Features of registration methods for clustered supersonic jets

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Abstract. We have considered the features of the supersonic underexpanded flows formation under conditions of developed condensation, as well as measurements in such jets by electron-beam and molecular-beam methods. It is shown that under the conditions of large clusters formation both the geometry and the structure of supersonic jets may change. It is determined that the use of a mass-analyzer for recording monomers and clusters in a molecular beam has a number of peculiarities caused by the molecular beam formation from a jet containing large clusters. A method of mass spectrometry of clustered flows during the ionization of gases in a jet before the formation of a molecular beam is proposed. The features of this method are illustrated.

1. Introduction

The main methods of producing gas clusters are currently based on the use of supersonic jets expanding into a rarefied space [1-2]. In the gaseous phase, the structure and composition of the clusters can markedly differ from the properties of clusters in the condensed state. The proportion of condensate can reach 20 – 30% of the total volume of the expiring gas, and the size of the clusters ranges from dimers to a thousand or more particles in a cluster. This depends on the gas used and the gas-dynamic parameters of the system, under the conditions of the supersonic jet outflowing from the prechamber through the sonic or supersonic nozzle at a high stagnation pressure P₀.

The registration of clustered (as well as nonclastered) flows is traditionally carried out using electron-beam [3], absorption infrared [4] or laser [5] spectroscopy, Rayleigh scattering, Mach-Zehnder interferometry [6], as well as molecular-beam mass spectrometry [7]. In this case, there are features that need to be taken into account to obtain reliable information about the objects under study. The purpose of this paper is to discuss the results obtained using mass spectrometry and electron-beam spectroscopy. All the experimental data given in this paper were obtained on a complex of gas dynamic stands of the Department of Applied Physics at Novosibirsk State University [8-9].

2. The size of the supersonic jet

The process of formation of clusters in a supersonic flow requires the provision of a high density of the expiring gas, at least at the initial stage of the expiration jet. This is the reason that in the majority of experimental installations, due to the limited total vacuum pumping rate of the vacuum systems and, accordingly, not very deep vacuum, a typical prolate ellipsoid-like structure is formed in which the free expansion zone of the cold gas jet is limited by lateral shock waves and the mixing zone with the background warm gas. In the case of developed condensation, as our measurements have shown,
the longitudinal and transverse dimensions of the jet increase in comparison with similar ones in non-condensing jets. In practice, the empirical formula [10]: \( X_m/d^* = k (P_0/P_h)^{0.5} \) is used to estimate the maximum length \( X_m \) of a supersonic jet expansion (from the nozzle to the Mach disk or the x-shaped configuration [3]). In the formula [10]: \( d^* \) is the diameter of the nozzle's sound section, \( P_h \) is the pressure of the surrounding space (background gas), \( k \) is the proportionality coefficient, depending on the flow regime and the properties of the expiring gas. For example, for supersonic jets of molecular nitrogen it is customary to assume \( k = 0.7 \). However, as shown by our measurements performed with sonic and supersonic nozzles, under the condensation conditions the coefficient \( k \) can increase up to 1.5 times. This result is shown in figure 1, where the coefficient \( k \) is given depending on the average cluster size \( N \) estimated according to [11]. The measurements were carried out by photographing supersonic jets, whose luminescence was initiated by a high-voltage electron beam. Since electronic excitation of atoms and molecules initiates, including long-lived excited states, we can obtain a picture of the glow of the jet at large linear dimensions. A similar result was obtained for supersonic argon jets. We believe that such change occurs in any supersonic jet provided that large clusters are formed.

![Figure 1](image)

**Figure 1.** The dependence of the proportionality coefficient \( k \) on the size of clusters. Nitrogen. Sonic nozzle: \( d^* = 0.22 \) mm. Supersonic nozzle: \( d^* = 0.17 \) mm, the throat nozzle diameter \( d_a = 2.40 \) mm, nozzle length \( L_D = 8.10 \) mm

The structure of the supersonic jet can change no less noticeably under conditions of developed condensation. Under certain flow parameters, in addition to the traditional primary jet, a prolate ellipsoid-like structure region of a larger size was formed by cluster particles [12]. We assume that large clusters relatively freely penetrate through the lateral compression jumps and the gas jet mixing zone with the background gas and form their own structure of a much larger size than the primary jet. It was also possible to visualize this process when a high-voltage electron beam was used to the luminescence excitation. An example of an image obtained in a supersonic argon jet is shown in figure 2. A brighter area corresponds to a higher density of radiating particles. In the photograph, in addition to the primary ellipsoid-like structure, a secondary structure, formed approximately from the middle of the primary jet, is clearly visible.

### 3. Clusters in a molecular beam

The formation of a molecular beam is a necessary condition for a mass spectrometry of supersonic flows. However, in the formation of a molecular beam from a clustered jet, in addition to the traditional problems of skimmer interaction and post-skimmer scattering [13], other factors should be considered. In particular, the velocity ratio \( S \) of the clusters, with considering the difference by orders of magnitude in mass, can significantly exceed \( S \) of the monomers. This difference leads to the particle size selection on the jet axis even if we will take into account the effect of clusters slippage with respect to monomers.
Figure 2. Photograph of the clustered supersonic jet expansion when a radiation is excited by a high-voltage electron beam. Argon. $P_0 = 600$ kPa; $P_h = 4.5$ Pa. Supersonic nozzle: $d_* = 0.17$ mm, $d_a = 2.4$ mm, $L_D = 8.1$ mm.

Since in the molecular beam we can neglect the collisions between the particles of the flow, the monomers and clusters move along the trajectories determined at the entrance to the skimmer. Therefore, as the gas passes through the diaphragms to the detector, near the axis of the molecular beam mainly heavy clusters are accumulated. The result of registration depends on the input aperture of the detector and the solid angle inside which particles from the skimmer along direct trajectories can get into the detector of the mass spectrometer. The consequence of this selection is the difference in the results obtained by different authors and at different experimental settings under seemingly similar conditions. For example, in [14-16], bimodality of the transverse distribution of the intensity of molecular beams was noted, which is associated with a wide distribution of the monomeric component, but a narrower and larger by the amplitude of the cluster component.

We performed measurements in molecular argon beams at approximately the same gas dynamic parameters (stagnation pressure and temperature, supersonic nozzle sizes, skimmer parameters), as in [16]. However, in our case, the path length of the molecular beam from the skimmer to the detector was larger, the aperture of the input diaphragm of the detector was smaller, and the detector was a quadrupole mass spectrometer. The result of measuring the transverse profile of the molecular beam density is shown in Figure 3.

Figure 3. The transverse profile of a molecular beam of argon. $P_0 = 400$ kPa. Supersonic nozzle: $d_* = 0.17$ mm; $L_D = 8.1$ mm; $D_a = 2.4$ mm. Skimmer $d_s = 0.46$ mm

The red solid line in the graph is the monomer distribution ($m/e = 40$) across the axis of the molecular beam, the red dashed line is the dimers ($m/e = 80$). Estimating the average cluster size by [11] in the
given regime gives the value \( <N> = 1380 \). The selected distance from the nozzle corresponds to the position of the skimmer at about the first quarter of the size of the first "barrel" of the supersonic jet. The monomer component recorded by the mass spectrometer has the complex structure. The first mode is a wide transverse profile (about 10 mm from the axis), which consists of the "primary" particles of the stream, i.e. monomers moving along the streamlines due to the finiteness of the Mach number at the skimmer entrance. A narrow intense central peak (1 ÷ 2 mm from the axis) determines the fraction of argon monomers formed from clusters upon ionization in the detector of the mass spectrometer. The high intensity of this mode indicates the concentration in the near axis region of the beam of a relatively small size clusters, since it is these clusters that decay primarily into monomers and small oligomers [17-18]. This is confirmed by the presence of a sufficiently intense peak of dimers, also shown in Figure 3. Such a bimodality, as noted above, was recorded by many researchers.

However, quite unexpectedly, a third mode is registered in a narrow range near 0.3 mm from the axis. In this range of transverse distances, the intensity of the monomeric peak falls by 2 orders. As a result, on the molecular beam axis, the oligomeric components, and in particular the dimers exceed the monomer component in amplitude. The explanation of this fact consists in the presence on the axis of the molecular beam of predominantly large clusters, which is disintegrated during ionization mainly into large fragments. When the skimmer - nozzle distance increased, the dip in the signal intensity of monomers near the molecular beam axis (3-d mode) decreased, and after leaving the first "barrel" disappeared completely. This is confirmed by the data (blue curves, monomers - solid line, dimers - dotted) also shown in the figure. The nozzle - skimmer distance corresponds to the position in the region of the x-shaped configuration. The change in this mode is due to the drop in the density of the clusters on the axis of the jet due to the expansion along the current lines (see the explanation to Figure 2), as well as the dissipation of the clusters as they pass through the shock wave and the mixing region. The absence of the third mode indicates the absence of large clusters on the molecular beam axis for the given nozzle-skimmer distance.

Thus, the demonstrated feature causes significant changes in the intensity of monomers on the axis of the molecular beam as a function of the distance from the nozzle when the mass spectrometer is used as a detector in regimes with developed condensation [7]. In the case of using an integral full-pressure sensor as a molecular beam detector, the intensity distribution across the beam axis in a similar regime is bimodal. Consequently, the measurement results in flows with clusters depend on the solid angle within which the particles of the molecular beam reach the detector, and also of the detector type.

4. Destruction of clusters during ionization

Most methods of mass spectrometry are based on the ionization of neutral particles by electrons. The electron energies used for this vary, as a rule, from a few tens to several hundred eV. When an electron beam is used to diagnose a supersonic jet, the electron energy can reach even several tens of keV. Since the gas clusters are connected by van der Waals forces with a binding energy of a fraction of eV, the ionization of the clusters is accompanied by their destruction. As noted above, small clusters break down primarily into monomers and dimers, large clusters break down into large fragments. The process in this case is of a probabilistic nature and depends on the size, structure, and composition of the clusters, as well as on the energy of the electrons. Therefore, obtaining large clusters by the expansion of supersonic jets into vacuum and measuring the size distribution of clusters is a very difficult task.

In our work, we tested the use of a high-voltage electron beam in a jet for mass spectrometry of clustered flows. For this purpose, a high-voltage electron beam with an energy of 8 ÷ 12 keV intersected the axis of the supersonic jet between the nozzle and the skimmer. The diaphragms of the molecular beam system were fed with potentials carefully chosen to achieve the maximum efficiency of transporting charged particles to a quadrupole block of a mass spectrometer with its own ionizer turned off. The result of the comparison of mass spectra is shown in figure 4. In both cases the same gas dynamic parameters were chosen: \( P_0 = 300 \text{ kPa}, T_0 = 298 \text{ K} \), the same supersonic nozzle, the
fixed distance between the nozzle and the skimmer. For convenience of comparison, maximum values coupled by a solid line are given, rather than mass peaks. Blue indicates the data for ionization by a high-voltage electron beam with an energy of 10 keV, red - using the own block of the mass spectrometer (electron energy 70 eV).

**Figure 4.** Comparison of the mass spectra of a supersonic jet 20% CH₄ + 80% He

It should be noted that the spectra are plotted without normalization. It seems difficult to compare the absolute amplitudes for the two measurement methods on a single scale. On the given spectra, the peak amplitude has monomeric methane peaks not completely removed by water (m/e = 18 and 17), as well as a number of hydrocarbon peaks. Therefore, the normalization to the sum of all the amplitudes or to the selected peak (for example, m/e = 16) does not give a reliable picture of the ratio of real amplitudes between these two methods. Nevertheless, we can draw conclusions based on the qualitative picture. With standard ionization in a mass spectrometer, with an increase in the mass number, the amplitudes of the peaks are systematically reduced. In ionization in the jet and transport of ions to the detector of the mass spectrometer, the amplitude of the oligomeric components decreases more sharply, but with a further increase in the mass number, the peak amplitudes decrease very slowly, local peaks are found consisting of groups of peaks. The ionization by a high-voltage electron beam in a jet gives significantly larger amplitudes of clusters with an average size N > 25. This may be due both to a change in the process of destruction of clusters at high electron energies (this fact was noted by the authors of [19]), and with different collision conditions for neutral and charged particles after ionization. In any case, the proposed method of ionization in the jet makes it possible obtaining a more complete picture of the clusters size distribution.

5. Conclusions

It is shown that condensation in a jet affects the dimensions of a supersonic jet, its shape and structure. For certain gas-dynamical parameters in supersonic jets, an especial secondary structure, formed in the conditions of cluster formation, was first discovered. It is determined that mass-spectrometric measurements in molecular beams under clustering conditions depend to a large extent on the detection method used, and the obtained distributions for the masses of the clusters depend not only on the energy of the ionizing electrons, but also on the location of ionization and the method of delivery of ionized particles to the mass spectrometer detector. Consequently, the measurement results in flows
with clusters depend on the solid angle within which the particles of the molecular beam reach the detector, and also of the detector type. Thus, we have illustrated the complexity and features of measurements in cluster supersonic jets and proposed recommendations that should be taken into account with respect to the observed characteristics.

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References
[1] Smirnov B M 2003 Physics – Uspekhi 46 589-628
[2] Wyslouzil B E and Wölk J 2016 J. Chem. Phys. 145 211702
[3] Kislyakov N I, Rebrov A K and Sharafutdinov R G 1975 J. Appl. Mech. Tech. Phys. 16 187-95
[4] Zischang J and Suhm M A 2013 J. Chem. Phys. 139 024201
[5] Chen G, Boldarev A S, Geng X, Li X, Cao Y, Wang L and Kim D E 2016 AIP Adv. 6 115015
[6] Gupta K C, Jha N, Deb P, Mishra D R and Fuloria J K 2015 J. Appl. Phys. 118 114308
[7] Zarvin A E, Kalyada V V and Khudozhitkov V E 2017 Thermophys. Aeromech. 24 671-81
[8] Zarvin A E, Kalyada V V, Yaskin A S, Khodakov M D, Korobeishchikov N G, Khudozhitkov V E, Madirbaev V Z and Ezdin B S 2016 Instr. Exp. Tech. 59 820–6
[9] Zarvin A E, Kalyada V V, Madirbaev V Z, Korobeishchikov N G, Khodakov M D, Yaskin A S, Khudozhitkov V E and Gimelshein S F 2017 IEEE Trans. Pl. Sci. 45 819-27
[10] Ashkenas H Z and Sherman P S 1966 RGD Proc. 4th Int. Symp. Ed J. H. De Leeuw Toronto Acad. Press 2 84-105
[11] Hagena O F 1992 Rev. Sci. Instr. 63 2374-9
[12] Zarvin A E, Yaskin A S, Kalyada V V and Ezdin B S 2015 Tech. Phys. Let. 41 1103–6
[13] Zarvin A E and Sharafutdinov R G 1979 J. Appl. Mech. Tech. Phys. 20 744-9
[14] Sharma P K, Knuth E L and Young W S 1976 J. Chem. Phys. 64 4345-51
[15] Yang S, Daineka D V and Chatelat M 2003 Chem. Phys. Let. 377 595-600
[16] Korobeishchikov N G and Penkov O I 2016 Vacuum 125 205-8
[17] Buck U and Meyer H 1986 J. Chem. Phys. 84 4854-61
[18] Bonhommeau D, Halberstadt N and Viel A 2006 J. Chem. Phys. 124 184314
[19] Schütte S and Buck U 2002 J. Mass Spec. 220 183-92