Nanoscale vortices in transport of salty solution through a graphene nanopore

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Summary Molecular dynamics simulation is used to investigate the ionic transport of NaCl in solution through a graphene nanopore under an applied electric field. Results show that the electric conductance is proportional to the nanopore diameter. The occurrence of vortical structures is observed by reconstructing the flow field, and the physical mechanism behind it, as well as its competition with the thermal fluctuations is discussed in detail in the present study.

INTRODUCTION

Transport characteristics of ionic solutions through nanometer sized channels or pores are commonly encountered in numerous natural phenomena as well as in chemical engineering. Examples include biological channels in membranes, nanopore sequencing, and water purification. This field has attracted increasing interest in the past decade in both the experimental and theoretical domain. 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 been reported on in the literature. In the present study, we report on the formation of nanoscale hydrodynamic vortices in the ionic solution near a graphene nanopore and their role in determining the electrical conductance of the pore.

METHOD

The molecular simulations are conducted in a cubic box with a dimension of L_x=5.112nm, L_y=5.184nm, L_z=10nm. The origin of the coordinates is set at the center of the box. The graphene sheet, which consists of an array of carbon atoms with a planar hexagonal structure (neighboring atoms have a bond lengths of 0.142nm), is located in the middle of the box in the plane z=0. A nanopore is constructed with radius a by removing the carbon atoms in a circular path in the central region of the graphene sheet. The box is then filled with water molecules described by extended simple point charge (SPC/E) model, which is considered to be reasonable when the external electric field strength is below 10 *V/nm*. Salt (NaCl) is introduced at a given concentration of 1M by replacing the required number of water molecules with Na and Cl ions. The simulations are performed at a constant temperature 300K and pressure of 1 bar with large scale MD package GROMACS 4.5.4. The van der Waals interaction of the carbon atoms are modeled as uncharged Lennard-Jones (LJ) particles.

A uniform external electric field is applied in a direction perpendicular to the graphene sheet (z-direction), and 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 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 be 2*fs*.

RESULTS

The variation of the current with the applied electric potential is shown in Fig. 1a for a number of different diameter d of the nanopore. The current obtained depends linearly on the voltage applied. The available experimental data appeared to show contradictory results on the relation between the conductances of the nanopore with the pore diameter. For instance, Garaj et al. [1] reported that the conductance is proportional to the pore diameter of the graphene, whereas Schneider et al. found it is proportional to the pore area [2]. Theoretically, the former result should be expected if the pore radius is much larger than the graphene thickness whereas the latter result is expected in the opposite limit where the membrane is much thicker than the pore radius [3]. In either case, it is assumed that the medium behaves as a homogeneous conductor with no bulk motion. Fig. 1b indicates that the electric resistance, calculated from the slope of the I - V curves, is proportional to the inverse of the pore diameter, in agreement with the experiments by Garaj et al. [1] and the MD simulations of Sathe et al. [4]

The simulation shows that the existence of the applied electric field together with a non-penetrable membrane forces the creation of an electric double layer (EDL) next to the graphene sheet where unbalanced ionic charges exist. The tangential electric field acting on the unbalanced charge in the EDL together with the variation of the electric pressure

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along the graphene sheet is expected to generate electro-osmotic flow in the vicinity of the pore. The flow fields for the nanopore of diameter d=1.5nm and the distribution of the water density, are illustrated in Fig. 2 with different electric strengths, in which nanoscale hydrodynamic vortices can be observed for sufficiently large electric strengths, e.g., E=0.5 and 1.0 V/nm.

The ordered hydrodynamic flow is in competition with thermal fluctuation. When E=0.2V/nm, the EDL seems to be too weak to generate any ordered electro-osmotic flow Thus the thermal fluctuations dominate and no obvious hydrodynamic circulation is observed. For E=0.5V/nm, the thermal fluctuation has evident influence on the streamlines although the entire vortical structures visibly exist. Comparatively, the smoothness of the streamlines for E=0.5V/nm implies that the nanoscale vortices is dominant over the effects of thermal fluctuation.

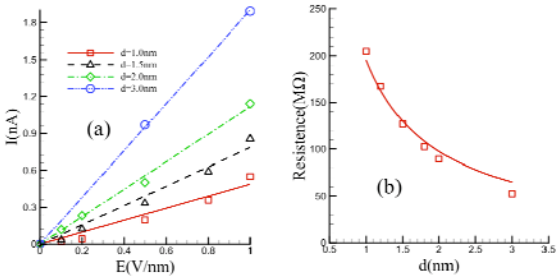

Fig. 1 (a) Variation of current with voltage applied for different diameter of nanopore, (b) Dependence of resistance on nanopore diameter.

Another remarkable characteristic is the asymmetry in the distribution of the ionic concentrations or the water density on the two sides of the graphene sheet. We attribute this to two causes. The first is the difference of mobility between sodium and chlorine ions. The second aspect is the direction of the electric field which could have significant effects on the interfacial water structures, as well as the wetting behavior of the solid membrane, due to the polar nature of the water molecules.

As a consequence of the asymmetry, a net hydrodynamic transport occurs through the nanopore, as shown in Fig. 2. The average velocities v_p, describing water crossing the nanopore, are presented in Fig. 3 for different electric strength and the nanopore diameters. It shows, that generally, the average velocity v_p of water through the nanopore is proportional to the applied voltage, and nearly independent of the diameter of the nanopore for the parameter range that we simulated.

The distribution of water density is explored by analyzing the reorientation of dipole moment under the electric fields. The influence of the base ionic concentration on the ionic distribution and the vortical structures is also discussed in the present study.

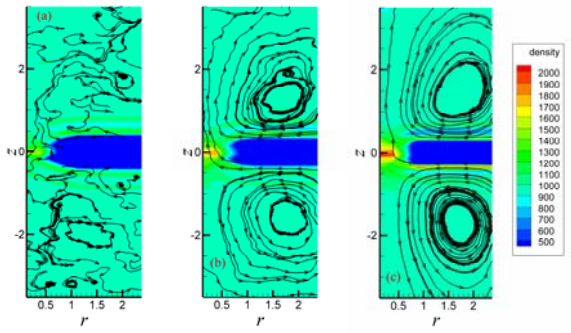

Fig. 2 Flow fields and liquid density distribution of salt solution for nanopore of diameter d=1.5nm. (a) E=0.2V/nm; (b) E=0.5V/nm; (c) E=1.0V/nm. The region with low density (color blue near z=0) represents the graphene sheet.

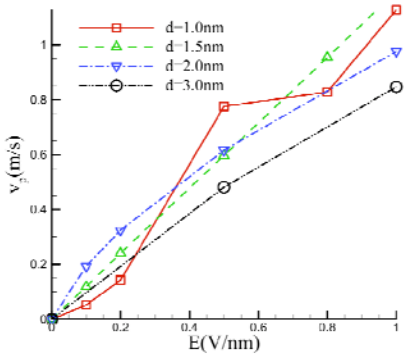

Fig. 3 Variation of water velocity at the nanopore with applied voltage for different nanopore diameters.

CONCLUSIONS

To study the transport properties of a salty solution through a nanosized pore, molecular dynamics simulation is performed in the present paper. The conductance of the system is found to vary linearly with the nanopore diameter, which helps clarify the mutually contradictory results reported in previous experiments. By extracting the velocity field, it is shown that nanoscale vortices exists near the pore and possibly play a role in determining the pore conductance. The mechanism behind this phenomenon is discussed.

References

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