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Molecular dynamics simulation of electroosmotic flow in rough nanochannels☆

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ABSTRACT

A three-dimensional molecular dynamics model of electroosmotic flow in rough nanochannels is developed and numerically analyzed to investigate the role of surface roughness on microscale electroosmotic flow. The water and ion concentration distributions in the fluid, velocity profiles in rough nanochannels are examined and compared with the corresponding smooth nanochannel. In addition, the role of roughness height on electroosmotic velocity and zeta potential is presented. The results indicate that the electroosmotic behavior in nanochannels is sensitive to the surface roughness. The plug-like velocity in nanochannel is reduced by the presence of surface roughness, which owes to the variation in electrical double layer and additional viscous dissipation for flow past rough surface. There is a layering distribution of water molecules and Cl^- ions in the near wall region, and some ions and molecules are confined at the concave region due to fluid/solid interaction. In addition, increases in roughness height lead to a smaller electroosmotic velocity in bulk solution and also a smaller zeta potential.

1. Introduction

Electroosmotic flow is fluid motion driven by an electric field acting on the net fluid charge produced by charge separation at a fluid–solid interface. Resulting from the presence of electrical double layer at the fluid–solid interface, the electroosmotic flow behaves as a uniform plug-like velocity profile and possesses the inherent advantage of selectivity, throughput and robustness. Due to this fact, the electroosmotic flow has a great potential in microfluidics, such as DNA identification [1], biological analysis and segregation technology [2–4], nanofabrication [5–7]. The underlying insight of electroosmotic flow has received considerable attention in the recent years.

Ever since the electroosmotic flow was firstly reported in 1809 by Reuss and the electrical double layer (EDL) theory was proposed by Helmholtz et al. [8], there has existed a substantial body of electroosmotic flow research by theoretical analysis, experimental measurement and engineering application. With the advance in computation, the simulation method during the past decade has emerged as a powerful tool for probing the microscopic behaviors of electroosmotic flow, especially the fluid–solid interaction at interfaces. The molecular dynamics simulation [9–11] and lattice Boltzmann simulation [12] are usually used to elucidate the mechanisms of electroosmotic flow. In general, the electroosmotic flow is mainly dependent on the imposed electric fields, channel wall and analyte fluid properties. As another critical parameter of microchannel, the channel surface roughness directly affects the fluid–solid interaction, which in turn controls the behavior of electroosmotic flow.

Considering the significance of surface topography to fluid–solid interaction, several attempts have been made to correlate the electroosmotic flow characteristics with surface roughness [13–17]. However, till now, how the roughness affects the fluid microscopic behavior (including ion and solvent distribution) in the electrical double layer is still less understood. In addition, the available investigation via Navier–Stokes description fails to probe the microscopic details of electroosmotic flow in nanochannels, such as the formation of EDL, special fluid distribution, ion–ion interaction, ion and molecule trajectory, especially the role of atomic-scale roughness on electrical double layer. Compared with the continuum flow theory, molecular dynamics simulation is capable to capture these details of electroosmotic flow stated above.

Therefore, a molecular dynamics model of electroosmotic flow in rough nanochannels is developed and numerically analyzed to investigate the role of surface roughness on nanoscale electroosmotic flow. In addition, the fluid concentration distributions in EDL, velocity profiles and zeta potential in rough nanochannels are evaluated and compared with the corresponding smooth nanochannel, in an effort to identify surface roughness role in microscale electroosmotic flow.

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2. Molecular dynamics simulation

In order to analyze the role of surface roughness on electroosmotic flow in nanochannels, a three-dimensional molecular dynamics simulation of NaCl solution flow imposed by electric field in rough nanochannels characterized by rectangular element is conducted. As shown in Fig. 1, the electrolyte solution is confined between two parallel solid planar walls. The upper smooth wall is composed of four layers of atoms, while the rough wall is constructed by adding extra partial layers of wall atoms to produce the rectangular roughness element. All the wall atoms are arrayed in the form of face centered cubic (FCC) lattice. The wall composed by four layers of atoms is 0.81 nm in thickness. The wall atoms are fixed to their lattice sites by a spring. The nanochannel height (distance between the two innermost layers) is 5.75 nm. The whole model has a lateral dimension of $L_x \times L_y = 4.86 \times 0.81\ \text{nm}^2$ and a height of $L_z = 7.37$ nm, and the rough lower wall has a surface roughness height H. The electrolyte solution is composed of 800 water molecules and 80 ions (40 Na^+ ions and 40 Cl^- ions). The fluid density is 1.3 g/cm^3. The upper wall, lower wall and electrolyte solution are similar to a sandwich-like structure. In the simulation, 12 positive charges are discretely distributed on the two innermost layers of each solid wall of nanochannel, remaining other wall layers uncharged. The surface charge density is 0.49 C/m^2.

The Newtonian equation for each particle can be written as [18]

$$m_i \frac{d\vec{r}^2}{dt^2} = \sum_{j\neq i,j=1}^{N} \vec{F}_{ij} + \sum_{j_w\neq i,j=1}^{N_w} \vec{F}_{ij_w} + \vec{F}_{out}\,\vec{i} \tag{1}$$

where subscript i and j represent the particle, and $\vec{i}$ is the unit vector in x-coordinate. The first term of the right-hand side of Eq. (1) is the molecular force due to Lennard-Jones (LJ) potential between particle i and other fluid molecules j in the computational domain, and the second term is the molecular force between particle i and all the solid wall particles j_w. The last term in Eq. (1) represents the external force, i.e. the electric force in our work, which makes the fluid deviate from the equilibrium. The LJ potential is given by:

$$U_{ij} = D_0\left[\left(\frac{R_0}{R_{ij}}\right)^{12} - 2\left(\frac{R_0}{R_{ij}}\right)^{6}\right] + C\frac{q_iq_j}{\varepsilon R_{ij}} \tag{2}$$

where the first term in Eq. (2) is the van der Waals interaction and the second term is the electrostatic interaction. In the first term, R_{ij} is the distance for the pair i and j, R_0 is the equilibrium distance between two atoms and D_0 is the equilibrium well depth. The LJ potential parameters between atoms i and j could be determined by Lorentz–Berthelot rules ($R_0 = (R_{0i} + R_{0j})/2$, $D_0 = \sqrt{D_{0i}D_{0j}}$). In the simulation, these parameters for LJ potential are listed in Table 1. For the second term, C is the constant, q_i, and q_j are the charge number of atoms i and j respectively, and ε is the dielectric constant. Note that as to the water molecules, oxygen–ion/wall interaction parameters are mainly considered instead of water–ion/wall interaction parameters in the LJ potential, which is usually applied in the investigation of the electroosmotic flow in a nanochannel [14].

The periodic boundary conditions are applied along the x and y directions. Under the periodic boundary conditions, particles that leave the domain at one side reenter the domain at the opposite side with the same velocity. In other words, when the fluid particle is leaving the boundary at $x(y) = 0$ or $x(y) = L_x(L_y)$, another particle will enter the unit cell at $x(y) = L_x(L_y)$ or $x(y) = 0$ with the same velocity. During the simulation, the fluid temperature may be raised, so it is necessary to control the system temperature variations so as to keep the temperature fluctuation at the canonical average. In this paper, a Nose thermostat [19] is used to maintain the system temperature at 300 K with $Q_{ratio} = 0.01$ ($Q_{ratio} = Q\,/\,(\tau_2 N_f k_B T_0)$, in which Q is the mass of extended system, N_f is the number of degrees of freedom in the structure, k_B is the Boltzmann constant, and T_0 is the target temperature.) at a relaxation time of 1 ps. Starting from a random configuration, geometry optimization is carried out firstly using smart

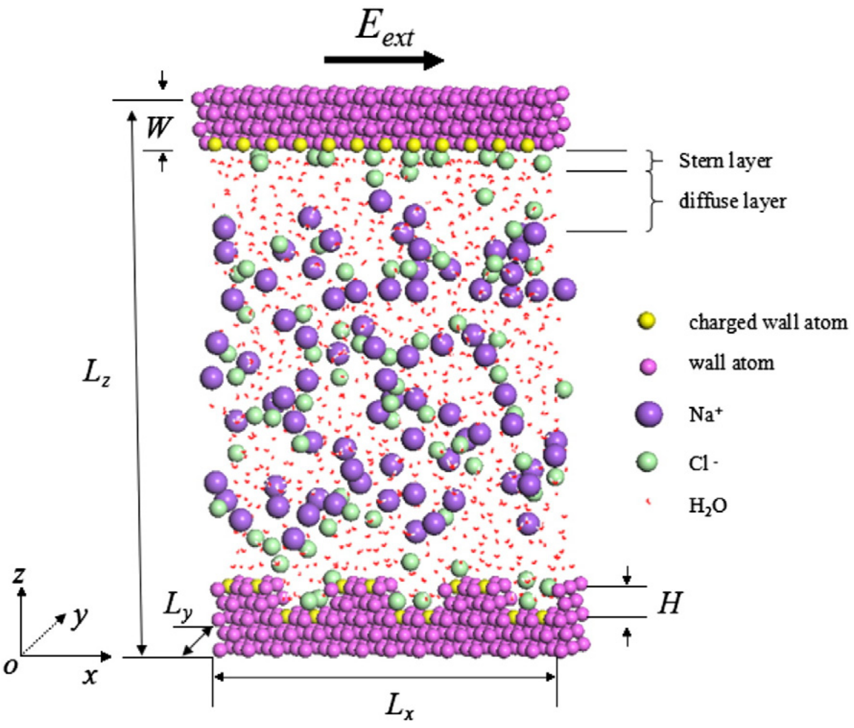

Fig. 1. Snapshot of solution distribution in a rough nanochannel.