Features of using traditional diagnostic tools for recording supersonic jets of rarefied gases in flows with clusters

A E Zarvin, K A Dubrovin, V E Khudozhitkov, S T Chinenov, V V Kalyada and A S Yaskin

Department of Applied Physics, Novosibirsk State University, 630090, Novosibirsk, Russia

E-mail: zarvin@phys.nsu.ru

Abstract. Features of the formation of supersonic underexpanded jets in condensation, as well as measurements in such jets by electron-beam and molecular-beam methods are considered. It is shown that the clusters in the flow can change both the geometry and the structure of the supersonic jets. It is determined that the readings of the mass analyzer used as a detector of a narrowly directed molecular beam depend to a large extent on the size of the clusters and the value of the detector’s solid angle. The examples which compare the traditional method of mass spectrometry with ionization and a new method ionization by high-voltage electron beam with the subsequent transport of ions to the mass spectrometer detector with its own turned-off ionization block illustrate changes in the detected clusters.

1. Introduction

In many cases the gas flow through the sonic and supersonic nozzles into the surrounding space with low pressure (rarefied gas) is accompanied by cluster formation in a supersonic jet [1–2]. At high stagnation pressure, the size of clusters can reach hundreds or thousands of atoms or molecules, and the proportion of condensate in the total gas flow can be up to 30%. Electron-beam [3], absorptive infrared [4] or laser [5] spectroscopy, as well as molecular-beam mass spectrometry are traditionally used for recording the supersonic jets of rarefied gases [6]. At the same time there are features that must be taken into account to obtain reliable information about the studied objects.

The purpose of the research is to discuss the results obtained using mass and electron-beam spectroscopy. All experimental data presented are obtained at the gas-dynamic complex of the Department of Applied Physics at Novosibirsk State University [7].

2. Changes in the size and structure of supersonic jet in clustering conditions

A typical form of a supersonic jet flowing into a submerged rarefied space (background gas) in most experimental facilities is one or more typical spindle-like structures (so-called “barrels”) following each other, formed as a result of the interaction of a supersonic gas flow from the nozzle with the background gas from the surrounding space. The borders of such a “barrel”, which occurs in the form of lateral and closing shock waves and areas of flowing and background gases mixing, are determined by the ratio between the stagnation pressure in the nozzle pre-chamber, P0, and the pressure of the surrounding background gas jet, Pb. The article proposes an empirical formula defining the longitudinal size of the initial “barrel”, Xm, from the nozzle exit to the closing shock wave (Mach disk or X-shaped [3] configuration) [8]: Xm/d* = k·(P0/Pb)0.5, where d* is the diameter of the sonic nozzle.
section, \( k \) is the proportionality coefficient, depending on the flow mode and the properties of the exhaust gas. For example, \( k = 0.67 \div 0.7 \) for the molecular nitrogen supersonic jets.

Since in electron collisions with atoms or molecules, the long-lived states excited, it is possible to obtain a picture of the jet glow on the large linear dimensions. This fact is used to visualize and measure the size of nitrogen and argon supersonic jets under various flow conditions. As our measurements made with sonic and supersonic nozzles in condensation, the jet longitudinal and transverse dimensions increase compared to similar ones in non-condensing jets. This growth can be represented as the dependence of the \( k \) coefficient on the cluster size and the condensate fraction.

Figure 1 shows the dependence of \( k \) coefficient in molecular nitrogen jets on the average cluster size \( N \), estimated according to the formulas proposed by O. Hagen [9]. The measurements were carried out by the supersonic jet photometry, which glow was initiated by a high-voltage electron beam. The graph shows that with the growth of \( N \), \( k \) increases, reaching the limit value at the cluster sizes of 100 and more.

We suggested that this result was caused by more efficient scattering of monomers background particles on heavy cluster particles. The cluster growth in strong condensation, i.e. at larger sizes, continues mainly due coagulation and coalescence, when the condensate proportion is almost not changing. It can be assumed that the condensate proportion is the determining factor. Unfortunately, we do not have the tools to diagnose the condensate proportion, and simply state the fact that condensation influences the supersonic jet size. A similar increase in the \( k \) coefficient is found in the argon jets, although fixed value is achieved at large values of the estimated [9] \( N \).

In modes with condensation, a change in the structure of the supersonic jet was also detected. Under certain conditions of outflow, in addition to the traditional primary jet, we also observed a spindle-shaped, but larger area, which we called the “trace”, formed, as expected, by cluster particles [10]. We assume that large clusters pass relatively easily through lateral shock waves and the gas mixing zone of the jet with the background gas and form a much larger structure of their own than the primary jet. It was also possible to visualize this process when a high-voltage electron beam is applied to the outgoing gas. It is most convenient to observe the “trace” parameters in argon jets, the glow of which has sufficient intensity in the visible region of the spectrum.

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 photo, besides the primary spindle-shaped structure, the “trace” structure, formed approximately from the middle of the primary “barrel”, is clearly visible. The threshold for the appearance of a “trace” in terms of the average cluster size is established. It is shown that the dimensions of the “trace” depend on the magnitude of the background pressure: as \( P_b \) increases, the dimensions of the “trace” decrease. It was also established that the addition of molecular nitrogen or oxygen to the background gas changes both the intensity and the predominant color of the “trace”. In a supersonic carbon dioxide jet, the glow of the “trace” region is in the ultraviolet part of the spectrum.
Figure 2. Photo of the flow of a clustered supersonic jet upon excitation of a glow by a high-voltage electron beam. Argon. \( P_0 = 600 \text{ kPa} \); \( P_h = 4.5 \text{ Pa} \). Supersonic nozzle: \( d_\ast = 0.17 \text{ mm} \), nozzle cutting diameter \( d_a = 2.4 \text{ mm} \), nozzle length \( L_D = 8.1 \text{ mm} \).

3. Clusters in a molecular beam

The formation of a molecular beam is a necessary condition for the mass spectrometry of supersonic flows. However, when forming a molecular beam from a clustered jet, in addition to the traditional problems of skim-dimensional interaction and after-skimmer scattering [11], it is necessary to take into account other factors. So, even when taking into account the effect of cluster slip relative to jet monomers, the speed ratio of S clusters, taking into account the difference in masses, significantly, by orders of magnitude, exceeds S monomers. This difference leads to selection by particle size. In a molecular beam, i.e. without particles colliding with each other and with the surrounding space, the monomers and clusters move along trajectories defined at the entrance to the skimmer. Therefore, predominantly heavy clusters accumulate near the axis of the molecular beam. The result of registration depends on the entrance aperture of the detector and the solid angle inside which the particles from the skimmer along straight paths 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 on different experimental setups under seemingly similar conditions. For example, in [12], the bimodality of the transverse distribution of the intensity of molecular beams was noted, which is associated with a wide distribution of the monomer component, but with a narrower and larger peak in the cluster component.

We carried out measurements in molecular beams of argon at a narrow solid angle of the detector. A quadrupole mass spectrometer was used as a detector. The result of a change in the \( \text{Ar}^+ \) monomer signal intensity (m/e = 40) depending on the deviation input aperture of the detector from the molecular beam axis for three distances from the nozzle to the skimmer of the molecular beam system is shown in figure 3: at a distance of 46 mm - approximately in the middle of the primary “barrels”, 115 mm - immediately after the x-shaped configuration, 172 mm - far downstream from the first “barrel”. The monomer component on the axis consists of the true monomers of the jet, as well as of the products of the collapse of the POI electron ionization clusters in the mass spectrometer detector. At large distances from the nozzle, the results obtained are quite traditional. However, the result inside the first “barrel” was completely unexpected.

Figure 3. The transverse profile of the molecular beam of argon at different distances of the nozzle is a skimmer. \( P_0 = 400 \text{ kPa} \). The nozzle is supersonic: \( d_\ast = 0.17 \text{ mm} \); \( L_D = 8.1 \text{ mm} \); \( D_a = 2.4 \text{ mm} \). Skimmer \( d_s = 0.46 \text{ mm} \).
Apparently, outside the region of \(-1 \leq y \leq 1\) mm, the dependence characterizes the change in the true monomeric component in the molecular beam. However, a sharp, tenfold increase in the intensity of the signal inside this area, and a no less sharp drop – in an even narrower interval near the axis, characterizes the change in “secondary” monomers, i.e. cluster degradation products. The increase in intensity is the concentration of small clusters near the axis [13], the fall is the concentration in a narrow axial region of large clusters that do not fall apart into monomers upon ionization [14] and the almost complete absence of true monomers in this area. As measurements have shown, on the molecular beam axis, Ar$_2^+$ dimers in amplitude can exceed the monomeric component.

Thus, the demonstrated feature can cause significant changes in the intensity of monomers on the axis of the molecular beam, depending on the distance from the nozzle, the solid angle, and the type of molecular beam detector.

4. Features of molecular beam mass spectrometry of clustered flows

Earlier it was mentioned the difference in the destruction of clusters during ionization and the dependence on their size. Much research has been devoted to the study of this process, as well as the dependence of destruction on the energy of ionizing electrons. This section compares the results of mass spectrometry of clustered streams in two different ways. The first, traditional, represented the selection of a neutral gas sample from a supersonic jet using a skimmer and molecular beam system with its analysis by ionization with electrons with an energy of 70 eV in its own ionizer quadrupole mass spectrometer (mode "SEM"). In the second one, proposed by us, a high-voltage (with an energy of 10 keV) electron beam is used, crossing the supersonic jet between the nozzle and the skimmer. The diaphragms of the molecular beam system (skimmer and collimator) were supplied with potentials carefully chosen to achieve maximum efficiency of transporting charged particles to the input diaphragm of a quadrupole mass spectrometer with its own ionizer turned off (SIMS mode).

The result of comparing the mass spectra for m/e multiples of 16 is shown in figure 4. In both cases, the same gas-dynamic parameters were chosen: $P_0 = 300$ kPa, $T_0 = 298$ K, the same supersonic nozzle. For comparison, the methods are not mass peaks, but their maximum values, connected by solid lines, red - for the SEM mode, blue - SIMS. In this case, the amplitudes of the signals are normalized so that the peaks of clusters of size $N = 6$, i.e. $m/e = 96$, had the same value, since, as we noted earlier [15, 16], these clusters are more stable. It can be seen that measurements in two modes give qualitatively identical results in the cluster size range of $3 \leq N \leq 26$. With increasing $N$, it is possible to obtain more reliable data in the mode with ionization directly in the jet.

![Figure 4](image_url)

**Figure 4.** Comparison of mass spectra of a supersonic jet of 20% CH$_4$ + 80% He.

Ionization by a high-voltage electron beam in a jet gives substantially large amplitudes of clusters with an average size of $N > 25$. This may be due to a change in the process of cluster destruction at high electron energies (this was noted by the authors [15]). It may also be due to other conditions of collisions of neutral and charged particles after ionization. In any case, the proposed method of ionization in the jet allows us to obtain a more complete picture of the cluster size distribution.
5. Conclusions
It is shown that condensation in a jet affects the size of a supersonic jet, its shape and structure. In particular, for certain gas-dynamic parameters in supersonic jets, a special secondary structure formed under conditions of cluster formation was first discovered. It was shown that mass spectrometric measurements in molecular beams under cluster formation conditions largely depend on the detection method used, and the resulting mass distributions of clustered particles depend on the site of ionization and the delivery method of ionized particles to the mass spectrometer detector. With the above results, we illustrated the complexity and features of measurements in clustered supersonic jets and gave recommendations for taking into account the detected features.

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] Gupta K C, Jha N, Deb P, Mishra D R and Fuloria J K 2015 J. Appl. Phys. 118 114308
[6] Zarvin A E, Kalyada V V and Khudozhitkov V E 2017 Thermophys. Aeromech. 24 671–81
[7] 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
[8] Ashkenas H Z and Sherman P S 1966 RGD Proc. 4th Int. Symp. Ed J. H. De Leeuw (Toronto Acad. Press) 2 84
[9] Hagena O F 1992 Rev. Sci. Instr. 63 2374–9
[10] Zarvin A E, Yaskin A S, Kalyada V V and Ezdin B S 2015 Tech. Phys. Let. 41 1103–6
[11] Zarvin A E and Sharafutdinov R G 1979 J. Appl. Mech. Tech. Phys. 20 744–9
[12] Yang S, Daineka D V and Chatellet M 2003 Chem. Phys. Let. 377 595–600
[13] Buck U and Meyer H 1986 J. Chem. Phys. 84 4854–61
[14] Bonhommeau D, Halberstadt N and Viel A 2006 J. Chem. Phys. 124 184314
[15] Schütte S and Buck U 2002 J. Mass Spec. 220 183–92
[16] Chinenov S T, Zarvin A E, Khudozhitkov V E, Kalyada V V and Yaskin A S 2018 IOP CS: MSE 387 012012
[17] Zarvin A E, Khudozhitkov V E and Kalyada V V 2018 IOP CS: MSE 387 012086