

Study on ion transport in nanochannels based on molecular dynamics simulation

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Keywords: Molecular dynamics; Nanochannel; Ion transport; Ion selectivity

Abstract: Based on the concept of "root", the mechanism of ion transport in one-dimensional carbon nanotubes is discussed by using molecular dynamics simulation and experimental data. The study revealed that in graphene nanotubes with a diameter of less than 5 nm, the migration rate of cations and anions would decrease as the diameter of the pipe became smaller. In addition, the wall of the negatively charged pipe will trap ions that are different from its electrical properties through electrostatic attraction, further slowing down the migration rate of these ions. Under the superposition of these two factors, we observed that the migration rate of sodium ion first accelerated with the increase of the wall charge density, and then slowed down, while the migration rate of chloride ion showed the opposite trend. This study deepens our understanding of the abnormal conduction phenomena in low-dimensional carbon nanotubes and provides a theoretical basis for designing the structures of such nanotubes. In addition, the research has a vital role in the innovation and development of membrane material technology, and can also play a prominent role in the field of seawater desalination.

1. Introduction

Nanochannel ion transport is an important biological and physical phenomenon, which plays an important role in information transfer and separation in organisms. With the development and popularization of nanotechnology, the study of ion transport in nanochannels has attracted increasing attention ^[1]. Molecular dynamics simulation is one of the important methods to study ion transport in nanochannels. By simulating the motion state of atoms and ions in nanochannels, we can reveal the law and mechanism of ion transport in nanochannels. The aim of this paper is to explore the law of ion transport in nanochannels by molecular dynamics simulation method, and to deeply analyze the selective regulation mechanism of ions in nanochannels. By studying the law of ion transport in nanochannels, we can also provide a theoretical basis for drug delivery, biosensors and other applications in the biomedical field, and provide reference and guidance for the development of nanotechnology ^[2]. It is hoped that through the study of this paper, we can deeply understand the mechanism of ion transport in nanochannels, and provide important reference for the research and application in related fields.

2. Research Methods

2.1 Molecular dynamics simulation methods

Using molecular dynamics simulation research methods, we can see the detailed conditions of molecular scale in the system, such as the specific location of atoms and their speed of movement, and use statistical methods to average such information, and then obtain macroscopic physical properties ^[3]. If the potential energy function of the intermolecular interaction properly maps reality, molecular dynamics simulations can accurately reproduce the physical behavior of the fluid in the standard state and explore its undiscovered behavior at the nanoscale. This method has been widely used in many aspects of nanohydrodynamics, including the simulation of fluid transfer properties in channels under the influence of nanosize limitations - a study that is still not easily accomplished by traditional experimental techniques. At the same time, the technique has also been used to verify

boundary conditions at the nanoscale [4].

2.2 Experimental methods for carbon nanotube channels

2.2.1 Preparation of carbon nanotube channels

The formation of small size carbon nanotube channels (CNTPs) and their functional detection include several stages as shown in Figure 1 below. At the beginning, the raw materials of carbon microtubules were purified by heat analysis technology [5]. Next, the carbon microtubules were dissolved with lipid molecules containing phosphorus; Next, the carbon microtubules are hit by ultrasonic waves and cut into short films of various lengths. The incomplete carbon microtubule fragments and other pollutants were removed by high speed centrifugation. After purification, carbon microcatheter wrapped by phospholipids was obtained. Eventually, these very thin tubes are added to the phospholipid fat body and their production is determined by a proton flow test [6].

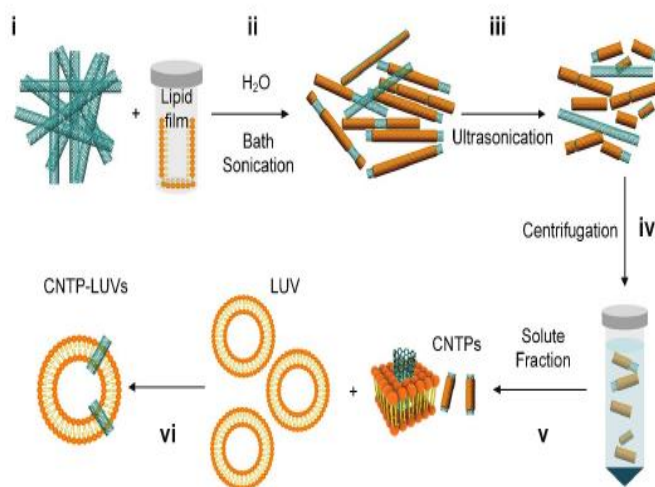


Figure 1 Preparation flow chart and structure diagram of small size carbon nanotube channels (CNTPs)

2.2.2 Measurement of fluid transport permeability

In order to accurately evaluate the movement of the fluid in the carbon nanotube, the carbon nanotube must first be inserted into the membrane of the liposome. The liposomes are then quickly mixed with the buffer solution. In this way, due to the concentration difference, the ions will move along the carbon nanotube; Similarly, if there is a difference in osmotic pressure, water molecules will also flow through carbon nanotubes. For the different fluids to be observed, appropriate fluorescent markers need to be selected and placed inside the liposome. When the internal ion concentration changes or water molecules flow out, the liposome shrinks, resulting in changes in the density of the internal fluorescent marker, and its fluorescence intensity will also change accordingly [7]. Next, the change in the fluorescence intensity of the marker is converted into the change in ion concentration or the flow momentum of water molecules through the calibration operation, and the transport rate of the fluid in the carbon nanotube is calculated. The most important step in the experiment is to quickly and immediately mix the liposomes with the buffer to measure the change in fluorescence. This process captures the instantaneous flow rate of the fluid at the beginning of the flow and avoids underestimating the rate of fluid passing through the pipe. Therefore, it is necessary to use stop-flow spectroscopy to ensure that the liposomes and buffers can be mixed quickly to achieve the expected experimental results [8].

As shown in Figure 2, instead of monitoring the chemical reaction along the flow path, flow stop spectroscopy sets a monitoring point near the mixing area and follows the chemical reaction immediately after a quick stop of the advancing syringe. This reaction is triggered by a tiny switch located in the syringe piston. A stepper motor is usually used to control the advance of the syringe, and its speed should be as high as possible without causing cavitation effects. Cavitation refers to

the formation of bubbles when the local pressure is reduced to the point of bubble formation, which affects the mixing of the sample and the optical detection process.

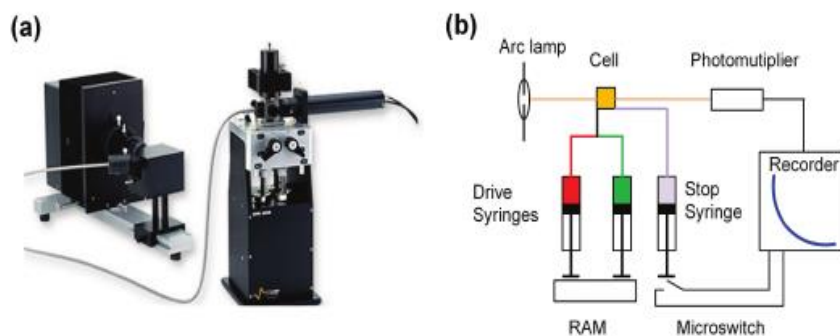


Figure 2 Stop-flow spectrometer. (a) Physical drawings of the stop-flow spectrometer (SFM2000); (b) Schematic diagram of key components

3. Study on the microscopic mechanism of ion transport in graphene nanochannels

3.1 Model Building

To carry out the simulation process, we chose NAMD2.12, a publicly available molecular dynamics software, set the time step to 2 femtoseconds, and applied periodic constraints on the three-dimensional space limits of the model. The TIP3P scheme was used to describe the structure of water molecules, and the interaction between atoms was explained by the CHARMM36 potential field equation, in which the carbon atoms in the graphene layer were classified as CA type. For non-bonded interactions, the effective distance is set at an upper limit of 1.2 nanometers, while the lower limit is fixed at 1.0 nanometers. The interaction between electron loads is estimated by the particle-grid-Ewald technique, which selects four femtoseconds as the operation step size and the grid scale of one hundredth of a micron. In the preliminary simulation phase, we first performed 0.1 nanosecond energy optimization operations on the system; Secondly, the system enters a 10-nanosecond steady-state equilibrium process, during which the Nose-Hoohu-Langevin thermal statistics technique is used to ensure that the pressure level is stabilized at the standard value of atmospheric pressure, so that the entire system is kept constant in the number of atoms, pressure and temperature (that is, following the conditions of the NPT ensemble). At the same time, the cycle frequency of the system and the reduction interval are set to 0.2 picoseconds. Under the control of Langevin temperature control equipment, the oxygen and carbon atoms are controlled by constant temperature, which stabilizes the system temperature at 300 Kelvin level and sets the damping coefficient to an inverse ratio of 0.2 per picosecond. Based on the previous conditions, a 10-nanosecond potential-driven simulation start-up procedure was then performed. In this process, I use the NVT ensemble of constant particle number (N), constant volume (V) and constant temperature (T). In order to achieve the application of potential, the system applies an electric field E_z in the direction of the Z axis, and the voltage value is obtained by dividing the electric field E_z by the length of the Z axis L_z , and adding a negative sign, that is, the voltage V_s can be expressed as $V_s = -L_z E_z$. Finally, the analysis of data from 100ns to 800ns was carried out based on the trend of ion velocity and the number of ion penetration.

3.2 Results and discussion

3.2.1 Influence of size and wall charge on ionic conductivity and mobility

In this simulation experiment, applied voltage $V_s = 2V$, channel diameter $d = 3nm$, $L_p = 3.4nm$, $c_{NaCl} = 1.0M$. $\mu_{[Na]^+} = 4.55 \times 10^{-8} m^2 / (V, s)$ and $\mu_{[Cl]^-} = 7.53 \times 10^{-8} m^2 / (V)$, the posture of Na^+ ion in $NaCl$ solution and the mobility of Cl^- ion when s is 1.0 M, $k_b = 11.65s / M$ is the corresponding solution conductivity. If the wall conductance effect is taken into account, we can see that the ion current presents an approximate linear upward trend with the increase of the wall charge density, as shown in Figure 3.

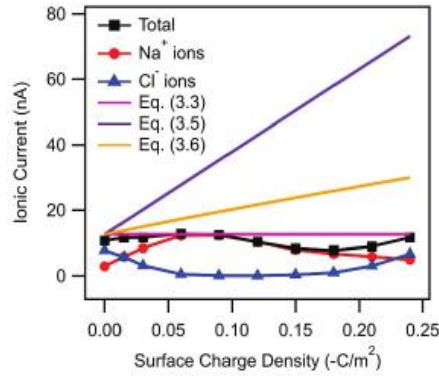


Figure 3 Comparison between simulation results of nanochannel currents and theoretical predictions.

As shown in Figure 4, the current flow of sodium ions increases to a peak and begins to decline after a transition at about $-0.1\text{C}/\text{m}^2$, while the current flow of chloride ions exhibits a relative behavior pattern. This current change phenomenon cannot be explained by the current theoretical equation. Further, in order to verify whether this is a phenomenon commonly seen in thin nanopores, it was simulated.

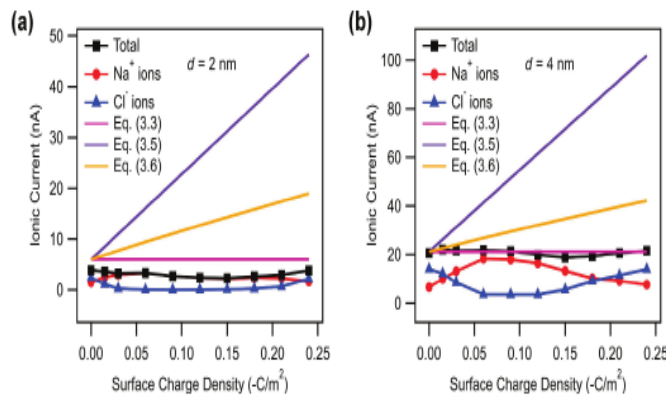


Figure 4 Comparison between the simulated results of nanochannel current and the theoretical predicted values

As shown in Figure 5, if the charged state of the wall is not considered, the theoretical calculation is that the current remains constant regardless of the amount of charge on the wall.

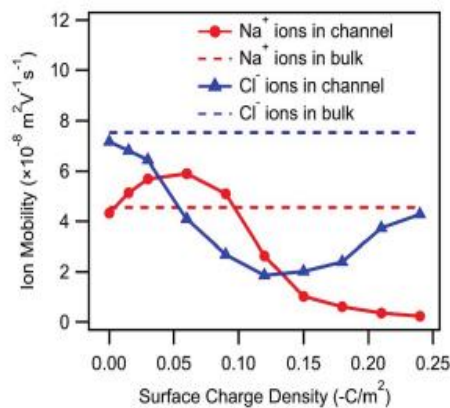


Figure 5 Mobility of ions in nanochannels

Figure 5 shows how the migration rates of sodium and chloride ions in a 3nm diameter nanotube vary with the concentration of charge on the tube wall. The results show that with the increase of the concentration of charge on the wall of the tube, the migration rate of sodium ions first increases

to exceed the normal state in solution, but it decreases rapidly under the condition of higher concentration of charge. In contrast, the migration rate of chloride ions has been lower than its natural state in solution, and it continues to decline with increasing charge concentration until it begins to pick up at about $-0.1\text{C}/\text{m}^2$. A similar phenomenon was seen for the other two nanochannels with diameters of 2 and 4 nanometers, respectively (As shown in Figure 5). In general, the total number of ions shows an increasing trend as the charge density increases. According to the traditional Debye-Hückel theory, the migration speed of ions decreases with the increase of concentration, so theoretically the migration speed of sodium ions and chloride ions should decrease with the increase of charge concentration.

3.2.2 Ion pair events during transport

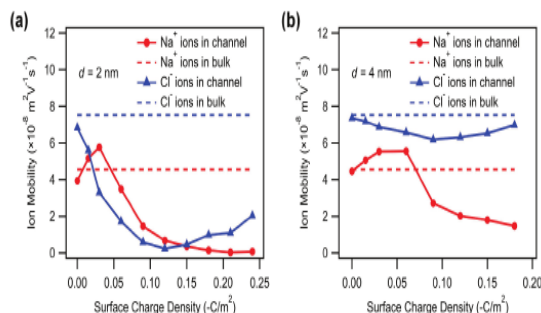


Figure 6 Mobility of ions in nanochannels.

According to the results shown in Figure 6, uncharged nanotubes of various diameters have different effects on ion transport. As can be seen from the figure, if the diameter of the pipe is less than 5nm, the migration speed of sodium ions and chloride ions in the pipe will be lower than their speed in the ordinary state, and with the reduction of the diameter of the pipe, the movement speed of ions will further slow down. In addition, although the diameter of the pipe changes, the proportion of various ions in the total amount remains constant (as shown in Figure 7). Figure 8 shows that through the analysis of the distribution of the time used by sodium ions to pass through the pipe, it is found that in the pipe with a width of only 1.4nm, the residence time distribution of sodium ions presents a long tail, which indicates that some ions will significantly slow down when passing through the pipe. When the width of the pipe decreases, the distribution of this "long tail" phenomenon becomes more significant. Further studies showed that the prolonged ion retention was caused by the ion pair crossing event, which directly led to a significant reduction in the mobility of sodium and chloride ions.

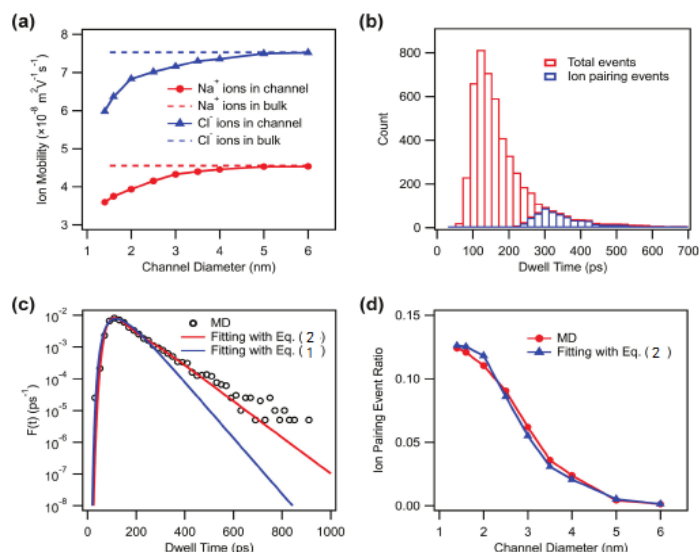


Figure 7 The ion transport operation in non-charged nanochannels with different diameters is the rule

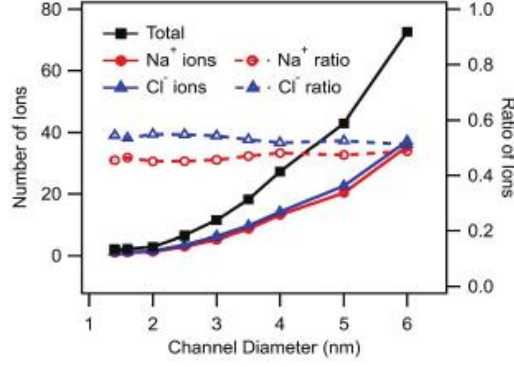


Figure 8 The number of Na⁺ ions, Cl⁻ ions, total ions and the proportion of different ions in non-charged nanochannels with different diameters

The first traversing mode is used to fit the residence time distribution of the passing case, and the boundary conditions of semi-infinity are used to convert the classical solution of the mode into:

$$F(t) = \frac{L_p}{\sqrt{4\pi Dt^3}} e^{-(L_p - tv_{ion})^2 / 4Dt} \quad (1)$$

F(t) - The first passage probability distribution, which represents the passage probability of ions per second.

D- Ion diffusion factor in the pipeline.

v_{ion} - the rate of ion migration in the pipe.

As shown in Figure 7(c), the results shown by formula (1) are generally consistent with the simulation data in the short time elapsed traffic events. As for the differences in the passage events completed over a long period of time, they can be attributed to the phenomenon of ions traveling through the channel in pairs. The probability p and (1-p) are used to represent the probability of single ion and paired ion crossing events, which correspond to the two distributions presented by F1(t) and F2(t), respectively. Therefore, the total current event distribution F(t) can be explained by the adjusted model.

$$F(t) = pF_1(t) + (1 - p)F_2(t) \quad (2)$$

According to the revised model, F1(t) and F2(t) both take the form shown in equation (1). For these two factors, the values of D/v_{ion} should be consistent according to Nernst-Einstein's law. As shown in Figure 7c, the adjusted model has a dense agreement with the simulation data. Figure 7d illustrates the proportion of ion pairs traversed by nanotubes of different sizes. When the nanotube diameter decreases, the ion pair crossing phenomenon occurs frequently. When the channel width exceeds 5nm, the proportion of pairs crossing is almost zero, but when the diameter shrinks to 1.4nm, this ratio rises to 12%. This increase in the proportion of pairs crossing helps explain why the migration rate of positive and negative ions in the nanotubes decreases.

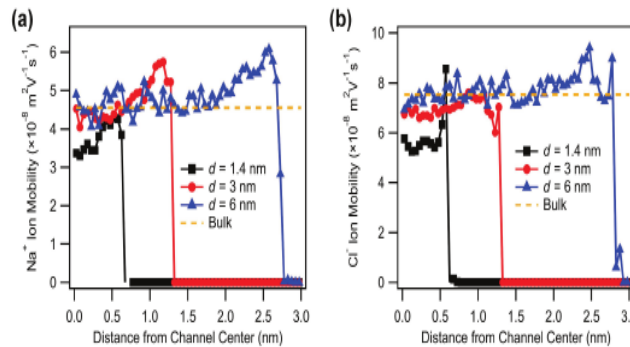


Figure 9 In non-charged nanochannels with different diameters

It is evident in Figure 8 that the migration rates of Na⁺ and Cl⁻ in the nanochannel decrease as the channel size decreases, especially in the center of the channel, which is due to the increased

binding effect leading to more frequent ion pairing crossing events. As can be seen from FIG. 9, comparing the proportion of ion pair passage under different concentration conditions, the number of ion pair passage occurrence increases with the increase of salt concentration, thus slowing down the ion migration rate.

4. Conclusion

In this paper, the ion transport in graphene nanochannels is investigated by molecular dynamics simulation. It is found that the ion current differs greatly from the prediction of the continuity theory formula, especially at high wall charge density. The analysis found that changing the size and wall charge density of the nanochannel would change the ion concentration in the channel, and the ion mobility would also change greatly, but the ion concentration inside the nanochannel could not explain this deviation. Moving the target to the mobility of ions within the nanochannel, it was found that ion pair events reduce ion mobility and become more pronounced in highly confined Spaces. When the electrostatic interaction between the wall charge and the anti-sign ion becomes stronger, the wall trapping effect will also reduce the mobility of the ion. At low wall charge density, the proportion of Na⁺ ions increases, which means that Cl⁻ ions form a weak interaction with the moving Na⁺ ions, resulting in an increase in the mobility of Na⁺ ions. For Cl⁻ ions, the opposite is true. With the further increase of the wall charge density, the trapping of Na⁺ ions by wall charge is enhanced, resulting in the decrease of the mobility of Na⁺ ions, while the mobility of Cl⁻ ions increases due to the decrease of pairs.

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