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TOPICAL REVIEW — Soft matter and biological physics

Theoretical studies and molecular dynamics simulations on ion transport properties in nanochannels and nanopores*

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Control of ion transport and fluid flow through nanofluidic devices is of primary importance for energy storage and conversion, drug delivery and a wide range of biological processes. Recent development of nanotechnology, synthesis techniques, purification technologies, and experiment have led to rapid advances in simulation and modeling studies on ion transport properties. In this review, the applications of Poisson–Nernst–Plank (PNP) equations in analyzing transport properties are presented. The molecular dynamics (MD) studies of transport properties of ion and fluidic flow through nanofluidic devices are reported as well.

Keywords: nanofluidic devices, ion transport, Poisson–Nernst–Plank (PNP) equations, molecular dynamics (MD) simulations

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1. Introduction

Ion transport and fluid flow through nanofluidic devices play important role in a broad spectrum of technological applications and biological processes,[1] including supercapacitor,[2] energy harvesting and conversion,[3,4] chemical separation, biosensors,[5–7] and drug delivery.[8] Due to the recent development of nanotechnology, nanofluidic devices have attained considerable attention. Therefore, a deep mechanistic understanding of ion transport and fluid flow through nanofluidic devices is not only helpful for us to reveal some biological activities, but also useful for the design of novel nanofluidic devices.

On one hand, nanofluidic system structures can be categorized into two groups, nanochannels and nanopores, according to the structural characteristics of nanofluidic system. More specifically, for nanochannels, the length is much larger than the radius, while for nanopores, the length and the radius are comparable to each other. Across a broad range of applications, such as molecular separation, detection, nanosensing, medicine release and seawater desalination (purification)[9–12] for nanofluidic materials, carbon nanotubes (CNTs) have regarded as one of the most promising candidates for nanofluidic devices.[13] Owing to the development of nanotechnology, CNTs can be easily synthesized to mimic nature ion channels, desalination, and energy harvesting. For example, the diameter and length of CNTs can be tuned, which makes the geometry of CNTs controllable. Aside from the regular structures with controllable geometry, CNTs also have smoothness and hydrophobic interior surfaces because of their graphitic walls. In addition, functional groups and charges on the surfaces of CNTs have significant influences on ion transport.[14–16] Particularly, the exceptional mechanical, optical, electrical, and thermal characteristics make CNT to be a promising material as an ion transporter and being extensively investigated.[17–23]

On the other hand, three major interactions, i.e., steric interactions, van der Waals interactions and electrostatic interactions, play a nontrivial role in nanofluidic systems with their varying depending on characteristic length scale. There are two treatments to nanofluidic systems concerning their theoretical investigations, depending on their characteristic length scale. When characteristic length is less than 5 nm, as the flow features in such nanofluidic systems strongly rely on the interactions among individual ions, thus the transport behaviors of ions are usually analyzed by using molecular dynamics driven by steric interactions, the dominant interaction player. While the characteristic length scales increase to range 5 nm–100 nm, electrostatic interactions have a profound effect on ion transport. Thus, in this case, continuum dynamics are often employed to elucidate the transport features. Typically, Debye length $\lambda_{\mathrm{D}} = \sqrt{\varepsilon\varepsilon_0 k_{\mathrm{B}} T / \sum_i n_i q_i^2}$, ranging from 1 nm to 100 nm, is one of the most important characteristic length scales, where ε is the dielectric constant of the solvent, ε_0 is the permittivity of vacuum, k_{B} is the Boltzmann constant, T is the absolute temperature, n_i and q_i are the bulk ion concentration and the charge of ion species i, respectively. In addition, as for van der Waals interactions, the characteristic length scales typically range from 1 nm to 50 nm.

Extensive phenomena in nanofluidics have been explored

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experimentally, including the current rectification, giant electroosmotic currents and cation-induced stochastic pore blocking, double-layer overlaps, ion permittivity, diffusion, surface charge effect and entropic forces.[1,24–30] In order to simulate nanofluidics in CNT, the ions are usually modelled to transport through a CNT by coupling water,[31] figure 1 is a cross-section view of ions and water molecules passing through a CNT. To better understand the underlying mechanisms of the considerable interesting phenomena of ion transport in CNTs, the rest part of this review paper is organized as follows. In Section 2, we will focus on the introduction of Poisson–Nernst–Plank (PNP) equations which are generally used to quantitatively illustrate the transport phenomena of ions in nanochannels or nanopores. In Section 3, we will pay attention to the application of molecular dynamics (MD) simulation in CNTs. Specifically, by using MD simulation, the effects of nanotubes size, functionalized nanotubes, ionic conditions, and unusual parameters on the transport properties are discussed. In Section 4, a summary is presented.

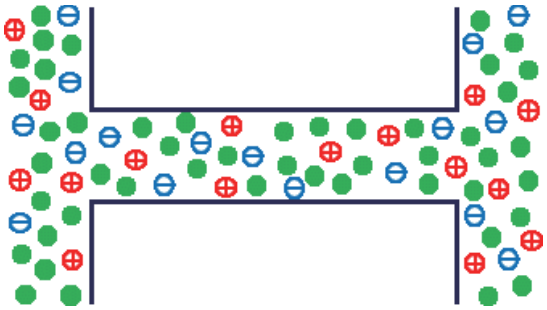


Fig. 1. (color online) Cross-section view of ions and water molecules (green spots) passing through a CNT.

2. Theoretical model: PNP model

Based on the three major interactions in nanofluidic systems (nanochannels and nanopores), when the size of system is larger than 5 nm, continuum dynamics is generally used to model the transport phenomena of ions. In this situation, what govern ion transport in nanofluidic systems are the well-known Poisson–Nernst–Plank (PNP) equations, which combine Poisson equation and Nernst–Plank equation. One of the prevailing method to predict the transport behaviors of ions inside such nanofluidic systhems is to numerically solve the PNP equations. Normally, nanofluidic systems do not include any chemical reactions between components, and therefore the flux of ions is constant in time, which can be described by a diffusion equation

$$\boldsymbol{J}_i = -D_i\left(\nabla n_i + \frac{n_i z_i e}{k_{\mathrm{B}}T}\nabla\phi\right), \tag{1}$$

where D_i, n_i, and z_i are the diffusion coefficient, the concentration, and the valence of ion species i, respectively, e is the electronic charge, ϕ is the electrostatic potential, k_{B} is the Boltzmann constant, and T is the absolute temperature.

Here the electrostatic potential obeys Poisson equation

$$\nabla^2\phi = -\frac{\rho_{\mathrm{e}}}{\varepsilon\varepsilon_0}, \tag{2}$$

where $\rho_{\mathrm{e}} = \sum_i n_i z_i e$ is the total charge density, ε is the dielectric constant of the medium, and ε_0 is the permittivity of vacuum.

The ion flux as given by Eq. (1) is governed by Nernst–Planck equation

$$\nabla\cdot\boldsymbol{J}_i = 0. \tag{3}$$

In practice, the current rectification is one of the most important phenomena in nanochannels and nanopores. In order to quantitatively understand the underlying physical mechanism, numerical solutions to PNP equations have been used extensively to shed light on some related interesting phenomena. In a pioneering work reported by Cervera and coauthors,[32] a theoretical model based on PNP equations was presented to give a quantitative description of the ionic transport across synthetic conical nanopores (Fig. 1 in Ref. [32]). Subsequently, by using spherical coordinates numerically solve the corresponding PNP equations, and eventually concluded a total electric current equation. This model was compared with corresponding experimental results with a relatively good agreement. To get more insights into the asymmetric properties of ion transport in charged conical nanopores, some tactics were also utilized to solve PNP equations, such as provide good initial values, decompose the equations, and multiply a coefficient in the nonlinear term proposed by Liu *et al.*[27] The fact that theoretical results accord well with experimental observations, indicates that PNP equations are a useful tool to quantitatively understand the transport properties of ions in nanofluidic systems. In order to study the ion current rectification in bipolar nanofluidic diode, a model based on PNP equations has been proposed by Constantin and Siwy to predict the ionic concentrations and electrical-potential profiles within the bipolar nanofluidic diode, as well as the current-voltage curves.[33] On the basis of PNP equations and Navier–Stokes equations, the characteristics of ion transport in a fluidic unipolar nanopore have been studied by Singh, and it is found that the length and location of surface charge on the walls of fluidic unipolar nanopore have a significant influence on ion transport and ion current rectification.[34] Through the combination of PNP and Navier–Stokes equations, the ionic transport and the liquid flow in conical nanopores were modeled.[35] Furthermore, the influence of the power-law index, surface charge of the nanopore, applied voltage, and the ratio of the tip radius to the Debye length on ionic current rectification and electroosmotic flow was investigated.[35] Recently, concerning the non-electrostatic interactions between the solution and channel, and between solvent molecules, a generalized PNP theory was derived by Park *et al.*[36]

3. Molecular dynamics simulation of ionic transport in carbon nanotubes

In the past decade, CNTs have been widely investigated in theory, experiment and simulation[31,37–43] due to their exceptional mechanical, optical, electrical, and thermal characteristics,[21–23] which makes CNT a promising material as an ion transporter in ion, water and electrolyte solution transportation.[44–50] For example, CNTs has been increasingly used to upgrade water purification technologies due to their mechanical and chemical characteristics, high aspect ratio and small influence on the environment.[51]

3.1. Size effects on ionic transport in carbon nanotubes

Thoroughly understanding the impacts of CNTs size on ion conduction is essential and helpful for designing optimal nanodevices for a wide variety of practical applications. Recently, by using MD simulation, broad investigations have been made to explore the size effects of carbon nanotubes on the transport and diffusion behaviors of ions and fluids in the nanoconfinement of CNTs. Concentrating on ion transport behaviors of aqueous electrolytes in CNTs with various radii, Samoylova *et al.* utilized all atom MD simulations (Fig. 1 in Ref. [41]) to study ion transport through CNTs under an electric field and the radius effect of CNT was elucidated.[41] They found that by decreasing the tube diameter from 8.15 nm to 4.09 nm, the behaviors of mean ionic current versus electric field deviate from linear to nonlinear (Fig. 2 in Ref. 41), and more specifically for the CNTs with radii 4.76 nm and 4.09 nm, no ionic current was detected. In addition, with the decrease of nanotube radius, the maximum ionic current passing through CNTs drops off dramatically (Fig. 3 in Ref. [41]). To further understand the transport behaviors of simple fluid, recently Ye *et al.* carried out an investigation on the static and dynamic properties of argon inside the carbon nanotubes with different sizes using molecular dynamics simulations.[52] Their simulation results concluded that there exist two atomic layers inside the (10,10) CNTs. However, the atomic layers tend to be obscure with the increase of the diameters of CNTs. On the other hand, for the dynamic property, the diffusion process of the argon along the axial and radial directions are discussed as well. Similarly, a series of MD simulations were also conducted by Ahmed *et al*. to analyze the transport properties of the same argon fluid, across CNTs with different sizes (altering diameters and lengths).[53] The results indicate close correlations between the liquid flow, occupancy, translocation time and CNT size.

3.2. Ionic transport in functionalized carbon nanotubes

Aside from the influence of CNTs size on ion conduction through CNTs, many studies have demonstrated the importance of functionalized CNTs in determining ionic transport. With the aim of studying ion transport through surface modified CNTs under an external electric field, some CNTs are modified deliberately by functional ring groups from outside or inside (Fig. 1 in Ref. [16]). Recent all-atom MD simulations results indicated that carbon nanotubes with various degree of modification are able to modulate the ionic current.[16] It is found that the ionic current passing through the nanotubes are not only remarkably increased, but also offer selectivity of the ionic current carriers. The ionic current in the functionalized CNTs increase profoundly compared with the unmodified CNTs of the same size (Fig. 3 in Ref. [16]). Inspired by the outstanding properties of biological protein channels, He *et al.* designed biomimetic nanopores to regulate ion transport via MD simulations,[54] and reported that chemically modified nanopores displayed an effective ion recognition ability and ion selectivity under transmembrane voltage bias. In addition, except for the functional groups, surface charges on CNTs also play a crucial role in regulating ionic transport. To investigate the ionic current flowing through a charged cylindrical nanopore, Xue *et al.* employed MD simulations and theoretical calculations based on PNP equations.[14] Simulation and calculation results both indicate that electric currents increase with the increase of surface charge density (Fig. 3 in Ref. [14]). Such a comparison between simulation results and theoretical nanalysis offers some clues to improve the calculation accuracy by modifing the parameters in the PNP equations. Subsequently, by using MD simulations, Xue *et al*. further studied the transport behaviors of electrolyte solution flowing through charged carbon nanotubes (CNTs),[15] and the simulation results revealed that the flow velocity as well as the slip length of the electrolyte solution are strikingly influenced by the number of surface charges and surface charge distribution pattern on the nanotube. Also, the effect of the surface charge upon the energy efficiency of nanofluidic battery was also estimated based on CNTs.

3.3. Ionic condition effects on ionic transport in carbon nanotubes

The transport behaviors of ions in CNTs are not only affected by the parameters of CNTs but also influenced by the ionic conditions including ionic species and concentration. Recently, by using MD simulations, Su and Huang comprehensively studied the coupling transport of water and ions through a carbon nanotube in electric fields.[42] The simulation results indicate that both cations and anions are capable to drag water molecules through the CNT (Fig. 2(a) in Ref. [42]), and the water flux and its direction are dominated by chloride ions flux (Fig. 2(b) in Ref. [42]), which reveals that the ion and water transport through CNTs can be remarkably tuned by salt species. Also, the water and chloride ions flux share the same variation trend, i.e., both increase in the

beginning then decrease gradually after reaching to a threshold value (Fig. 6 in Ref. [42]), while the sodium ions flux increase steadily and nearly linearly against ionic concentration. The dependence of water and ion flux on ionic concentration implies that ionic concentration plays a nontrivial role in the coupling transport of water and ion. To comprehensively understand ion transport through carbon nanotubes, Beu systematically investigated the influence of the solute specificity and concentration, the nanotube geometry and radius, and applied external electric field on transport features and solution structuring by using extensive MD simulations.[55–57] Their findings reflect that the increases of solute concentration would lead to a slightly nonlinear decrease of diffusion coefficients, by which the correlations between conductance, ion pairing times and solute concentration were established. In addition, via MD simulation, He *et al.* reported that some nanopores have voltage-dependent selectivity of cations.[54] By increasing the transmembrane voltage, Na^+ selectivity of graphene nanopores (3COO) is gradually turning into K^+ selectivity.

3.4. Unusual parameters effects on ionic transport in carbon nanotubes

In recent years, it is unexpected that some unusual parameters which were usually neglected in traditional MD simulations play dominant roles in specific situations. For example, traditional MD simulations include only the van der Waals forces between ions, water molecules and the CNTs. However, it has been shown that the cation-π interaction, the dominant electrostatic one in the model π system, should be taken into consideration.[58] Liu and coauthors have successfully explained the water blockage by ions in the narrow (6,6) CNTs by including the cation-π interactions into MD simulations.[59] Although the Na^+ cannot pass through such small CNTs, they are trapped in the entrance of the nanotubes due to the cation-π interactions between ions and CNTs. Therefore, the water flow is totally stopped. The method, in addition, can also be applied to helping people understand the bound ions inside the CNT channels and the trapped ions could escape from the channels with the application of a high value electric field.[59] Recently, Pham and coworkers' simulations show that the ion behaviors inside the CNTS can be strongly influenced by cation-π interactions. By doing MD simulations, they noted that the Na^+ and K^+ cations are much more closer to the carbon wall when the cation-π interactions were included.[60] Interestingly, the K^+ ions are more nearer to the wall than Na^+ ions whether the cation-π interactions are considered or not. Moreover, Liu and Patey showed that different water structures used in MD simulations lead to different ion flow rates in the CNTs.[61] Compared with the TIP3P model widely used in MD simulations, the TIP4P/2005 performed impressively well for a variety of properties and thermodynamic situations.[61,62] In Liu and Patey's earlier papers, they clarified that the water flow rates of TIP4P/2005 structure are significantly lower than those of TIP3P in different sizes of CNTs.[63,64] Furthermore, it is clear that the water molecules with small flow rate tend to become ring-bound, which is the primary barrier for ion entry. Therefore, the ion flow rate of TIP4P/2005 solutions is similarly slower than that of TIP3P, which is extremely true under low temperature conditions.[61]

As mentioned above, as long as the length scale of nanochannels or nanopores are larger than 5 nm under the condition of charged channel or pore, and the thickness of channel or pore is comparable to the Debye length, then the ionic current is controllable. Thus, the transport phenomena of ions can be well elucidated using continuum dynamics theory. On the other hand when the scale is smaller than 5 nm, it becomes not appropriate to analyze with continuum dynamics as its validity questionable. In this case, MD simulations become a useful tool to solve this problem, and dissect the molecular structure inside the nanodevices. What is more, the accuracy of the interactions involving different ions and channel wall can be well improved by simply adjusting the simulation method.

4. Conclusion

In summary, we have reviewed the numerical simulations and theoretical modeling in ionic transport and fluidic flow in nanofluidic systems. PNP model is widely utilized as a theoretical tool to model the transport behaviors. Furthermore, by employing MD simulations, it is shown that nanotubes sizes, functionalized nanotubes, ionic conditions, and unusual parameters influence the transport properties. According to the conclusions obtained from the literatures, it is found that (i) CNTs with large radius are more liable to conduct ions, while CNTs with small radius tend to hinder ions from passing through CNT. (ii) The ionic current, recognition capability and selectivity can be significantly increased for the functionalized CNTs. (iii) The ability of drive water flux for different ionic species are different, and the variation tendency of ions flux are different for different ionic concentration. (iv) Some unusual parameters such as cation-π interactions can profoundly affect the ionic transport behaviors. However, despite a number of deep insights, the understanding of ionic transport properties under nanoscale confinement is far from complete. Precise fabrication of biomimetic nanofluidic materials so as to mimic the exact biological process is still a big challenge. Developing new theoretical methods to model various ion, electrolyte and molecular transport properties are still in need, as the transport behaviors are rather sensitive to chemical and physical structural features, such as chemical groups, chemical reactions and polarization. Yet theoretical models rarely take the above factors into account. The combination

of experiment, theory and simulation is crucial to uncover the fundamental mechanistic origin of ionic transport in confined one-dimensional environment. Such a new horizon of understanding can also provide useful guidelines to the design of novel nanofluidic devices.

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