

CORRECTION OF THE GAS FLOW PARAMETERS BY MOLECULAR DYNAMICS

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Abstract. This work is devoted to the molecular dynamics calculations of real gases and mixtures thereof macroparameters at room and low temperatures. Necessity of such calculations is caused by both the lack of experimental data on the gases properties in selected parameters ranges and problems of multiscale modeling of technically complex microsystems that use gas medium as transport agents. In work modern molecular dynamic approach to calculation of gas macroparameters is set out in a concentrated form, as well as its approbation is carried out by the example of the calculation of nitrogen macroparameters at room and lower temperatures. In numerical experiments the temperature dependences of pressure, kinetic, potential, and total energies, enthalpy, coefficients of compressibility and heat capacity at constant volume are obtained, which agree well with the theoretical and experimental data. Further development of the methodology will be related to calculation of the coefficients of viscosity and thermal conductivity, as well as a generalization to the case of a gas mixture.

1 INTRODUCTION

The current stage of scientific evolution is characterized by a large number of studies carried out for the development and implementation of nanotechnology in the production. Nanotechnology implies a good knowledge of the properties of materials and media used in industrial processes. One way to obtain information about the properties of the medium is a molecular modeling.

This paper deals with the calculation of the properties of gaseous media used as transport agents in installations of supersonic cold gasdynamic sputtering nanoparticles on the surface of various materials [1, 2]. Modern computer technology allows to calculate the properties of the gaseous medium at a molecular level, which makes it possible to determine the macroscopic parameters of gases from first principles.

The problem of gaseous media macroparameters calculating by molecular dynamics simulation arises when either no experimental data on the parameters of a real gas or gas mixture in a range of temperatures and pressures, or when a precise calculation of the gaseous medium state in a multiscale is required. In this paper, there is the motivation of both types as the results of numerical experiments are planned to be used as a database for subsequent multiscale computations of supersonic flows of gas mixtures in installations of supersonic

cold gasdynamic sputtering of nanoparticles on the substrate. As part of this big theme present work is a preparatory step for the joint calculation by continuum mechanics and molecular dynamics of all stages of deposition.

In the work by the method of molecular dynamics [3-7] macroparameters calculation of real gas (nitrogen) is performed. The first step is to bring the gas dynamic computing system in equilibrium at the selected temperature, and then from molecular dynamics calculations of the equation of state of pressure and energy (coefficients of compressibility and heat capacity), the internal energy of the system and enthalpy are determined. The results are compared with known experimental data.

2 MATHEMATICAL STATEMENT OF A PROBLEM

Consider a system of nitrogen molecules N_2 , enclosed in a microvolume V , which is a cube with sides $Lx = Ly = Lz$. The total amount of gas particles depends on the microvolume's size, gas density ρ and particles mass m : $N = \rho \cdot V / m$, $V = Lx^3$.

The dynamics of particles in a microvolume is described by equations of Newton.

$$m \cdot \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i, \quad i = 1, \dots, N, \quad (1)$$

where i – particle's number, N – the amount of particles, m – the mass of a single particle (molecule), $\mathbf{r}_i(r_x, r_y, r_z)$ – the radius vector of the i -th particle, $\mathbf{F}_i(F_x, F_y, F_z)$ – the total force acting on the particle i .

The interaction forces of the particles are expressed through the gradient of the potential energy $U = \sum_{i=1}^N u_i$. As the potential for interaction between nitrogen molecules u_i a Lennard-Jones potential is [8] in form “n-6” from [9].

$$u_i = \frac{1}{2} \sum_{j \neq i} \varepsilon \frac{n}{n-6} \left(\frac{n}{6} \right)^{\frac{6}{n-6}} \left[\left(\frac{\sigma}{r_{ij}} \right)^n - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad i = 1, \dots, N, \quad (2)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ – the distance between i -th and j -th particles, ε – the energy of molecular interaction, σ – the effective radius of interaction.

Initial conditions include starting distribution of particle coordinates and velocities. Starting coordinates distribution of the gas particles is taken uniform and consistent with the density corresponding to the selected temperature T_0 and pressure P_0 . Starting velocity distribution of the particles in modulus is set according to the selected temperature and realizes Maxwell distribution. The velocity distribution of the particles on the solid angle is uniform and such that the total momentum of the system is zero.

Periodicity conditions with periods Lx, Ly, Lz on axes x, y, z are considered as the boundary conditions.

The system of equations (1) is solved using a Verlet method [10] in the velocity form:

$$\mathbf{r}^{n+1} = \mathbf{r}^n + \mathbf{v}^n \Delta t + \frac{\mathbf{F}^n (\Delta t)^2}{m} \frac{1}{2}, \quad \mathbf{v}^{n+1} = \mathbf{v}^n + \frac{\mathbf{F}^{n+1} + \mathbf{F}^n}{2m} \Delta t, \quad (3)$$

here Δt – the integration step, n – the step's number, \mathbf{F}^{n+1} – the force value on the current step.

Berendsen thermostat is used to achieve the desired temperature of the gas in thermodynamic equilibrium [11, 12].

The purpose of modeling is to obtain the average values of the gas macroparameters. The set of macroparameters consist of kinetic, potential, thermal, internal, and total energies; temperature and pressure; compressibility factors; enthalpy and heat capacity. Formulas below are for determining these macroparameters.

Kinetic energy of a system E_K and kinetic energy of a thermal moving E_T are calculated as sums of every particle energies the following way:

$$E_K = \sum_{i=1}^N \frac{m |\mathbf{v}_i|^2}{2}, \quad E_T = \sum_{i=1}^N \frac{m |\mathbf{v}_i - \mathbf{v}_m|^2}{2}, \quad \mathbf{v}_m = \frac{1}{N} \sum_{i=1}^N \mathbf{v}_i, \quad i=1, \dots, N, \quad (4)$$

where $|\mathbf{v}_i|$ – the velocity vector's \mathbf{v}_i length of the i -th particle, \mathbf{v}_m – the velocity of the center of mass.

Internal energy E_I and total energy E represent following sums:

$$E_I = E_T + U, \quad E = E_K + U. \quad (5)$$

The temperature of the system is determined by the thermal energy of the system [9, 10]:

$$T = \frac{1}{3 \cdot N \cdot k_b} \left\langle \sum_{i=1}^N m |\mathbf{v}_i - \mathbf{v}_m|^2 \right\rangle, \quad (6)$$

where $\langle \rangle$ – the average value on system states, k_b – Boltzmann constant.

The system pressure P is determined by the virial theorem [12-14]:

$$P = \frac{N \cdot k_b \cdot T}{V} + \frac{1}{3 \cdot V} \left\langle \sum_{i=1}^N \sum_{j>i} (\mathbf{r}_{ij} \cdot \mathbf{F}_{ij}) \right\rangle, \quad i=1, \dots, N, \quad (7)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, \mathbf{F}_{ij} – the interaction force between the i -th and j -th particles.

Compressibility factor Z_C describes the deviation of the thermodynamic properties of a real gas from the ideal gas and is expressed through the calculation result (7):

$$Z_C = \frac{P \cdot V}{N \cdot k_b \cdot T} = 1 + \frac{1}{3 \cdot N \cdot k_b \cdot T} \left\langle \sum_{i=1}^N \sum_{j>i} (\mathbf{r}_{ij} \cdot \mathbf{F}_{ij}) \right\rangle, \quad i=1, \dots, N, \quad (8)$$

Also in the literature expression describing the deviation of the properties of the gas from the properties of the same gas under normal conditions, is investigated:

$$Z_P = \frac{P \cdot V}{P_0 \cdot V_0}, \quad (9)$$

where P_0, V_0 – the pressure and the volume of the system under normal conditions.

Enthalpy H is another illustrative macroparameter of real gas, which in case of a real gas depends not only on the temperature, but also the pressure:

$$H = NE_I + PV. \quad (10)$$

To calculate the heat capacity C_V of the gas at constant volume, there are many ways of computing [3, 4, 12-17]. In this work calculations were made for the following variants:

$$C_V = \frac{3 \cdot k_b}{2} \left[1 - \frac{3 \cdot N}{2} \frac{\langle E_K^2 \rangle - \langle E_K \rangle^2}{\langle E_K \rangle^2} \right]^{-1}, \quad (11)$$

$$C_V = \frac{3 \cdot k_b}{2} \left[1 - \frac{3 \cdot N}{2} \frac{\langle T^2 \rangle - \langle T \rangle^2}{\langle T \rangle^2} \right]^{-1}, \quad (12)$$

$$C_V = \frac{3 \cdot N \cdot k_b}{2} \left[1 + \frac{2}{3 \cdot N \cdot (k_b \cdot \langle T \rangle)^2} (\langle E_P^2 \rangle - \langle E_P \rangle^2) \right], \quad (13)$$

$$C_V = \frac{3 \cdot N \cdot k_b}{2} \left[1 + \frac{3}{2 \cdot N} \frac{\langle E_P^2 \rangle - \langle E_P \rangle^2}{\langle E_K \rangle^2} \right]. \quad (14)$$

Equation (11) showed itself the most robust in the above mentioned conditions of the problem, so it was used in the preparation of the main results.

The total calculation algorithm is the following sequence of actions. At the initial time distributions of positions and velocities of all the particles are given, then solved the equations of motion, forces of the potential interaction (2), the new coordinates and velocities of the particles taking into account the boundary conditions and external influences on the system from the thermostat, kinetic (4), the internal and total of energies (5) are calculated at each step. Calculations are carried out before the stationary values of the temperature (6) and the pressure (7) which mean the establishment of the thermodynamic equilibrium. Then the rest macroparameters of the system (8) - (11) are calculated.

3 SIMULATION RESULTS

Among the strategies for calculating the gas macroparameters there are two main. The first and simplest of these is to fix the volume and number of particles. The result is "frozen" gas density. In this situation, you can change the pressure and calculate its temperature and other macroparameters (the first version of calculation), or vice versa, change the temperature and

calculate pressure and other macroparameters (the second version of calculation). As a result we obtain dependences of the fundamental gas macroparameters on the pressure or on the temperature (below results obtained by the second variant are discussed).

The second strategy is to fix the pressure through the using of the barostat. In this case, with a fixed number of the particles system volume changes, and thus the gas density changes. In this strategy also there are two variants of calculations, either at a given temperature (which is controlled by a thermostat) density and other gas macroparameters are calculated, or at given number of particles density, temperature and other gas macroparameters are calculated.

Obviously, the choice of a strategy is linked with the objective function of calculations. Calculation combining both strategies and the various options will be the most complete. In this work we restricted ourselves to the first strategy and the second option for calculating. In this situation, all the temperature dependences of the gas macroparameters are simply determined.

The method of obtaining the average characteristics within the chosen strategy was as follows. First, we calculated the starting point on the P-T diagram corresponding to normal conditions (when the gas pressure is 1 atm., and the temperature of the gas is equal to 273.15 K). For these conditions, the majority of the gas macroparameters, including nitrogen for example, which was chosen for a numerical experiment is well known. In particular, the density of nitrogen at these conditions is 1.24979 kg/m³.

The calculation of the starting point was performed for 27000 of nitrogen molecules in the volume 1004936 nm³. The calculation was performed in 3 stages. First, the system was equilibrated in the conditions of thermostat using the Berendsen thermostat. Thermostating time was 8 ns. Fluctuations in pressure and temperature are not more than 0.05% from average value. Then, also in regulated temperature conditions for 4 ns first calculation of gas average macroparameters was carried out. Further in conditions off the thermostat for a further 4 ns second calculation of gas average macroparameters was carried out. Comparison of the gas macroparameters in the first and the second calculations confirmed the achievement the gasdynamic equilibrium state of the system.

Further calculations of temperature dependences of the gas macroparameters were carried out. For this purpose, on the temperature scale reference points 273.15, 263.15, 253.15, ..., 93.15 K were selected, which were used for calculations. For each reference point, different from 273.15 K, the calculation started from the system state for 273.15 K at the moment of time 8 ns. At the same time thermostat is at once switched to the reference temperature. This calculation was carried out for 4 ns. Then the thermostat is turned off and for another 4 ns gas average macroparameters were calculated.

Fig. 1-5 shows the resulting temperature dependences of the pressure, kinetic and potential energies and enthalpy, calculated per molecule, the specific heat at constant volume, compressibility coefficient (shows the actual deviation of the equation of state of a real gas on pressure from the ideal gas). Analysis of the obtained dependences showed the following.

First, near the start reference point gas is close to ideal gas, and its parameters are close to the known tabular data.

Secondly, at low temperatures the tendency of gas liquefaction (see. Fig. 5) is clearly visible, as evidenced by qualitative and quantitative experimental data. In particular, the specific heat at constant volume close to the point of liquid nitrogen starts to increase

exponentially and eventually reaches not two, but three or more J/K.

Third, linear character of change of such the macroparameters as pressure, kinetic and total energy, compressibility factor Z_p near the point of liquid nitrogen (77 K), means that the chosen strategy for calculating in this area no longer reflects the state of the gas, and in this case it is necessary to move to the second strategy, that is, to use a barostat.

Thus, it can be noted that in general the presented method allows to calculate gas (or gas mixture) macroparameters in the range of room and low temperatures. At the same time near the point of gas liquefaction, both the above strategy for calculating with thermo- and barostats should be used.

To conclude this section, we should mention another issue. The temperature dependences of two major macroparameters of gas: the viscosity and thermal conductivity are not considered in the work. This is partly due to the additional processing costs of their receipt, but the main thing - with the instability of the known computational algorithms to determine them by using periodic boundary conditions. In connection with this in the future it is supposed to conduct a separate researching on a detailed study of the problem.

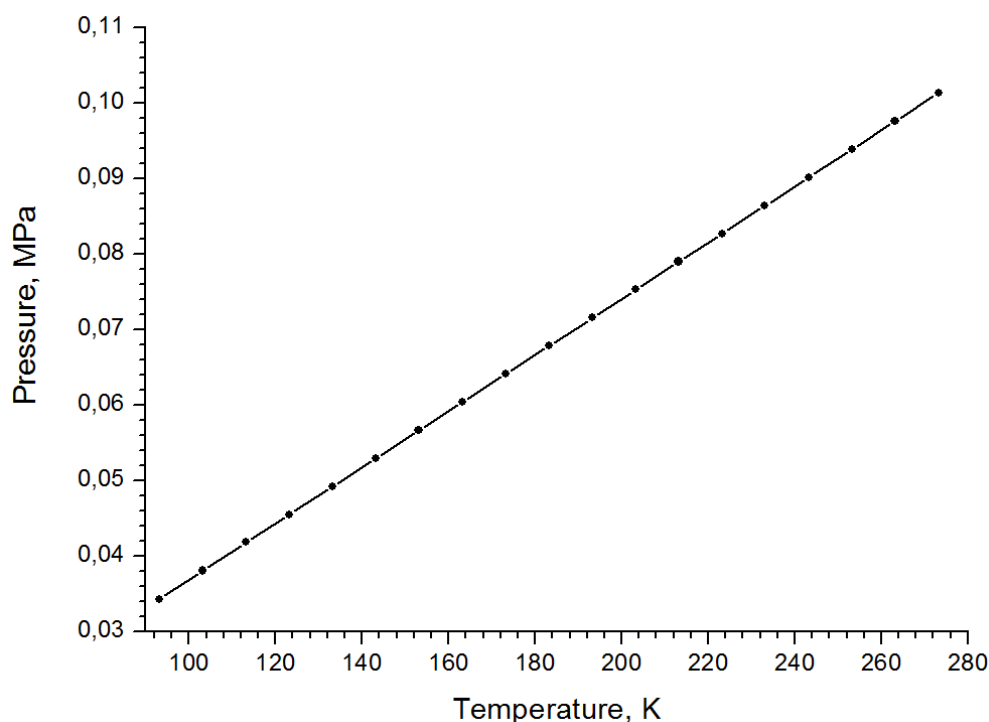


Figure 1: Dependence of pressure from temperature at constant density

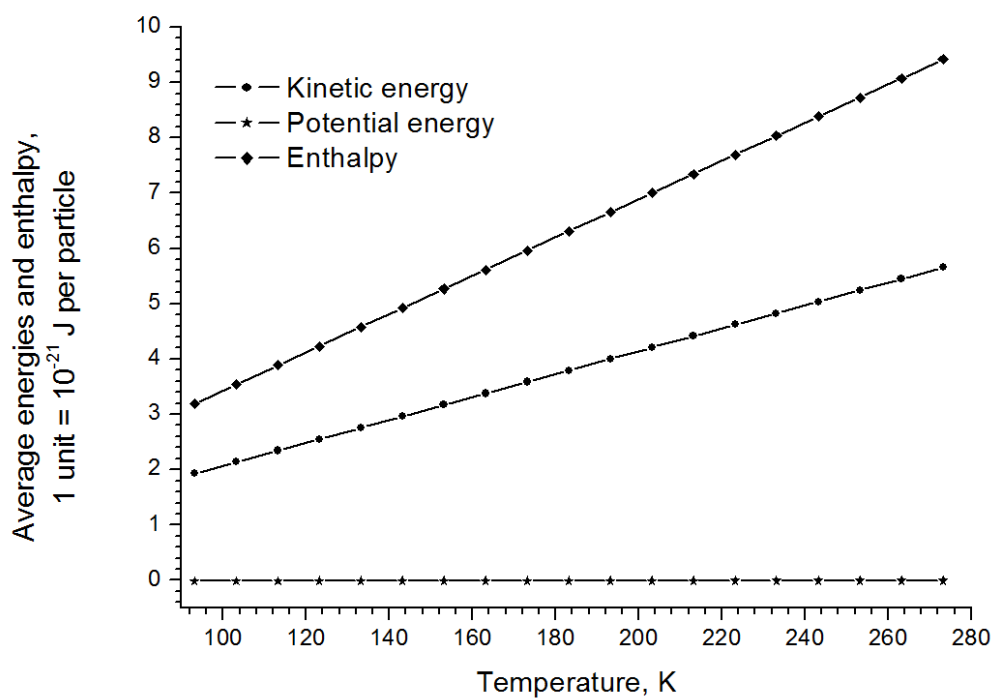


Figure 2: Dependence of average energies and enthalpy (calculated per molecule) from temperature at constant density

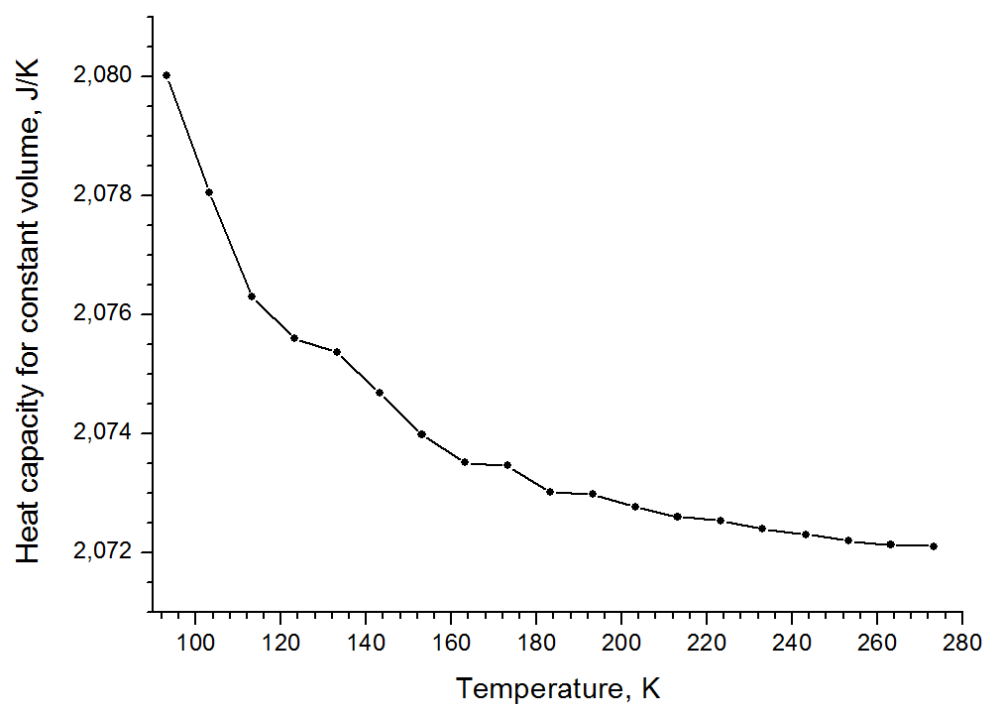


Figure 3: Dependence of heat capacity at constant volume from temperature

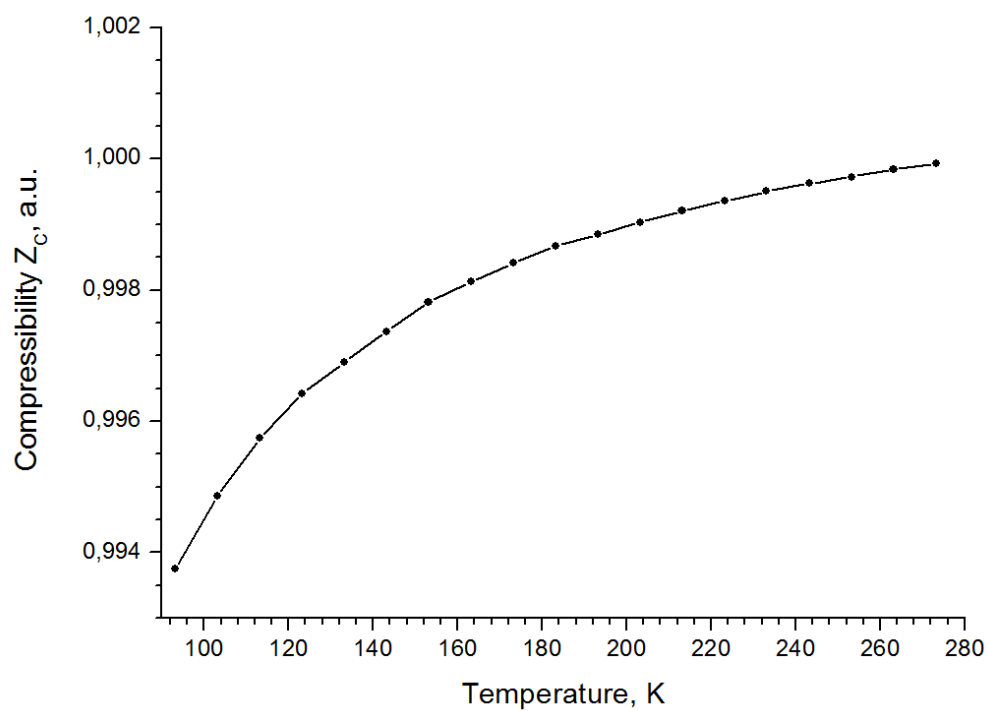


Figure 4: Dependence of compressibility Z_C (deviation from ideal) from temperature

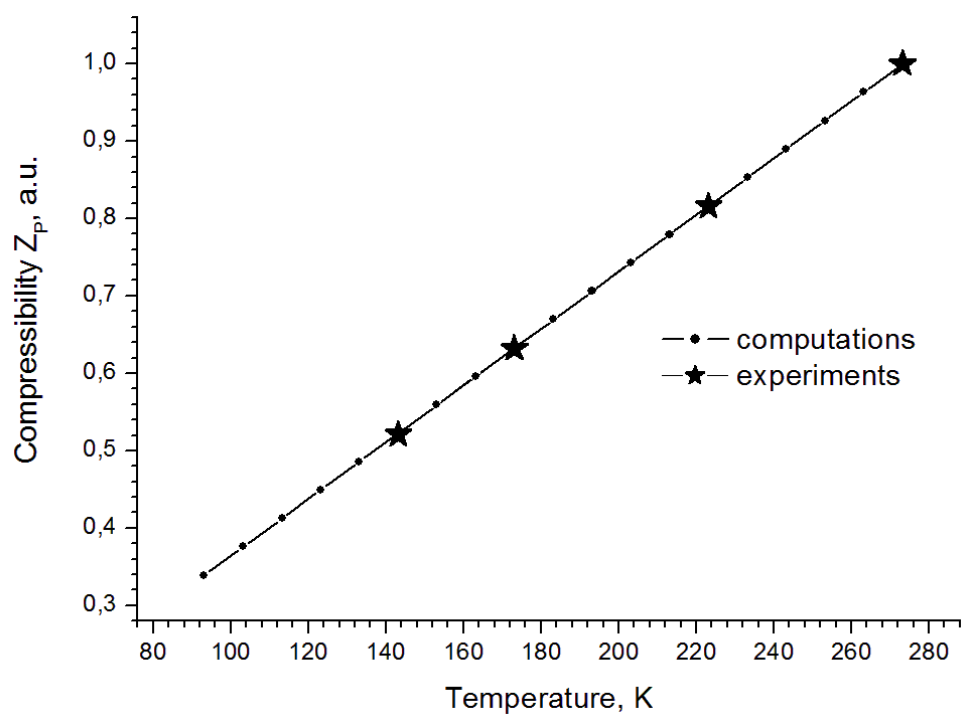


Figure 5: Dependence of compressibility Z_P from temperature

4 CONCLUSIONS

The paper considers the problem of calculating the macroparameters of gas media by molecular dynamics simulation. This issue is relevant for multiscale computing of supersonic flows of gas mixtures in plants sputtering nanoparticles on the surface of various materials. Under this theme, the present work is a preparatory step for the joint calculation of continuum mechanics and molecular dynamics of all stages of sputtering. The results of the work are as a approbation of calculation methods of basic gas or gas mixture macroparameters and received specific temperature dependences of the nitrogen macroparameters in the range of room and low temperatures (typical for gaseous media in installations of supersonic cold gasdynamic sputtering). Further development of the technique will be associated with the calculations of the coefficients of viscosity and thermal conductivity of nitrogen, and with the definition of macroparameters for nitrogen and hydrogen mixture in various proportions

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