The promising gas-dynamic schemes of vacuum deposition from the supersonic gas mixture flows.

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Abstract. Gas jet deposition (GJD) becomes promising method of thin film and nanoparticle deposition. This paper is focused on elaboration of new methods of GJD based on different gas dynamic schemes of flow formation and interaction with substrate. Using direct statistical simulation method, the analysis was performed for: a) interaction of the jet from the sonic nozzle with a substrate; b) fan flow in the result of interaction of two opposite jets; c) convergent flow from the ring nozzle, directional to the axis; d) interaction of the jet after convergent flow with the substrate; e) fan flow in the result of interaction of two opposite jets after convergent expansion.

Introduction.
The conceptual idea of GJD is confined in the using of the gas dynamic acceleration of precursor molecules in a flow by adiabatically expansion, followed by interaction of high energy molecules with elevated kinetic energy with a substrate. Extraordinary high kinetic energy of heavy atoms or molecules can be reached in the flow of light carrier gas. The ratio of kinetic energy of heavy and light molecules is proportional to the ratio of molecular masses. But total energy can be realized in the processes of interaction with substrate only in molecular beam system. In the continuum flow relaxation processes behind shock waves equalize the energy of heavy and light component. The part of the heavy molecule high kinetic energy exceeding the carrier gas energy is accessible for deposition only in non-equilibrium flows in the result of the gas separation, which is overlapped by energetic transformation. These processes were considered in the works devoted to aerodynamic problem and gas separation technology [1-6]. The review of papers concerning the deposition processes is presented in [7].

The elevated energy of organic molecules in a free jet was used, for example, in molecular beam system [8] and in the schemes with the gas separation in and behind shock waves in front of the substrate by deposition of the polytetrafluoroethylene (PTFE) film from the hypersonic flow of tetrafluoroethylene (TFE) [9]. The conception of this paper is based on experiments [9], followed by systematic analyses of different gas-dynamic schemes by direct simulation Monte-Carlo (DSMC) method [10]. The experimental procedure of [9] consists in the pyrolysis of the bulk PTFE to the almost pure gas C₂F₄ (TFE) at the stagnation partial pressure less than 10 torr and temperature less then 1000 K, followed by expansion of TFE or mixture TFE with helium into a low density
background. The substrate is located in the core of a free jet, where penetrating background molecules do not disturb the frontal flow.

The computational DSMC method is developed for analysis of mass, energy and impulse transformation in flows on the base of determination of macroscopic parameters from the calculated velocity and internal energy distribution function of molecules. It means that detail kinetics of molecule – substrate collisions can be analyzed.

**C\textsubscript{2}F\textsubscript{4} and hydrogen models in collision processes.**

For potential of colliding particles the variable soft spheres model [10] was used in calculations. Parameters of this model are evaluated from the temperature dependence of viscosity and diffusion coefficients given by Lennard-Jones model. The reference temperature \( T_{ref} = 1000 \) K, scattering factor \( \alpha = 1.3 \), viscosity power \( \omega \) is 0.71 for \( \text{C}_2\text{F}_4 \) and 0.64 for \( \text{H}_2 \), reference diameter \( d_{ref} \) is 5 Å for \( \text{C}_2\text{F}_4 \) and 2.55 Å for \( \text{H}_2 \).

Landau-Teller law for this particular case was used in calculations of \( \text{C}_2\text{F}_4 \) vibrational relaxation in the form \( \lg Z_{ff} = -26.86 \cdot \frac{T}{T} - 1/3 - 2.76 \). The vibrational heat capacity of \( \text{C}_2\text{F}_4 \) is given by polynomial on evidence derived from spectroscopic handbook. Details of the \( \text{C}_2\text{F}_4 \) simulation model elaboration can be found in [11].

1. **Interaction of the jet from the sonic nozzle with a substrate.**

The usual scheme of the jet deposition in the axially symmetric case [9] is presented in the figure 1 on the base of numerical Monte Carlo simulation of the precursor (\( \text{C}_2\text{F}_4 \)) supersonic jet interacting with the substrate in the form of a disk. The stream lines of the \( \text{C}_2\text{F}_4 \) flow are shown on the background of the temperature field. One can see the shock wave formation in front of the substrate. The latter has diameter equal to the sonic nozzle diameter \( d_* \) and located on the jet axis in the point \( Z / d_* = 0 \). The simulation provides the determination of all macroscopic parameters (temperatures, pressure, density, concentrations). In figure 2 they are shown along the axis. In the case of pure \( \text{C}_2\text{F}_4 \) the stagnation temperature of the gas at the substrate wall reaches the stagnation temperature in the source \( T_0 \). But in the case of expansion with helium as carrier gas the temperature of \( \text{C}_2\text{F}_4 \) in front of the substrate can reach \( 1.5 \cdot T_0 \) and higher. Besides, it is possible to obtain the translational and internal energy distribution for molecules colliding with a surface. Such information is of prime interest for analyses of deposition process. All specific conditions of deposition are determined by following parameters: source stagnation pressure and temperature, geometry of the nozzle, location of a substrate, Knudsen number of the flow over a substrate, its orientation and temperature. The elaborated methods of numerical simulation are admissible for any combination of above said parameters.

![Figure 1. Supersonic C\textsubscript{2}F\textsubscript{4} flow over substrate placed at Z/d\textsubscript{*} = 0 (3d\textsubscript{*} from the nozzle).](image1.png)

![Figure 2. Parameters on the axis for the flow over substrate (for figure 1).](image2.png)

2. **The fan flow in the result of interaction of two opposite jets from Laval nozzles.**

Figure 3 presents the special case of the precursor flow formation. It is the interaction of two identical opposite supersonic gas mixture jets (97.5 % of \( \text{H}_2 \) and 2.5 % of \( \text{C}_2\text{F}_4 \)). The streamlines of the heavy component are shown on the background of temperature of the light gas only as one left quarter of the
flow section. In the subsonic zone of the jet in front of symmetry plane the temperature of heavy component can be elevated few times higher than the initial stagnation temperature of mixtures. The relative concentration of C$_2$F$_4$ in this region exceeds this value in the stagnation chambers few times. After that gases endure the fan expansion, like along the mirror wall. The position of substrate in the form of a ring belt is shown by dashed line.

Figure 3. Interaction of the opposite H$_2$ + C$_2$F$_4$ jets. Stream lines for C$_2$F$_4$ flow.

Figure 4. The upper right quarter of the flow section. The streamlines show C$_2$F$_4$ flow to the axis and along it. The background is H$_2$ temperature.

3. Convergent flow from the ring sonic nozzle, oriented to the axis.

The C$_2$F$_4$ stream lines, issuing from the slot sonic nozzle in the form of a ring belt with h- wide are shown in figure 4 for the same mixture as in the previous case. As before, figure 4 presents only a quarter of the flow section. The convergent axially symmetrical flow oriented to the axis, is formed behind the nozzle on the cylindrical surface. The shock structure, surrounding the axis of symmetry at Z/h$^*$ < 100, is enriched by heavy gas component with temperature essentially higher than stagnation one. This scheme itself is promising for the deposition of films on the surface of stretched cylindrical bodies (wires, capillaries, fibers). Radial distribution of parameters is shown in figure 5. The relatively dense and high temperature cloud of C$_2$F$_4$ around the axis can be itself be source of hyperheated gas for deposition.

Figure 5. Velocities V$_{H_2}$, V$_{C_2F_4}$, H$_2$ and C$_2$F$_4$ translational temperatures T$_t$, relative number density n/n$_0$, number percentage of C$_2$F$_4$ θ in the symmetry plane.

Figure 6. Interaction of jets from two convergent sources (see Fig. 4). C$_2$F$_4$ streamlines on the background of H$_2$ temperature.

4. Interaction of the jet after convergent flow with the substrate.

The gas mixture behind the shock wave after convergent flow is spreading out along the axis in two sides. The substrate installed perpendicularly to axis will be subjected to the flow with elevated energy and concentration of heavy (precursor) gas. This scheme has likeness with a scheme on figure 3.
5. Fan flow in the result of interaction of two opposite jets after convergent expansion.

If two slot sources (see figure 4) are located on one axis, as it is shown on figure 6 for one quarter of flow section, the region of the interaction of two opposite supersonic flow along one axis has extremely high temperature and concentration of heavy component. After collision of these flows gas endures the fan expansion like in the scheme of figure 3. The substrate can be located on the periphery of the fan flow, as it is shown by the dashed line.

Conclusion.

DSMC method provides the data on distribution of all macroscopic parameters of gas mixtures, that allows analyze composition and energetic transformation in gas mixture flows and non-equilibrium state of gases including all energy distribution function for translational, rotational and vibrational modes.

The performed computational analyses open new ways of gas jet deposition. One of them, described in paragraph 1, has been realized experimentally.

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