Nano watermill driven by revolving charge*

Zhou Xiao-Yan(周晓艳)[a)b)], Kou Jian-Long(寇建龙)[b)], Nie Xue-Chuan(聂雪川)[c)], Wu Feng-Min(吴锋民)[a)b)†], Liu Yang(刘 扬)[d)‡], and Lu Hang-Jun(陆杭军)[b)§]

[a)] *Department of Physics and Institute of Theoretical Physics, Shanxi University, Taiyuan* 030006, *China*
[b)] *Department of Physics, Zhejiang Normal University, Jinhua* 321004, *China*
[c)] *Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai* 201800, *China*
[d)] *Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hong Kong* 999077, *China*

(Received 19 November 2014; revised manuscript received 13 February 2015; published online 29 May 2015)

A novel nanoscale watermill for the unidirectional transport of water molecules through a curved single-walled carbon nanotube (SWNT) is proposed and explored by molecular dynamics simulations. In this nanoscale system, a revolving charge is introduced to drive a water chain confined inside the SWNT, the charge and the tube together serving as a nano waterwheel and nano engine. A resonance-like phenomenon is found, and the revolving frequency of the charge plays a key role in pumping the water chain. The water flux across the SWNT increases with respect to the revolving frequency of the external charge and it reaches its maximum when the frequency is 4 THz. Correspondingly, the number of hydrogen bonds in the water chain inside the SWNT decreases dramatically as the frequency increases from 4 THz to 25 THz. The mechanism behind the resonance phenomenon has been investigated systematically. Our findings are helpful for the design of nanoscale fluidic devices and energy converters.

Keywords: water pumping, molecular dynamics simulations, carbon nanotube, revolving charge

PACS: 47.60.–i, 47.11.Mn, 83.10.Mj **DOI:** 10.1088/1674-1056/24/7/074702

1. Introduction

Actuation of a fluid flow in nanopores is of fundamental importance for progress in the design and utilization of novel nanofluidic devices, machines and sensors, which have a broad prospect of use in industrial applications, including nanofiltration, water purification, and hydroelectric power generation.[1–6] In fact, not only the externals of our daily life but also biological life itself depends on the transport of water through pipes, capillaries, and protein channels, controlled by pumps, valves, and gates.[7–14] Fluid pumping is an essential function of a nanofluidic system.[15] It has been recognized that the active transport of water through nanopores is technically difficult, or even impossible, using conventional methods due to the large surface to volume ratio, although there are various kinds of devices applied to conveniently pump water on a macroscopic level. Therefore, it is crucial to develop effective water pumping devices that can make a continuous unidirectional water flow on the nanoscale.

Over the last two decades, the field of nanofluidics has seen rapid development.[16,17] Various novel concepts and blueprints for nanoscale pumps based on carbon nanotubes have been proposed,[3,18–29] because the use of carbon nanotubes for the fabrication of nanofluidic devices has a number of attractive features.[30–32] In 1999, Král *et al.* proposed a laser-driven pump for atomic transport through carbon nanotubes.[33] A laser is applied to excite an electric current in the carbon nanotube, which drives intercalated atoms by a wind-like force. The experiments that followed have demonstrated that nanoparticles of iron inside the carbon nanotubes can be driven in the direction of the electron flow by electromigration force.[34] By using molecular dynamics simulation, Insepov *et al.* found that the gas inside the carbon nanotube can be driven by the Rayleigh surface wave.[3] Nanoscopic propellers, designed by robust macroscopic principles and possessing "chemically tunable" blades, were introduced by Wang and Král to pump solvent molecules.[35] In 2012, a rotary nano ion pump, inspired by the F_0 part of F_0F_1-ATP synthase biomolecular motor was investigated by molecular dynamics simulation.[36] The simulation results demonstrated that an ion gradient would be generated between the two sides of the nanopump when the rotor of the nanopump rotated mechanically. Duan *et al.* used a small portion of the initially twisted wall of a carbon nanotube to function as an energy pump for transportation of water molecules.[23] Using molecular dynamics simulations, Chang demonstrated that a domino wave along the longitudinal direction of the tube can be developed. The molecules inside the single-walled carbon nanotube (SWNT) can be pumped by a domino wave.[37] Ma's

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11005093 and 61274099), the Research Fund of Education Department of Zhejiang Province, China (Grant No. Y201223336), the Zhejiang Provincial Science and Technology Key Innovation Team, China (Grant No. 2011R50012), the Key Laboratory of Zhejiang Province, China (Grant No. 2013E10022), and the Hong Kong Polytechnic University, China (Grant No. G-YL41).

†Corresponding author. E-mail: wfm@zjnu.cn
‡Corresponding author. E-mail: yang.liu@polyu.edu.hk
§Corresponding author. E-mail: zjlhjun@zjnu.cn

© 2015 Chinese Physical Society and IOP Publishing Ltd

group demonstrated that water can be pumped by a revolving chiral carbon nanotube.[25] In addition, progress in moving water has been made by designing systems with an imbalance of surface tension or a chemical or thermal gradient,[24,38–40] but it is still difficult to make a controllable continuous unidirectional water flow.[22]

Recently, various nanopumps driven by electric fields or electric current have been proposed.[18–20,41–43] Král and Shapiro[44] predicted that electric current can be generated in metallic carbon nanotubes immersed in liquids flowing along them, which is consistent with the subsequent experimental results of Ghosh *et al.* which were described two years later.[45] Inspired by this result, Sun *et al.* demonstrated experimentally that a water flow can also be driven by the applied current of an SWNT.[1] In our previous work, we proposed nano water pumps based on a ratchet-like mechanism without osmotic pressure or hydrostatic drop.[27,39,46]

In this paper, we propose a novel blueprint for a nano watermill by numerical simulations, wherein a revolving charge serves as the waterwheel. Experimentally, the revolving charge can be achieved by an array of electrodes with a certain mode or by some molecular rotors.[47,48] It is noted that molecular rotors with a fixed off-center rotation axis have recently been observed by a scanning tunneling microscope.[49] Moreover, several fabrication methods for nanofluidic channels and nanotubes have been developed.[50,51] In fact, our idea is inspired by these experimental successes. We found that the continuous directional water flux can be pumped effectively by a revolving charge. The revolving frequency of the external charge plays a key role in water transportation. An interesting resonance was found where the water flux peaks at $f = 4$ THz. However, the water chain confined inside the SWNT is disturbed and the hydrogen bonds between them are ruptured. Therefore, the number of hydrogen bonds decreases dramatically. The mechanism behind the resonant phenomenon has been investigated systematically. Our simulation results demonstrate that a nano watermill can conveniently convert the energy of the revolving charge into the transport of the water molecules inside the curved carbon nanotube.

2. Methodology

The simulation framework is illustrated in Fig. 1. Membranes were created by two carbon sheets separated by a distance of 2.7 nm. A curved (6, 6) SWNT with 8.1-Å diameter was embedded in the membranes along the z direction, as shown in Fig. 1. The curvature radius of the SWNT is 1.755 nm. A positive charge with a quantity of q $(= +e)$ is introduced outside the tube. It rotates in a circle of radius r $(= 1.0$ nm) with a constant angular velocity ω. The radial distance of the circle's central point O from the carbon tube wall is 1.35 nm. To keep the simulation system electronically neutral, a contrary charge $-q$ is assigned close to the boundary.

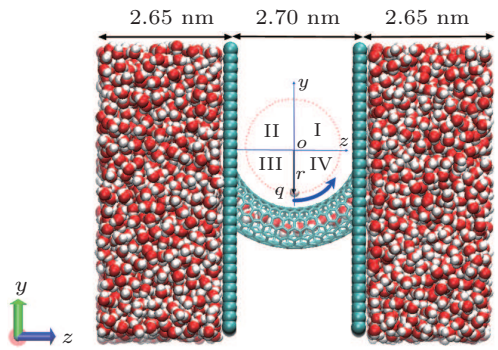


Fig. 1. (color online) Sectional view of the simulation framework: the charge (white ball) q rotates around the origin O with radius r = 1.0 nm. The carbon nanotube with 8.1-Å diameter and two carbon sheets is shown in light blue. Water molecules are depicted in VDW representation (image created with VMD [1.8.7]).

MD simulations were performed with GROMACS 4.0.7[52,53] at a constant volume with the initial box size dimensions of $L_x = 6$ nm, $L_y = 6$ nm, $L_z = 8$ nm, and a temperature of 300 K for 100 ns. Periodic boundary conditions were applied in all directions. The simulation box contains 8317 water molecules, which are modeled by using the TIP3P model.[54] A time step of 2 fs was adopted when the revolving frequency is less than 10 THz and 1 fs was adopted for other frequencies. Simulation data were collected every 1 ps. The last 95 ns were collected for analysis. The carbon nanotube is regarded as a large molecule. The total potential energy function of CNT can be expressed in the form:

$$V_{\text{total}} = \sum_{\text{VDW}} 4\varepsilon_{\text{CC}}\left[\left(\frac{\sigma_{\text{CC}}}{r}\right)^{12} - \left(\frac{\sigma_{\text{CC}}}{r}\right)^{6}\right] + \sum_{\text{bond}} \frac{1}{2}k_b(r - r_0)^2 + \sum_{\text{angles}} \frac{1}{2}k_\theta(\theta - \theta_0)^2 + \sum_{\text{dihedrals}} \frac{1}{2}k_\xi(\xi - \xi_0)^2,$$

where $\sigma_{\text{CC}} = 0.34$ nm, $\varepsilon_{\text{CC}} = 0.3612$ kJ·mol^{-1}, bond length of $r_0 = 0.142$ nm, bond angle of $\theta_0 = 120^\circ$, the spring constant of $k_{\text{b}} = 393960$ kJ·mol^{-1}·nm^{-2} and $k_\theta = 527$ kJ·mol^{-1}·deg^{-2}, $k_\xi = 52.718$ kJ·mol^{-1}·deg^{-2}. The Lennard–Jones parameters for the interaction between a carbon atom and the water oxygen are $\varepsilon_{\text{CO}} = 0.4802$ kJ·mol^{-1} and $\sigma_{\text{CO}} = 0.3275$ nm. With periodic boundary conditions, long range electrostatic interactions with a cutoff for real space of 1.4 nm were computed by using a particle-mesh Ewald method. In each simulation, the carbon sheets are fixed.

3. Results and discussion

To study the directional transport of the water through the curved SWNT, driven by a revolving charge, we define flux as the difference between the number of water molecules leaving from the left end and the right end (again, having entered from the opposite end) per nanosecond.

Figure 2 shows the water flux and the average number of water molecules inside the curved nanotube as functions of the revolving frequency of the charge. For $f = 50$ GHz, the curved SWNT is occupied by about 12 water molecules, which is determined by local excess chemical potential.[30] Water molecules not only penetrate into but are also conducted through the SWNT. The water flux is about 2.35 water molecules per nanosecond through the nanotube. This value is comparable to the measured 3.9 ns^{-1} for aquaporin-1.[55] From Fig. 2, we can see that the net flux is very sensitive to the revolving frequency f. It increases remarkably to 10.6 ns^{-1} when the frequency f increases from about 0.05 THz to 4 THz. This maximum value is about four times the water flux (about 2.35) at $f = 0.05$ THz. Interestingly, there are two peaks, at $f_1 = 4$ THz and $f_2 = 12.5$ THz. Correspondingly, the average number of water molecules inside the curved SWNT decreases dramatically to about 5, indicating that the single file of water chain is disturbed dramatically. The net flux decreases sharply when the frequency is larger than f_2. Surprisingly, the average number of water molecules inside the curved SWNT recovers to 12, indicating that the curved SWNT is again filled by water molecules. Moreover, the direction of the flux even reverses at $f = 25$ THz. The critical frequency of the single-file water chain can be determined by using the relation $E_{HB} = m\omega^2 A^2/2$, where E_{HB} is the binding energy of the hydrogen bond, m is the mass of the water molecule, and A is the amplitude of allowed radial motion. The value of E_{HB} is about 16 kcal/mol and the amplitude is about 0.3–0.9 Å.[56] The classical resonant frequency of the water chain inside the (6, 6) SWNT is estimated to lie between 4.8 THz and 14.5 THz. Our simulation results show that the water flux peaks at $f_1 = 4$ THz and $f_2 = 12.5$ THz, which is in good accord with the theoretical values and results in the previous work.[56,57]

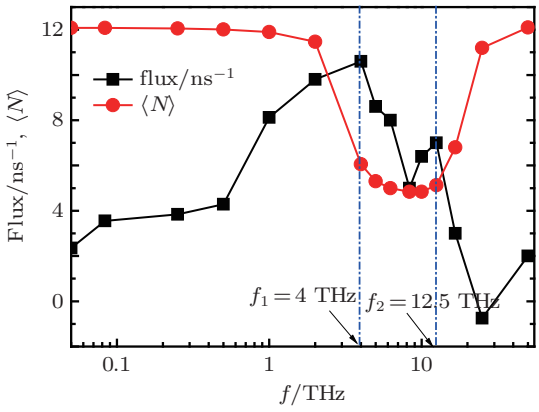


Fig. 2. (color online) Water flux and average number of water molecules N inside the curved SWNT as functions of the revolving frequency f of the external charge.

Water molecules are connected by hydrogen bonds inside the SWNT, which are shielded from fluctuations in the bulk water. Hydrogen bonds are really a special case of dipole forces,[58] and they play a key role in the molecular transportation through the nanotube. Here, we focus on the hydrogen bonds connecting between the water molecules inside the SWNT. A geometric definition of hydrogen bonds is adopted. A water pair is hydrogen-bonded if the O–O distance is less than 3.5 Å and simultaneously the bonded O–H···O angle is less than 30°.

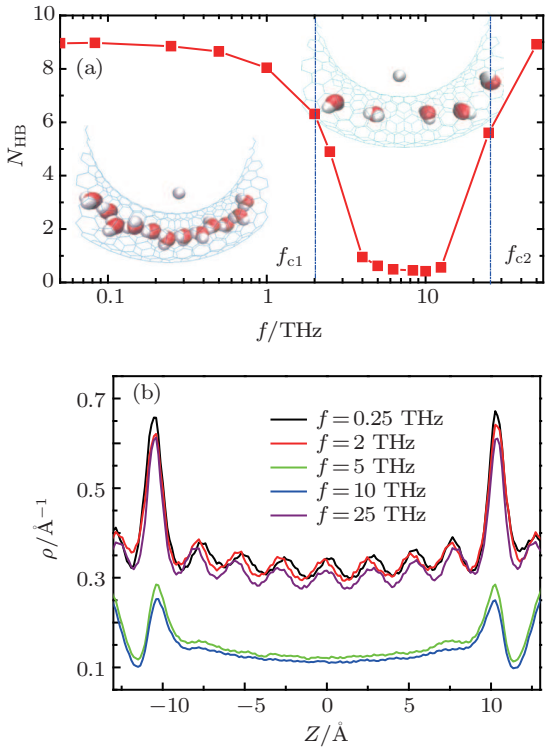


Fig. 3. (color online) (a) Average number of the hydrogen bonds inside the curved SWNT for different rotation frequencies. (b) Water density distributions inside the nanotube along the z axis under different rotation frequencies.

The average number of hydrogen bonds (shown in Fig. 3(a)), denoted by N_{HB}, shows the same trend as the average number of water molecules inside the tube (shown in Fig. 2): it decreases very slowly for $f < f_{c1} = 2$ THz. The average number of water molecules is about 12 and the average number of hydrogen bonds is about nine in the range of $f < f_{c1}$. The average number of water molecules and hydrogen bonds are both almost unchanged, indicating that the single-file water chain inside the SWNT is affected slightly by the external revolving charge. Furthermore, from Fig. 3(b), we can see a wavelike pattern of the water density distribution along the z direction. The wavelike pattern is sharp near the ends of the curved SWNT. However, when f_{c1} $(= 2$ THz$) < f < f_{c2}$ $(= 25$ THz$)$, the average number of water molecules decreases dramatically to about five. Correspondingly, the average number of hydrogen bonds, N_{HB}, decreases sharply to 0.5. All of the hydrogen bonds are almost disrupted by the revolving charge. The water molecules transport across the nanotube individually, not collectively. As shown in Fig. 3(b), the

wavelike pattern of water density distribution is quite flat near the center of the nanotube. Surprisingly, when the frequency is larger than 25 THz, N_{HB} increases with the frequency. In the range of $f > f_{c2}$, N_{HB} increases sharply to nine. The wavelike pattern of water density distribution again becomes obvious. The influence of the charge rotation on the structure of the water chain becomes negligible.

Formations and ruptures of hydrogen bonds occur not only in water but also in some alcohols and their aqueous solutions. We have also conducted simulations to study the effect of revolving charge on the behavior of methanol confined inside a carbon nanotube. We found a similar resonance phenomenon. However, a downshift of the critical frequencies is found for the methanol system compared to the water system. This is due mainly to the different strengths of their hydrogen bonds and their molecular mass. Water is a strongly polar molecule, while methanol is intermediate between nonpolar and strongly polar molecules.[59]

To understand the mechanism behind the nano water pump, we calculated the water charge interaction energies for different frequencies of the revolving charge. Because the external charge rotates around the center point O, the position of the charge can conveniently be depicted by the angle θ, as shown in Fig. 1. That is, θ is the angle between the position vector $\boldsymbol{r}$ of the revolving charge and the z axis. The size of the angle, θ, is measured in degrees. At time $t = 0$, the point charge is on the reference line (z axis). The axes (y and z) of a two-dimensional Cartesian system divide the plane into four regions, which are called quadrants. When $0 < \theta < 90°$, the point charge is located in the first quadrant, denoted by I. Similarly, the other three quadrants are denoted by II, III, and IV, respectively (see Fig. 4).

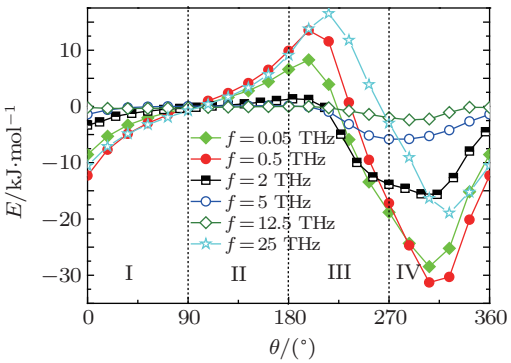


Fig. 4. (color online) The interaction energies between the revolving charge and the water molecules inside the curved SWNT for different frequencies.

From Fig. 4, we can find that the profile of interaction energy is asymmetrical. When the revolving charge moves through quadrant I, the interaction energies are negative, indicating that the charge drags water molecules inside the SWNT. The attractive energies decrease with θ due to the increase of the distance between the charge and the water molecules. The distance reaches its maximum when θ is 90°, resulting in the charge–water interaction energies decreasing to about zero. In contrast, interaction energies increase and become positive in quadrant II, indicating that the revolving charge pushes water molecules through the carbon nanotube. Furthermore, $180° < \theta < 225°$, the majority of the interaction energies are positive, because the dipoles of the water molecules inside the SWNT cannot flip synchronously. When $\theta > 225°$, the interaction energies between the charge and water molecules inside the SWNT become negative. However, the peaks do not appear when $\theta = 270°$, in which the average distance between the charge and the water molecules inside the SWNT decreases to its minimum. Therefore, the pumping effect is attributed to the asymmetrical interaction energy acting on the water molecules inside the nanotube.

The profiles of the interaction energies depend on the revolving frequency of the charge. When $f < f_{c1}$ or $f > f_{c2}$, the interaction energies vary obviously with the θ (or the position of the point charge). In the range of $f_{c1} < f < f_{c2}$, the interaction energies become weak because the average number of water molecules inside the SWNT decreases dramatically.

4. Conclusions

In the present work, we design a novel nanopump with a SWNT and a revolving charge outside. We have shown the excellent pumping effect of this water pump. The net flux increases rapidly with the frequency of the revolving charge. An interesting resonance phenomenon is found. As $f = 4.0$ THz, the net flux reaches 10.6 ns^{-1}, which is about three times the measured 3.9 ns^{-1} for AQP. We find that the remarkable pumping effect is attributable to the asymmetric interaction energy acting on the water-chain inside the nanochannel. When the revolving charge moves into quadrants III and IV, the interaction acting on the water chain is strong enough to drag the water chain across the right outlet of the SWNT. Then, when the charge moves into regions I and II, the interaction is so weak that it is difficult to push the water chain toward the left entrance. Interestingly, we found that the single-file water chain remains in good order even the frequency of the charge rotation reaches a large value of 1.5 THz. Our design is expected to have a number of implications in nanotechnology, such as hydroelectric power converters, fluid separation, drug delivery, and sensor applications.

Acknowledgments

We thank Fang Hai-Ping and Zhou Ru-Hong for helpful discussion.

References

[1] Zhao Y, Song L, Deng K, Liu Z, Zhang Z, Yang Y, Wang C, Yang H, Jin A, Luo Q, Gu C, Xie S and Sun L 2008 *Adv. Mater.* **20** 1772
[2] Darhuber A A and Troian S M 2005 *Annu. Rev. Fluid Mech.* **37** 425
[3] Insepov Z, Wolf D and Hassanein A 2006 *Nano Lett.* **6** 1893
[4] Holt J K, Park H G, Wang Y M, Stadermann M, Artyukhin A B, Grigoropoulos C P, Noy A and Bakajin O 2006 *Science* **312** 1034
[5] Shannon M A, Bohn P W, Elimelech M, Georgiadis J G, Marinas B J and Mayes A M 2008 *Nature* **452** 301
[6] Yuan Q and Zhao Y P 2009 *J. Am. Chem. Soc.* **131** 6374
[7] Tyree M T 2003 *Nature* **423** 923
[8] Tornroth-Horsefield S, Wang Y, Hedfalk K, Johanson U, Karlsson M, Tajkhorshid E, Neutze R and Kjellbom P 2006 *Nature* **439** 688
[9] Tajkhorshid E, Nollert P, Jensen M O, Miercke L J W, O'Connell J, Stroud R M and Schulten K 2002 *Science* **296** 525
[10] Murata K, Mitsuoka K, Hirai T, Walz T, Agre P, Heymann J B, Engel A and Fujiyoshi Y 2000 *Nature* **407** 599
[11] Su J and Guo H 2012 *J. Phys. Chem. B* **116** 5925
[12] Ku D N 1997 *Annu. Rev. Fluid. Mech.* **29** 399
[13] He J X, Lu H J, Liu Y, Wu F M, Nie X C, Zhou X Y and Chen Y Y 2012 *Chin. Phys. B* **21** 054703
[14] Zhou X Y and Lu H J 2007 *Chin. Phys.* **16** 335
[15] Wang X Y, Cheng C, Wang S L and Liu S R 2009 *Microfluid. Nanofluid.* **6** 145
[16] Liu Z, Zhao Y C and Sun L F 2010 *Physics* **4** 251 (in Chinese)
[17] Fang H P and Tu Y S 2010 *Physics* **2** 002 (in Chinese)
[18] Joseph S and Aluru N R 2008 *Phys. Rev. Lett.* **101** 064502
[19] Rinne K F, Gekle S, Bonthuis D J and Netz R R 2012 *Nano Lett.* **12** 1780
[20] Wang Y, Zhao Y J and Huang J P 2011 *J. Phys. Chem. B* **115** 13275
[21] Qiu H, Shen R and Guo W 2011 *Nano Res.* **4** 284
[22] Gong X J, Li J Y, Lu H J, Wan R Z, Li J C, Hu J and Fang H P 2007 *Nat. Nanotechol.* **2** 709
[23] Duan W H and Wang Q 2010 *ACS Nano* **4** 2338
[24] Zhang Z Q, Dong X, Ye H F, Cheng G G, Ding J N and Ling Z Y 2014 *J. Appl. Phys.* **116** 074307
[25] Feng J W, Ding H M, Ren C L and Ma Y Q 2014 *Nanoscale* **6** 13606
[26] De Luca S, Todd B D, Hansen J S and Daivis P J 2014 *Langmuir* **30** 3095
[27] Zhou X, Wu F, Kou J, Nie X, Liu Y and Lu H 2013 *J. Phys. Chem. B* **117** 11681
[28] Li X P, Kong G P, Zhang X and He G W 2013 *Appl. Phys. Lett.* **103** 143117
[29] De Luca S, Todd B, Hansen J and Daivis P J 2013 *J. Chem. Phys.* **138** 154712
[30] Hummer G, Rasaiah J C and Noworyta J P 2001 *Nature* **414** 188
[31] Joseph S and Aluru N R 2008 *Nano Lett.* **8** 452
[32] Noy A, Park H G, Fornasiero F, Holt J K, Grigoropoulos C P and Bakajin O 2007 *Nano Today* **2** 22
[33] Král P and Tománek D 1999 *Phys. Rev. Lett.* **82** 5373
[34] Svensson K, Olin H and Olsson E 2004 *Phys. Rev. Lett.* **93** 145901
[35] Wang B and Král P 2007 *Phys. Rev. Lett.* **98** 266102
[36] Lohrasebi A and Feshanjerdi M 2012 *J. Mol. Model.* **18** 4191
[37] Chang T 2008 *Phys. Rev. Lett.* **101** 175501
[38] Longhurst M and Quirke N 2007 *Nano Lett.* **7** 3324
[39] Kou J, Zhou X, Lu H, Xu Y, Wu F and Fan J 2012 *Soft Matter* **8** 12111
[40] Kou J, Mei M, Lu H, Wu F and Fan J 2012 *Phys. Rev. E* **85** 056301
[41] Vaitheeswaran S, Rasaiah J C and Hummer G 2004 *J. Chem. Phys.* **121** 7955
[42] Dzubiella J and Hansen J P 2005 *J. Chem. Phys.* **122** 234706
[43] Su J and Guo H 2011 *ACS Nano* **5** 351
[44] Král P and Shapiro M 2001 *Phys. Rev. Lett.* **86** 131
[45] Ghosh S, Sood A K and Kumar N 2003 *Science* **299** 1042
[46] Lu H, Nie X, Wu F, Zhou X and Kou J 2012 *J. Chem. Phys.* **136** 174511
[47] Seldenthuis J S, Prins F, Thijssen J M and van der Zant H S J 2010 *ACS Nano* **4** 6681
[48] Tierney H L, Murphy C J, Jewell A D, Baber A E, Iski E V, Khodaverdian H Y, McGuire A F, Klebanov N and Sykes E C H 2011 *Nat Nano* **6** 625
[49] Gao L, Liu Q, Zhang Y, Jiang N, Zhang H, Cheng Z, Qiu W, Du S, Liu Y and Hofer W 2008 *Phys. Rev. Lett.* **101** 197209
[50] Maleki T, Mohammadi S and Ziaie B 2009 *Nanotechnology* **20** 105302
[51] Park S, Vosguerichian M and Bao Z 2013 *Nanoscale* **5** 1727
[52] Hess B, Kutzner C, van der Spoel D and Lindahl E 2008 *J. Chem. Theory Comput.* **4** 435
[53] Lindahl E, Hess B and van der Spoel D 2001 *J. Mol. Model.* **7** 306
[54] Jorgensen W L, Chandrasekhar J, Madura J D, Impey R W and Klein M L 1983 *J. Chem. Phys.* **79** 926
[55] Zeidel M, Ambudkar S, Smith B and Agre P 1992 *Biochemistry* **31** 7436
[56] Zhang Q L, Jiang W Z, Liu J, Miao R D and Sheng N 2013 *Phys. Rev. Lett.* **110** 254501
[57] Lu H J, Gong X J, Wang C L, Fang H P and Wang R Z 2008 *Chin. Phys. Lett.* **25** 1145
[58] Li X Z, Walker B and Michaelides A 2011 *Proc. Natl. Acad. Sci. USA* **108** 6369
[59] Pagliai M, Cardini G, Righini R and Schettino V 2003 *J. Chem. Phys.* **119** 6655