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Anomalous flow behavior in closed and open thin walled nanochannels

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ABSTRACT

Molecular dynamics simulations have been carried out to examine water flow in symmetric and asymmetric open and closed ends nanochannels with hydrophilic surfaces. The results are counterintuitive and the opposite of what is observed in macro-systems–closed channels fill faster with fluid than do their open counterparts. In addition, hybrid closed–open asymmetric channels fill up even faster. These results can be explained on the basis of the fluid–structure interaction that arises through the different vibrational behaviors of the surface molecules that are part of the wall forming these channels. Such effects are not expected to be of significance in macro-channels, and point to an important case where macro and nanochannels exhibit contrary behavior. Since these effects results from strong interactions between the fluid molecules and solid surface, one would not expect them with hydrophobic walls, and our simulations confirm such behavior.

Fluid confinement and flow [1,2] in nanoscale channels occurs often in nature, e.g., in cell membranes during ion and water transport [3], and in rocks [4]. The physical properties of nanoscale water are known to differ from those of its bulk counterpart [5]. Studies on carbon nanotubes and hydrophobic surfaces have shown that the flow is virtually frictionless [6,7], being limited primarily by the barriers at the entry and exit of the nanotube pore [8], indicating that the structure outside a nanochannel has a significant influence on the flow within it [9]. On the other hand with hydrophilic surfaces, the flow experience considerable resistance to flow in the nanochannel [7]. We consider water flow in hydrophilic nanochannels that are constructed in various configurations through molecular dynamics (MD) simulations [10,11] and show that the fluid–structure interaction arising through different vibrational behaviors of hydrophilic surface molecules bounding nanochannels can have a profound influence in driving water flow. Most surfaces will have surface thermal fluctuations, so the effects we are observing may affect a whole range of nanopores/nanoslits in nature. While natural nanopores can have various shapes and configurations that could couple fluid behavior with the free and driven vibrations of solid surfaces [12–14], the influences of geometry and the corresponding fluid–structure interactions on fluid flow have remained unexplored beyond interfacial issues such as fluid slip [15], and hydrophobic or hydrophilic interactions [16]. A better understanding of such behavior [17] would help in the development nanoscale devices from a more fundamental perspective than simply mimicking macroscale design methodologies.

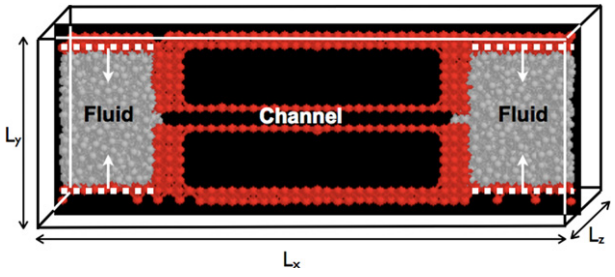

Fig. 1. Schematic diagram of the domain for an arbitrary simulation where $L_x = 11.2$ nm, and $L_y = L_z = 3.73$ nm. The hydrophilic walls are moved in the directions shown to compress the fluid into channels that have different end configurations, as shown in Fig. 2.

The MD simulations nominally consider 3968–3984 molecules in the basic cyclically replicated parallelepiped shown in Fig. 1. The system dimensions are $L_x = 11.2$ nm axially, and $L_z = L_z = 3.73$ nm in each transverse direction. As shown in Fig. 1, two moveable walls uniformly compress fluid reservoirs, forcing fluid into 0.5 nm wide and infinitely deep channels that are initially evacuated. These channels are constructed in the four configurations shown in Fig. 2, namely, continuous (Type 1), open–open (Type 2), closed–closed (Type 3), and closed–open (Type 4). The solid walls are modeled after Si and have 2096–2112 sites, depending upon the configuration. The Si molecules are tethered to their equilibrium sites with a simple harmonic potential with a spring constant of 44.7 N/m. These walls enclose 1872 water molecules. All molecules are provided with initial Gaussian velocity distributions. Both the fluid and the wall temperatures are maintained at 334 K using a Gaussian thermostat. The simulated results do not

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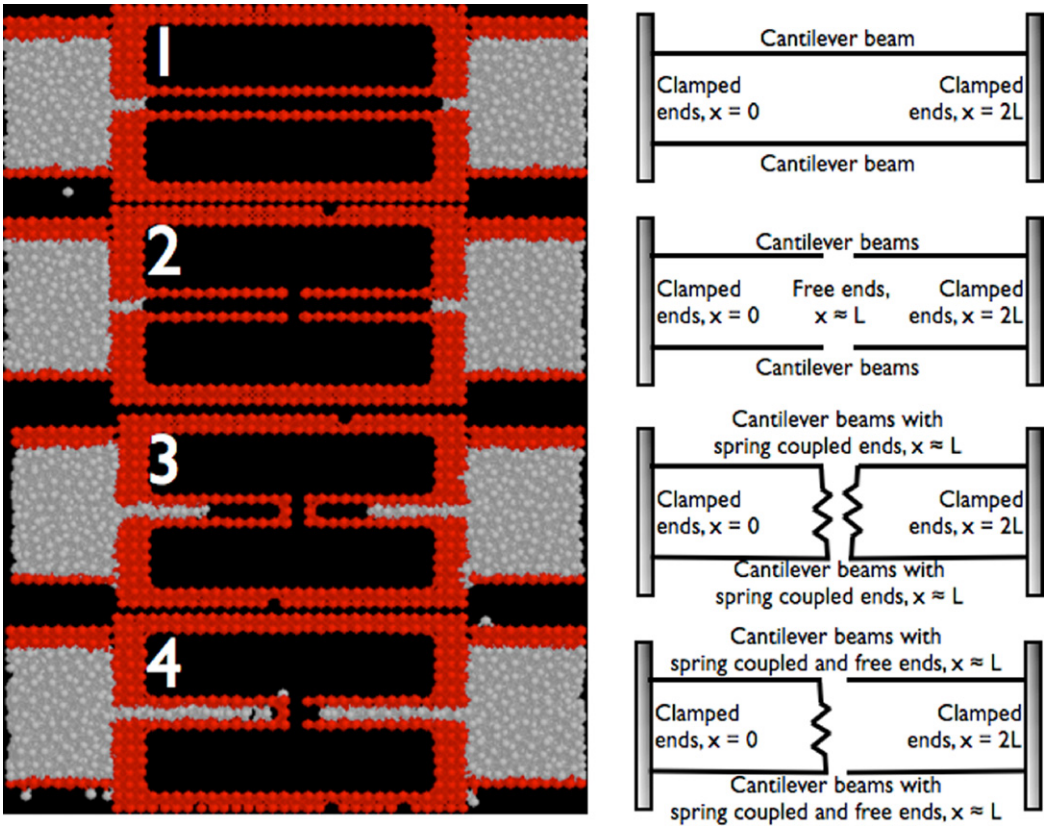

Fig. 2. Fluid penetration into evacuated channels after 500,000 time steps, each of 0.176 fs duration, for four different channel configurations: (a) continuous, (b) open–open, (c) closed–closed, and (d) closed–open. The few water molecules seen outside the walls leak through the tethered wall molecules at high pressures.

Table 1
Values of the Lennard-Jones interactions parameters σ, ε, and q. Cross interactions are modeled based on Lorentz–Berthelot mixing rules.

	s 10^{-10} m	e (KJ mol^{-1})	q e
O	3.17	0.65	−0.82
H	0	0	0.41
Wall	4.028	0.87	0

change if other techniques, such as simple velocity rescaling, are used.

The simulation algorithm uses the quaternion method with a fifth-order Gear predictor–corrector algorithm for translational motion and a fourth-order predictor–corrector algorithm for rotational motion [18,19]. Intermolecular interactions are described by the potential model $u_{ij} = 4\varepsilon_{ij}((\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^{6}) + q_i q_j / r_{ij}$, where σ_{ij} and ε_{ij} denote the LJ interaction parameters, r_{ij} the scalar distance between sites i and j, and q_i and q_j charges on sites when applicable. Cross interactions are modeled based on Lorentz–Berthelot mixing rules [11] and the reaction field method is used for long-range interactions [20,21]. The water parameters σ and ε, presented in Table 1, represent experimental geometries, energies of ion–water complexes, and energies of solvation [22] for water, which is modeled after the SPC potential [23]. Wall atoms are modeled as LJ sites. The hydrophilic interaction between water and the wall surfaces is controlled by placing random or systematic negative and positive charges on the wall atoms (or sites) while maintaining overall charge neutrality [16,24,25]. The atoms that constitute the nanochannel and walls are tethered using a simple harmonic potential. If some of these tethering sites are selectively moved, the walls are also dragged along (as illustrated in Fig. 1) while allowing for thermal fluctuations. A typical simulation runs for either 1,500,000 steps or until the channel fills up, whichever occurs first, with 0.176 fs time steps.

Fig. 2 presents images of fluid flow though the four channels after 500,000 time steps, while Fig. 3 shows the fluid penetration for a range of time steps to provide a more detailed picture of the differences in the flow rates in these channels. These figures show that continuous and open–open channels offer far more resistance to fluid flow than do closed–closed and closed–open channels. The shortest fill time occurs for Type 4 closed–open asymmetric channels, which is counterintuitive. These results are the opposite of what one would expect in macro-channels. However, it should be noted that most macro-channels are usually initially filled with air. In our studies we evacuated the channels, but did allow for the fluid to evaporate in the channels naturally as determined by the thermodynamics of the system. In our system, since the channels are evacuated, the pressure gradients at the leading edges of the flows are identical in all four cases. The more obvious expectation was that the flow rate in all channels would be equal, since we saw little evidence of evaporation of the fluid during the simulation times, and in any case no evaporated fluids actually left the channel (thus the system would not be effected by the open/closed status of the channel via the fluid–fluid interactions at least). Thus the only possible explanation would be the fluid–solid interactions. The interaction parameters between the surface–water were identical, so the only possible explanation must lie with the “mechanical” behavior of the solid surface itself. We therefore hypothesized that the difference arises not from distinctions in the inherent fluid mechanics, but from the dissimilar fluid–structure interactions for the four cases. Thus the only remaining obvious difference could be due to the vibrational state of the surface molecules. The rational behind these differences is