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PROBLEMS WITH THE MODELING OF WATER FLOW IN NANOCHANNELS

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Abstract

The aim of the paper is to examine the effect of various molecular models on the Molecular Dynamics (MD) simulation of water nanoflows. The simulations of water nanoflows in copper channels for three molecular models: TIP4P, PPC, TIP5P were performed. The MD simulation input parameters characterizing the systems were identical. Various values of velocity profile in nanochannels were obtained.

Key words: *nanoflows, Molecular Dynamics, computer simulations*

INTRODUCTION

Dynamic behavior of water in nanochannels is crucial for the design of molecular sensors, devices, machines and for many biological applications.

The understanding of the water transport inside graphene flat nanochannels is highly desired for practical applications. The study of diffusion of water molecules through nanochannels can help to explain operating mechanisms of water channels, which are responsible for many important biological processes in the cell (Karniadakis et al., 2005).

When characteristic dimension of the flow is less than approximately ten molecules, the continuum hypothesis breaks down (Kucaba at al., 2009) and the Molecular Dynamics method should be employed to simulate the atomistic behavior of such system. To simulate a nanoflow by use of the MD, the atomistic description is necessary for liquids contained in nanochannels and a substrate forming the channel. The computer simulations need specific input parameters characterizing systems in question, which either come from theoretical considerations or are provided by an experiment.

The anomalies that exist in the bulk properties of water caused that a large number of atomistic models of water has been developed. It seems to be very important to understand properly the effect of various atomistic water models on MD results, before they can be used for a nanotechnology design.

MOLECULAR MODELS OF WATER

The structure of a water molecule (Fig. 1) is relatively complex and can be properly described only in the framework of quantum mechanics. However, this kind of description is not applicable for the Molecular Dynamics simulation, therefore a number of simplified models have been proposed. Unfortunately, each of them has a limited range of applications.

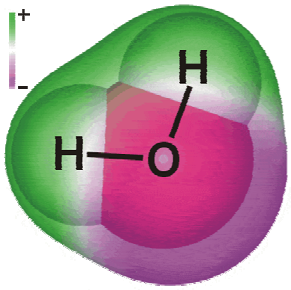


Fig. 1. The approximate shape and a charge distribution for a water molecule

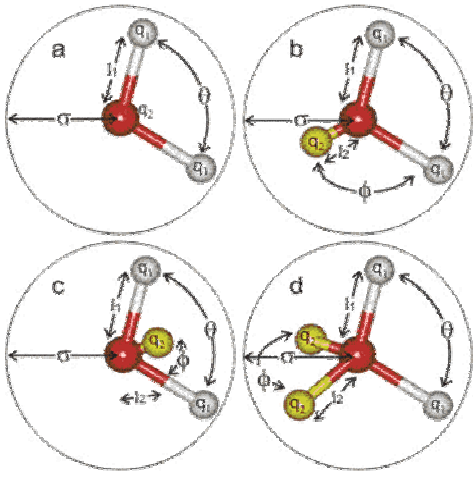


Fig. 2. The most frequently used geometrical model shapes of a water molecule (Chaplin, 2008)

In Table 1 and Fig. 2 we present three molecular models of water, selected for our Molecular Dynamics simulations of flow in nanochannels.

Table 1. Parameters of the water molecular models used in simulation (Chaplin, 2008).

Model	Geo-metrical confi-guration (Fig. 2)	Lennard-Jones molecul. diameter б, $1*10^{-10}$m	Lennard-Jones potential well depth ε kJ/mol	l_1, $1*10^{-10}$ m	l_2 $1*10^{-10}$ m	q_1 (e)	q_2 (e)	θ°	Φ°
TIP4P	C	3.15365	0.6480	0.9572	0.15	+0.5200	-1.0400	104.52	52.26
PPC	B	3.23400	0.6000	0.9430	0.06	+0.5170	-1.0340	106.00	127.00
TIP5P	D	3.12000	0.6694	0.9572	0.7	+0.2410	-0.2410	104.52	109.47

MOLECULAR DYNAMIC SIMULATION

Molecular Dynamics is a computer simulation technique describing the time behaviour of a set of interacting molecules. The laws of classical mechanics are followed. The force exerted on a molecule *i* by its neighbours consists of two components:

$$\mathrm{F_i} = \sum_{\mathrm{j}} \sum_{\beta} \sum_{\alpha} \mathrm{f}_{\mathrm{i}\alpha\mathrm{j}\beta} + \sum \mathrm{f}_{\mathrm{il}} \qquad (1)$$

where $\mathrm{f}_{\mathrm{i}\alpha\mathrm{j}\beta}$ – short range van der Waals force exerted on α atom of molecule *i* by β atom of molecule *j*,

f_{il} – long range Coulomb force acting on molecule *j*

The motion is governed by the Newton – Euler equations:

$$M_i \ddot{\boldsymbol{R}}_{\boldsymbol{i}} = \boldsymbol{F}_i + \boldsymbol{F}_x \qquad I_i \cdot \dot{\boldsymbol{\omega}}_i - \omega_i \times I_i \cdot \boldsymbol{\omega}_i = \boldsymbol{N}_i \qquad (2,3)$$

where M_i – the total mass of the molecule i,
R_i – the position vector of its centre of mass,
F_x – the force necessary to set water in motion,
I_i – the inertia tensor,
ω_i – the angular velocity,
N_i – the torque

Stages of simulation:

Initiation: Placing the molecules of water and the copper atoms in the knots of crystalline mesh. After that the velocities of the molecules are initialized. Their values are sampled at random from the Maxwell – Boltzmann distribution for the assumed temperature.

Equilibration: After initiation the positions of molecules are far from equilibrium. The whole ensemble is allowed to move freely for some time to attain equilibrium positions. This is always connected with decreasing the potential and increasing the kinetic energy of molecules, i.e. increasing the temperature of the medium. This excess temperature must be removed by a suitable "thermostat".

Actual simulation: After attaining equilibrium the actual simulation starts. The required data are accumulated in "dump-files" in the preselected time intervals.

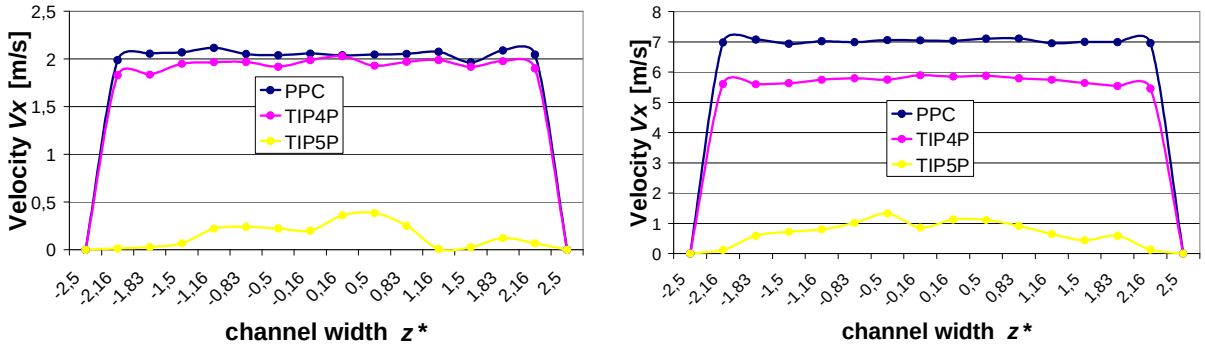
RESULTS

The simulations of water nanoflows in copper channels for three molecular models: TIP4P, PPC, TIP5P were performed. The MD simulation input parameters characterizing the systems were identical.

In the performed simulation, MD unit cell was in the form of a rectangular prism and contained water molecules bounded by walls consisting of another kind of molecules/atoms and was identical as in (Kucaba at al., 2009). The number of water molecules in the MD cell with cooper walls was equal to 280. The nanochannel walls were built of copper atoms and their width was equal to 5 diameters of the water molecule. The physical properties of materials and their electrostatic interactions were taken into account. The Lennard-Jones potential was assumed for interactions between water molecules and between water molecules and wall (copper) atoms. All Lennard-Jones parameters (δ, ε) were taken from (Allen et al., 1987). The program MOLDY (Refson, 2001), suitably modified, was used for this purpose. The Gaussian thermostat was applied to control the temperature of water molecules during the whole simulation. On the beginning this temperature was fixed at 300 K.

To drive the flow, a constant nondimensional force F_x was applied to the centre of mass of each water molecule. The calculations were carried out over 100 000 time steps Δt = 0.5 fs

long, after the system has reached the equilibrium, positions and velocities of all molecules were recorded in dump files every 100 time steps, for the further use.
Figure 3 shows the velocity profile obtained from the MD simulation. We observe that the velocity obtained from the MD simulation by use the TIP5P model is much smaller than by use of the PPC and the TIP4P models.

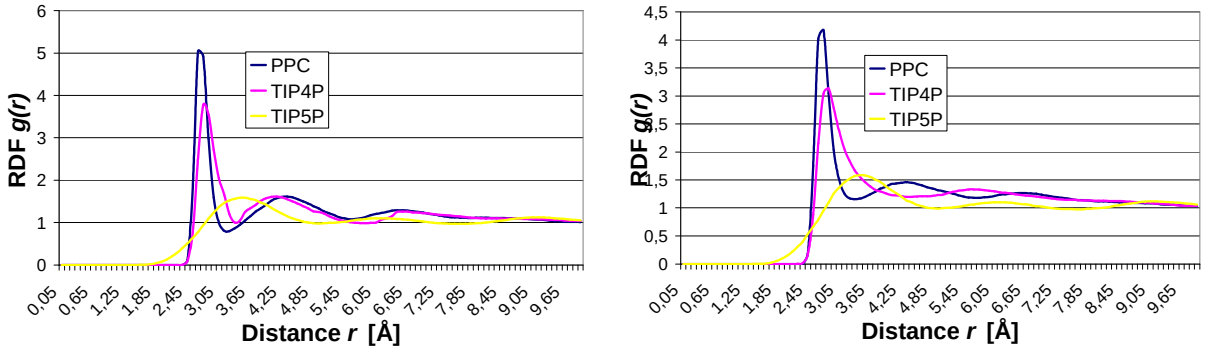


a) b)

Fig. 3. Velocity distributions for two water flows in nanochannel. The flows driven by various nondimensional force F_x was applied to the centre of mass of each water molecule, a) F_x=2.5, b) F_x=5.0. Points • denote the values from simulation, ─ - denote approximating curves

We can observed that value of forces F_x effects on the velocity values of the flow. The velocity changes from 2.5 m/s (Fig. 3a) to 5.5 m/s (Fig. 3b) and the values depend on molecular model water used to nanoflow simulation as well.

To clear this situation corresponding Radial Distribution Function (RDF) was plotted on Figure 4. The Radial Distribution Function (RDF) is a basic measure of the structure of the matter, its shape is different for different states of matter, gases, liquids and solids.



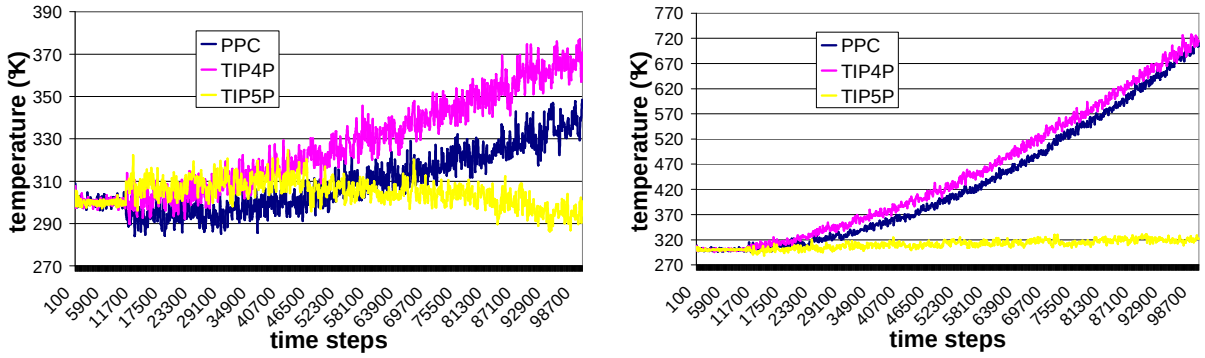
a) b)

Fig. 4. The Radial Distribution Function for simulated two water nanoflows. Flows driven by use of the force a) F_x=2.5, b) F_x=5.0

When the flow is driven by the force F_x = 2.5, the RDF shape for nanoflow of water modelled by use of the TIP5P model is typical like for a solid state of matter and RDF's function shapes for nanoflows of water modeling by use of the PPC and the TIP4P models are typical like for a liquid state of matter (Fig. 2a).

However, when the value of force increases, i.e. F_x = 5.0. the RDF's shape for nanoflows of water modelled by use of the TIP5P model is typical like for a liquid state of matter, RDF shape for nanoflows of water modelled by use of the PPC and TIP4P models is typical like for a gaseous state of matter (Fig. 4b).

To clear this situation we plot values of the water temperature T as a function of time step of the performed nanoflow simulations.
From results presented in Fig. 5, we can note that computer model of water effects on the water nanoflow temperature.
When the force F_x = 2.5 (Fig. 5a) is applied to drive the nanoflow and the TIP5P model to represent a water molecule, the temperature T decreases after 87 000 time steps. The water temperature of nanoflows simulated by use of the PPC and the TIP4P models increases, but for the PPC does not exceed the temperature of the boiling of water (373 K).
However, when force F_x = 5.0 is applied to drive the flow (Fig. 5b), the water temperature for nanoflows simulated by use of the TIP5P water model is constant, but for simulation based on the PPC water model and the TIP4P water model the temperature quickly increases above the temperature of the boiling of water.



a) b)

Fig. 5. The water temperature of nanoflows – the Gaussian thermostat applied, the flow driven by the force a) F_x=2.5, b) F_x=5.0.

Results presented in Fig. 4 and Fig. 5 indicate, that during the nanoflows simulation based on various water computer models the water temperature depends strongly on a) computer model used in simulation, b) force F_x applied to drive the flow. The simulation, for which results are presented above, were performed for identical parameters. The Gaussian thermostat was applied to controlling the temperature of water molecules during the whole simulation. The initial temperature was T = 300 K, time steps Δt = 0.5 fs, when the system reached the equilibrium the positions and velocities of all molecules were recorded in dump files every 100 time steps.

Therefore we can conclude that for each computer model of a water molecule we should individually choose parameters of the MD simulation.

Below we want to show how effects the time step value on the water temperature during nanoflows simulation. We want to present results for water nanoflows driven by use of the nondimensional force F_x = 5.0 and for two cases, when simulation was performed by use of the TIP4 water model and the second one, when simulation was performed by use of the TIP5P water model.

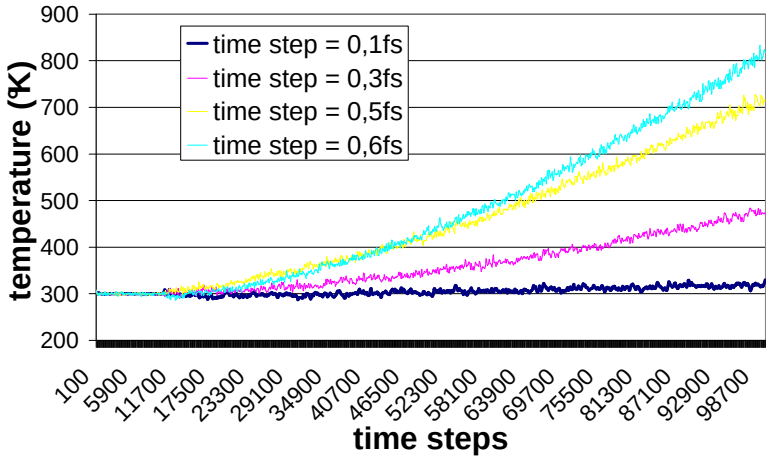


Fig. 6. The temperature of the system – Gaussian thermostat used with different time steps for the model of water TIP4P (force $F_x = 5.0$).

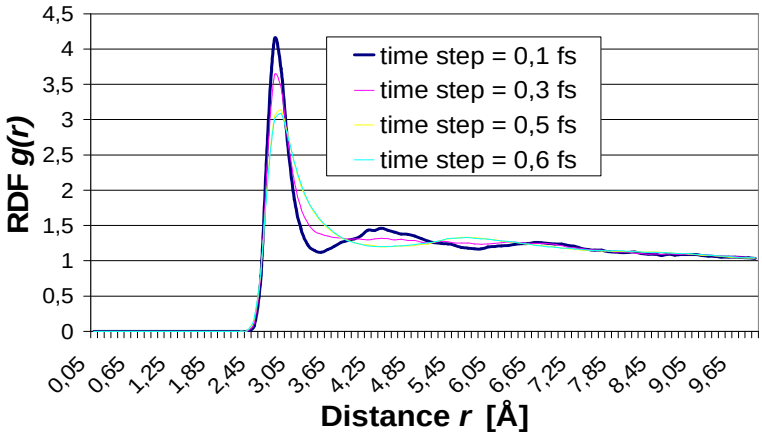


Fig. 7. The Radial Distribution Function – Gaussian thermostat used with different time steps for the model of water TIP4P (force $F_x = 5.0$).

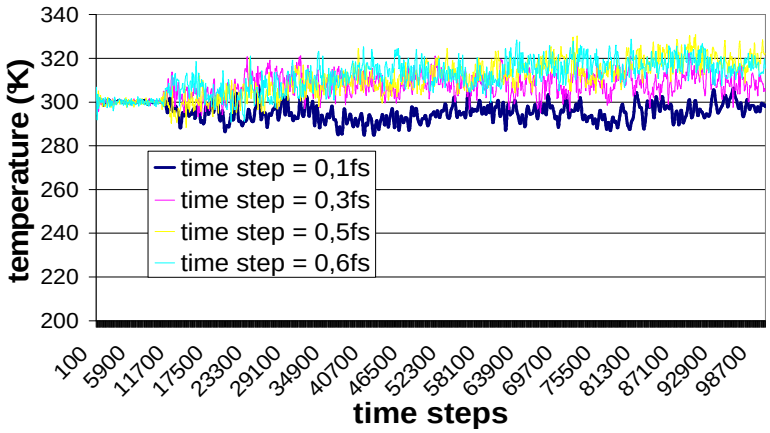


Fig. 8. The temperature of the system – Gaussian thermostat used with different time steps for the model of water TIP5P ($F_x = 5.0$).

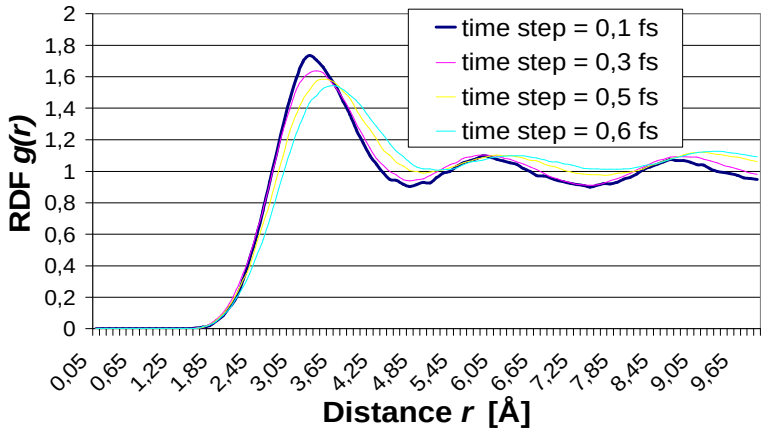


Fig.9. The Radial Distribution Function – Gaussian thermostat used with different time steps for the model of water TIP5P (F_x = 5.0).

From the results presented in diagrams (Fig. 6 – 9) we can conclude, that the temperature of water remains constant during nanoflows simulated by use of the TIP4P and the TIP5P models, if we chose small time step Δt = 0.1 fs. Inappropriate time step can effect quick increment of the temperature (Fig. 6 and Fig. 8) and the change of the water state from liquid to gas (Fig. 7 and Fig. 9).

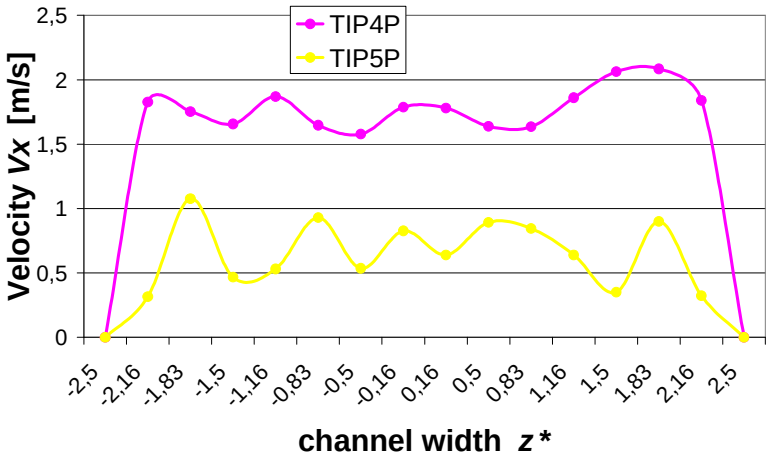


Fig. 10. Velocity distributions for flow of water in a nanochannel, force F_x=5.0, time step Δt = 0.1 fs. Points • denote the values from simulation, ─ - denote approximating curves

Moreover it can be seen that the velocity values obtained from the MD simulation by use of the TIP5P model are smaller than by use of the TIP4P model. Comparing results from Fig. 3b and Fig. 10 we can see that the difference between values of velocity distribution for the TIP4P and the TIP5P decreases when simulation time step decreases to Δt = 0.1 fs.

In conclusion: for each simulation and each computer model of a water molecule we should individually choose the parameters of the MD simulation.

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