The large clusters influence on the supersonic flows gas dynamics in a rarefied medium

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Abstract. The processes of Van der Waals clusters formation in supersonic gas flows expanding into a rarefied medium are discussed in this report. The necessary conditions for cluster formation, methods for measuring the average size and size distribution of clusters in a rarefied gas flow are considered. The problems associated with electron-beam ionization of clusters during mass spectrometry of clustered flows are analyzed. The process of intraccluster energy exchange in mixtures, that leads to the possibility of inverse pumping of electronic levels of atoms, is illustrated. The problems arising during optical measurements of density in cluster flows are demonstrated. The effect of large clusters formation on the shape and structure of supersonic flows is shown.

1. Introduction
Van der Waals cluster is an associate of gas particles bound by the Lennard-Jones potential. Gas clusters are of interest in terms of their participation in physicochemical processes, and their applications in various technologies. The chemical properties of clusters are primarily due to the increasing role of surface particles. In fact, for small clusters all of the combined particles turn out to be surface. It explains their heightened chemical activity. In technological processes a useful property of clusters is the high specific energy of large ones and, at the same time, the low energy required for their fragmentation. This property has found application in smooth polishing technology using a molecular beam of clustered particles [1]. Cluster beams are also used for the manufacture of thin films, for the production of new materials, and in other similar applications [2].

The formation of gas clusters in supersonic flows occurs at certain initial flow parameters. This process requires high stagnation pressure and low initial temperature in supersonic flow. An important factor is the configuration of nozzle used for flow formation. It is established that the adding of a small admixture of a easily condensable gas to the outflowing mixture leads to catalysis of the cluster formation process at an early stage of condensation [3].

The fundamentally important parameters in the study and usage of clusters are their average size and size distribution. A number of techniques for measuring cluster sizes in a gas stream are known: mass spectrometric [4–5], spectral [6–8], electron diffraction [9], and complex [10]. The proposals to determine the velocity ratio from measurements of the transverse profiles of the density of the molecular beam are also considered. Assuming a mass as a known quantity, it is possible to measure the translational temperature [11], and, knowing the translational temperature, the particle mass distribution can be determined [12]. The submitted experimental methods, within the framework of their limitations, make it possible to calculate the average size of clusters 〈N〉. However, in practice,
most experimenters use dependence (1) proposed by O. Hagen [13–14]. According to [14], the dependence of the formed clusters average size is represented as:

$$\langle S \rangle = b(\Gamma^*)^a,$$

(1)

where $\Gamma^*$ is the non-dimensional similarity parameter of condensation presented as a function of the gas stagnation parameters and nozzle shape; $a$ and $b$ are constants. For an axisymmetric flow, $\Gamma^*$ has the form:

$$\Gamma^* = wP_0d_{eq}^{-a}T_0^{-\frac{s-2}{4}}r^{-1},$$

where $w$ and $q$ are constants depending on the gas type; $s$ is the number of active degrees of particles freedom. As experience showed, the formula proposed by O. Hagen accurately describes the value of $\langle S \rangle$, and all the amendments introduced by other authors into it do not significantly change the result.

In the present report, we demonstrate the distortion effect of gas dynamics and energy exchange in supersonic flows expanding into a rarefied medium in conditions of clusters formation.

2. Experimental setup

In the NSU’s Applied Physics Department was developed functioning now an experimental laboratory stand LEMPUS-2 [15] designed to study the flows of gases or gas mixtures with known composition expanding into a vacuum or a very rarefied medium. The schematic of the stand is shown in figure 1. A prechamber with a nozzle (1) is located inside the expansion chamber (2) on the coordinate device. The design of the prechamber allows the installation of nozzles of sonic and supersonic configurations. The gas flowing out of the nozzle forms a supersonic jet (3).

![Figure 1. Schematic of the LEMPUS-2 experimental complex: 1 - prechamber with a nozzle, 2 - expansion chamber, 3 - gas flow, 4 - electron source, 5 - optical window, 6 - optical measurement system.](image)

The vacuum system of the stand includes high-vacuum turbomolecular pumps manufactured by SHIMADZU with the corresponding fore-vacuum oil-free pumps by KASHIYAMA and ANEST IWATA, and Cryo Torr-8 helium cryogenic pumps from HELIX TECHNOLOGY. The pumps are installed in a parallel circuit. Operating pressure range in the background medium of the vacuum chamber: $10^{-4}$ - $10^{2}$ Pa at a gas consumption of up to 0.2 g/s in continuous and up to 10 g/s in pulsed flow regime. Using an electron source (4), radiation is initiated in the gas flow. It is monitored through an optical window (5) by means of an established variation of the optical system (6), which can consist of a quartz lens with a spectrometer/scanner or photo camera mounted outside the window (5).

3. Results and discussion

Illustrations discovered and identified by the authors of the effects associated with the clusters formation in supersonic flows are presented as follows.

a. Reducing radiation intensity when applying electron-beam diagnostics to measure local density in a flow of condensing gases. The density profiles of the supersonic argon flow obtained from measurements of the particles radiation intensity in accordance with the technique proposed in [16] are located below the empirical-theoretical dependence [17], and this deviation increases in proportion to the increase in pressure $P_0$. This effect can be explained by the fact that, according to [18], in a
collision with an electron, only one particle in a cluster is excited and emitted. Therefore, a cluster, sometimes consisting of 1000 or more particles, is perceived as one particle in this technique. Since the fraction of condensate in the flow and the average cluster size increase with increasing \( P_0 \), this leads to a proportional decrease in the radiation intensity.

\( b. \) Changing the structure of the emitted spectrum. In the presence of easily condensing admixtures of monosilane, methane or carbon dioxide in argon emission an inverse anomalous increase in the radiation intensity is observed. Figure 2 shows the dependences of the radiation intensity recorded at a wavelength of 549.6 nm (neutral argon – \( \text{Ar-I} \)) on the value of \( P_0 \cdot d_* \) in argon flows with the addition of methane (a) and methane-monosilane (b) admixtures to the carrier gas, the proportion of which does not exceed 5%. The dashed line indicates a linear increase in the radiation intensity observed in a pure argon flow. Discovered effect is observed only on individual argon emission lines. The addition of a easily condensable component to argon leads to a shift in the onset of condensation to a region of lower values of \( P_0 \cdot d_* \). Clusters of admixture, which are the nuclei of condensation, appear first in the flow. Clustering of the admixture prevents the condensation of argon. As a result, at the initial stage of cluster formation, there are no trimers and heavier argon clusters in the flow. The most probable sequence of processes for the energy exchange in a flow is as follows:

\[
[X] + e \rightarrow [X]^* - \text{the admixture particle is excited and possibly ionized by electron impact. The assumption of possible ionization is due to the interaction cross section.}
\]

\[
[X]^* + \text{Ar}_n[X]_m \rightarrow (\text{Ar}_n[X]_{m+1})^* - \text{the excited particle of admixture, transfers energy to the cluster (interacting with it) and joins it.}
\]

\[
(\text{Ar}_n[X]_{m+1})^* \rightarrow \text{Ar}^* \text{Ar}_n-1[X]_{m+1} - \text{due to the intra-cluster energy exchange, individual argon energy levels are excited with following photon emission. This process is possibly proceeding with ejection of excited atomic argon from the cluster.}
\]

**Figure 2.** An increase in the radiation intensity (\( \lambda = 549.6 \text{ nm} \)) in an argon flow with the addition of methane (a) and methane-monosilane (b) admixture in comparison with the traditional linear dependence.

c. Gas dynamics distortion. The effect was detected during photometric measurements of the spindle-shaped argon jet diameter \( Z_j \) in its maximum cross-section with variation of the initial outflowing parameters. According to [17], this size should be directly proportional to the value \( d_* \sqrt{P_0/P_h} \). This fact is confirmed by varying the pressure in the background medium \( P_h \) with fixing the remaining initial parameters (see figure 3, a). However, when carrying out measurements with a variation in the stagnation pressure \( P_0 \), similar dependence has a nonlinearity due to the fact that the proportionality coefficient proposed in [17] is not constant and depends on the formed clusters size or on the fraction of condensate.

d. The formation of a secondary cluster flow. During the experiments to study developed condensation, in conditions of large clusters formation in the jet [14], an additional flow larger than traditional jet is found.
Figure 3. Approximations of the results obtained by measuring the traditional jet diameter in the maximum cross-section $Z_j$ with variations in $P_h$ (a) and $P_0$ (b).

An example of visualization of a discovered new effect in an argon flow is presented in figure 4. For improved visualization of the effect, the image is divided into fragments with comparable radiation intensity. The secondary flow (a "wake") expands from the middle of the first traditional "barrel" and exceeds its diameter by about 2 times and its length by 6-7 times. It is shown that this flow is formed due to large clusters, which have a large momentum and energy and are able to overcome the shock waves of a traditional jet and form cluster flow.

Figure 4. Visualization of an argon jet flowing out under conditions of developed condensation.

4. Conclusion

This report demonstrates the effect of clusters formation in a supersonic flow on gas dynamics and energy exchange, which should be taken into account when working with clustered jets.

Acknowledgements

The work was performed using the shared equipment center "Applied physics" of the NSU Physics Department with the financial support of the RFBR (grant №20-01-00332/20).

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