VERIFICATION AND VALIDATION OF MOLECULAR DYNAMICS SIMULATIONS

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Abstract. *We present some problems related to the influence of molecular models and different parameters of algorithms on Molecular Dynamics simulation of water nanoflows. We study the effect of water molecular models and thermostats on convergence to equilibrium in Molecular Dynamics simulation of the nanoflows of water. Out of large number of existing models of water we present the results for four selected ones, namely: TIP4P, PPC, TIP4P-2005, TIP5P, and for two thermostats – Gaussian and Nosé Hoover.*

1 INTRODUCTION

Numerical modeling and simulation is widely used in the practice of scientific research, engineering design and industrial applications throughout the world. Physical prototype models are now being improved and sometimes replaced with computer models, which have made significant economical and social impact. In many numerical simulations, the fundamental problems usually occur at the contact of the continuous model, consisting of the initial system of differential equations and boundary conditions, and the discrete model.

Computer simulations are a very powerful tool for solving many-body problems in statistical physics, physical chemistry and biophysics. The deterministic method of Molecular Dynamics (MD) simulations [1] is employed mainly for liquids and solids in nanoscale. Molecular Dynamics requires description of geometry of the molecules and the forces acting between them. The results of MD simulations of water flows in rectangular nanochannels, induced by gravitational force field are presented in [2, 3]. As the structure of the water molecule is relatively complex, a number of simplified models have been proposed in the literature [4]. Here we study the effect of the water molecular models on simulation of the nanoflows. The aim of the present work is to learn how the quality of the simulated properties of the molecular system depends on the used molecular model of water. The results for simulated water flows in copper nanochannels, for four molecular models: TIP4P, PPC, TIP4P-2005, TIP5P and for two thermostats – Gaussian and Nosé-Hoover, are presented and discussed.

Verification and Validation is the multi-disciplinary process of demonstrating credibility in simulation results. Credibility is built by collecting evidence that the numerical model is being solved correctly and the simulation model adequately represents the appropriate physics. The former activity is called Verification and requires intimate knowledge of the mathematical model representing the physics, the numerical approximation derived from that model, software quality engineering practices, and numerical error estimation methods. The latter, termed Validation is accomplished by comparing simulation output with experimental data and quantifying the uncertainties in both. Broad knowledge of modeling and experimentation, augmented with a deep understanding of statistical methods, are necessary for Validation.

The V&V are the questions whose methodology was examined well and described in the literature wide in the case many of classic computational methods e.g. CFD.

The methods of V&V for Molecular Dynamics were not processed until now, though problems this, because consideration the development of nanotechnology, is unusually significant.

2 MOLECULAR DYNAMICS SIMULATIONS

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.1)

- 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 [5] 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 + Δt). With such procedure the evolution of the system can be followed for long times [6].

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,

$$F_i = m_i * a_i \qquad (1)$$

for each atom i in system constituted by N atoms. Here mi is the atom mass,

$$a_i = d^2 r_i / dt^2 \qquad (2)$$

its acceleration, and F_i the force acting upon it, due to the interactions with other atoms [6].

The motion is governed by the Newton-Euler equations

$$M_i \ddot{R}_i = F_i + F_x \qquad \qquad I_i \cdot \dot{\omega}_i - \omega_i \times I_i \cdot \omega_i = N_i \qquad (3,4)$$

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, ω_i is the angular velocity of the molecule, I_i is the inertia tensor.
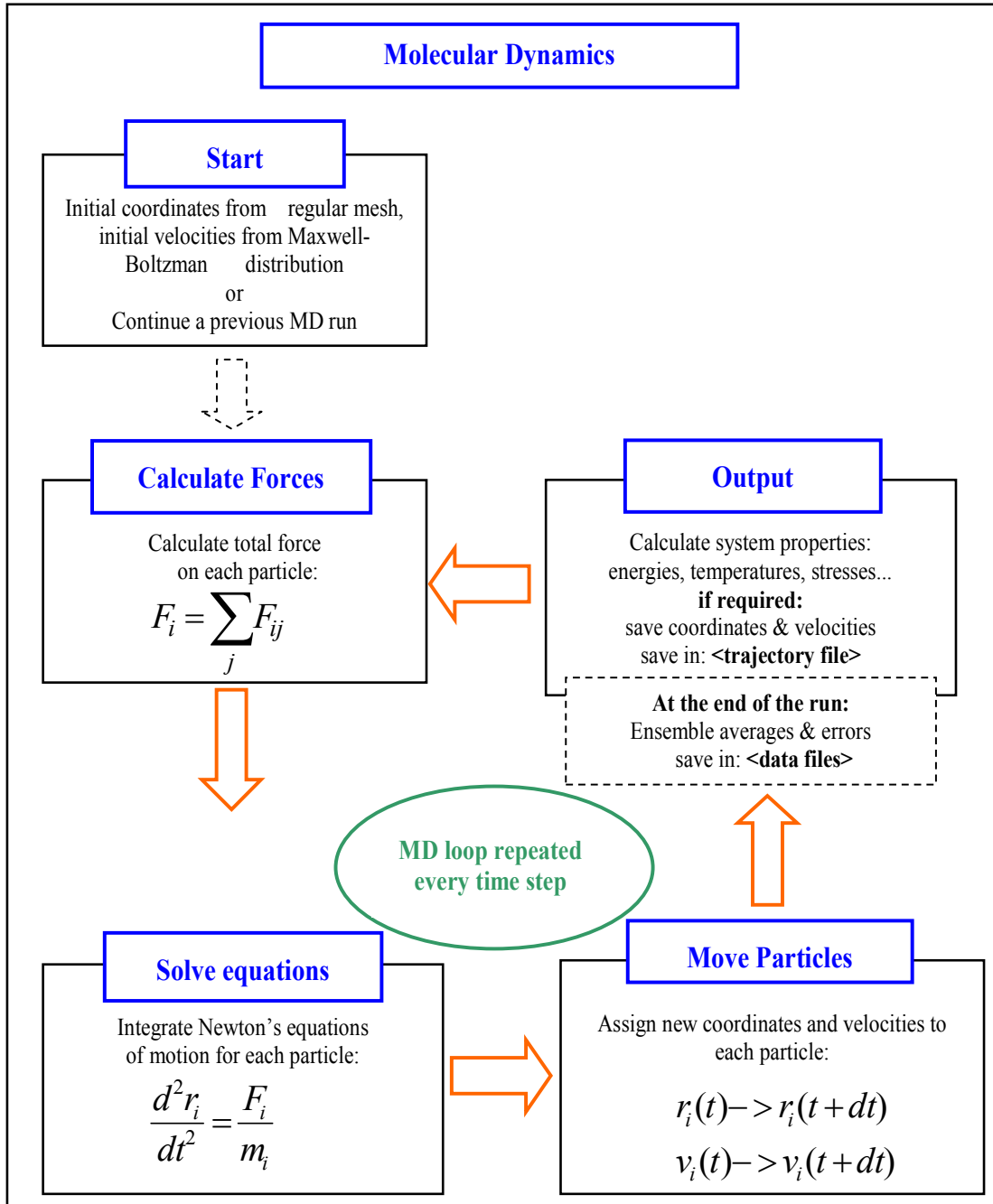
Molecular Dynamics

Start

Initial coordinates from regular mesh, initial velocities from Maxwell-Boltzman distribution

or

Continue a previous MD run

Calculate Forces

Calculate total force on each particle:

$$F_i = \sum_j F_{ij}$$

Output

Calculate system properties: energies, temperatures, stresses...

if required:
save coordinates & velocities
save in: **<trajectory file>**

At the end of the run:
Ensemble averages & errors
save in: **<data files>**

MD loop repeated every time step

Solve equations

Integrate Newton's equations of motion for each particle:

$$\frac{d^2 r_i}{dt^2} = \frac{F_i}{m_i}$$

Move Particles

Assign new coordinates and velocities to each particle:

$$r_i(t) -> r_i(t + dt)$$
$$v_i(t) -> v_i(t + dt)$$

Fig. 1: Simplified algorithm of Molecular Dynamics.

3   RESULTS

The simulations were carried out for four models of water: TIP4P, PPC, TIP4P-2005 and TIP5P. The program MOLDY [5], suitably modified, was used for this purpose. The nanochannel walls were built from copper atoms and its width was equal to 5 diameters of the water molecule. The physical properties of materials and their electrostatic interactions were taken into account. The number of copper atoms in the wall was equal to 236; the number of water molecules was equal to 280. The periodic boundary conditions were applied. The Lennard-Jones potential was assumed for

interactions between water molecules and also between water molecules and wall atoms [2, 3]. To drive the flow, a constant force F_x was applied to the centre of mass of each water molecule (see Section 2).

3.1   Temperature control

As mentioned before, some means of temperature control are necessary during the simulation. At the initial stage the excess heat comes from the potential energy of nonequilibrium configuration of the molecules. Later, when water flows under the influence of the mass force F_x, the heat results from friction at the walls.

The program MOLDY offers several mechanisms to control the temperature. The Nosé-Hoover thermostat couples the system to a heat bath of the desired temperature T, using a fictitious dynamical variable ξ:

$$\dot{\xi} = \frac{g}{Q}(t - T) \tag{5}$$

where g is the number of degrees of freedom in the system, Q is the associated fictitious "mass",

The Gaussian thermostat replaces the Newton-Euler equations by variants, in which the kinetic energy is a conserved quantity [5].

$$\ddot{R}_i = \frac{F_i}{M_i} - \xi_T \dot{R}_i \qquad \qquad \xi_T = \frac{\sum_j v_j \cdot F_j}{\sum_j M_j v_j^2} \tag{6,7}$$

$$I_i \cdot \dot{\omega}_i - \omega_i \times I_i \cdot \omega_i = N_i - \xi_R I_i \cdot \omega_i \qquad \qquad \xi_R = \frac{\sum_j \omega_j \cdot N_j}{\sum_j \omega_j I_j \omega_j} \tag{8,9}$$

Results of simulations show the equilibration process for four water molecular models and the two described thermostats.
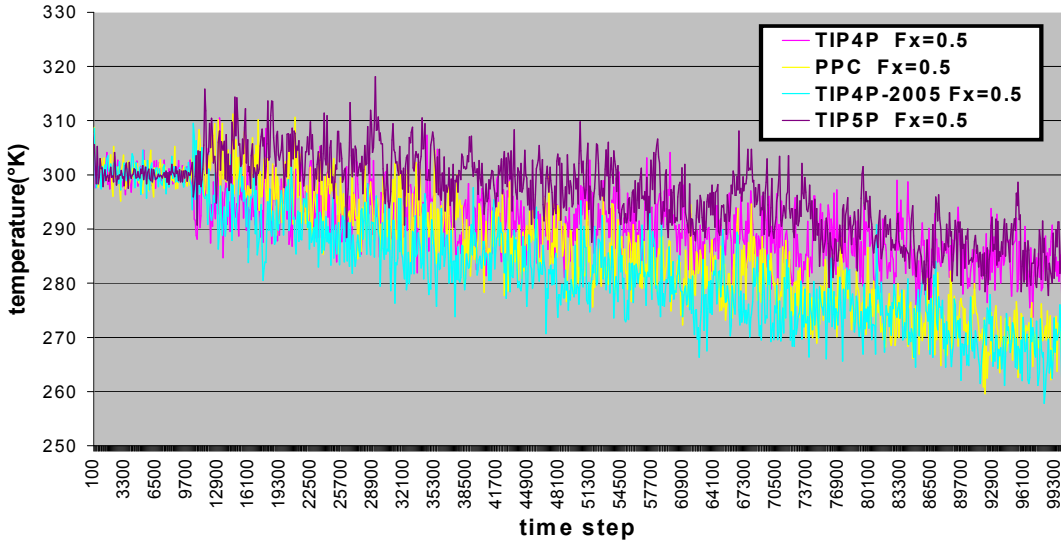

Fig. 2: Temperature of the system – Gaussian thermostat used for various models of water
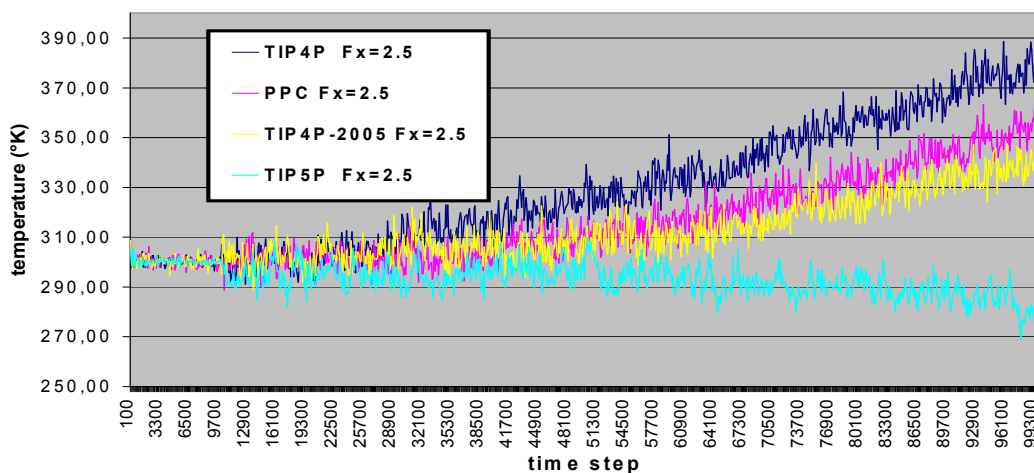Force $F_x = 0.5$

5

Fig. 3: Temperature of the system − Gaussian thermostat used for various models of water
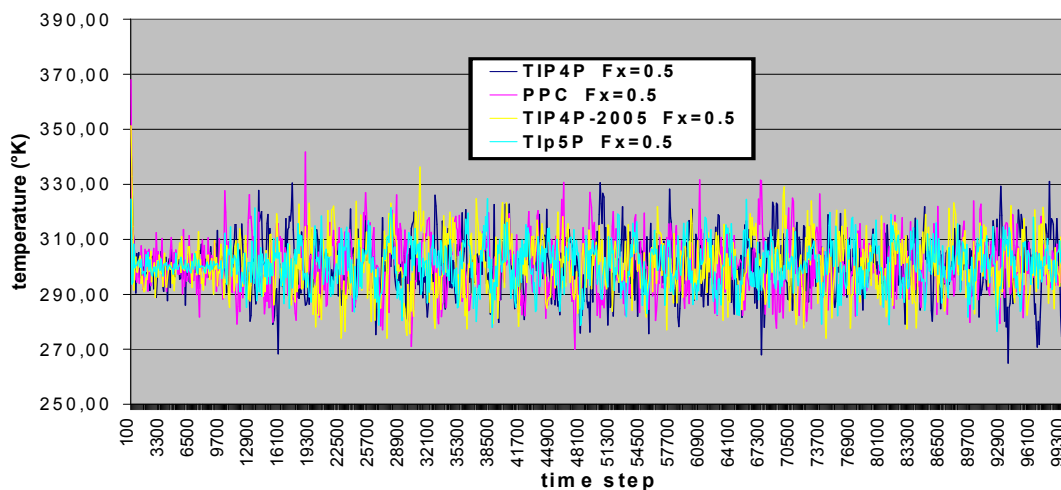Force $F_x = 2.5$

Fig. 4: Temperature of the system − Nosé-Hoover thermostat used for various models of water
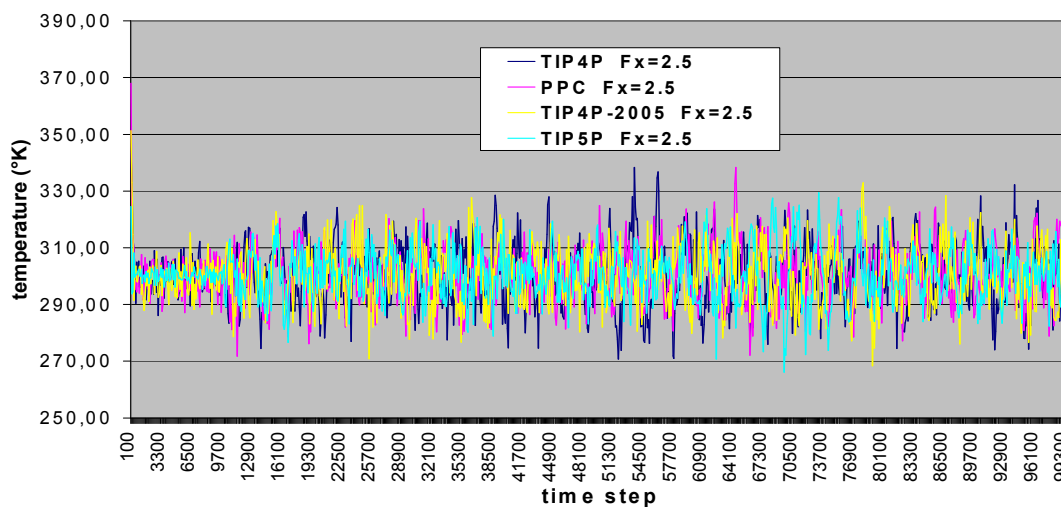Force $Fx = 0.5$

Fig. 5: Temperature of the system − Nosé-Hoover thermostat used for various models of water
Force $F_x = 2.5$

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3.2   Integration algorithms and time step

A standard method for solution of ordinary differential equations such as 3 and 4 (see section 2) is the finite difference approach.

The general idea is as follows. Given the molecular positions, velocities, and other dynamic information at time t, we attempt to obtain the positions, velocities etc. at a later time t + Δt to a sufficient degree of accuracy. The equations are solved on a step-by-step basis.

In MOLDY the dynamical equations 3 and 4 are integrated using of the Beeman algorithm[7]. For atomic systems the accuracy is of the same order as the commonly used Verlet algorithm[8].

The calculations were carried out over 100 000 time steps $\Delta t = 0,0006$, $\Delta t = 0,0005$ and $\Delta t = 0,0003$ 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.

Results shows the influence of the choice of time step on the correct functioning of the thermostat method and the authenticity of the results of the whole simulation.
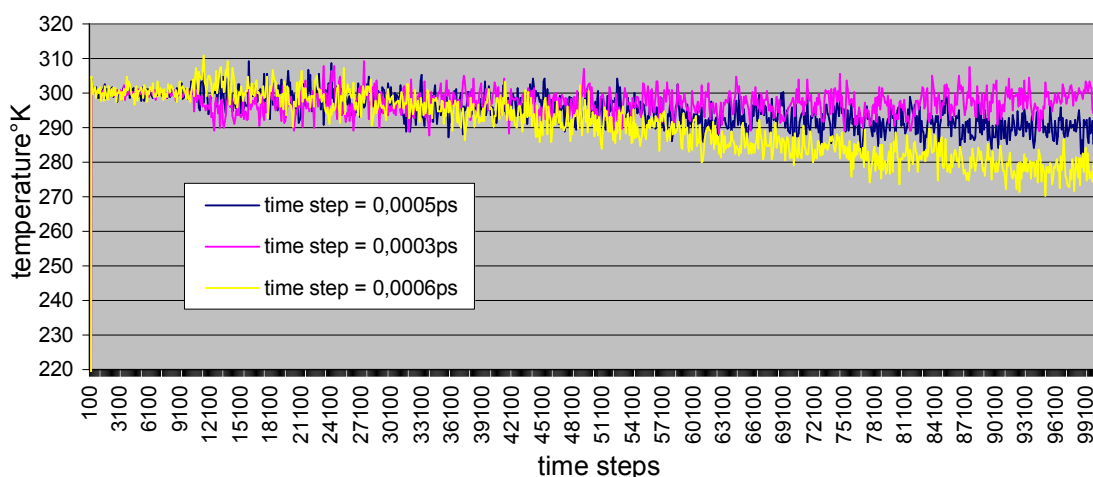

Fig. 6: Temperature of the system − Gaussian thermostat used with different time step for model of water TIP4P. Force $F_x = 2.5$
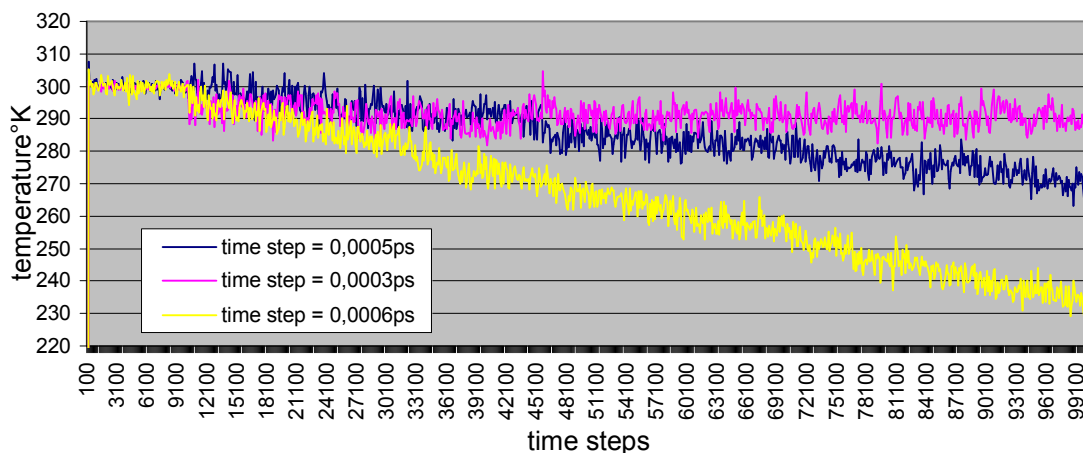

Fig. 7: Temperature of the system − Gaussian thermostat used with different time step for model of water PPC. Force $F_x = 2.5$

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4   CONCLUSIONS

The results show, that for the simulations of nanoflows with Gaussian thermostat, the temperature of the system increases in time when water models TIP4P, PPC, TIP4P-2005 are used, and decreases when TIP5P is used (see Fig.3). During simulations with Nosé-Hoover thermostat the value of the mean temperature of the system remains almost constant for all considered water models (see Fig.4 and Fig.5). The convergence to equilibrium is very fast in this case. It seems, that for the problems considered the Nosé-Hoover thermostat is much more efficient than the Gaussian. The physical explanation of other peculiarities of the presented diagrams, particularly the temperature oscilations and the behaviour for TIP5P model, requires further investigation.

From the presented diagrams it is clear, that for the problems considered, i.e. flows in nanochannels, the Gaussian thermostat is much more efficient if the time step Δt is smaller (see Fig.6 and Fig.7).

The smaller time step effects enlargement of the time of the whole simulation and the required memory, however the larger temporary step can effect generating the inaccurate trajectory of motion. Clearly, the larger time step, the less accurately will our solution follow the correct classical.

The study of V&V methods gives the possibility of the construction of the correct computer model to the description of the studied phenomenon, how also receipt of the exact and authentic results of computer simulations.

Influence on the results of the simulation in the Molecular Dynamics method has e.g. Integration algorithms and time step, molecular model of water or another material, mechanisms to control the temperature of the system. Therefore the study of the methods of V&V will be connected with above mentioned factors exactly.

The study of the procedures of Verification and Validation for the Molecular Dynamics has the large signification, because correct simulating real processes in nanoscale will make possible.

REFERENCES

[1] M.P. Allen, D. J. Tildesley: Computer simulations of Liquids, Oxford University Press, 1987;

[2] A. Kucaba-Pietal: Microflows modelling by use micropolar fluid model, OW RUT, Rzeszow, 2004;

[3] A. Kucaba-Pietal, Z.A. Walenta, Z. Peradzyński: Water flows in copper and quartz nanochannels, [in] Mechanics of the 21-th Century. (Ed. W.Gutkowski, T.Kowalewski), Springer, Dodrecht, 2005;

[4] M. Chaplin: Water Structure and Science, Water Models, http://www.lsbu.ac.uk/water/, 17.07.2008;

[5] K.Refson: "Moldy User's Manual". Chapter II, ftp://ftp.earth.ox.ac.uk/pub;

[6] F. Ercolessi: A molecular dynamics primer, Spring College in Computational Physics, ICTP, Trieste, Italy, 1997;

[7] D. Beeman: Some multistep methods for use in molecular dynamics calculations, J. Comp. Phys. 20 (1976), 130-139;

[8] L. Verlet: Computer `experiments' on classical fluids. I. thermodynamical properties of lennard-jones molecules, Phys. Rev. 165 (1967), 201-214;