Transport of ions through a (6,6) carbon nanotube under electric fields*

Shen Li(沈 力), Xu Zhen(徐 震), Zhou Zhe-Wei(周哲玮), and Hu Guo-Hui(胡国辉)†

Shanghai Institute of Applied Mathematics and Mechanics, Shanghai Key Laboratory of Mechanics in Energy Engineering, Shanghai University, Shanghai 200072, China

(Received 19 March 2014; revised manuscript received 15 May 2014; published online 24 September 2014)

The transport of water and ions through carbon nanotubes (CNTs) is crucial in nanotechnology and biotechnology. Previous investigation indicated that the ions can hardly pass through (6,6) CNTs due to their hydrated shells. In the present study, utilizing molecular dynamics simulation, it is shown that the energy barrier mainly originating from the hydrated water molecules could be overcome by applying an electric field large enough in the CNT axis direction. Potential of mean force is calculated to show the reduction of energy barrier when the electric field is present for (Na^+, K^+, Cl^-) ions. Consequently, ionic flux through (6,6) CNTs can be found once the electric field becomes larger than a threshold value. The variation of the coordination numbers of ions at different locations from the bulk to the center of the CNT is also explored to elaborate this dynamic process. The thresholds of the electric field are different for Na^+, K^+, and Cl^- due to their characteristics. This consequence might be potentially applied in ion selectivity in the future.

Keywords: nanostructured materials in electrochemistry, carbon nanotube, molecular dynamics, ion exchange

PACS: 82.45.Yz, 88.30.rh, 83.10.Mj, 82.39.Wj **DOI:** 10.1088/1674-1056/23/11/118201

1. Introduction

Carbon nanotubes (CNTs) have been widely applied in nanotechnology and biotechnology because of their superior mechanical properties, ideal geometry, and chemical inertia. Carbon nanotubes have attracted great interest in biological applications and have been extensively explored in biosensors,[1,2] tissue engineering,[3] and biomedical devices,[4] etc. They are also prosperous in many areas of nanotechnology, such as water desalination,[5] nanochannels,[6,7] and ion channels.[8,9]

Many researchers have realized the passage of either water molecules or ions through the carbon nanotubes. Previous experimental[10] and numerical studies[11,12] indicated that water can permeate through (5,5) or (6,6) CNTs. However, ions are faced with a different situation in comparison to water molecules. That is, ions might not be able to permeate through carbon nanotubes,[13] even when their diameters are smaller than the CNTs' because of their hydration shells. Available studies[14–16] showed that ions are able to pass through the (7,7) or larger CNTs. Nevertheless, it was found[17] that ions are not capable of transporting through (6,6) CNTs under a certain pressure. This phenomenon can be ascribed to the hydrating water molecules around the ion.[18] Due to the hydration shells, ions encounter an energy barrier, mainly arising from dehydration,[19] when they try to pass through the narrow CNTs. This implies that ions need to peel off some solvent molecules before they get into the CNTs. Since the dehydration energies of diverse ions differ significantly,[20] scientists might take this advantage to achieve ion selectivity, which is crucially important in biological and nano-technical applications. Song and Corry[19] found that both Na^+ and K^+ are able to permeate through the (8,8) SWNT under 100 MPa, but only Na^+ has the ability of passing through the (7,7) SWNT membranes under 200 MPa. This phenomenon provides a possible method to separate different types of ions, such as a solution in which Na^+, K^+, and Cl^- coexist. Gong *et al.*[21] showed that controllable Na^+ or K^+ selectivity can be obtained by using different modified patterns of carbonyl oxygen inside the (9,9) CNT. Their positions in the carbon nanotube mimic the arrangement of amino acids in the filter structure of potassium channels. They both attain the ion selectivity under the relatively large radius of a CNT.

What about the narrower CNT such as (6,6) CNT? Rapid water conduction through narrow (6,6) carbon nanotubes has been widely investigated in previous literatures. However, ions are considered to hardly permeate through the (6,6) CNT because of the large energy barrier under certain pressure. Using molecular dynamics (MD) simulation, we show that ions are able to overcome the energy barrier (mainly dehydration energy[19]), and pass through (6,6) CNTs under specific electric fields in the present study. The energy barrier is estimated by potential of mean force (PMF) that allows a more detailed, quantitative characterization of permeation events.[22] The coordination number of ions is calculated to illustrate the change of hydrating molecules in the process of the transportation. Because the ions' characteristics, the threshold of the electric

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11272197 and 11372175) and the Innovation Program of Shanghai Municipality Education Commission, China (Grant No. 14ZZ095).

†Corresponding author. E-mail: ghhu@staff.shu.edu.cn

© 2014 Chinese Physical Society and IOP Publishing Ltd

field that makes the ion pass through (6,6) CNTs is different. For example, the threshold value of Na^+ is higher than K^+. Therefore, it is possible to differentiate the ions by (6,6) CNTs with a particular electric field. It provides another method to achieve the ion selectivity, which might have a potential perspective in nanotechnology and biotechnology.

2. Method

The system is constructed by a 1.35-nm-long (6,6) CNT, two layers of graphene, water molecules, and ions in a 3 nm×3 nm×5.35 nm box (Fig. 1). The (6,6) CNT with radii of 0.407 nm parallel to the z axis is positioned at the center of the system. The two layers of graphene are located at the two ends of the CNT. The CNT and graphene are considered to be fixed and previous studies[23] indicated that this only has little influence on the outcome. They are solvated by 2-nm-thick layers of water on both sides, and ions are randomly placed, yielding a net concentration of 250 mM NaCl or KCl solution. Molecular dynamics simulation is utilized to simulate for 305 ns and the data in the last 300 ns are collected for analysis. The MD simulations are performed with the large-scale MD package GROMACS 4.5.4.[24] The TIP3P water model is used to describe the water molecules and the Charmm27[25] force field for ions (Na^+, K^+, and Cl^-). All carbon atoms are considered as uncharged Lennard–Jones (LJ) particles with the parameters of $\sigma_{CC} = 0.34$ nm and $\varepsilon_{CC} = 0.3612$ kJ·mol^{-1}. The CNT–water interaction is considered by a carbon–oxygen LJ potential with the parameters of $\sigma_{CO} = 0.3275$ nm and $\varepsilon_{CO} = 0.4802$ kJ·mol^{-1}.[26,27] The LJ interactions are treated with a cut-off distance of 1 nm and the particle mesh Ewald (PME)[28] method with a real-space cut-off of 1 nm is used to calculate the full electrostatic interactions. Periodic boundary conditions are imposed in all directions. The electric field applied is parallel to the z axis. In the present work, the electric field ranges from 0 to 3 V/nm. Previous studies indicated that water dissociation will not occur under such strength electric fields. Only for fields beyond about 3.5 V/nm, Saitta *et al.*[29] started to observe much more frequent water molecular dissociations. In Rothfuss *et al.*'s study,[30] water dissociation was found to occur under external fields of 3.2 and 4.4 V/nm. A very recent experimental study provided a thorough review of the process of water ionization in high electric fields induced by Pt electrodes.[31] In particular, an interesting analysis of the interplay between the local field and the external field, as estimated by Geissler *et al.*,[32] concludes that the latter should enhance water ionization for intensities of 3–6 V/nm. A Monte Carlo study[33] found that the polarization of a water molecule by the external field becomes negligible below field strengths of $\sim$ 10 V/nm. Therefore, neglecting water polarization is not expected to have a substantial impact on our numerical results. In the simulation, the system is under a constant pressure of 1 atm and a temperature of 300 K and the time step is set to be 2 fs, and the data are collected every 0.2 ps. Coordination numbers are determined by the average number of ligands within the distance of the first minimum in the radial distribution function.[19]

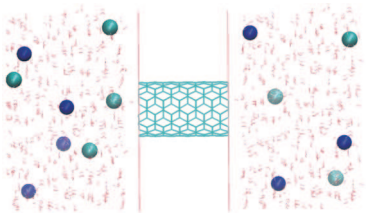


Fig. 1. (color online) Physical model of the simulated system. The red paralleling sheets stand for graphene. The green tube is the CNT. The red particles are water molecules, while the blue and green spheres represent Na^+ and Cl^-, respectively.

To analyze the mechanics of the passage of ions, the potential of mean force (PMF) is utilized to calculate the free energy of ions by the steered molecular dynamics (SMD) simulations based on Jarzynski's equality[34] which is a relation between equilibrium free energy differences and work done through non-equilibrium processes. This method is an effective approach for accurate estimation of the free energy and it has been successfully used in transporting small molecules through channels.[35] Considering a process that changes a parameter λ of a system from λ_0 at time zero to λ_t at time t, the second law of thermodynamics states that the average work W done on the system cannot be smaller than the difference between the free energies F corresponding to the initial and the final values of λ: $\Delta F = F(\lambda_t) - F(\lambda_0) \leq \langle W \rangle$, where the equality holds only if the process is quasi-static. According to this inequality, a non-equilibrium process provides only an upper limit for the free energy difference. However, Jarzynski proposed an equality that holds regardless of the speed of the process:[36] $e^{-\beta \Delta F} = \langle e^{-\beta W} \rangle$, where $\beta = 1/(k_B T)$ is the inverse temperature, and k_B is the Boltzmann constant.

In the SMD simulations, ions were set along the center axis of the (6,6) CNT, and 0.675 nm (half length of CNT) away from the mouth of CNT initially. An external force is applied to the ion to pull it into the center of the CNT from the bulk. The pulling distance is set to be 1.35 nm, which equals the length of the CNT. The pulling spring constant k was set as 2.4 kcal/(mol·Å^2), and the pulling velocity is fixed at 0.002 nm·ps^{-1}. For each different electric field, the SMD simulations were repeated and averaged over five times to make the potential of mean force (PMF) profile convincing and reliable.

3. Result and discussion

The PMF in Fig. 2 shows that ions experience a distinct free energy barrier upon entering the pore, which originates mainly from the dehydration effect.[19] The hydrated radius of

Na^+, K^+, and Cl^- is 0.32 nm, 0.36 nm, and 0.385 nm, respectively, which can be obtained through Fig. 2(a). That is to say, considering that the distance between oxygen and carbon is about 0.3 nm, the radius of (6,6) CNT (0.407 nm) is not large enough for ions and its hydrated water to transport through. If the ion is expected to pass through the pore, it needs to overcome the energy barrier due to dehydration. As shown in Fig. 2(b), the magnitude of free energy barriers upon entry follows $\triangle G^+_{Na} > \triangle G^-_{Cl} > \triangle G^+_K$, which means that it is the easiest for K^+ to enter the (6,6) CNT and the hardest for Na^+.

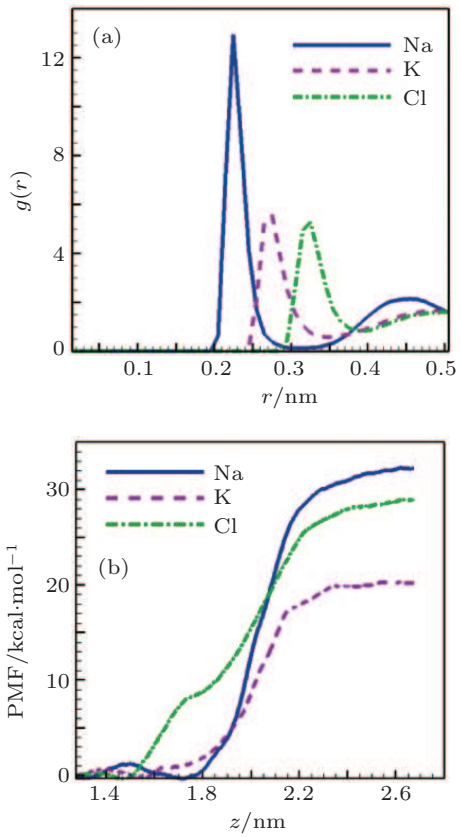


Fig. 2. (color online) (a) Ion–oxygen radial distribution functions (RDFs) for Na^+, K^+, and Cl^- in the bulk. (b) PMF profile of different ions in the (6,6) CNT without electric field. The mouth of CNT is located at $z = 2.0$ nm and the center of CNT is located at $z = 2.675$ nm.

To the best of our knowledge, the previous literature has not reported that ions could pass through (6,6) CNT. In the present study, our simulation indicates that an electric field is able to drive ions to pass through (6,6) CNT. Numbers of ions passing through the CNT per nanosecond are shown in Fig. 3 under different electric fields. Obviously, the flux of ions increases with the electric field strength after a threshold electric voltage. The simulations indicate that the threshold value ranges from 1.7 V/nm to 1.8 V/nm for Na^+ and 1.3 V/nm to 1.4 V/nm for K^+ according to the ionic flux we measured. We can also find that the ionic flux varies for different kinds of ions. Specifically, the flux of K^+ is larger than that of Cl^- generally and Cl^- is easier to pass through the CNT than Na^+, which is consistent with our results of PMF. A set of PMF profiles are plotted in Fig. 4 under different strengths of electric field to manifest their influence on the energy barriers.

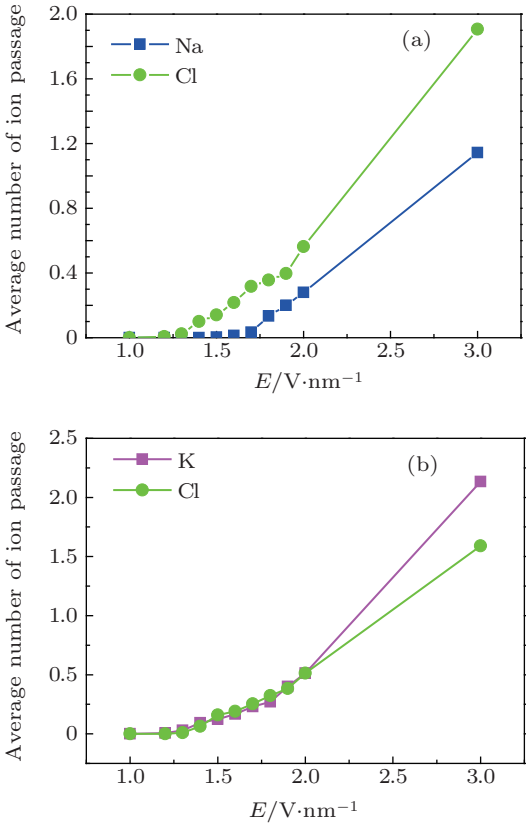


Fig. 3. (color online) Average total numbers of ion passages per nanosecond for NaCl (a) and KCl (b) solutions under different electric fields.

Among various ions, Na^+ and K^+ have received special attention because of their important role in biological and chemical fields. Many researchers[20,37] focused on the ion selectivity between Na^+ and K^+, so we mainly discuss the mechanism of Na^+ and K^+ transporting through the CNT under an electric field. In Fig. 4(a), with the application of the electric fields, the curves of PMF decline remarkably in the vicinity of the entrance of the nanopore. It can be found that even under the electric field of 1 V/nm, there is a little bulge around the entrance, which indicates an energy barrier preventing K^+ from passing through the CNT. There are no ions detected in the pore in the statistic from simulations at this voltage. At a threshold value $E = 1.3$ V/nm, the curve is nearly a horizontal close to the mouth of the CNT, and consequently a small quantity of K^+ is found to pass through the CNT.

It is worth mentioning that a potential well appears at $z = 1.6$ nm, approximately outside the CNT, which originates from the attraction of the ions and the water molecules with the carbon molecules. Previous studies[38–41] also revealed that the electric fields have significant effects on the interfacial water structures, and enhance the hydrophilicity of the solid substrate. Therefore, the depth of the potential well increases

with the electric field as expected. After $z > 1.6$ nm, the PMF curves raise again because the ions have to overcome the energy barriers due to dehydration before they enter the CNT.

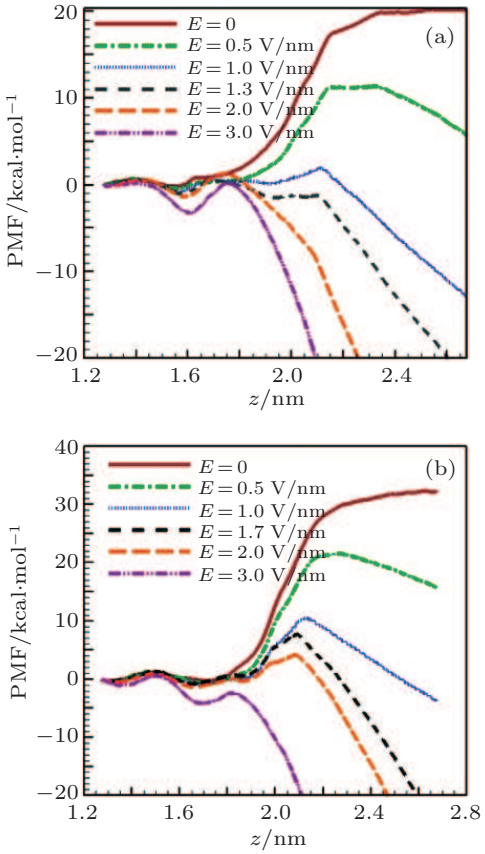


Fig. 4. (color online) PMF profiles of K^+ (a) and Na^+ (b) passing through the (6,6) CNT under different electric fields. The mouth of CNT is located at $z = 2.0$ nm and the center of CNT is located at $z = 2.675$ nm.

The tendency of PMF profile of Na^+ is similar to K^+, as depicted in Fig. 4(b). In comparison to K^+, although the statistic from molecular simulations indicates that there is a small amount of ions passing through the pore at $E = 1.7$ V/nm and 2.0 V/nm, the bulge is still located at the mouth of the CNT. This discrepancy implies that the translocation of the ions is a complicated process related to the interaction between carbon and ions, dehydration, ionic radius, etc., and deserves further investigation.

The radius of the first hydration shell of Na^+, K^+, and Cl^- is 0.32 nm, 0.36 nm, and 0.385 nm, respectively, as mentioned above, which is obtained from the first minimum value along the profile of radial distribution functions of ion–oxygen in bulk. The coordination number of each ion is estimated to be 6, 7, and 8 in the bulk respectively, which agree with previous study.[19] Figure 5 shows that the variation of the coordination number for Na^+ and K^+ along the axis of CNT under an electric field of 2 V/nm. Taking Na^+ as an example, it can be found that the coordination number is about 6 in the bulk water. However, it declines significantly as the ion approaches the mouth of the nanopore. When the electric fields are applied, the dehydrating process starts at about $z = 1.7$ nm, 0.3–0.4 nm away from the entrance of the pore. It might be worth mentioning that this distance is approximately equal to the radius of the first water shell. After the ion completely enters into the tube, the coordination number reduces to 3. Figure 6 shows the snapshots of dehydration of Na^+entering the CNT under an electric field of 2 V/nm (a movie is also provided in the supplemental file). The four pictures indicate the variation of hydrating water molecules as the ion enters the CNT. The reason for dehydrating is that the ions are imposed by an electrophoretic force under the electric fields, which pushes the ion to move towards the nanopore. When ions travel to the location around $z = 1.7$ nm, the first shell of hydrated water molecules just touches the mouth of the pore. Because the radius of the (6,6) CNT is smaller than the radius of the hydrated ion, the ion cannot pass through the fixed CNT. Therefore, the ion should overcome the energy barrier of dehydrating water and the existence of an electric field can help achieve this purpose. With the action of the pushing electrophoretic force and the obstacle of the CNT, some hydrated water molecules are peeled off. When the strength of the electric field is large enough, the ion will overcome the energy barrier and dehydrate adequate water molecules to make the radius fit the pore. As a result, the ion gets through the (6,6) CNT.

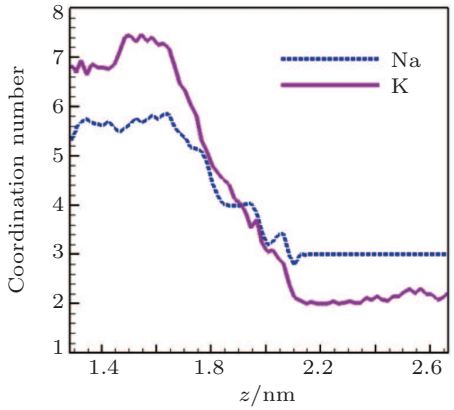


Fig. 5. (color online) Coordination number of K^+ under the electric field of 2 V/nm. The mouth of the CNT is located at $z = 2.0$ nm and the center of the CNT is located at $z = 2.675$ nm.

Another interesting phenomenon is that the coordination number for K^+ reduces more dramatically than that for Na^+. In the bulk, the potassium ion has the ability to attract more water molecules due to its larger radius in comparison to the sodium ions, and its hydrating energy E_h is relatively smaller according to $E_h \sim q^2/r_i$,[42] where q is the electrical charge of the ion, and r_i is the ionic radius. This implies that the water molecules around K^+ are easier to be peeled off under external forces. On the contrary, when they are located in the nanopore, the spatial confinement prevents the potassium ions, which have a larger radius, from attracting more

water molecules, resulting in the reduction of the coordination number inside the CNT.

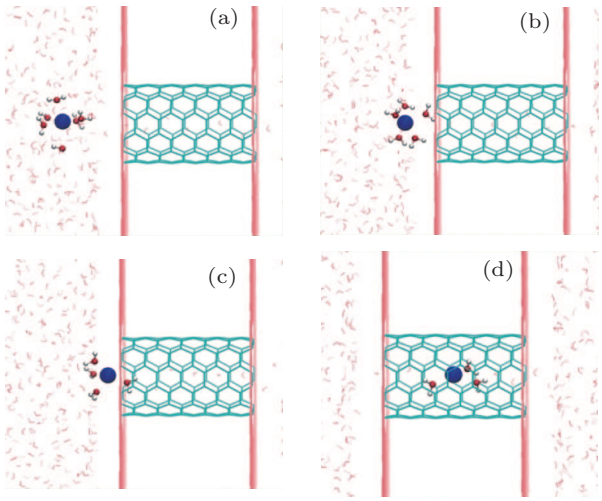


Fig. 6. (color online) Dehydrating process of Na^+ entering the CNT under $E = 2$ V/nm. (a) Ion is in the bulk water ($z = 1.363$ nm), and the hydration number is 6; (b) ion is ready to enter the CNT ($z = 1.664$), and the hydration number is 5; (c) ion is entering the CNT and a part of the ion is in the CNT ($z = 1.852$), and the hydration number is 4; (d) ion is totally in the CNT ($z = 2.675$), and the hydration number is 3.

4. Conclusion

By using the molecular dynamics simulations, we have demonstrated that the role of an electric field on the ions' transportation through a (6,6) CNT. Without the effect of an electric field, the ions are confronted with a significant energy barrier when they try to enter the (6,6) CNT. Due to the existence of the hydrated water molecules, the ion and water molecules are too large to pass through the (6,6) CNT. When the applied electric field is present, the ion is imposed by an electrophoretic force, which helps ions overcome the energy barrier. If the strength of the electric field is beyond a threshold value, some water molecules of the first water shell are peeled off due to the action of the pushing electrophoretic force when the ion moves to the access of the tube, then the ions are pushed into the CNT. Because of their properties, such as radius, hydrating energy, and interaction with the CNT, the thresholds for different ions are diverse. To pass through the (6,6) CNT, Na^+ needs an electric field of 1.8 V/nm, K^+ needs an electric field of 1.4 V/nm, and Cl^- requires an electric field of -1.4 V/nm. This mechanism of thresholds might provide a potential approach for ion selectivity and is expected to be applied in nanotechnology.

References

[1] Besteman K, Lee J O, Wiertz F G M, Heering H A and Dekker C 2003 *Nano Lett.* **3** 727
[2] Ouyang F P, Peng S L, Zhang H, Weng L B and Xu H 2011 *Chin. Phys. B* **20** 058504
[3] Chen X, Tam U C, Czlapinski J L, Lee G S, Rabuka D, Zettl A and Bertozzi C R 2006 *J. Am. Chem. Soc.* **128** 6292
[4] Kam N W S, O'Connell M, Wisdom J A and Dai H 2005 *Proc. Natl. Acad. Sci. USA* **102** 11600
[5] Kalra A, Garde S and Hummer G 2003 *Proc. Natl. Acad. Sci.* **100** 10175
[6] Hummer G, Rasaiah J C and Noworyta J P 2001 *Nature* **414** 188
[7] Gong X J and Fang H P 2008 *Chin. Phys. B* **17** 2739
[8] Park K H, Chhowalla M, Iqbal Z and Federico S 2003 *J. Biol. Chem.* **278** 50212
[9] Li Y, Zheng L P, Zhang W, Xu Z J, Ren C L, Huai P and Zhu Z Y 2011 *Chin. Phys. Lett.* **28** 066101
[10] Holt J K, Park H G, Wang Y, Stadermann M, Artyukhin A B, Grigoropoulos C P, Noy A and Bakajin O 2006 *Science* **312** 1034
[11] Wang J, Zhu Y, Zhou J and Lu X H 2004 *PCCP* **6** 829
[12] Striolo A 2006 *Nano Lett.* **6** 633
[13] Dinadayalane T, Murray J S, Concha M C, Politzer P and Leszczynski J 2010 *J. Chem. Theory Comput.* **6** 1351
[14] Beu T A 2010 *J. Chem. Phys.* **132** 164513
[15] Beu T A 2011 *J. Chem. Phys.* **135** 044515
[16] Beu T A 2011 *J. Chem. Phys.* **135** 044516
[17] Corry B 2008 *J. Phys. Chem. B* **112** 1427
[18] Liu H, Murad S and Jameson C J 2006 *J. Chem. Phys.* **125** 084713
[19] Song C and Corry B 2009 *J. Phys. Chem. B* **113** 7642
[20] Liu H, Jameson C J and Murad S 2008 *Mol. Simulat.* **34** 169
[21] Gong X, J. Xu L K, Wang J and Yang H 2010 *J. Am. Chem. Soc.* **132** 1873
[22] Zhang Y and Voth G A 2011 *J. Chem. Theory Comput.* **7** 2277
[23] Dietzel D, Faucher M, Iaia A, Aime J, Marsaudon S, Bonnot A, Bouchiat V and Couturier G 2005 *Nanotechnology* **16** S73
[24] Hess B, Kutzner C, van der Spoel D and Lindahl E 2008 *J. Chem. Theory Comput.* **4** 435
[25] MacKerell A D, Bashford D, Bellott M, Dunbrack R, Evanseck J, Field M J, Fischer S, Gao J, Guo H and Ha S A 1998 *J. Phys. Chem. B* **102** 3586
[26] Gong X, Li J, Zhang H, Wan R, Lu H, Wang S and Fang H 2008 *Phys. Rev. Lett.* **101** 257801
[27] Xiu P, Zhou B, Qi W, Lu H, Tu Y and Fang H 2009 *J. Am. Chem. Soc.* **131** 2840
[28] Darden T, York D and Pedersen L 1993 *J. Chem. Phys.* **98** 10089
[29] Saitta A M, Saija F and Giaquinta P V 2012 *Phys. Rev. Lett.* **108** 207801
[30] Rothfuss C J, Medvedev V K and Stuve E M 2003 *J. Electroanal. Chem.* **554** 133
[31] Stuve E M 2012 *Chem. Phys. Lett.* **519** 1
[32] Geissler P L, Dellago C, Chandler D, Hutter J and Parrinello M 2001 *Science* **291** 2121
[33] Yang K L, Yiacoumi S and Tsouris C 2002 *J. Chem. Phys.* **117** 337
[34] Park S, Khalili-Araghi F, Tajkhorshid E and Schulten K 2003 *J. Chem. Phys.* **119** 3559
[35] Liu Z, Xu Y and Tang P 2006 *J. Phys. Chem. B* **110** 12789
[36] Jarzynski C 1997 *Phys. Rev. Lett.* **78** 2690
[37] Shao Q, Zhou J, Lu L, Lu X, Zhu Y and Jiang S 2009 *Nano Lett.* **9** 989
[38] Bratko D, Daub C D, Leung K and Luzar A 2007 *J. Am. Chem. Soc.* **129** 2504
[39] Hu G H, Xu A J, Xu Z and Zhou Z W 2008 *Phys. Fluids* **20** 102101
[40] Xu Z, Hu G H, Wang Z L and Zhou Z W 2014 *Appl. Math. Mech.* **35** 1
[41] Xu Z, Hu G H, Wang Z L and Zhou Z W 2014 *Appl. Math. Mech.* **35** 5
[42] Burgess J 1978 *Metal Ions in Solution* (Ellis Horwood) p. 181