Jets in scientific research and technological applications

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Abstract. A brief review of the work carried out at the Institute of Thermophysics of the SB RAS on the use of supersonic jets in scientific research to obtain relaxation process constants is presented, such as, effective cross sections for quenching of electronic states, atoms, molecules and ions. Also a review of the work directed to the use of jets and electron beams in various plasma-chemical technologies is given, namely, deposition of functional layers of thin-film silicon solar cells and conversion of hydrocarbon gases into useful products.

1. Introduction
A supersonic highly underexpanded free jet, which is created using various nozzles or nozzle devices in geometry, has a unique property. In such jet, in the region of the nozzles immediately adjacent to the exit, a supersonic flow is formed, so-called jet core. The jet core is limited by barrel shock waves and the closing shock wave. The uniqueness of this jet core is that its gas-dynamic parameters remain unchanged in a wide range of initial conditions, for example on the flow rate of gases through the nozzles or on the gas pressures in the flooded space where gas expands. Moreover, these parameters can be accurately predicted by a fairly simple calculation of the isentropic outflow of gas into vacuum, since the flow in the core of the free jet is the same as when the gas is expanded into a vacuum. This uniqueness of the supersonic jet can be used both in scientific research and in technological applications for organizing various plasma chemical technologies. This work is devoted to these two aspects of a supersonic gas jet application.

2. Jets in scientific research
In the supersonic jet core, parameters such as gas density and translational temperature change sharply with increasing distance from a nozzle exit. For example in the stream behind the sound nozzles at a distance of ten calibers, the density decreases by three orders of magnitude. At the same time, the temperature can reach several Kelvin degrees, despite the fact that it falls more slowly, and under certain conditions, for example with dilution by a light gas, can reach a fraction of the Kelvin degree. This property makes it possible to use the gas jet core as a gas thermostat in which the exact values of the gas temperature and density can vary due to a change in the distance from the nozzle exit and from the initial conditions in the forechamber, such as pressure and temperature, which can be measured very accurately by modern devices. Such gas thermostat can serve as a gas target in obtaining cross sections for the interaction of accelerated particles, in particular electrons, with atoms and molecules. This gas target is also very interesting in molecular spectroscopy, since cooling the gas greatly simplifies the interpretation of the spectra.
Another useful application of the flow in the jet core from the scientific instrument point of view, is following: by changing the initial conditions and the distance from the nozzle exit, it is possible to create in the jet arbitrary deviations from the equilibrium between the internal and translational degrees of freedom of the molecules up to the disturbance of the Maxwell distribution in the translational degrees of freedom themselves.

Observation of the deviation from the Maxwell-Boltzmann equilibrium occurring in the forechamber at moving from it makes possible to determine the relaxation times. It is also possible to determine the characteristics of the relaxation processes by looking after the approximation to the equilibrium flow as the gas flow increases. In addition, comparison of experimental data with theoretical calculations makes it possible to select adequate models of collisional processes. The useful properties of the jet core described above can be used not only for investigating the relaxation processes between internal and translational degrees of freedom, but also for the study of many other physicochemical processes, in particular condensation kinetics.

Let us illustrate the theses presented above with the results of the research. Examples of the results of using the jet core as a gas target for obtaining cross sections and effective quenching constants are given in [1, 2]. It should be noted that the measurement of these physical constants in such wide temperature range is unattainable by any other methods, except for the use of gas cooling in supersonic expansion in the jet core.

Figure 1 compares the experimental and calculated data [3, 4] with the population of the rotational levels in the ground state of the nitrogen molecule.

**Figure 1.** Comparison of the calculation results (solid lines) performed in the model of sudden collisions [3] of populations of rotational levels of $N^0_{\nu}$ in $N^2_2$, $B^2\Sigma^+_g (\nu = 0)$ states with experimental data (symbols).

**Figure 2.** Characteristic number of collisions for rotational relaxation in the $N_2+N_2$ system. a - experiment: 1-4 - ultrasound; 5-11 - thermotranspiration; 12-14 - shock waves; 15 - free jet [5-7]; b - theory: 1-5 - classical calculations; 6-9 - trajectory calculations; 10 - eikonal approximation.
The calculation was made by G.I. Sukhinin in the approximation of sudden collisions. As can be seen from this figure, an excellent coincidence of calculation and experiment is observed. This makes it possible to use the found transition probabilities matrix to calculate the populations of rotational levels from the spectra of the first negative nitrogen ion system. Figure 2 shows the dependence of the characteristic number of collisions of the rotational relaxation of nitrogen on the temperature in a wide range from units to $10^4$ Kelvin [5-7] to illustrate the use of the jet core for determining the relaxation process constants. Such range of temperatures is unattainable for other methods, as evidenced by comparisons made in the same figure.

Based on the experience of using supersonic jets and electron beams in scientific research, a gas-jet plasma chemical method for initiating chemical reactions in the gas phase and on the surface was developed [8, 9]. The engineering realization of this method is a cold plasmatron, which is a combination of an electron gun forming an electron beam and a nozzle block that provides feed to the processing in the form of a supersonic jet. The nozzle unit performs one more important task, it is a gas gate providing the pressure drop necessary for the operation of the electron gun. This pressure drop is created between the reaction chamber and the volume of the electron gun. A low-temperature electron-beam plasma is formed by the interaction of a gas jet and an electron beam in the volume of the reaction chamber. The main definitive features of cold plasma are that in it the rates of direct chemical reactions are orders of magnitude higher than in the case of thermal activation of processes, and the rates of reverse reactions at translational temperatures close to room temperature are frozen. This means that the reaction products obtained in the plasma chemical process are not destroyed by the heating of the gas. The fields of application of this plasma chemical method are very wide – from technologies associated with processes of deposition of films and surface treatment to technologies of low-tonnage gas chemistry [10]. The flows of working gas and the level of vacuum for these technologies can differ by several orders of magnitude, but the devices providing the technological process – cold plasmatrons, will be practically identical, slightly differing from each other in the dimensions and parameters of the nozzle blocks.

3. Jets in technological applications

We give some examples of the application of the gas-jet plasma chemical method for the deposition of thin films having various structures and different chemical composition. Thin-film structures are the basis of microelectronics, they are used as functional layers in various types solar of cells, they are also used for the formation of corrosion resistant and wear resistant coatings of machine parts, etc. Gas-jet plasma-chemical vapor deposition in combination with a roll-to-roll process has a huge potential for creating compact productions, the products of which are accumulated in the form of flexible tape-substrate (for example, thin-film solar cells, thin-film electrodes for lithium-ion batteries, etc.). The core of these technologies is a reaction chamber equipped with the necessary number of cold plasmatrons. Through this chamber a tape-substrate moves using the "roll-to-roll" technology, onto which the layer of material is deposited continuously. The finished product accumulates in the form of a roll. When creating a product having a multilayer structure, the production unit includes several reaction chambers equipped with plasmatrons configured to deposit the corresponding coating. Table 1 presents the experimental results and technological features of the gas-jet plasma chemical method for solving various practical problems.

Another example of the use of a gas-jet plasma chemical method relates to the processing of gaseous hydrocarbons into useful products of different chemical composition. Plasma chemical synthesis in the gas phase has a huge potential for creating compact, modular production, for example, in natural gas fields. The core of these technologies is a plasma chemical reactor equipped with the necessary number of cold plasmatrons and a device for supplying an external electro-magnetic field. Obtained product is separated from the unprocessed feedstock and is removed from the process in the form of gas, liquid or solid. Table 2 presents the experimental results and technological features of the gas-jet plasma chemical method for various practical problems. In such applications it is necessary to
process large amounts of feedstock (by several orders of magnitude) in comparison with the deposition
of thin films.

**Table 1.** Technological application of the jet the gas-jet plasma chemical method for deposition of
layers on industrial size substrates.

| Task | Experimental results | Technological features |
|------|----------------------|-----------------------|
| Deposition of silicon layers for thin-film solar cells. | High deposition rates of the intrinsic semiconductor layers at the level of 5 nm/s have been achieved, layers of silicon with different crystalline structures from amorphous to microcrystalline have been obtained. | High deposition rate of layers. Possibility to obtain a material with a different crystal structure. Possibility of depositing layers on non-conductive substrates at low temperature. |
| Deposition of silicon layers deposition for lithium-ion batteries. | A specific discharge capacitance was achieved at the first cycle of 3200 mAh/g at a theoretical capacity of 4200 mAh/g. When using substrates of carbon nanotubes, the number of charge-discharge cycles (up to a 2-fold drop in capacity) increased by 8 times. | Versatility of the technology for various applications. Good adhesion of silicon to the substrate. Ability to create multi-layer structures. |
| Deposition of transparent conductive coating ZnO:Al. | Conductive films with a specific resistance of 0.005 Ωcm and a transmittance of visible light of 80% are obtained. | The possibility of modification of the process for evaporation of metals. Plasma oxidation. |
| Deposition of carbon layers for ionistors and lithium-ion batteries. | The layers of disordered graphene with conductivity at the level of 100 S/cm are obtained. | Versatile process for the raw materials used. The uniformity of deposition. |
| Epitaxial silicon deposition. | The deposition rate was reached at 15 nm/s. | The highest speed of deposition of layers. Clean process. |
| Production of solar grade silicon. | Silicon of solar quality with energy inputs at the level of 50 kWh/kg from monosilane was obtained, with a conversion factor of more than 50% on substrates with an area of 0.15 m². | Low specific energy consumption. High coefficient of raw material use. Large area of deposition. |

**Table 2.** Practical application of the gas-jet plasma chemical method for low-tonnage plasma gas chemistry.

| Task | Experimental results | Technological features |
|------|----------------------|-----------------------|
| Conversion of silicon tetrachloride (SiCl₄) to trichlorosilane (SiHCl₃). | A plasma-chemical reaction was performed with a conversion factor of 30% in a single cycle. | Compact equipment. High process selectivity. |
| Conversion of natural and associated petroleum gases into commercial products (methanol, broad fraction of light hydrocarbons, etc.). | Gaseous and liquid hydrocarbons of various composition were obtained. A high selectivity for methanol production (at 80%) was achieved with a processing ratio of 4% in a single-step regime. | Compact modular equipment for gas processing at production sites. Direct synthesis of methanol without the isolated stage of syngas production. |
4. Summary
It is shown that the supersonic core of a free jet is a good scientific tool for obtaining the quenching rate constants of electronic states, relaxation times, and the probabilities of electron-vibrational-rotational transitions at an electron impact. Also, supersonic gas jets and the cold electron-beam plasma created in them offer unique opportunities for creating new technologies on this basis. At the moment, a number of works have been performed on the use of a gas-jet plasma chemical method in various directions associated with the deposition of thin films and the processing of model associated petroleum gas into liquid products, such as methanol, and broad fraction of light hydrocarbons.

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