Ion transport through a graphene nanopore

Guohui Hu\textsuperscript{1}, Mao Mao\textsuperscript{2} and Sandip Ghosal\textsuperscript{2}

\textsuperscript{1} Shanghai Institute of Applied Mathematics and Mechanics, Shanghai Key Laboratory of Mechanics in Energy Engineering, Modern Mechanics Division, E-Institutes of Shanghai Universities, Shanghai University, 149 Yanchang Road, Shanghai 200072, People’s Republic of China
\textsuperscript{2} Department of Mechanical Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA

E-mail: s-ghosal@northwestern.edu

Received 8 June 2012, in final form 17 August 2012
Published 7 September 2012
Online at stacks.iop.org/Nano/23/395501

Abstract

Molecular dynamics simulation is utilized to investigate the ionic transport of NaCl in solution through a graphene nanopore under an applied electric field. Results show the formation of concentration polarization layers in the vicinity of the graphene sheet. The nonuniformity of the ion distribution gives rise to an electric pressure which drives vortical motions in the fluid if the electric field is sufficiently strong to overcome the influence of viscosity and thermal fluctuations. The relative importance of hydrodynamic transport and thermal fluctuations in determining the pore conductivity is investigated. A second important effect that is observed is the mass transport of water through the nanopore, with an average velocity proportional to the applied voltage and independent of the pore diameter. The flux arises as a consequence of the asymmetry in the ion distribution which can be attributed to differing mobilities of the sodium and chlorine ions and to the polarity of water molecules. The accumulation of liquid molecules in the vicinity of the nanopore due to re-orientation of the water dipoles by the local electric field is seen to result in a local increase in the liquid density. Results confirm that the electric conductance is proportional to the nanopore diameter for the parameter regimes that we simulated. The occurrence of fluid vortices is found to result in an increase in the effective electrical conductance.

(Some figures may appear in colour only in the online journal)

1. Introduction

Ionic conduction through nanometre-sized channels or pores is a common theme in biological systems as well as in various manufactured materials such as membranes and synthetic nanopores [1–6]. Theoretical as well as experimental aspects of the problem have attracted increasing interest in the past decade. Molecular dynamics (MD) simulation is an effective tool for exploring these nanoscale phenomena. It has the advantage of being able to relate the observables directly to the molecular properties of the solid and liquid, once an appropriate intermolecular potential is given, without the need for too many simplifying assumptions. Various aspects of the problem, such as ionic current rectification, DNA translocation and water transport have already been reported in the literature [7–12].

MD simulations in the context of translocation of single stranded and double stranded DNA through biological α-Haemolysin and synthetic nanopores have been reported [13, 8, 9, 14]. It was found that the open-pore current increases linearly with the applied voltage, and obeys Ohm’s law for voltages that are no more than of the order of a volt. The distribution of the electric potential around the pore, the translocation speed of DNA, the interactions between the DNA molecule and the pore wall, as well as strategies for controlling the translocation speed have been considered [15, 16]. Recently, Sathe \textit{et al} [11] investigated the translocation of DNA through a graphene nanopore using MD simulations,
and suggested that nucleotide pairs can be discriminated using graphene nanopores under suitable bias conditions.

There are, however, a number of open problems that have not been understood. First, due to the geometry of the system, the ions may accumulate and form a concentration polarization layer (CPL) in the vicinity of the membrane. The influence of the nonuniformity of the ion concentration in this charged separated Debye layer on the ionic current has not been well understood. Secondly, open questions remain on the effect of hydrodynamic flow on the ionic current as well as on DNA translocation speeds. Ghosal [17, 18] presented a simple hydrodynamic calculation for the electrophoretic speed of the polymer, modelled locally as a long cylindrical object centred on the axis of the pore. The calculation yielded analytical results in close agreement with experimental measurements [19, 20]. In a related problem where the electrophoretic force was measured with the DNA immobilized in the pore, numerical [21] as well as analytical [22] models based on the hypothesis that the hydrodynamic drag was the primary resistive force yielded results in close agreement with the experiments. These results point to the possibility that hydrodynamics might play an important role in determining DNA translocation speeds. Hydrodynamics also plays an important role in a related problem; when a direct current is applied across an ion-selective nanoporous membrane or through a nanochannel with overlapping Debye layers, it is known that micro-fluid vortices may be observed due to hydrodynamic instability, and these vortices are capable of enhancing the ionic current in the so called ‘overlimiting regime’ [23].

The purpose of the present study is to discuss the influence of the CPL and fluid convection on ionic transport through nanochannels using MD simulations. The rest of this paper is organized as follows: in section 2, we present the physical model and describe the numerical approach. The simulation results are analysed in detail in section 3. Finally, some concluding remarks are made in section 4.

2. Method

2.1. System setup

The molecular simulations are conducted in a cubic box with dimensions of $L_x=5.112$ nm, $L_y=5.184$ nm, $L_z=10$ nm. The origin of the coordinates is set in the centre of the box. The graphene sheet with the size of $L_x \times L_y$, consists of an array of carbon atoms with a planar hexagonal structure (neighbouring atoms have a bond lengths of 0.142 nm), localized at the mid-plane, $z=0$. A nanopore, with radius $a$, is constructed by removing the carbon atoms in a central circular patch of the graphene sheet: $x^2+y^2 < a^2$. The remainder of the box is then filled with water molecules described by the extended simple point charge (SPC/E) model [24]. Polarization of water molecules is neglected, prior investigations have shown that this is reasonable as long as the field strength does not exceed about 10 V nm$^{-1}$ [25]. Salt (NaCl) is introduced at a given concentration of 1 M by replacing the required number of water molecules with Na$^+$ and Cl$^-$ ions.

2.2. Molecular dynamics (MD) simulation

The simulations are performed at a constant temperature 300 K and pressure of 1 bar with the large scale MD package GROMACS 4.5.4 [26]. The van der Waals (vdW) interaction of the carbon atoms is modelled as uncharged Lennard-Jones (LJ) particles. The graphene–water interaction is considered by a carbon–oxygen LJ potential. This general set up and parameter values have been employed in previous studies [27–29].

A sketch of the computational setup of the present simulations is depicted in figure 1. A uniform external electric field is applied in directions perpendicular to the graphene sheet ($z$-direction). The contributions of the external electric field are described as $U_i = -\sum q_i \mathbf{r}_i \cdot \mathbf{E}$, where the $q_i$ and $\mathbf{r}_i$ denote the charge and location of the charged atoms $i$ respectively, and $\mathbf{E}$ is the strength of the external electric field. The LJ interactions are truncated at the cut-off distance $r_0 = 1.0$ nm and the particle mesh Ewald (PME) method [30] with a real-space cut-off of 1 nm is utilized to treat the long-range electrostatic interactions. Periodic boundary conditions are imposed in all directions. The time step in all simulations is set to 2 fs.

For the sake of computational efficiency, all of the carbon atoms are frozen during the simulations [12]. Previous investigations have shown that this only has a minor influence on the dynamics of the adjacent water [31, 32]. Further, although edge dynamics [33], partial charges [34], or out-of-plane displacement [35] might affect the ionic and water transport, following Suk and Aluru [12], they are not considered in this study for the sake of simplicity. Minimization of energy is performed with the steepest descent method on the initial system. Then the system is evolved for 2 ns to achieve a state of statistical equilibrium. In all cases, statistics are collected during the last 8 ns and samples are taken every 0.2 ps.

2.3. Data analysis

To analyse the statistics of the macroscopic physical variables, the spatial location and velocity vectors of the particles are transformed to cylindrical coordinates. Data is presented in the $r$-$\phi$ plane, which is partitioned into gridded cells with interval range ($\Delta r$, $\Delta \phi$).

Ionic concentration. The number density of Na and Cl ions in the cells are calculated by $n_i = N_i/V_c$, where $N_i$ and $V_c$ are the number of ions and volume of the corresponding cell respectively.

Water flux. The number of oxygen atoms $N_w$ through the nanopore in time interval $\Delta t$ is calculated to obtain the water flux. The average water velocity $v_p$ in the axial direction through the nanopore is given by $v_p = mN_w/\Delta t\rho_0A$, in which $m$ is the mass of a water molecule, $\rho_0$ is water density in the bulk and $A = \pi a^2$ is the area of the nanopore.

Flow field. For the cell at $(r,z)$ containing $N_c$ water molecules, the transient local velocity vector can be obtained by

$$v(r, z, t) = \frac{1}{\Delta t N_c} \sum_{i=1}^{N_c} \left[ \mathbf{r}_{Oi}(t + \Delta t) - \mathbf{r}_{Oi}(t) \right]$$ (1)
where $\mathbf{r}_i(t_j)$ is the location vector of oxygen atom \(i\) at time \(t_j\). \(\Delta t\) is the time interval between two successive frames. We take \(\Delta t = 2\) ps in the present study. The velocity field \(\mathbf{v}(r, z)\) of the equilibrium state is then calculated by averaging the transient velocity over time. To check the independence of physical quantities with respect to grid size, the probability density function (PDF) of the axial velocity \(v^O_z\) of water at \((0, 0)\) is plotted in figure 2 for different grid sizes. After determining the average velocity \(\bar{v}^O_z\) and standard error \(\sigma\), it is seen that the PDF is well represented by a Gaussian:

$$P(v^O_z) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[ -\frac{(v^O_z - \bar{v}^O_z)^2}{2\sigma^2} \right]. \quad (2)$$

Furthermore, the PDFs are nearly independent of the computational grid size. In the present study, we set \(\Delta z = 0.2\) nm.

**Ionic current.** The ionic current is obtained by \(I = eN_i/\Delta t\), where \(N_i\) stands for the number of Na or Cl ions across the graphene nanopore in time interval \(\Delta t\), \(e\) is the amount of charge per electron.

### 3. Results and discussions

#### 3.1. Concentration polarization

If the pore size approaches zero, clearly a polarized double layer would form adjacent to the graphene sheet. For a finite, but nevertheless sufficiently small pore size, a nonuniform ion distribution (concentration polarization) is expected adjacent to the sheet. The profiles of ionic number density along \(z\)-axis are plotted in figure 3, where \(z = 0\) corresponds to the graphene sheet. It is interesting that the sodium and chlorine ions both form concentration polarization layers (CPL) on either side of the graphene sheet. However, their distributions show some asymmetry. Due to size exclusion, the ions cannot approach the graphene sheet closer than about an ionic radius. The combination of electrostatic and these steric forces result...
Figure 3. Number density profile of Na and Cl ions in the z-direction with $d = 1.5$ nm for different field strength, to show the presence of concentration polarization layer.

Figure 4. Nonuniform distributions of number density (in units of M) of chlorine (left panel) and sodium (right panel) ions with $d = 1.5$ nm and $E = 0.5$ V nm$^{-1}$. The grey rectangles at $z = 0$ mark the graphene sheet. Ionic gradients lead to electric pressure, which drives nanoscale vortices near the pore.

In the appearance of a concentration peak. In the case of the chlorine ions, the concentration peak is located a distance $D_{Cl} = 0.375$ nm from the sheet. This distance is found to be independent of the applied field strength. The CPL can also be observed for the sodium ions on the other side; however, the amplitude of the peak is comparatively weak. For weak applied fields (e.g. $E = 0.2$ V nm$^{-1}$) the CPL is not as well defined. A second smaller peak of sodium ions may be observed on the other side of the membrane. The asymmetry between the two kinds of ions may be partly due to the higher mobility of the chlorine ions, and, partly due to differences in the van der Waals interactions between the two kinds of ions with the carbon atoms in the graphene sheet. The peak in the ionic concentration profile is found to increase monotonically with increasing electric field.

3.2. Flow fields

The formation of the CPL is expected to generate a fluid flow in the vicinity of the interface. This is indeed seen in the simulations. The flow streamlines for the nanopore of diameter $d = 1.5$ nm, together with the distribution of water density is shown in figure 5 for different values of electric field strength. When the field is sufficiently large, e.g., $E = 0.5$ and $1.0$ V nm$^{-1}$, vortices of a spatial scale on the order of nanometres are clearly observed. When $E = 0.2$ V nm$^{-1}$, the electric pressure appears too weak to generate sustained micro-vortices against the influence of thermal fluctuations.

An interesting physical insight that emerges from these simulations is that there appears to be a marked asymmetry in the distribution of the cations and anions and that of water density. This is most likely due to a combination of pressure are to be expected, which might drive a flow, as long as these forces are strong enough to overcome viscous resistance and are not completely masked by the fluctuating Brownian forces (thermal fluctuations).
Flow fields and water density (in units of kg m$^{-3}$) distribution of salt solution for a nanopore of diameter $d = 1.5$ nm with (a) $E = 0.2$ V nm$^{-1}$; (b) $E = 0.5$ V nm$^{-1}$; (c) $E = 1.0$ V nm$^{-1}$. The rectangles (colour grey near $z = 0$) mark the graphene sheet. For strong fields, as in panel (c), a well defined vortical flow is seen, but for weak electric fields the bulk motion of the fluid is difficult to distinguish from the background thermal fluctuations.

three factors. First, as we have mentioned above, there is an approximately 30% difference in mobility between sodium and chlorine ions. Second, the van der Waals interactions between Na and C, Cl and C differ significantly. The third, which has been reported by previous researchers [36–39], is that the direction of the electric field could have significant effects on the interfacial water structures, as well as on the wetting behaviour of the solid membrane, due to the polarity of the water molecules. A consequence of this asymmetry, is that there is a flux of water through the nanopore, as may be seen in the appearance of the streamlines in figure 5. The average flow velocity $v_p$, describing water crossing the nanopore, is presented in figure 6 for different electric field strengths and pore diameters. It shows that generally the average velocity at the nanopore is proportional to the applied voltage, and nearly independent of the diameter of the nanopore for the parameters we simulated.

A region of high water density is seen at the centre of the nanopore. For $E = 1.0$ V nm$^{-1}$, the local water density can be as high as 2043 kg m$^{-3}$. The accumulation of water in the nanopore appears to originate from re-orientation of the water dipole moments when the external voltage is applied. To describe the orientation of water molecules, we define an average over the $x$–$y$ plane of the angle $\phi$ between the dipole moment vector of the water molecule and the $z$-axis. In the absence of an electric field, the orientation of the dipoles is completely random, corresponding to $\phi = 90^\circ$. Figure 7 shows that with increasing electric field strengths, the dipoles prefer an axial orientation. For a given $z$-location, it increases with the field strength. The degree of ordering increases as one approaches the pore, where the dipoles favour to be parallel to the wall of the nanopore. This is consistent with previous studies on SWCNT, where a similar ordering has been observed [40]. Such ordering allows closer packing of the water molecules, leading to a rise in density in the pore region.

3.3. Voltage current relations

Recent experimental measurements have produced apparently conflicting results on the dependence of pore conductance on pore radius. Garaj et al [41] reported that the pore conductance is proportional to the pore diameter, whereas Schneider et al [42] reported it to be proportional to the pore area. The former result would correspond to a hole in an infinitely thin membrane in a homogeneous infinite conducting medium. The latter would correspond to a cylindrical conduit of diameter much less than the length of the cylinder [43]. Since
Figure 7. Average angle between the dipole moment and the $z$-axis for a pore diameter of $d = 1.5$ nm. Reduction of the angle due to the re-orientation of the dipole moment by the field is strongest in the pore region, where the dipoles favour to be parallel to the wall of the nanopore.

The former result is to be expected if the thickness of graphene can be ignored and the electrolyte solution is assumed to obey Ohm’s law, some researchers [3] have speculated that the discrepancy between the experiment of Schneider et al and the theoretical result for a hole in a thin sheet might originate from the fact that their graphene sheet was treated with a polymer coating (to reduce non-specific surface adsorption of DNA). To clarify this, Sathe et al [11] conducted molecular dynamics simulations for a KCl solution with pore diameters in the range of 2–7 nm. They found the dependence of resistance $R$ on pore diameter follows the relationship $R \sim 1/d^2$, which is qualitatively in agreement with the experiment of Schneider et al [42]. However, quantitatively the resistances they obtained in their simulations were three to four times smaller than the experimental measurements. They attributed the discrepancy to a number of factors, including inaccuracies in the force field in their simulations, unknown charge distribution and uncertainties about the exact shape of graphene pores.

The variation of the current with the applied electric field was extracted from our simulations and is shown in figure 8 for a number of different pore diameters, $d$. A linear regime is observed at weak fields ($E$). For higher applied voltages, it is found the current shows super-linear growth and the nonlinearity is stronger for pores of smaller diameter. Hydrodynamic transport due to the nanoscale vortices could be responsible for this faster than linear increase of the current. A similar phenomenon has also been observed when an external electric field is applied normal to the surface of an ion-selective nanoporous membrane immersed in an electrolyte solution. There, at a critical value of the applied field, the quiescent state undergoes a hydrodynamic instability, resulting in the appearance of micro-vortices that are responsible for an ‘overlimiting current’ in the current–voltage relationship [23]. In the nanopore problem however, there is no instability. The hydrodynamic flow is always present, its strength simply increases with the electric field.

Figure 8(b) shows the electric conductance ($G$) at low fields, which is calculated from the slope of the initial linear segment of the $I$–$V$ curves. It is seen to be proportional to the nanopore diameter $d$, which is qualitatively in agreement with the experiments by Garaj et al [41] and is as expected from the theoretical model where the pore is regarded as a hole in an infinitely thin insulating sheet in a uniform conductor. The resistance obtained for $d = 3$ nm is $R = 199$ M$\Omega$, which is comparable to the values reported by Schneider et al [42], though we do not observe their $G \propto d^2$ dependence on pore diameter. The theoretical result $G = \sigma d$ for a hole of diameter ‘$d$’ in an insulating sheet in a conducting medium of conductivity ‘$\sigma$’ may be used to extract an ‘effective’ conductivity from the data shown in the inset in figure 8. The conductivity obtained in this way is $\sigma = 1.879$ Sm$^{-1}$, which is about a factor of 5 smaller than the bulk conductivity, $\sigma = 9.3$ Sm$^{-1}$, for a 1 M NaCl solution. The discrepancy

Figure 8. The current versus applied field (left panel) for several different pore diameters. The pore conductance determined from the slope of the initial linear region of the current–voltage characteristic is also shown as a function of the pore diameter (right panel).
may arise from the fact that there are significant differences between a graphene nanopore immersed in an electrolyte and a hole in an insulating sheet in an Ohmic medium. As we have seen, one important difference lies in the existence of the concentration polarization layer, which modifies the electric field distribution near the pore as well as drives a hydrodynamic flow that affects transport properties. The influence of these phenomena on pore conductance is still an open problem. A second source of discrepancy may be a due to a limitation of our computation. In a physical experiment, the nanopore radius is vanishingly small in comparison to the reservoir dimensions, so that essentially all of the electrical resistance arises from the pore. This assumption might not be satisfied as well in our simulated model, since, due to limitations of computational capabilities, the area of the graphene sheet that we constructed, 5 nm × 5 nm, is quite comparable to the pore diameter of 3 nm. These issues will be investigated further in future studies.

4. Conclusion

Molecular dynamics simulations were performed to study the transport properties of an electrolyte through a nanometer-sized pore. Due to the partial blockage of the ionic current by the graphene membrane, a concentration polarization layer (CPL) develops next to the membrane when an external voltage is applied. The CPL is able to induce electric pressure in the fluid adjacent to the pore. If the applied voltage is large enough to overcome the effects of viscosity and Brownian fluctuations, vortices are generated in the fluid near the pore. These nanoscale vortices enhance the ionic current through a mechanism similar to the effect known as ‘overlimiting current’ for perm-selective membranes. Owing to the polarization of water molecules, the direction of the electric field might have significant influence on water structure near the graphene surface. This effect, together with the differing mobility and van der Waals attraction to C exhibited by the Cl and Na ions, brings about an asymmetric distribution of ions, and a net flux of water in the direction of the electric field through the pore. The average velocity of this hydrodynamic flow is found to increase approximately linearly with the nanopore diameter and appears to be independent of the pore diameter. Orientational order created in the water dipoles by the electric field enhances closer packing of the water dipoles. This is manifested in the appearance of regions of high water density within the pore. The electrical conductance of the system is found to vary linearly with the nanopore diameter, as one might expect from the classical theoretical relation $G = \sigma d$ for a hole in an insulating membrane within a conductor. However, the effective conductivity, $G/d$, is found to be nearly five times the bulk conductivity of the electrolyte. The linear dependence of $G$ on $d$ is in accord with the experiments of Garaj et al but we do not observe the $G \propto d^2$ dependence reported by Schneider et al. This could be due to differences in experimental techniques, as a result of which their situation does not correspond to the model studied in this paper.

Acknowledgments

This work was supported by the National Science Foundation of China (Grant No. 11272197), Research Fund for the Doctoral Program of Higher Education of China (Grant No. 20103108110004), and Shanghai Program for Innovative Research Team in Universities. This project was supported in part by the American Recovery and Reinvestment Act (ARRA) funds through grant number RO1 HG001234 to Northwestern University (USA) from the National Human Genome Research Institute, National Institutes of Health.

References

[1] Doyle D A, Morais Cabral J, Pfuetzner R A, Kuo A, Gulbis J M, Cohen S L, Chait B T and MacKinnon R 1998 The structure of the potassium channel: molecular basis of K+-conduction and selectivity Science 280 69–77
[2] Rhee M and Burns M A 2006 Nanopore sequencing technology: research trends and applications Trends Biotechnol. 24 580–6
[3] Venkatesan B M and Bashir R 2011 Nanopore sensors for nucleic acid analysis Nature Nanotechnol. 6 615–24
[4] Branton D et al 2008 The potential and challenges of nanopore sequencing Nature Nanotechnol. 26 1146–53
[5] Roux B, Allen T, Bernèche S and Im W 2004 Theoretical and computational models of biological ION channels Q. Rev. Biophys. 37 15–103
[6] Demming A 2012 Nanopores—the ‘Holey Grail’ in nanotechnology research Nanotechnology 23 250201
[7] Aksimentiev A, Brunner R, Cruz-Chu E, Comer J and Schulten K 2009 Modeling transport through synthetic nanopores IEEE Nanotechnol. Mag. 3 20–8
[8] Aksimentiev A and Schulten K 2005 Imaging α-Hemolysin with molecular dynamics: ionic conductance, osmotic permeability, and the electrostatic potential map Biophys. J. 88 3745–61
[9] Comer J, Dimitrov V, Zhao Q, Timp G and Aksimentiev A 2009 Microscopic mechanics of hairpin DNA translocation through synthetic nanopores Biophys. J. 96 593–608
[10] Cruz-Chu E R, Aksimentiev A and Schulten K 2009 Ionic current rectification through silica nanopores J. Phys. Chem. C 113 1850
[11] Sathe C, Zou X, Leburton J-P and Schulten K 2011 Computational investigation of DNA detection using graphene nanopores ACS Nano 5 8842–51
[12] Suk M E and Alur N R 2010 Water transport through ultrathin graphene J. Phys. Chem. Lett. 1 1590–4
[13] Aksimentiev A, Heng J B, Timp G and Schulten K 2004 Microscopic kinetics of DNA translocation through synthetic nanopores Biophys. J. 87 2086–97
[14] Gracheva M E, Xiong A, Aksimentiev A, Schulten K, Timp G and Leburton J-P 2006 Simulation of the electric response of DNA translocation through a semiconductor nanopore-capacitor Nanotechnology 17 622–33
[15] Luan B and Aksimentiev A 2010 Control and reversal of the electroosmotic force on DNA in a charged nanopore J. Phys.: Condens. Matter 22 454123
[16] Mirsaidov U, Comer J, Dimitrov V, Aksimentiev A and Timp G 2010 Slowing the translocation of double-stranded DNA using a nanopore smaller than the double helix Nanotechnology 21 395501
[17] Ghosal S 2006 Electrophoresis of a polyelectrolyte through a nanopore Phys. Rev. E 74 041901
[18] Ghosal S 2007 The effect of salt concentration on the electrophoretic speed of a polyelectrolyte through a nanopore Phys. Rev. Lett. 98 238104
[19] Storm A J, Chen J H, Zandbergen H W and Dekker C 2005 Translocation of double-strand DNA through a silicon oxide nanopore Phys. Rev. E 71 051903
[20] Smeets M M R, Keyser U F, Krapf D, Wu M, Dekker N H and Dekker C 2006 Salt dependence of ion transport and DNA translocation through solid state nanopores Nano Lett. 6 89–95
[21] van Dorp S, Keyser U F, Dekker N H, Dekker C and Lemay S G 2009 Origin of the electrophoretic force on DNA in solid-state nanopores Nature Phys. 5 347–51
[22] Ghosal S 2007 Electrokinetic-flow-induced viscous drag on a tethered DNA inside a nanopore Phys. Rev. E 76 061916
[23] Chang H-C, Yossifon G and Demekhin E A 2012 Nanoscale electrokinetics and microvortices: how microhydrodynamics affects nanofluidic ion flux Annu. Rev. Fluid Mech. 44 401–26
[24] Berendsen H J C, Grigera J R and Straatsma T P 1987 The missing term in effective pair potentials J. Phys. Chem. 91 6269–71
[25] Yang K-L, Yiacoumi S and Tsouris C 2002 Canonical Monte Carlo simulations of the fluctuating-charge molecular water between charged surfaces J. Chem. Phys. 117 337–45
[26] Hess B, Kutzner C, van der Spoel D and Lindahl E 2008 GROMACS 4: algorithms for highly efficient, load-balanced, and scalable molecular simulation J. Chem. Theory Comput. 4 435–47
[27] Gong X, Li J, Lu H, Wan R, Li J, Hu J and Fang H 2007 A charge-driven molecular water pump Nature Nanotechnol. 2 709–12
[28] Hummer G, Rasaiah J C and Noworyta J P 2001 Water conduction through the hydrophobic channel of a carbon nanotube Nature 414 188–90
[29] Zhou X-Y and Lu H-J 2007 The structure and dynamics of water inside armchair carbon nanotube Chin. Phys. B 16 335–9
[30] Darden T, York D and Pedersen L 1993 Particle mesh Ewald: an N. log(N) method for Ewald sums in large systems J. Chem. Phys. 98 10089
[31] Thomas J A and McGaughey A J H 2008 Density, distribution, and orientation of water molecules inside and outside carbon nanotubes J. Chem. Phys. 128 084715
[32] Werder T, Walther J H, Jaffe R L, Halicioglu T and Koumoutsakos P 2003 On the water–carbon interaction for use in molecular dynamics simulations of graphite and carbon nanotubes J. Phys. Chem. B 107 1345–52
[33] Girit Ç Ö et al 2009 Graphene at the edge: stability and dynamics Science 323 1705–8
[34] Jiang De-en, Cooper V R and Dai S 2009 Porous graphene as the ultimate membrane for gas separation Nano Lett. 9 4019–24
[35] Cong C, Yu T, Sato K, Shang J, Saito R, Dresselhaus G F and Dresselhaus M S 2011 Raman characterization of ABA- and ABC-stacked trilayer graphene ACS Nano 5 8760–8
[36] Bratko D, Daub C D, Leung K and Lazar A 2007 Effect of field direction on electrowetting in a nanopore J. Am. Chem. Soc. 129 2504–10
[37] Daub C D, Bratko D, Leung K and Lazar A 2006 Electrowetting at the nanoscale J. Phys. Chem. C 111 505–9
[38] Daub C D, Bratko D and Lazar A 2012 Topics in Current Chemistry vol 307 (Berlin: Springer) pp 155–79 (Nanoscale wetting under electric field from molecular simulations)
[39] Hu G-H, Xu A-J, Xu Z and Zhou Z-W 2008 Dewetting of nanometer thin films under an electric field Phys. Fluids 20 102101
[40] Walther J H, Jaffe R, Halicioglu T and Koumoutsakos P 2001 Carbon nanotubes in water: structural characteristics and energetics J. Phys. Chem. B 105 9980–7
[41] Garaj S, Hubbard W, Reina A, Kong J, Branton D and Golovchenko J A 2010 Graphene as a subnanometre trans-electrode membrane Nature 467 190–3
[42] Schneider G F, Kowalczyk S W, Calado V E, Pandraud G, Zandbergen H W, Vandersypen L M K and Dekker C 2010 DNA translocation through graphene nanopores Nano Lett. 10 3163–7
[43] Siwy Z S and Davenport M 2010 Nanopores: graphene opens up to DNA Nature Nanotechnol. 5 697–8