Keldysh Institute of Applied Mathematics
Russian Academy of Sciences
National Research Nuclear University MEPhI

Multiscale Multilevel Approach to Solution of Nanotechnology Problems

Sergey V. Polyakov, Yuri N. Karamzin,
Tatiana A. Kudryashova, Viktoriia O. Podryga,
Dmitry V. Puzyrkov

polyakov@imamod.ru

Moscow, Russia, MMCP, 2017

OUTLINE OF THE PRESENTATION

- Technology problem
- Statement of the model problem
- Macroscopic model
- Molecular interaction model
- Boundary conditions
- Numerical scheme
- Parallel implementation
- Results
- Conclusion

TECHNOLOGICAL PROBLEM

- ***TECHNOLOGICAL PROCESS***

-supersonic cold gas spraying of nanopowders on the surface of products in electronics

- ***TOPICALITY AND PERSPECTIVES***

-the creation of new systems of nanoprinting, new electronic circuits with specified nano-sizes and configuration, implementation of chips on quantum effects (quantum wires, arrays of quantum dots, etc.).

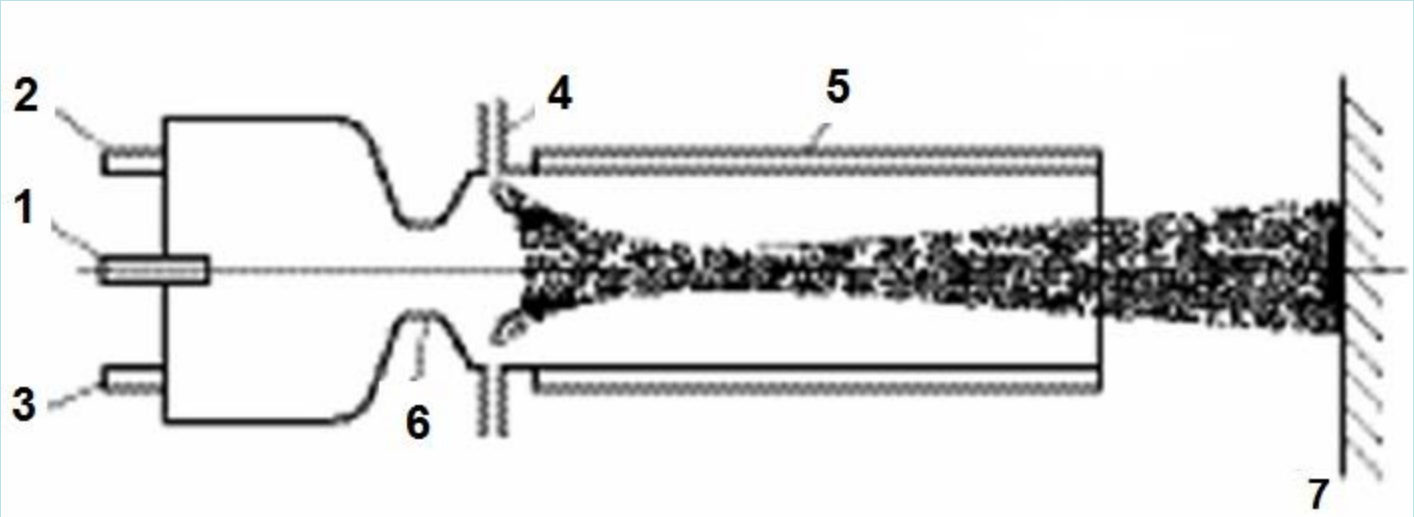
- ***TECHNICAL PROBLEMS TO BE RESOLVED BY MODELING***

- providing specified accuracy and speed of nanoprinting,
- providing maximum purity of products,
- providing mass release of products

- ***MATHEMATICAL PROBLEMS***

- lack of adequate mathematical models and simulation tools

SCHEME OF HIGH-SPEED SPRAY



1 – input of powder (axial);
2,3 – input of gas mixture components;
4 – input of powder (radial);
5 – trunk;
6 – nozzle.
7 - substrate

FEATURES OF SELECTED FORMULATION OF THE PROBLEM

- neutral conditions without combustion and chemical reactions
- temperature range is (80-800) K (below the melting point of the nanopowder)
- deposition using a mixture of neutral gases (pure)
- many technical systems use a mixture of N_2 + H_2
- micron and sub-micron sizes of channel and nozzles
- matrix delivery system of nanoparticles
- the size of the powder nanoparticles ~ 5-10 nm
- nanoparticles materials: Cu, Al, Ni, Ta
- substrate materials: polysilicon, SiO_2, SiC

SPECIFICS OF THE PROBLEM AND SOLUTIONS

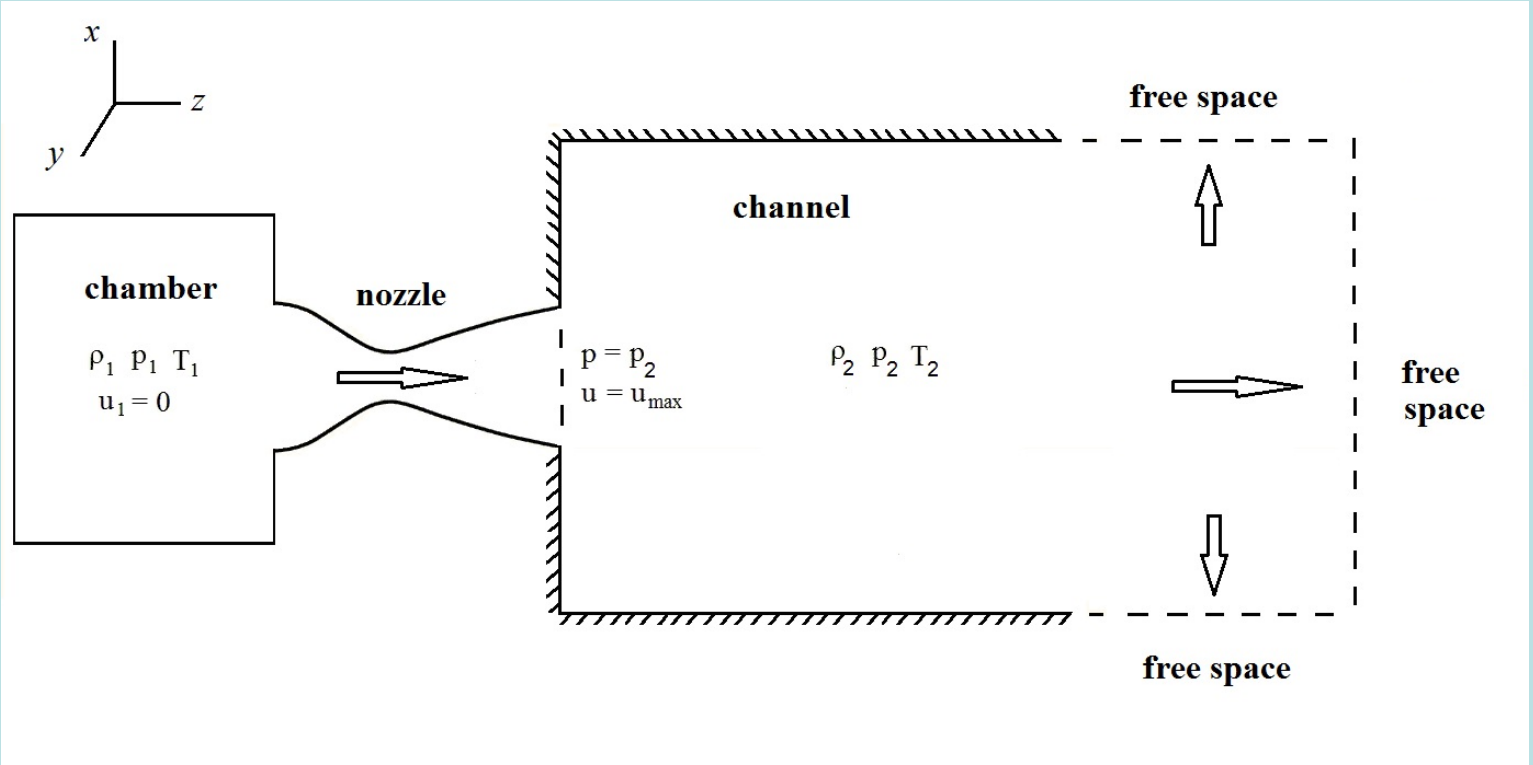
SPECIFICS OF THE PROBLEM

- Rarified gas mixture
- Interaction of gases with metals on boundaries
- Multiscalability
- Unknown properties of materials

PROPOSED SOLUTIONS

- New multiscale numerical approach
- Base macroscopic model is quasi-gasdynamics equation system
- Base microscopic model is Newton's dynamics equation system
- Grid and sub-grid parallel computations
- Compute of data base for properties of materials

STATEMENT OF THE MODEL PROBLEM



MODEL PROBLEM PARAMETERS

- Nitrogen-Hydrogen gas mixture
- Nickel walls of the channel
- Normal temperature conditions (T_1,T_2=273.15 K)

MULTISCALE APPROACH

Multiscale approach consists of the using of two or more scale levels.

For the considered problem we use 2 levels: **macro-** and **micro- levels**

Macrolevel sizes: 10-1000 mean free paths of gas molecules

Microlevel sizes: 0.001-10 mean free paths of gas molecules

For T=273.15 K free paths is $<\lambda> \sim 100$ nm

Channel diameter: 10 – 10000 nm (Knudsen numbers: 0.01 – 10)

Channel length: 10 – 10000 μm (Knudsen numbers: 0.01 – 0.00001)

Model on macrolevel: **QuasiGasDynamics** (QGD)

Model on microlevel: **Molecular Dynamics** (MD)

Why MD?

MD is effective alternative of Boltzmann equation by the Monte-Carlo methods

MD allows:

- to calculate of the momentum exchange and energy exchange between components of gas mixture

- to analyze the interaction of gas with microchannel surface: boundary conditions

- to determine the gases macroparameters: EoS (equation of state) for real gas

- to obtain the transport coefficients and other flow parameters

MULTISCALE ALGORITHMS

1st Class Algorithms: calculating the gases and solids properties using only MD => MD Database

2nd Class Algorithms: calculating the gases flows in microchannels using QGD + MD Database (no “online” MD calculations)

3rd Class Algorithms: calculating the gases flows in microchannels using QGD + MD Database for the boundary area and MD calculations in the flow

4th Class Algorithms: calculating the gases flows in microchannels using QGD + MD (MD calculation on every step, in every microvolume)

MACROMODEL: QGD EQUATIONS

$$\frac{\partial \rho_l}{\partial t} + div\, \mathbf{W}_l^{(\rho)} = 0, \quad \mathbf{W}_l^{(\rho)} = \rho_l \mathbf{u}_l - \rho_l \mathbf{w}_l, \quad \mathbf{w}_l = \tau \left[(\mathbf{u}_l, \nabla)\mathbf{u}_l + \frac{1}{\rho_l} \nabla p_l \right],$$

$$\frac{\partial}{\partial t} \rho_l u_{l,k} + div\, \mathbf{W}_l^{(\rho u_k)} = S_l^{(\rho u_k)},$$

$$W_l^{(\rho u_k)} = \rho_l \mathbf{u}_l u_{l,k} + \mathbf{e}_k \left(p_l + \frac{2}{3} \mu_l\, div\, \mathbf{u}_l \right) - \mu_l \left(\nabla u_{l,k} + (\nabla, \mathbf{e}_k)\mathbf{u}_l \right) - \left(\rho_l w_{l,k} \mathbf{u}_l + \rho_l \mathbf{w}_l u_{l,k} \right),$$

$$S_l^{(\rho u_k)} = \nu_{ll'} \rho_l \left(\overline{u}_{l,k} - u_{l,k} \right), \quad l = a, b, \quad l' = b, a, \quad k = 1, 2, 3,$$

$$\frac{\partial}{\partial t} E_l + div\, \mathbf{W}_l^{(E)} = S_l^{(E)},$$

$$\mathbf{W}_l^{(E)} = \left(\rho_l \mathbf{u}_l - \rho_l \mathbf{w}_l \right) H_l - \chi_l \nabla T_l + \left(\frac{2}{3} \mu\, div\, \mathbf{u}_l \right) \mathbf{u}_l - \sum_{k=1,2,3} \mu \left(\nabla u_{l,k} + (\nabla, \mathbf{e}_k)\mathbf{u}_l \right) + (\rho_l \mathbf{w}_l, \mathbf{u}_l)\mathbf{u}_l,$$

$$S_l^{(E)} = \nu_{ll'} \rho_l \left(\overline{E}_l - E_l \right), \quad l = a, b, \quad l' = b, a,$$

$$E_l = \frac{1}{2} \rho_l \left| \mathbf{u}_l \right|^2 + \rho_l \varepsilon_l, \quad p_l = Z_l \rho_l \Re_l T_l, \quad \varepsilon_l = c_{V,l} T_l$$

QGD model details: T.G. Elizarova, B.N. Chetverushkin, Yu.V. Sheretov, A.A. Zlotnik

MACROMODEL: BOUNDARY CONDITIONS FOR PURE QGD

- **At the nozzle exit**

$$u_n = v_{max}(t), \quad u_\tau = 0, \quad p = p_{lav}(t), \quad T = T_{lav}(t)$$

- **At the walls (sliding conditions)**

$$u_n = 0, \qquad \frac{\partial u_\tau}{\partial n} = 0, \qquad \frac{\partial p}{\partial n} = 0, \qquad \frac{\partial T}{\partial n} = 0$$

- **DE, EF,AF boundaries (undisturbed flow):**

$$\frac{\partial u_x}{\partial x} = 0, \qquad \frac{\partial u_y}{\partial x} = 0, \qquad \frac{\partial p}{\partial x} = 0, \qquad \frac{\partial T}{\partial x} = 0$$

MICROMODEL: MD EQUATIONS

$$\begin{cases} m_l \dfrac{d\mathbf{c}_{l,i}}{dt} = \mathbf{F}_{l,i} \\ \dfrac{d\mathbf{r}_{l,i}}{dt} = \mathbf{c}_{l,i} \end{cases}$$

System of Newton's equations

$$\mathbf{F}_{l,i} = -\frac{\partial U\left(\mathbf{r}_{l,1},\ldots,\mathbf{r}_{l,N}\right)}{\partial \mathbf{r}_{l,i}} + \mathbf{F}_{l,i}^{ext}, \quad l = a,b,c, \quad i = 1,\ldots,N_l$$

For 3 types of particles 6 potential functions:

$$U = U_{aa} + U_{bb} + U_{ab} + U_{ac} + U_{bc} + U_{cc},$$

U - potential energy, F^{ext}- external force, a - nitrogen, b - hydrogen, c - nickel

MICROMODEL: BOUNDARY CONDITIONS FOR PURE MD

1. Periodic boundary conditions inside of area (Fig. 1)
2. Mirror boundary conditions for gas area (Fig. 2)
3. Input conditions (Fig. 3)
4. Output conditions (Fig. 4)

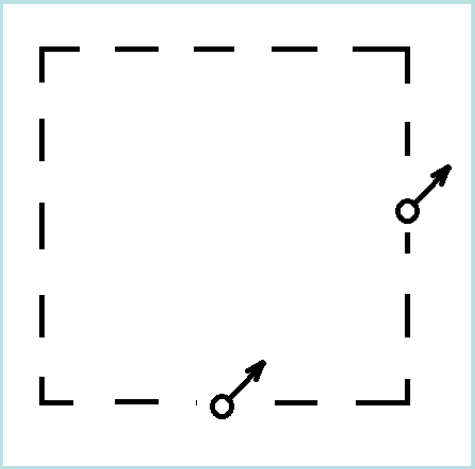


Fig. 1

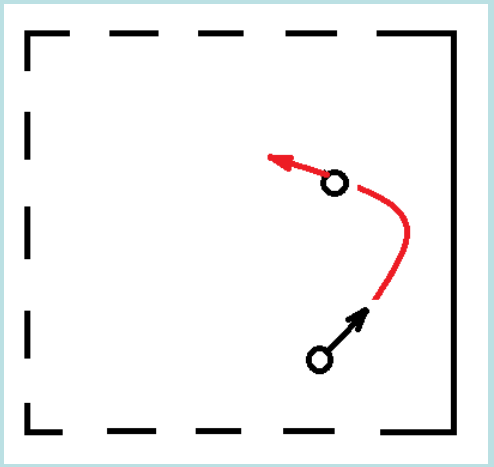


Fig. 2

HYBRID MODEL: QGD and MD EQUATIONS

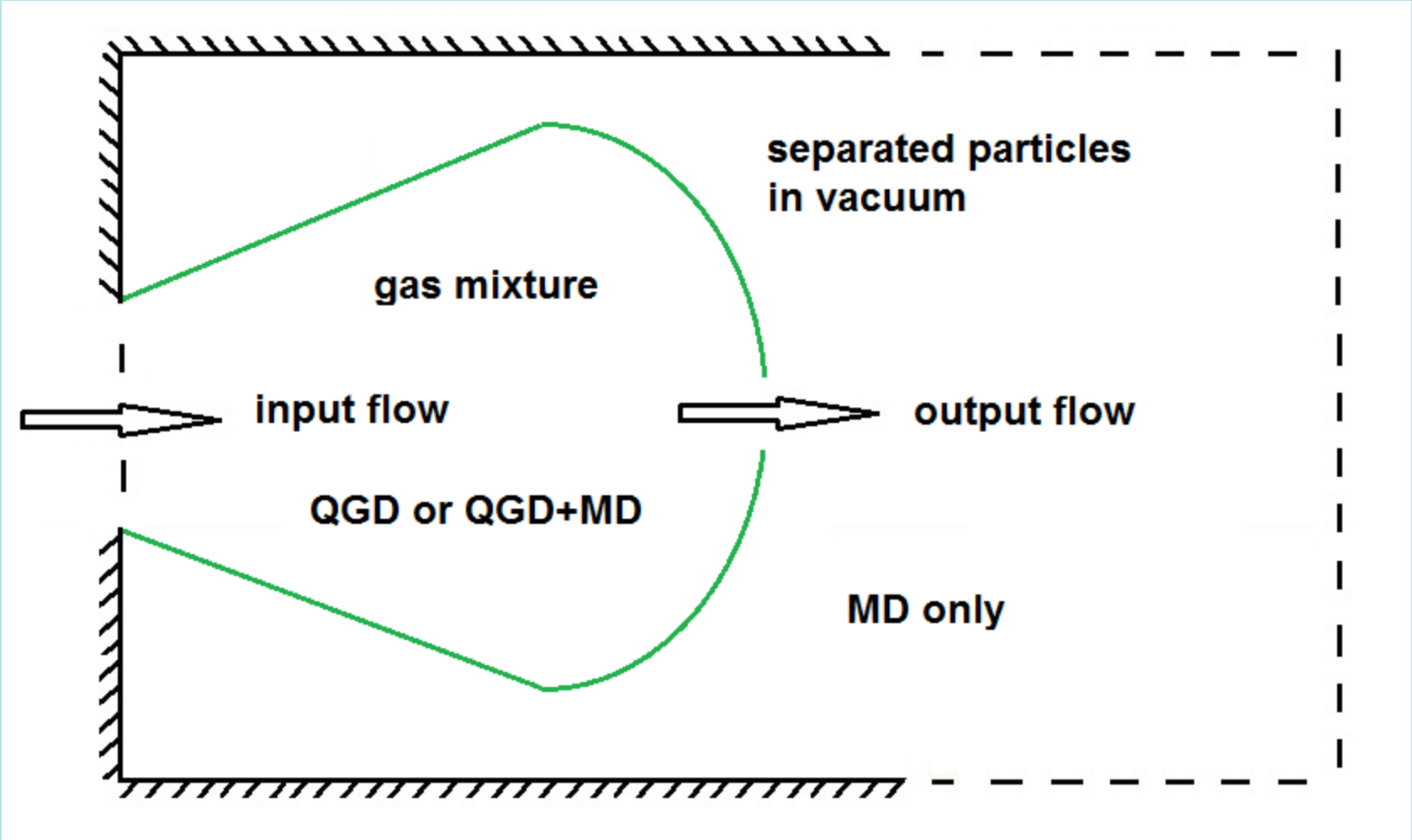
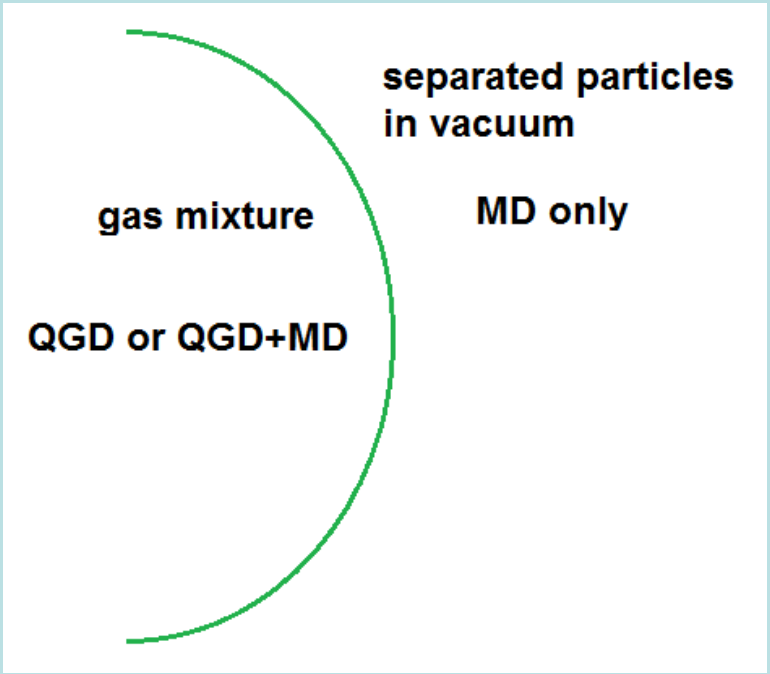


Fig. 3

HYBRID MODEL: BOUNDARY FLOWS

Computation of density, impulse, energy flows throught gas-vacuum boundary (left Fig.) and through Knudsen layer boundary (right Fig.) with the help of MD model



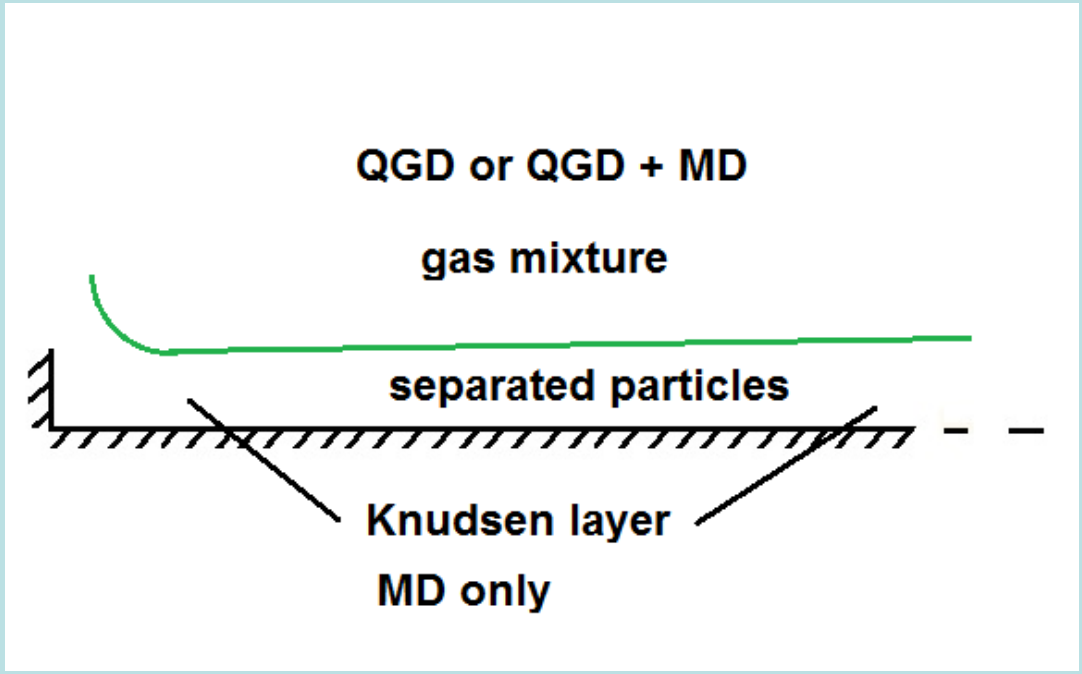


Fig. 4

NUMERICAL METHODS AND ALGORITHMS

On macrolevel:
Grid approach
Finite difference or finite volume space approximations
Explicit or Implicit schemes on time

On microlevel:
The Verlet integration scheme

General numerical algorithm:
Splitting into physical processes
Local and connected MD computations

Creation Data base on materials properties:
MD computaions of kinetical coefficients for gases and metals
MD computations of real gas state parameters
MD computations of boundary gas and metal flows parameters

COMPUTATION OF MACROPARAMETERS

Temperature:

$$T = \frac{2}{3}\frac{\langle E_T \rangle}{k_b}, \qquad E_T = \frac{1}{N_l}\sum_i \frac{m_{l,i}\left|\mathbf{v}_{l,i} - \mathbf{v}_{l,m}\right|^2}{2}, \; \mathbf{v}_{l,m} = \frac{1}{N_l}\sum_i \mathbf{v}_{l,i}, \; i = 1,\ldots,N_l \;, \; l = a,b$$

Pressure:

$$P = \frac{1}{3}\left(P_{xx} + P_{yy} + P_{zz}\right)$$

$$P_{\alpha\alpha} = \frac{1}{V}\sum_i m_i \left(v_{i,\alpha} - v_{m,\alpha}\right)^2 + \frac{1}{V}\sum_i \sum_{j>i} r_{ij,\alpha} \cdot F_{ij,\alpha} \;, \; \alpha = x,y,z$$

E_T - thermal kinetic energy

$\mathbf{v}_{l,m}$ - the center of mass velocity for *l* type particles system

$P_{\alpha\alpha}$ - diagonal components of pressure tensor

V - volume

COMPUTATION OF GAS MACROPARAMETERS

Compressibility factor:

$$Z_C = \frac{P \cdot V}{N \cdot k_b \cdot T} = 1 + \frac{1}{3 \cdot N \cdot k_b \cdot T} \left\langle \sum_{i=1}^{N} \sum_{j>i} \left(\mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \right) \right\rangle$$

$$Z_P = \frac{P \cdot V}{P_0 \cdot V_0}$$

Heat capacity at constant volume:

$$C_V = \frac{3 \cdot k_b}{2} \left[1 - \frac{3 \cdot N}{2} \frac{\left\langle E_K^2 \right\rangle - \left\langle E_K \right\rangle^2}{\left\langle E_K \right\rangle^2} \right]^{-1}, \quad \left\langle E \right\rangle = \frac{1}{M} \sum_{m=1}^{M} E_m$$

Enthalpy:

$$H = NE_I + PV$$

Internal energy:

$$E_I = E_T + U$$

M - the number of calculated system states

COMPUTATION OF GAS KINETIC COEFFICIENTS

Shear viscosity:

$$\eta = \frac{m_0^2}{2k_B T V t}\left\langle \frac{1}{3}\sum_{\alpha<\beta}\left(\sum_i \left[r_{i,\alpha}(t_0+t)\cdot v_{i,\beta}(t_0+t) - r_{i,\alpha}(t_0)\cdot v_{i,\beta}(t_0)\right]\right)^2\right\rangle,$$

$$t = NSTEPS\cdot\Delta t;\ \ \alpha\beta = xy, xz, yz;\ \ i = 1...N$$

t_0 - start time for one state

Thermal conductivity coefficient:

$$\lambda = \frac{1}{2k_B T^2 V t}\left\langle \frac{1}{3}\sum_{\alpha}\left(\sum_i \left[\delta\varepsilon_{i,\alpha}(t_0+t) - \delta\varepsilon_{i,\alpha}(t_0)\right]\right)^2\right\rangle,$$

$$\alpha = x, y, z,\ \ \delta\varepsilon_{i,\alpha} = r_{i,\alpha}\left(\varepsilon_i - \langle\varepsilon_i\rangle\right),\ \ \varepsilon_i = \frac{m\,\mathbf{v}_i^{\,2}}{2} + \frac{1}{2}\sum_{j\neq i}^{N} U_{ij}$$

ε_i - momentum full energy of particle i

S. Polyakov, Yu. Karamzin, T. Kudryashova, V. Podryga, D. Puzyrkov, KIAM RAS

COMPUTATION OF GAS KINETIC COEFFICIENTS

Diffusion coefficient via Einstein relation:

$$D = \frac{1}{6Nt}\left\langle \sum_i \left(\mathbf{r}_i(t_0+t) - \mathbf{r}_i(t_0)\right)^2 \right\rangle,$$

$$t = NSTEPS \cdot \Delta t; \quad i = 1...N$$

t_0 - start time for one state

Diffusion coefficient via Green-Kubo formula:

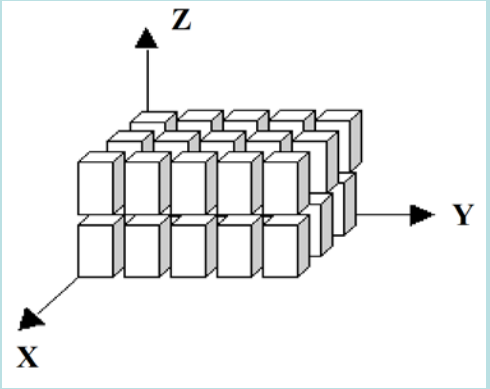
$$D = \frac{1}{3N}\int_0^\infty \langle CorrDif \rangle dt,$$

$$CorrDif = \sum_i \left(v_i(t_0+t)\cdot v_i(t_0)\right),$$

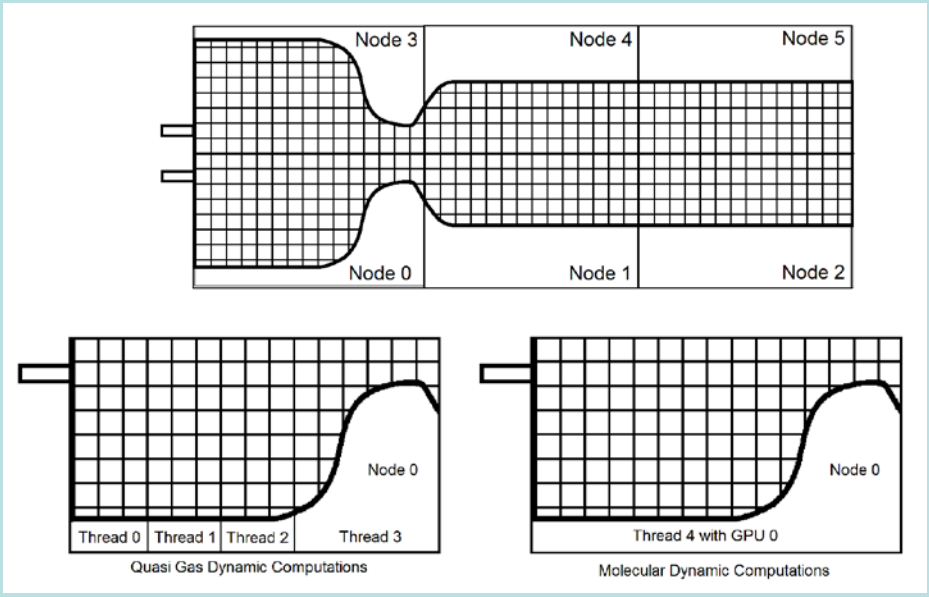
$CorrDif$ - autocorrelation function of the velocity

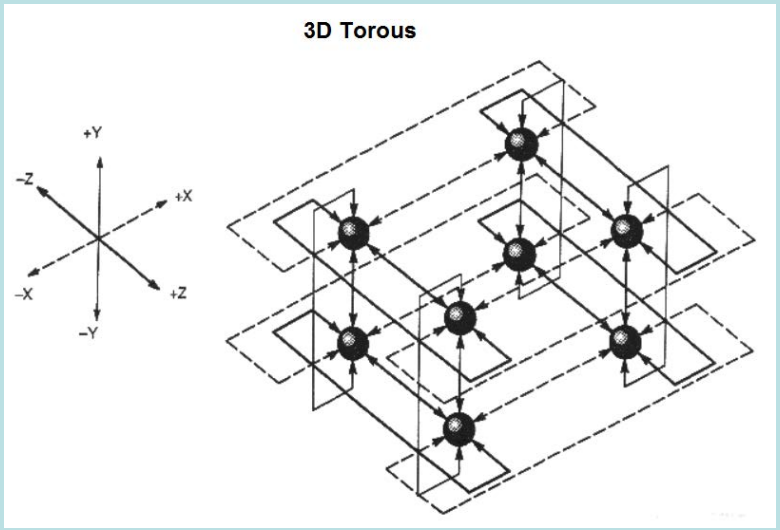
PARALLEL REALISATION

- The main method of parallelization - partition into domains of equal power.
- Each domain is divided into "boxes of interaction".
- Topology distribution on domains and boxes - a three-dimensional lattice.
- Topology exchanges - a three-dimensional torus.
- Realisation – MPI + OpenMP || MPI + CUDA



QGD+MD domain decompositions





SIMULATION RESULTS: Flow correction

QGD+MD: 3D flow

$$S_a^E = \nu_{ab}\left(\overline{E}_a - E_a\right), \quad S_b^E = \nu_{ba}\left(\overline{E}_b - E_b\right),$$

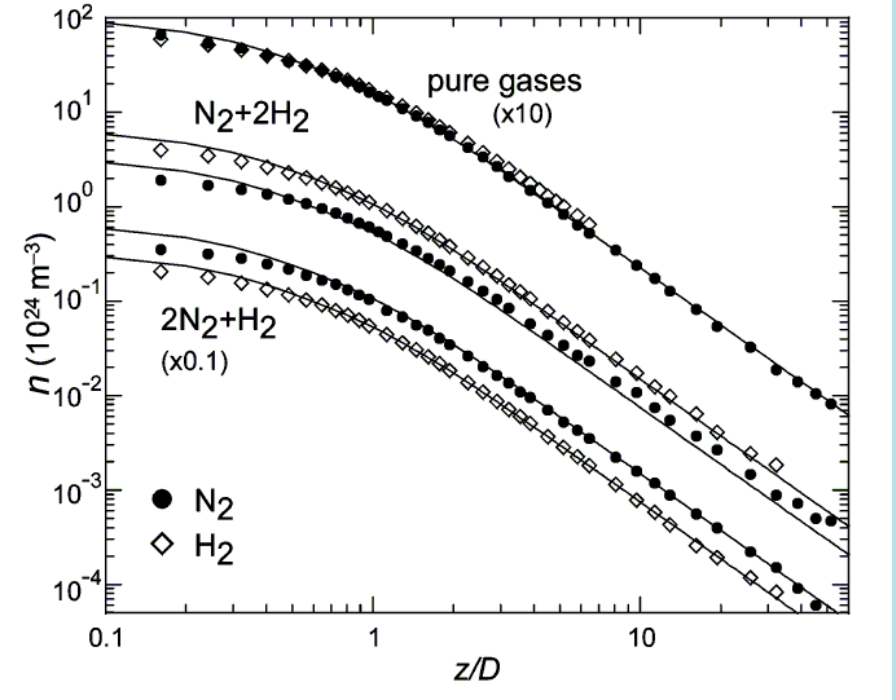
$$S_a^u = \nu_{ab}\rho_a\left(\overline{\mathbf{u}}_a - \mathbf{u}_a\right), \quad S_b^u = \nu_{ba}\rho_b\left(\overline{\mathbf{u}}_b - \mathbf{u}_b\right),$$

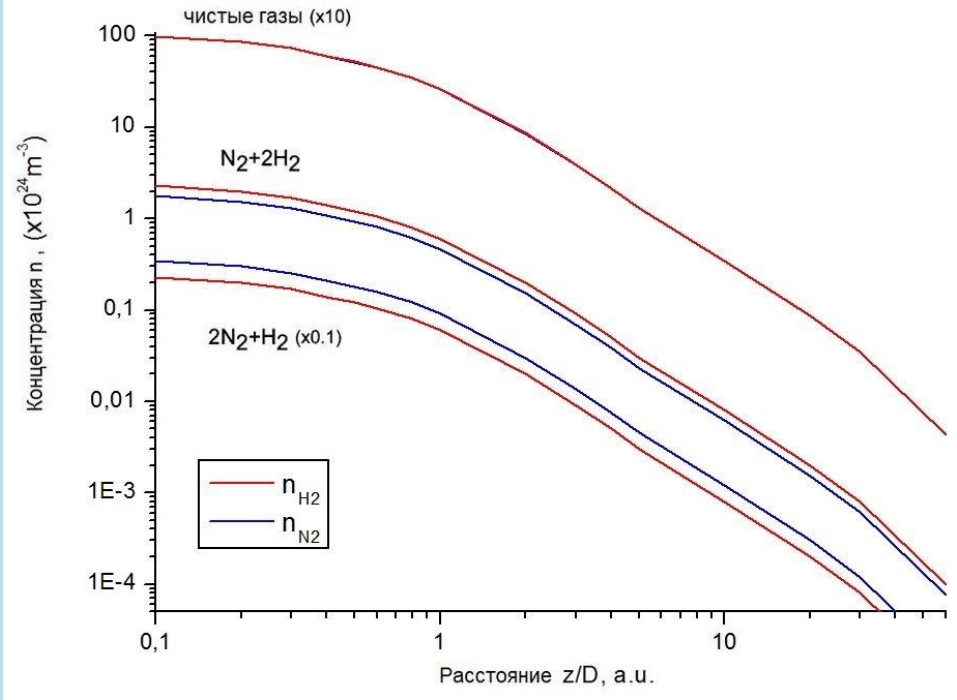
sample	$X_0(N_2)$
N_2	1
$2N_2 + H_2$	0.66(1)
$N_2 + 2H_2$	0.34(1)
H_2	0

The physical experiment to determine the parameters of N2 + H2 mixture supersonic flow in microchannels:

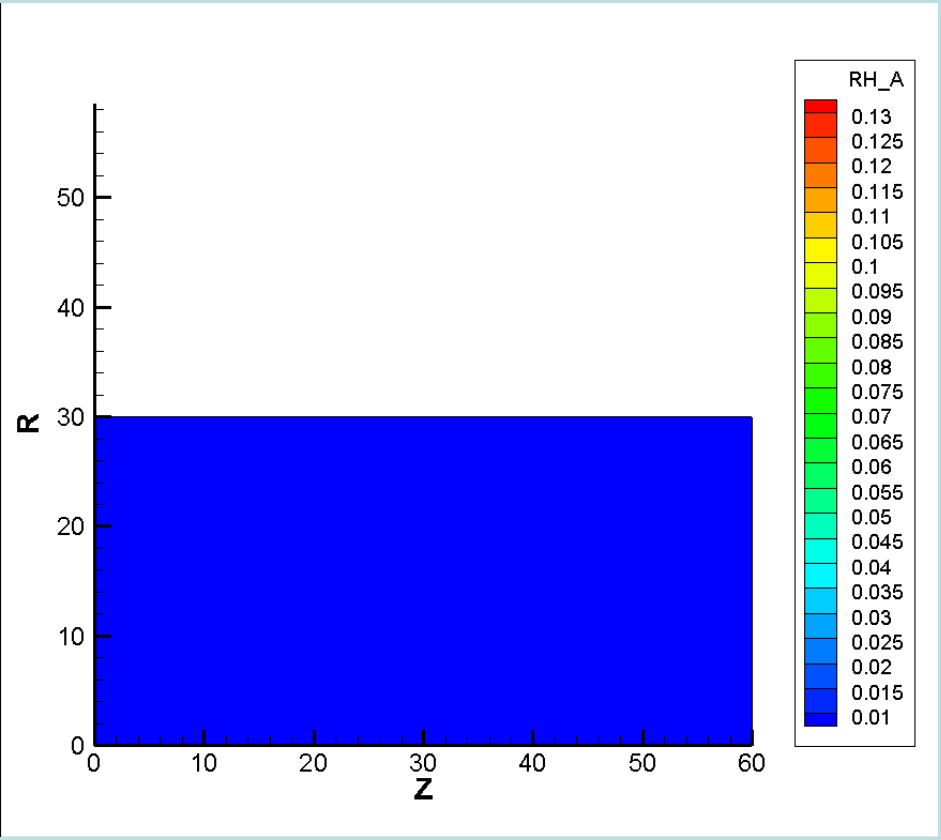
Ramos, G. Tejeda, J.M. Fernandez, S. Montero.

***J. Phys. Chem. A* 2009, 113, *P.* 8506–8512**

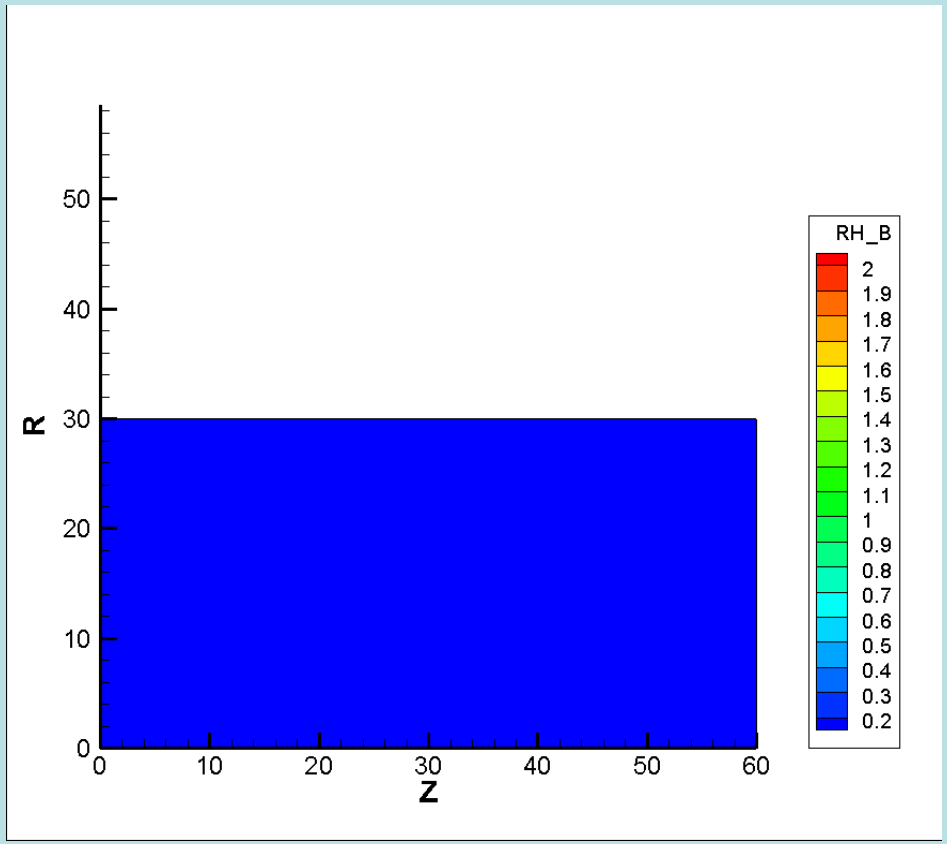




SIMULATION RESULTS: DENSITY OF COMPONENTS

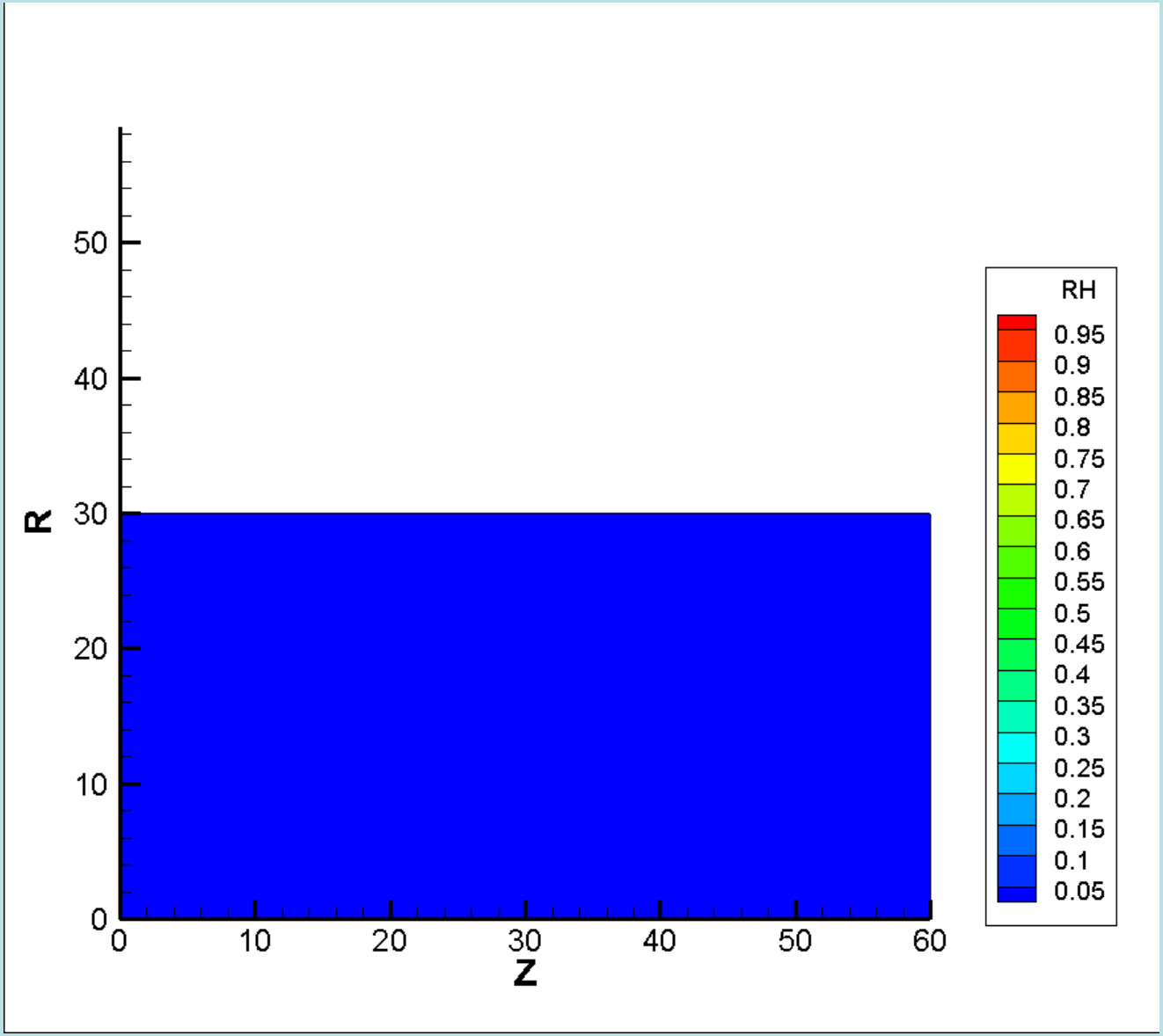


Hydrogen



Nitrogen

SIMULATION RESULTS: DENSITY OF MIXTURE

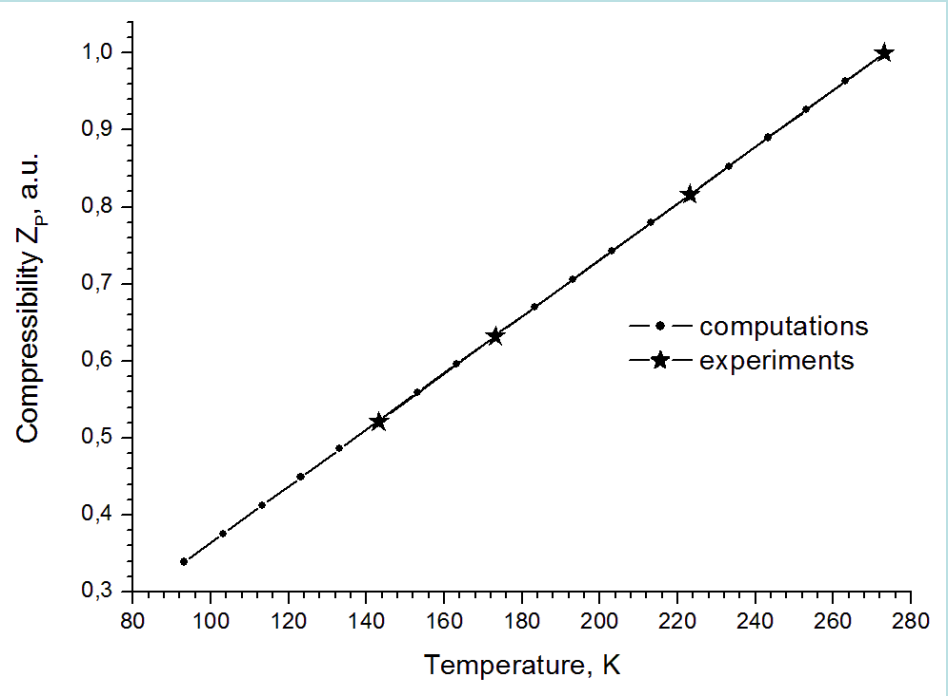


SIMULATION RESULTS: Computation of gas state

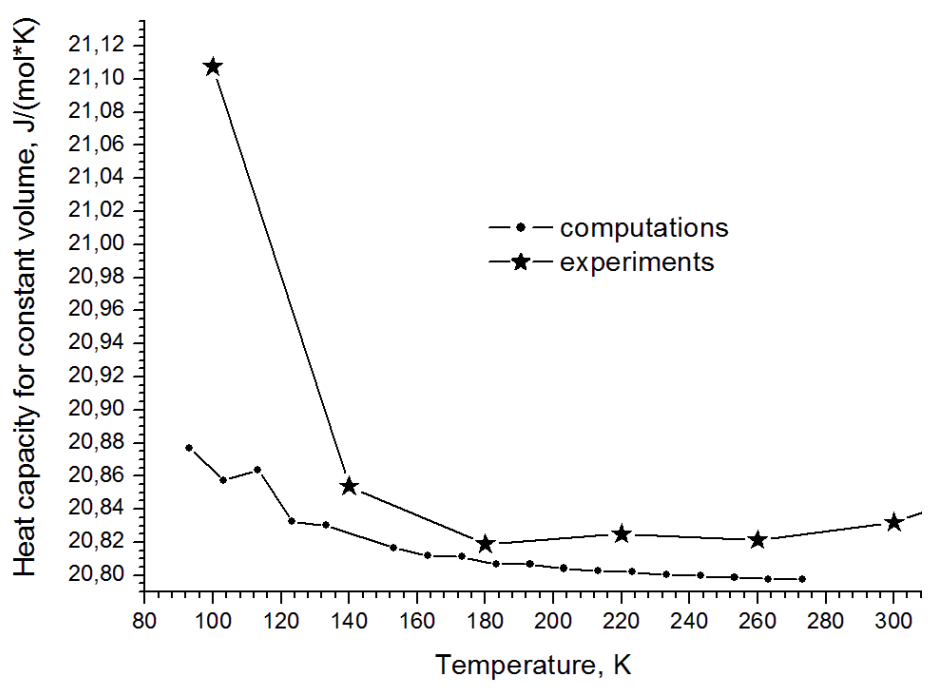
MD calculating the parameters for equation of state (EoS) for real gases (nitrogen, hydrogen and their mixture) in the range of desired temperatures and pressures, creation of EoS database.

Particle number: 27000,
Temperature range: 93.15 K - 273.15 K,
Calculation time: 4ns + 4 ns + 2 ns, 1 step = 2 fs

Thermal EoS (P, T, V)



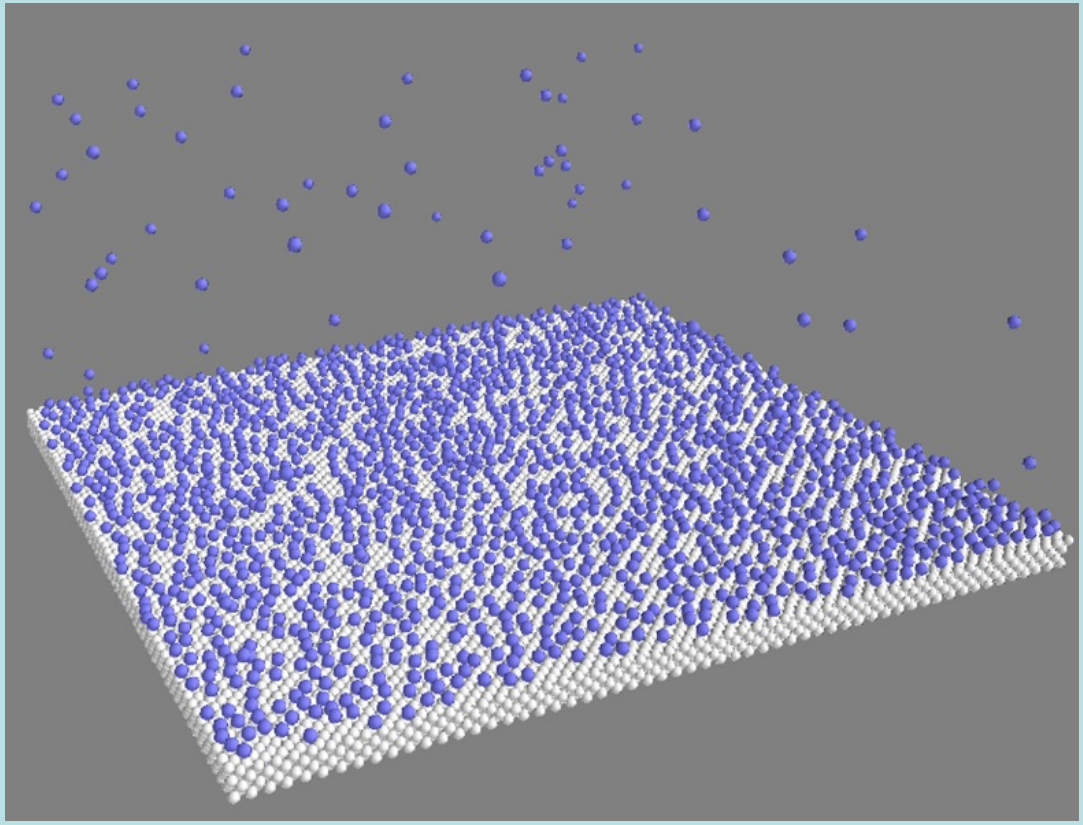
Caloric EoS (E, P, T)



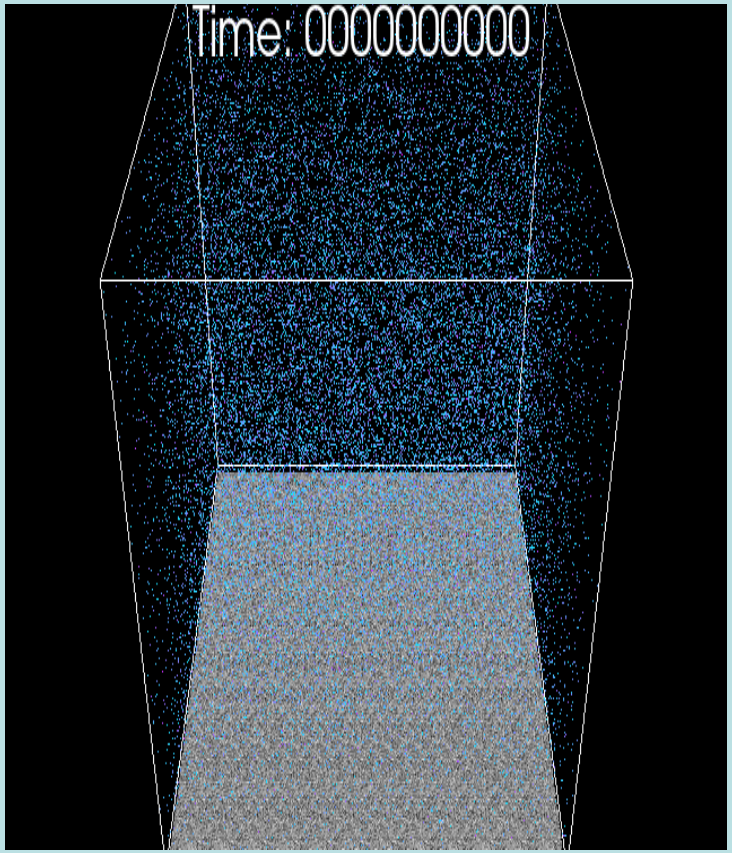
SIMULATION RESULTS: Interaction of gas with metal

Calculation of the nitrogen molecules interacting with the wall of nickel channel

Particle number: 8 128 512 + 423 840 = 8 552 352,
Thermostats temperature: T_{Ni} = 273.15 K, T_{N2} = 273.15 K
Number of time steps: 1 150 000 steps, 1 step = 2 fs
System size: 102x102x1534 nm^3

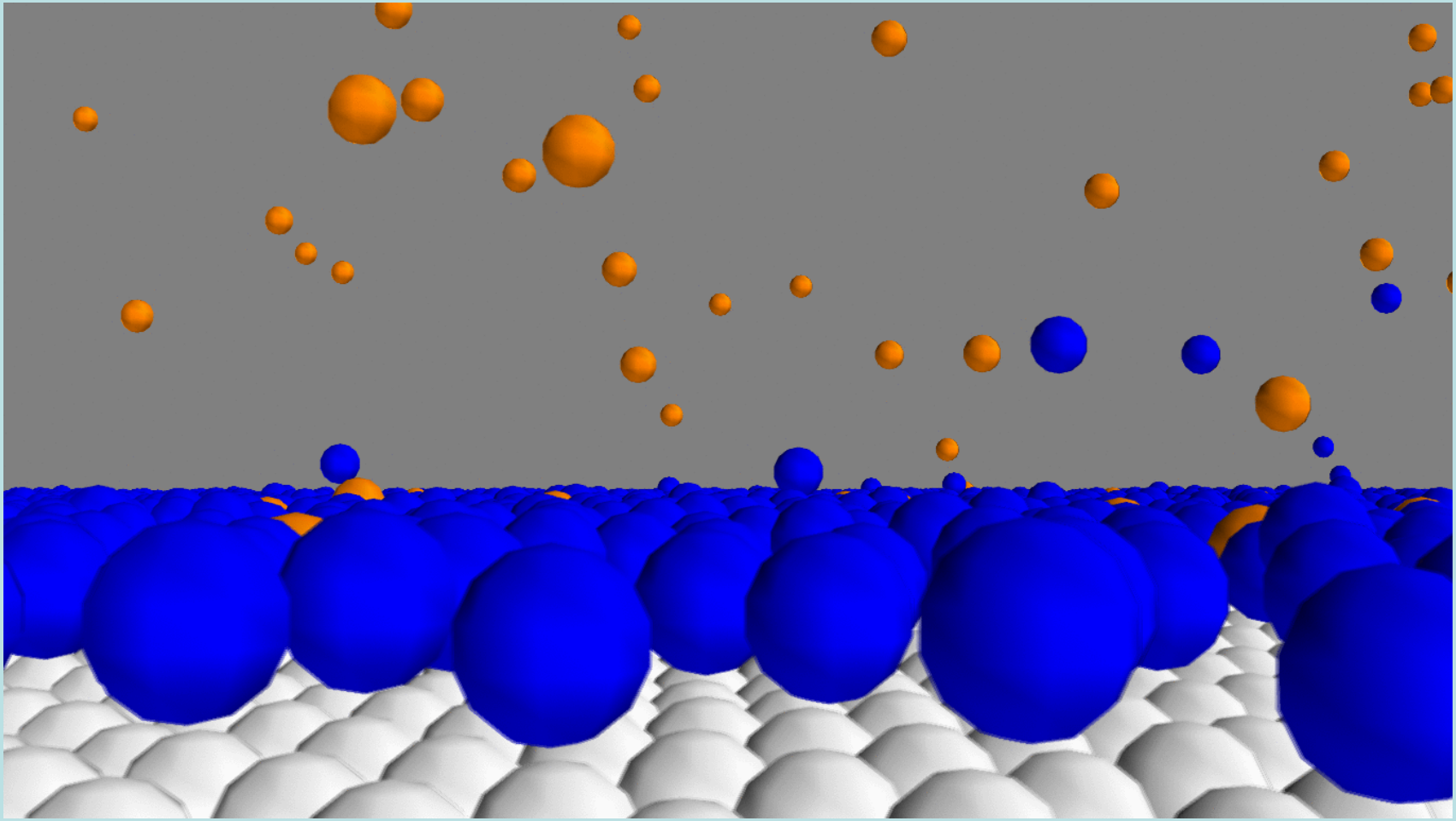


Distribution of nitrogen molecules (domain 20x20 nm^2) on nickel plate surface, at time 2.3 ns



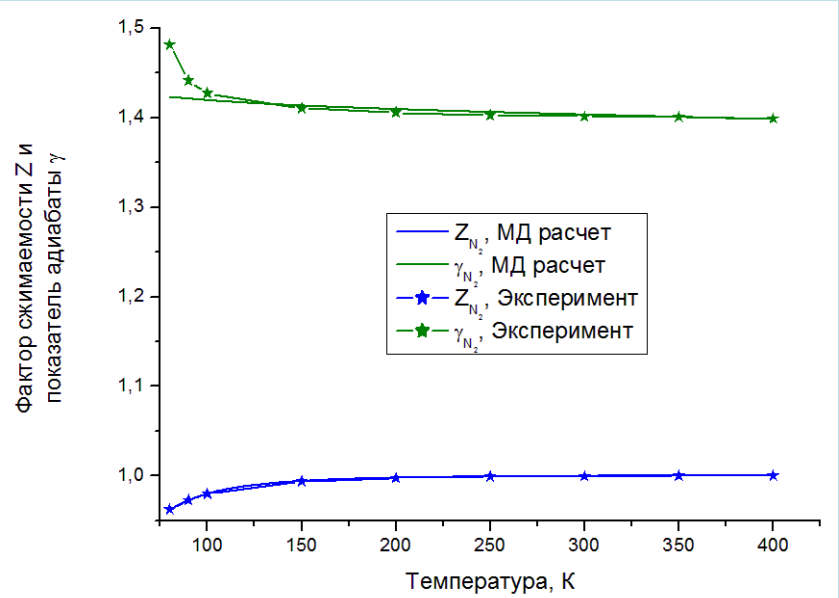
Microvolume near the wall of the microchannel (100x100x1500 nm^3)

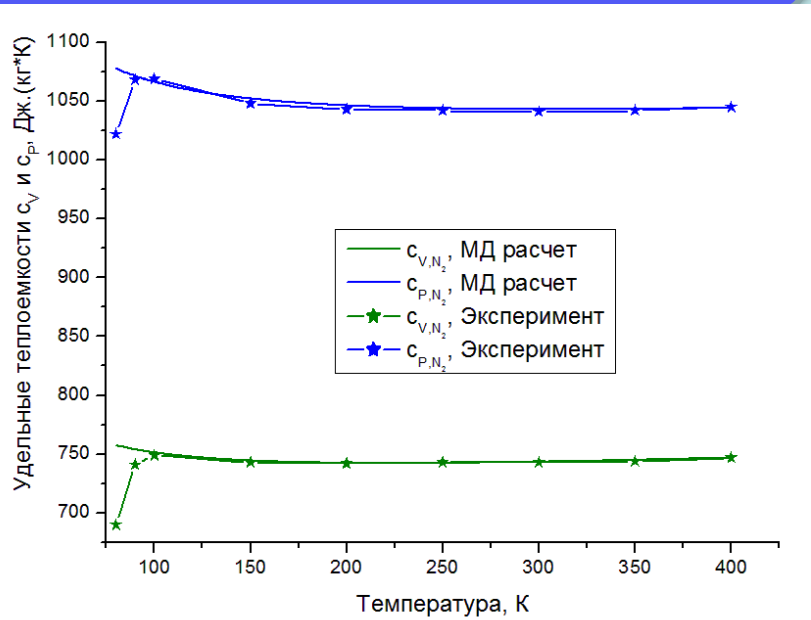
SIMULATION RESULTS: Absorption effect

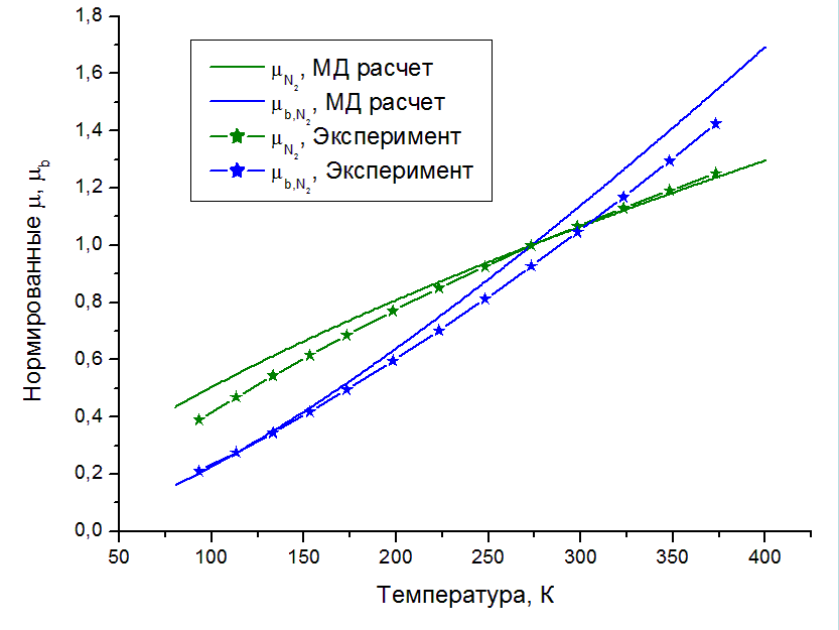


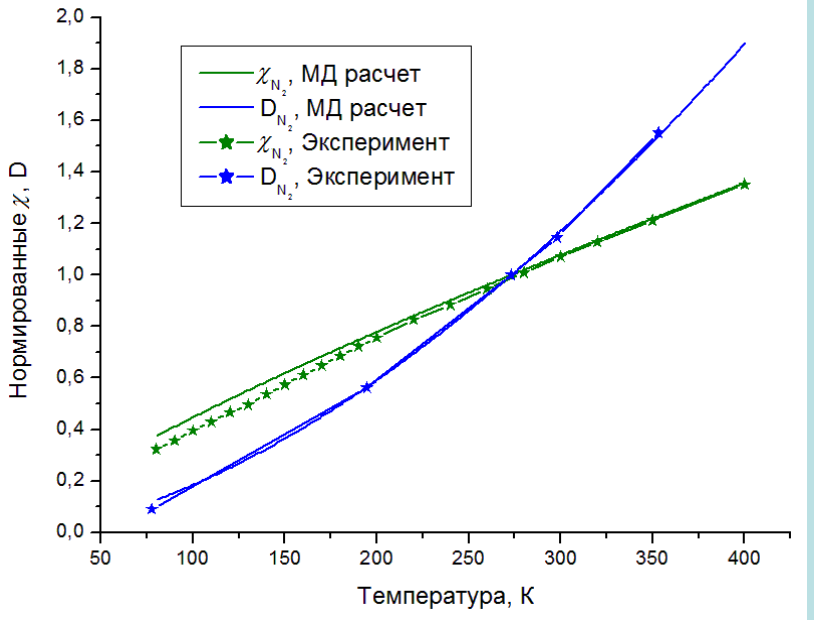
Orange color corresponds to hot gas molecules
Blue color corresponds to cold gas molecules adsorbed on metal surface

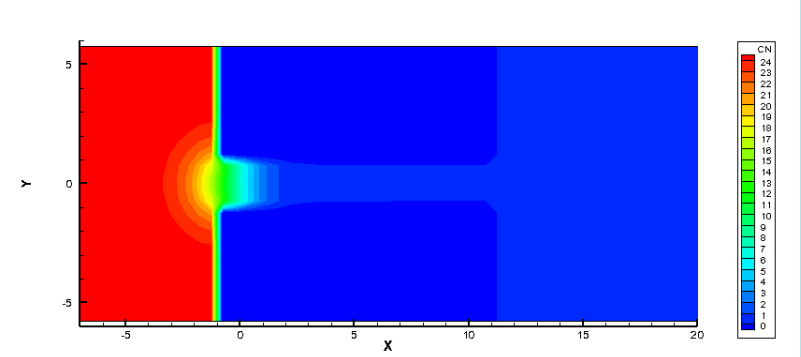
SIMULATION RESULTS: MD calculation of base coefficients for real gas

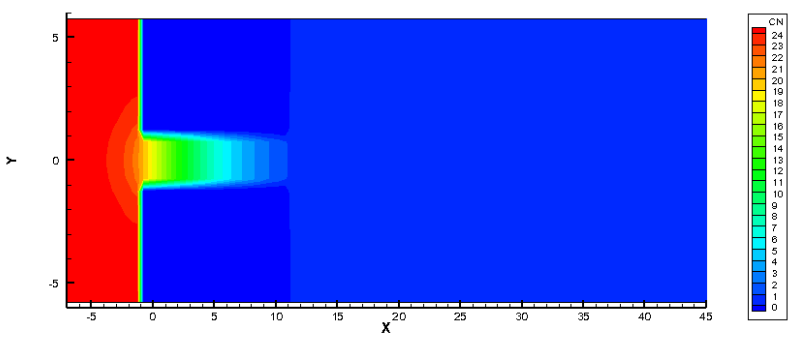










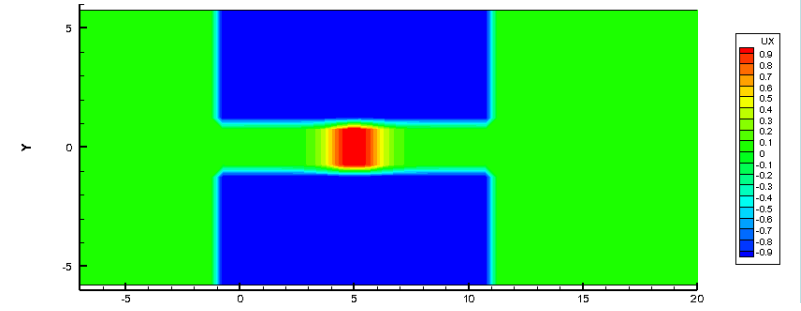


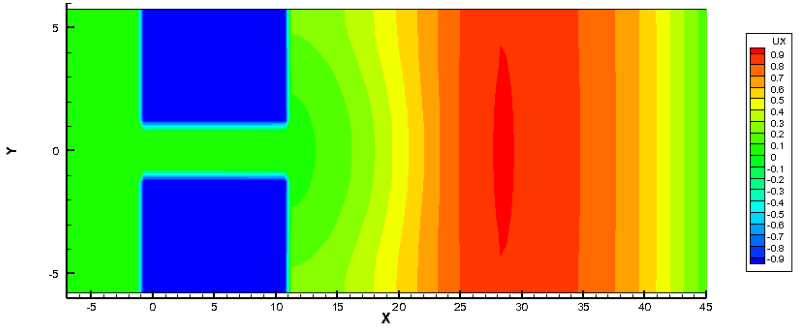
0.053 mks

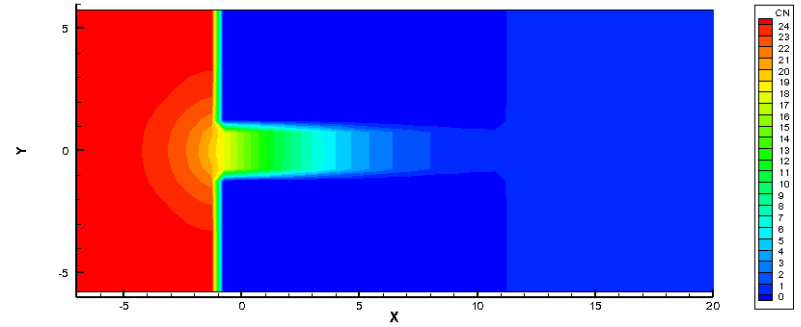
←

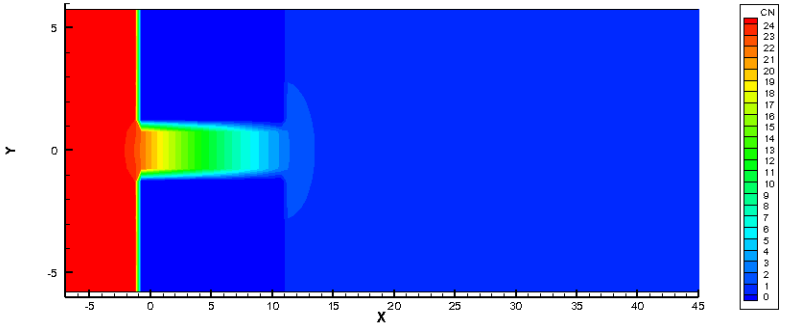
→

1.106 mks







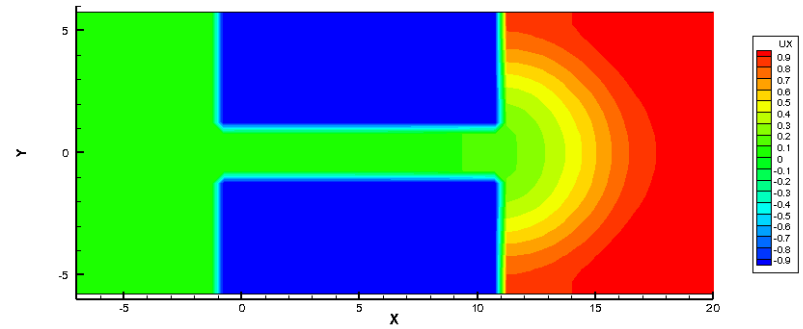


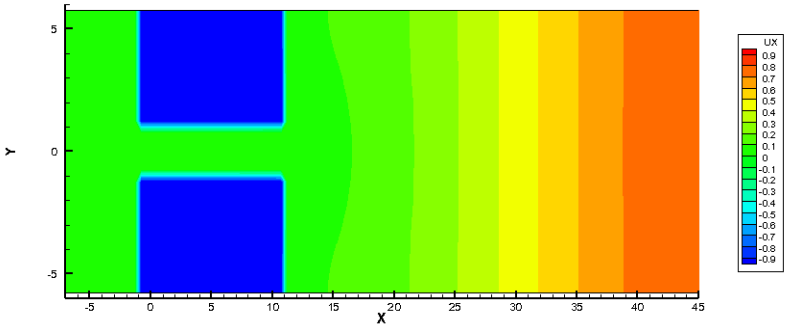
0.553 mks

←

→

2.211 mks





CONCLUSION

- *Multiscale numerical approach to 3D simulation of non-linear interaction of gas with metal in microsystems was developed.*
- *Parallel realization of the approach using hybrid parallel computing technology was performed.*
- *Verification of numerical approach and validation of parallel software were performed.*
- *Proposed numerical approach allows to simulate qualitatively the behavior of gas – metal complex microsystems under the real conditions.*
- *Future: direct 3D simulation of specific nanotechnology problems.*

Thanks you!