

Influence of molecular models of water on computer simulations of water nanoflows

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Abstract—We present some problems related to the influence of molecular models on Molecular Dynamics simulation of water nanoflows. Out of large number of existing models of water we present some results of the MD simulation of water nanoflows for four molecular models: TIP4P, PPC TIP4P-2005, TIP5P.

I. INTRODUCTION

COMPUTER simulation methods have become a very powerful tool for solving many-body problems in statistical physics, physical chemistry and biophysics. Although theoretical description of complex systems in the framework of statistical physics is well developed and the experimental techniques for obtaining detailed microscopic information are quite sophisticated, it is often only possible to study specific aspects of those systems in detail via simulation. On the other hand, simulations need specific input parameters characterizing systems in question, which either come from theoretical considerations or are provided by experiment [1].

The deterministic method of Molecular Dynamics (MD) simulation [2], although theoretically valid for the whole range of densities, is employed mainly for liquids and solids. The long flight paths between collisions of gas molecules make the method of Molecular Dynamics prohibitively expensive, while other methods, like e.g. Direct Monte-Carlo Simulation, can give satisfactory results at much lower computational cost. In liquids the molecules are densely packed and remain in constant contact with the neighbours. Under such conditions Molecular Dynamics seems to be the most accurate and, at the same time, the most efficient simulation method.

Molecular Dynamics requires description of the molecules and the forces acting between them. Perhaps the most often, to describe the forces, the Lennard-Jones potential is used; it assumes that the molecules are spherically symmetric, repelling one another at close and attracting at far distances.

The motivation for this research stems from real nanochannel flow problem. For flows of liquids in nanochannels the continuum description is no longer valid and the Molecular Dynamic Simulation seems to be the only appro-

appropriate approach to the problem. In the following some MD flow simulation results will be presented to illustrate usefulness of the method.

II. MOLECULAR MODELS OF WATER

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

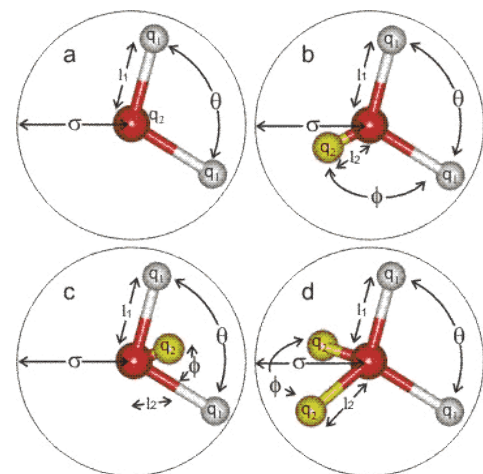


Fig. 1 Most frequently used geometrical model shapes of water molecule

In Table 1 and Fig. 2 we present four molecular models of water, selected for our Molecular Dynamics simulations of flow in nanochannels. Table 2 contains the values of some physical parameters of water, calculated with the use of those models, together with corresponding experimental data. The molecular parameters of copper from [6] and [7] were used.

TABLE I.
PARAMETERS OF THE WATER MOLECULAR MODELS USED IN OUR SIMULATION [13]

Model	Geometrical configuration (Fig. 2)	Lennard-Jones molecular diameter σ , $1*10^{-10}$ 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
TIP4P/2005	c	3.1589	0.7749	0.9572	0.1546	+0.5564	-1.1128	104.52	52.26
TIP5P	d	3.12000	0.6694	0.9572	0.7	+0.2410	-0.2410	104.52	109.47
PPC	b	3.23400	0.6000	0.9430	0.06	+0.5170	-1.0340	106.00	127.00

TABLE II.
CALCULATED PHYSICAL PROPERTIES OF THE WATER MODELS USED IN OUR SIMULATION [13]

Model	Dipole moment $\mu = qi*li$, m	Dielectric constant	Self diffusion 10^{-9} m ² /s	Average configurational energy kJ/mol	Density maximum, °C	Expansion coefficient 10^{-4} °C ⁻¹
TIP4P	2.18	53	3.29	-41.8	-25	4.4
TIP4P/2005	2.305	60	2.08	-	+5	2.8
TIP5P	2.29	81.5	2.62	-41.3	+4	6.3
PPC	2.52	77	2.6	-43.2	+4	-
Experimental	2.65	78.4	2.30	-41.5	+3.984	2.53

III. MOLECULAR DYNAMICS

Molecular Dynamics simulation method treats the medium as an ensemble of molecules. Each molecule may consist of one or more atoms attached to each other in the way specific for given substance. It is assumed that:

- each atom is treated as a point mass,
- simple force rules describe the interactions between atoms; force acting on a molecule is a sum of forces acting on all constituent atoms,
- Newton's equations of motion are integrated to obtain coordinates and velocity of each molecule as a function of time (see Fig.2)
- thermodynamic statistics are extracted from positions and velocities of the molecules.

The orientation of the molecules can be represented in several ways, however the use of quaternions [4] seems to be the most advisable. The most important advantage of quaternions is the fact, that they lead to equations of motion free of singularities (which is not the case for e.g. Euler angles). This, in turn, leads to good numerical stability of the simulation.

Integration algorithms used in Molecular Dynamics simulation are based on finite difference methods, with discretized time and the time step equal to Δt . Knowing the positions and some of their time derivatives at time t (the exact details depend on the type of algorithm), the integration scheme gives the same quantities at a later time ($t + \Delta t$). With such procedure the evolution of the system can be followed for long times [3].

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.
- Balancing: 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 the 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 simulation starts. The required data (specified in advance) are accumulated in “dump-files” in preselected time intervals. Any property of interest, dynamic or static, may then be evaluated with the use of the data in the dump.

In molecular dynamics we follow the laws of classical mechanics,

$$F_i = m_i * a_i$$

for each atom i in system constituted by N atoms. Here m_i is the atom mass, $a_i = d^2 r_i / dt^2$ its acceleration, and F_i the force acting upon it, due to the interactions with other atoms [3].

The motion is governed by the Newton-Euler equations

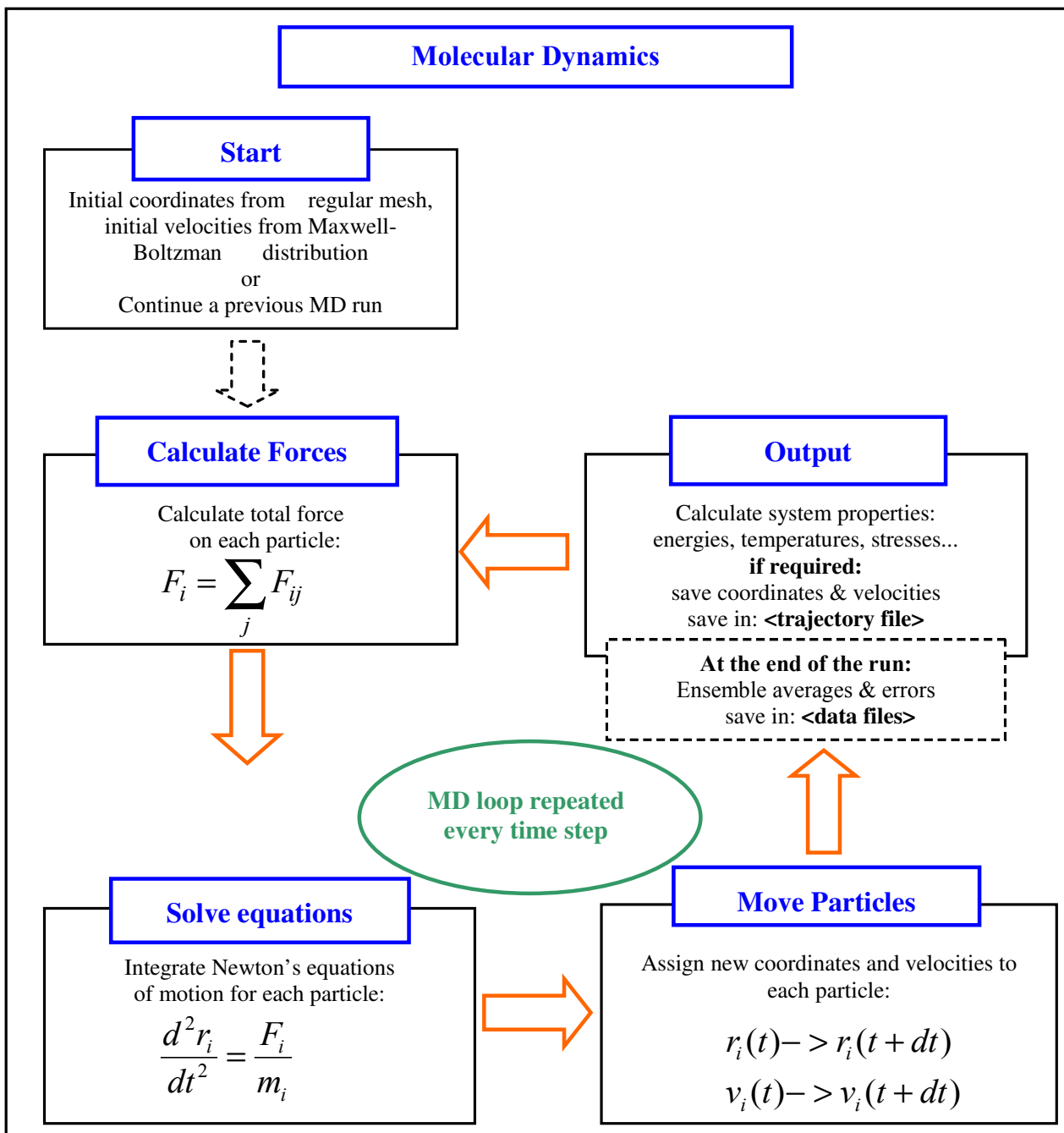


Fig. 2 Simplified algorithm of Molecular Dynamics

$$M_i \ddot{R}_i = F_i + F_x$$

where M_i is total mass molecule i , R_i is the centre of mass of molecule i , F_i is the total force acting on molecule i , F_x is a mass force necessary to set water in motion (see Section IV).

IV. MOLECULAR DYNAMICS SIMULATIONS OF PLANE NANOFLOWS

In the present chapter the results of the simulations of plane flows of water through narrow copper channels [9,10,11,12] are presented.

Simulations were carried out for four models of water, as described in Section 2. The assumed channel width was equal to approximately 5 diameters of the water molecule. Physical properties of the materials and, in particular, their electrostatic interactions were taken into account.

To set water in motion, a mass force F_x , directed along x – axis, in positive direction, was applied to every water molecule. Three values of F_x were selected: 0.5, 2.5 and 5.0. Mass force is nondimensional. This force set the only molecules of water. Wall of channel is stable during flows of water.

The simulations were performed with the program MOLDY [4], suitably modified for our purposes. Moldy is a computer program for performing molecular dynamics simulations of condensed matter. Moldy is free software; which may redistribute it and/or modify it under the terms of the GNU.

As mentioned before, some methods of temperature control may sometimes be necessary during the simulation. At the initial stage of equilibration the excess heat comes from potential energy of nonequilibrium configuration of the molecules (first 10000 time step - Fig 3 and Fig 4). Later, when

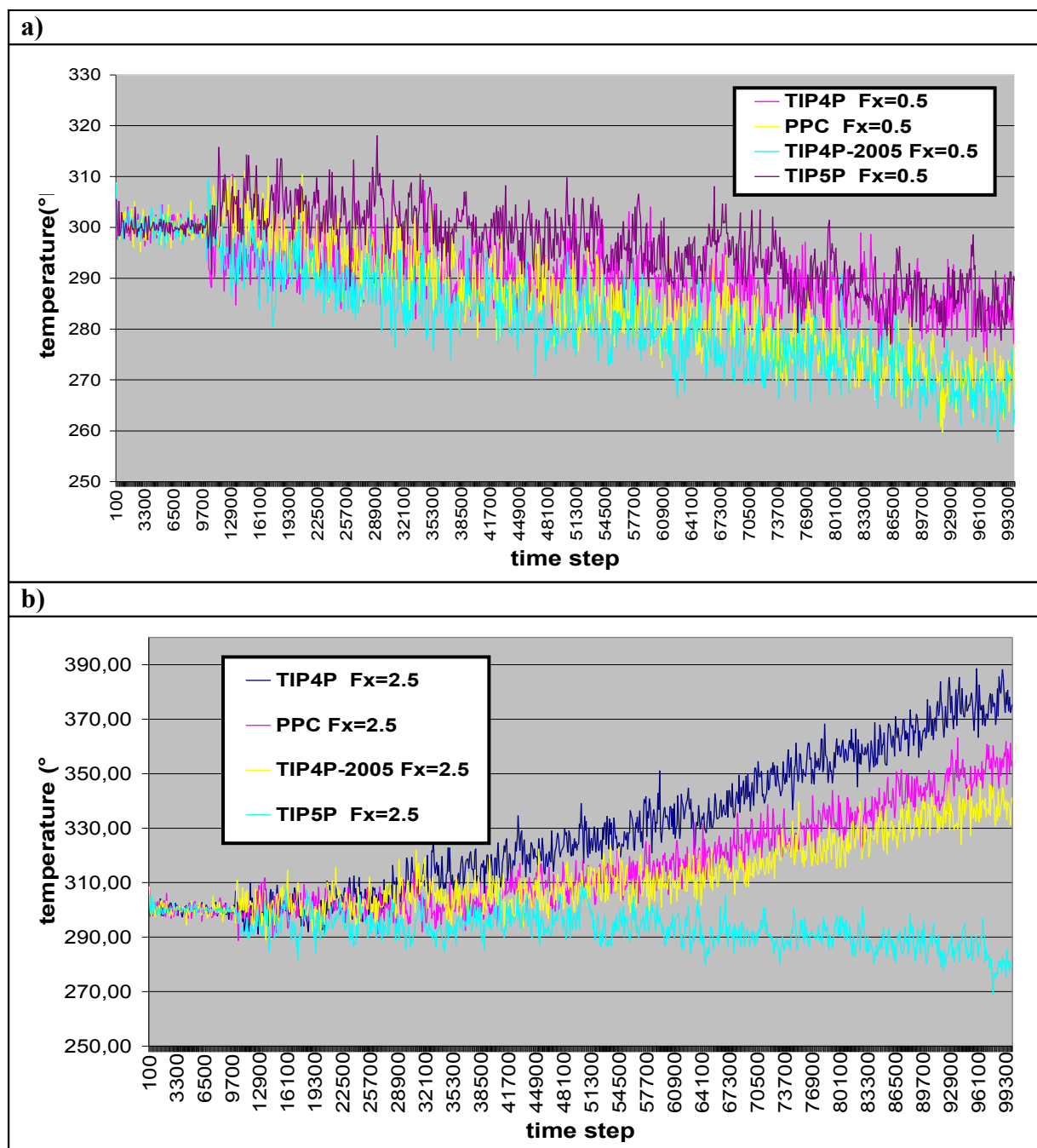


Fig. 3 Temperature of the system – Gaussian thermostat used for various models of water
a) mass force $F_x = 0.5$, b) mass force $F_x = 2.5$.

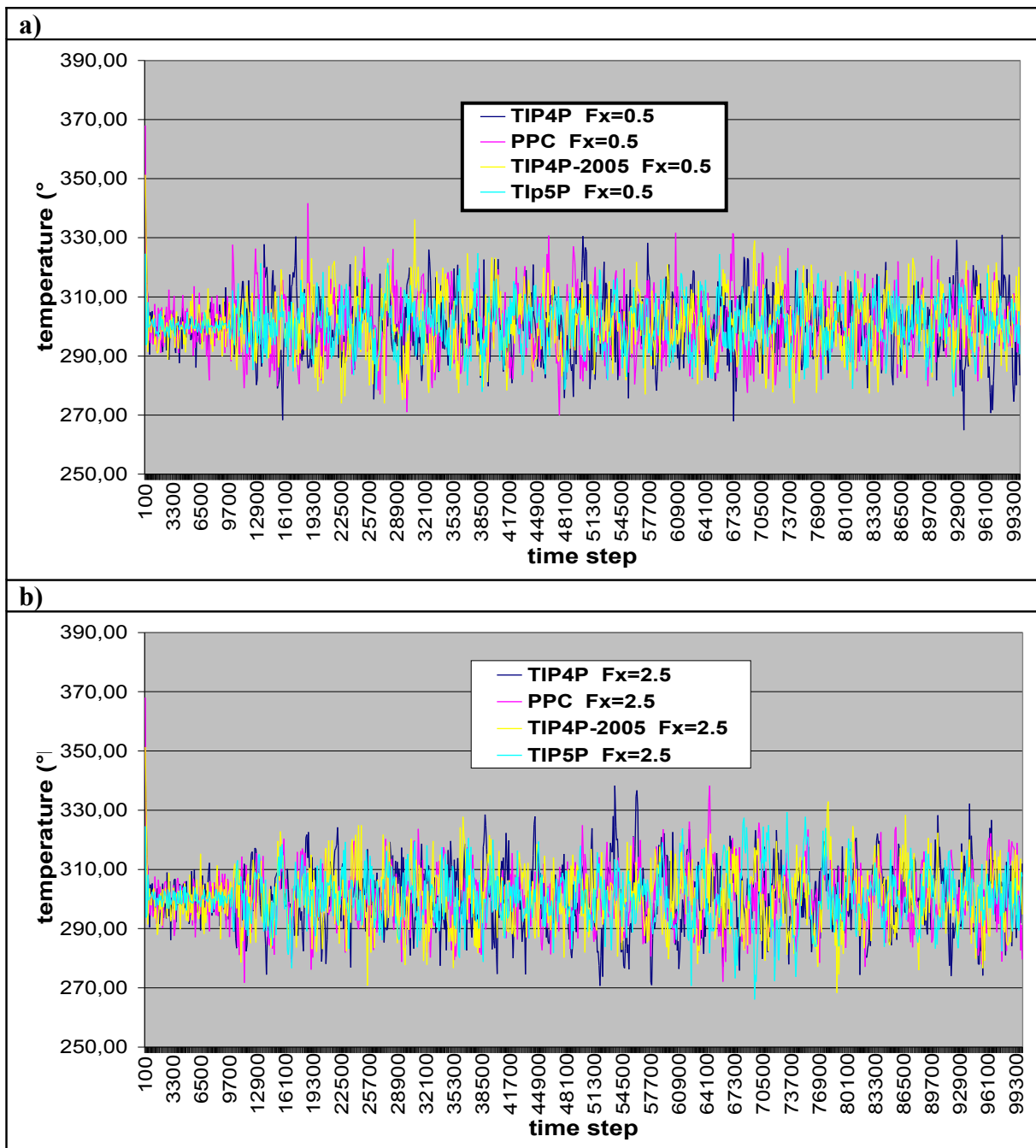


Fig. 4 Temperature of the system – Nosé-Hoover thermostat used for various models of water
 a) mass force $F_x = 0.5$, b) mass force $F_x = 2.5$.

water flows under the influence of a mass force, heat is produced due to “friction” at the walls, which in molecular scale are always rough.

The program MOLDY offers three mechanisms of temperature control. In our simulations the technique of “velocity scaling” (multiplication of the molecular velocity components of all molecules by square root of the required temperature divided by the actual temperature of the medium) has been used during the equilibration period only, as it does not generate correct particle trajectories.

The Nosé-Hoover method couples the system to a heat bath using a fictional dynamical variable, while the Gaussian

thermostat replaces the Newton-Euler equations by variants of which the kinetic energy is a conserved quantity [4]. The last two methods have been used to control temperature after equilibration of the system.

The calculations were carried out over 100 000 time steps $\Delta t = 0.005$ picosecond long, after the system has reached the equilibrium. The positions and velocities of all molecules were recorded in dump files every 100 time steps, for further use.

Figures 3 – 7 present some selected results of our simulations. Figures 3 and 4 illustrate the efficiency of the two thermostats – Gaussian and Nosé-Hoover – for considered flows,

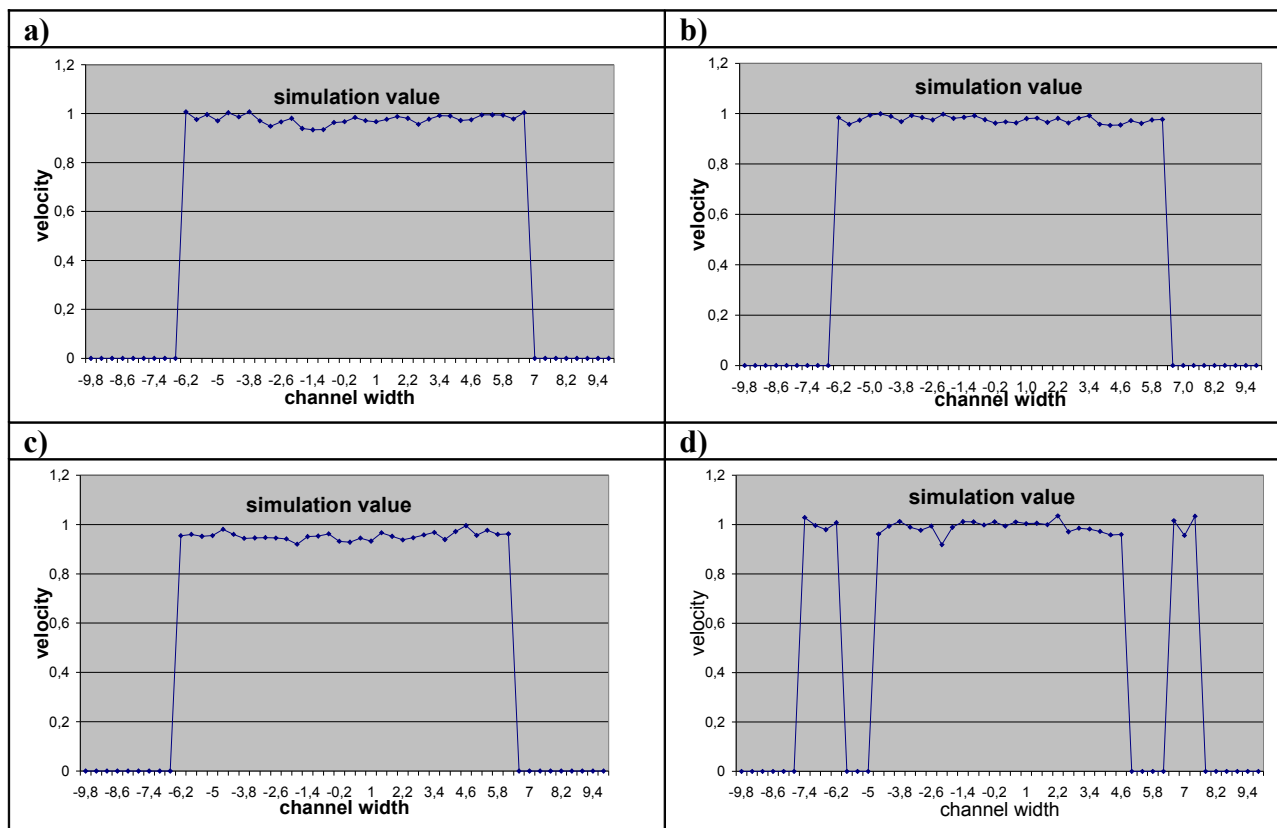


Fig. 5 Velocity distributions for flow of water in nanochannels, ($F_x=0.5$, Gaussian thermostat)
a) PPC, b) TIP4P, c) TIP4P-2005, d) TIP5P.

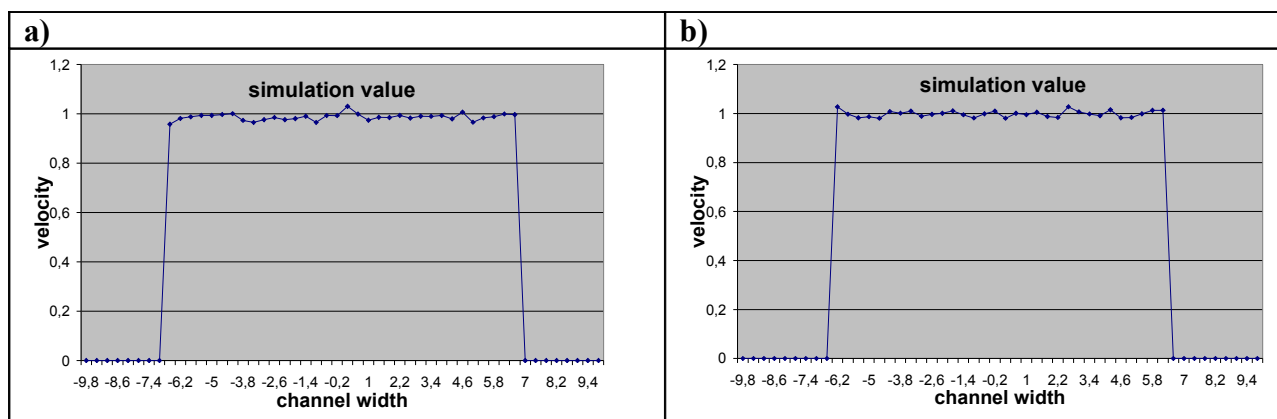


Fig. 6 Velocity distributions for flow of water in nanochannels, ($F_x=0.5$, Nosé-Hoover thermostat)
a) PPC, b) TIP4P.

at different mass forces acting on the molecules and different water models. On figure 3 we can see that for some the models of water the growth of force calling out the flow of water the growth of temperature effects.

Figures 5, 6 and 7 present velocity distributions in the channel cross-section perpendicular to the x – axis. Quickly increasing and declining graph it shows the wall of channel.

From the presented diagrams it is clear, that for the problems considered, i.e. flows in nanochannels, the Nosé-Hoover thermostat is much more efficient than the Gaussian one. The physical explanation of other peculiarities of the di-

agrams, particularly the behaviour of different models of water, requires further investigation. All our simulations be realized on our server on which programme MOLLY was compiled and started with different entrance described parameters overhead.

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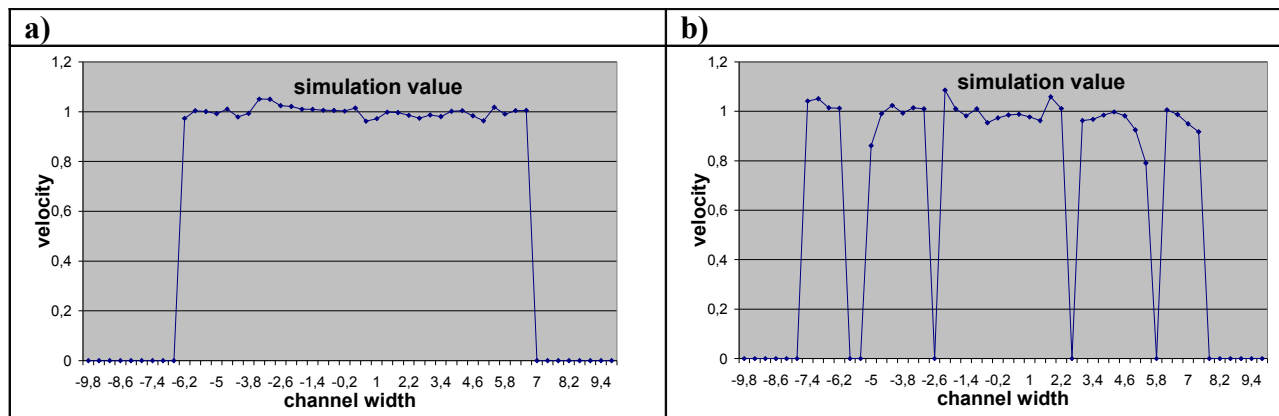


Fig. 7 Velocity distributions for flow of water in nanochannels, ($F_x=0.5$, Nosé-Hoover thermostat)
 a) TIP4P-2005, b) TIP5P

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