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Clusters as a diagnostic tool for gas flows

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Abstract. The example of a gas flowing through an orifice into the surrounding rarefied space is used to demonstrate the possibility of using clusters for diagnosing gas flows. For the conditions studied (it takes a cluster velocity about the same time to relax to the gas velocity as it does to reach the orifice), information on the flow parameters inside the chamber is obtained from the measurement of the cluster drift velocity after the passage through an orifice for various gas consumptions. Other possible uses of clusters in gas flow diagnostics are discussed as well.

Keywords: clusters, gas flows with clusters, size distribution function of clusters, gasdynamics of gas flows, cluster beams

1. Introduction

Gas transfer to a region of low pressure is accompanied by the formation of gas fluxes or gas beams, and this gas, with various additions in the form of ions, excited atoms, molecules, clusters and microparticles, has various applications (see, for example, books [1–3]). It is convenient to insert microparticles into a gas flux in order to visualize the gas laminar motion where individual gas elements move along certain streamlines. Since these particles are entrained by a gas flow, scattered light allows the gas flow lines to be seen if obstacles are placed in the gas path or the gas outflows into a surrounding space. This approach has received acceptance for a dusty plasma where reliable optical methods had been elaborated for the determination of microparticle positions in a space and their displacements in time. The latter allows finding gas flow lines, in particular, as a result of streamlining bulk objects. Then, the assumption is made that particles are entrained by a gas flow and move together with the gas.

In the case of variation of the gas velocity or the motion direction, it is necessary that the relaxation time for particle motion in a gas be small compared to the variation time of the gas velocity, and then particles move together with the gas. This criterion is often violated under laboratory conditions, and then the character of particle motion and the particle relaxation time in a gas flow allow the motion of the gas flow to be restored before the region of particle registration.

In this paper, we demonstrate this for the motion of clusters — nano-sized particles — in a gas stream outflowing through an orifice into a vacuum or the surrounding rarefied space. Measurement of the distribution function of charged clusters over velocities and motion directions after the gas passes through an orifice allows one to understand the character of gas motion ahead of the orifice and to retrieve the parameters of this motion.

2. Formation of a gasdynamic flow

Figure 1 gives a schematic of laminar gas motion in a chamber and the outflow of gas into the surrounding rarefied space. Precisely this setup is used in cluster experiments (see, for example, Refs [4, 5]), the basis of which is the NC-200 cluster source designed at Oxford Applied Research (Great Britain). A gas flows along a wide tube, or chamber, and the radius of orifice r in the chamber end significantly exceeds the mean free path λ of atoms in a gas, so this gas outflows from the chamber in the form of a gasdynamic jet. Since the rate of gas flow near an orifice is on the order of the gas sound velocity, whereas this rate inside the chamber is several orders of magnitude less, a strict gas acceleration takes place near the orifice. Clusters located in a gas have no time to follow atoms near an orifice because of their inertia, and the average cluster

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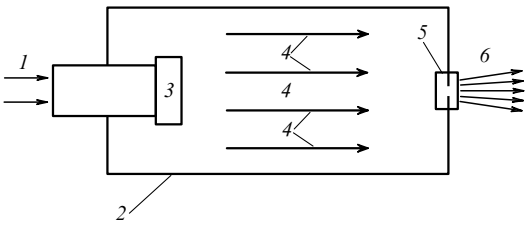

Figure 1. Schematic of the formation of a gasdynamic flow with clusters: *1* — injection of a gas flux into the wide tube, *2* — chamber, *3* — magnetron, *4* — gas flow with clusters in a chamber, *5* — orifice, *6* — beam outside the chamber.

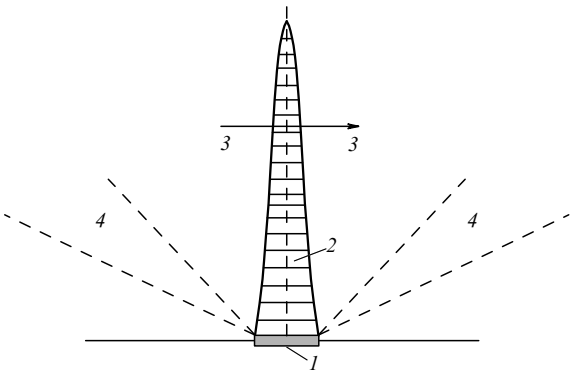

Figure 2. Beam destruction in the course of its propagation: *1* — an orifice, *2* — a region occupied by a beam, *3*, *4* — regions outside the beam; the arrow indicates the distance from the orifice where the distribution function plotted in Fig. 3 is valid.

velocity at the orifice is lower than that of atoms. Correspondingly, the velocity distribution function of clusters behind the orifice gives information about the character of variation of the gas velocity ahead of the orifice.

Let us consider the evolution of a gasdynamic stream as it expands behind an orifice in a vacuum or rarefied gas. Since the flow radius is large compared to the mean free path of atoms in a gas, internal atoms propagate downstream from the orifice in the form of a beam which is stabilized due to collisions with neighboring atoms. Because this stabilization is absent for periphery atoms, the atoms located at distances of order the mean free path of atoms away from the beam boundary propagate freely in the surrounding space. As a result, the gasdynamic atomic beam spreads with distance from the orifice, as shown in Fig. 2.

Figure 3 displays the space distribution function of atoms in and near a beam for the above-mentioned character of beam formation and propagation. Then, inside a beam (region *2*), the atom number density is constant over the beam cross section and is determined by the equation of state for an ideal gas. At the beam boundary, the atom number density decreases sharply, because atoms travel freely into the surrounding space (region *3* in Fig. 3). The thickness of the transition layer between regions *2* and *3* in Fig. 3 is of the order of the mean free path of atoms in a gas. Region *3* corresponds to an effusion beam which outflows from the gasdynamic beam surface in the radial direction, so that, in accordance with the beam cylinder symmetry, the atom number density in this region decreases as we move from the beam center. The boundary of region *3* is determined by the

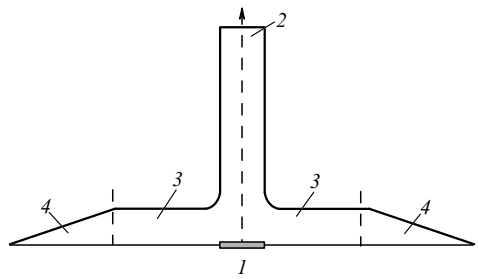

Figure 3. Space distribution of atoms in and near a beam at a distance that is marked by the arrow in Fig. 2: *1* — orifice projection, *2* — beam region, *3*, *4* — regions outside the beam.

distance from the center, which is attainable by most periphery atoms. Only fast atoms may reach region *4*.

The gasdynamic regime of beam formation and propagation corresponds to the criterion where the atom mean free path λ in a beam is small compared to orifice radius r, which corresponds to small values of the Knudsen number Kn:

$$\mathrm{Kn} = \frac{\lambda}{r} \ll 1 \,. \tag{2.1}$$

It is convenient to invoke the rarefaction coefficient δ defined as [6–8]

$$\delta = \frac{\sqrt{\pi}}{2\,\mathrm{Kn}} = \frac{\sqrt{\pi}}{2}\,\frac{r}{\lambda} \tag{2.2}$$

for a small beam parameter $1/\delta$. This parameter will be used below in the analysis of processes of formation and propagation of a gasdynamic beam.

3. Clusters in a gas flow

The schematic of the generation of an atomic gasdynamic beam in Fig. 1 is simultaneously a schematic of the generation of cluster beams in a magnetron discharge [9, 11]. Metal clusters are formed here from the bombardment of the cathode by fast ions in a magnetron discharge, and metal atoms resulting from cathode erosion partake in a certain sequence of processes [10]. The clusters are entrained by the slow gas flux and remain in the gas beam after its formation and subsequent beam evolution after passing through an orifice of the magnetron chamber.

Let us analyze the character of cluster interaction with a gas in the course of cluster motion under given conditions. A low cluster density is a natural requirement for this system, at which one can neglect interactions between clusters. The interaction of gas atoms with a cluster has a simple character. Indeed, strong cluster interaction with an incident atom takes place only near the cluster surface at distances on the order of atomic sizes, i.e., on the order of the Bohr radius a_0. Being guided by clusters consisting of a hundred atoms or more, clusters can be considered to be spherical particles of a certain radius r_0, where $r_0 \gg a_0$. Assuming angles of atom scattering on a cluster to be random, we can obtain the following relation for the diffusion cross section σ_0 of atom scattering on a cluster: $\sigma_0 = \pi r_0^2$.

We are guided by the kinetic regime of cluster motion in a gas, $\lambda \gg r_0$, where a strong cluster interaction at any time takes place with one atom only. Figure 4 represents conditions for the kinetic and diffusion regimes of cluster motion in

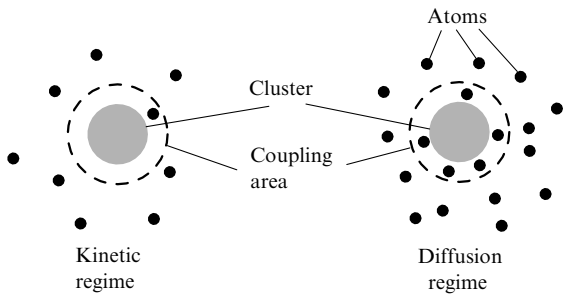

Figure 4. Cluster interaction with atoms of a surrounding gas for the kinetic and diffusion regimes of cluster motion in a gas.

a gas. In particular, the kinetic regime at atmospheric pressure is signified if the number of cluster atoms is significantly less than 10^{10}. Thus, we consider the following hierarchy of cluster sizes:

$$r \gg \lambda \gg r_0 \gg a_0 \,, \tag{3.1}$$

where notations are given above for each size.

If a cluster is located in a gas and its average velocity w differs from the average directed gas velocity v_g, these velocities must be equalized in the end as a result of cluster–atom collisions. The relaxation character for the cluster velocity is described by the relaxation time τ_{rel} that is a parameter of the cluster equation of motion:

$$\frac{d\mathbf{w}}{dt} = \frac{\mathbf{v}_g - \mathbf{w}}{\tau_{rel}} \,. \tag{3.2}$$

The relaxation time in the kinetic regime is given by the following formula [12] that takes into account atom–cluster collisions:

$$\tau_{rel} = \frac{3M}{8\sqrt{2\pi mT}\,N_a r_0^2} = \frac{n^{1/3}}{k_{rel} N_a} \,, \qquad k_{rel} = \frac{8\sqrt{2\pi mT}\,r_W^2}{3m_a} \,, \quad r_0 \ll \lambda \,. \tag{3.3}$$

Here, M is the cluster mass, m_a is the mass of cluster atoms, m is the mass of gas atoms, N_a is the number density of gas atoms, r_W is the Wigner–Seitz radius [13, 14], and n is the number of cluster atoms. Notably, for water drops traveling in atmospheric air at the temperature $T = 300$ K, formula (3.3) gives $k_{rel} = 2.8 \times 10^{-11}$ cm^3 s^{-1}. As is seen, the relaxation time of the cluster velocity depends on the number of cluster atoms as $\tau_{rel} \sim n^{1/3}$ according to formula (3.3), since the cluster mass is $M \sim n$, and the cluster radius is estimated as $r_0 \sim n^{1/3}$.

One can also use formula (3.3) as an estimate for atoms moving in a gas. As is seen, the difference between the relaxation times for average velocities of atoms and clusters is characterized by the factor $n^{1/3}$, if the masses of atoms which belong to a gas and clusters have the same order of magnitude. In particular, this fact is used in impactors (see, for example, Refs [15–17]) which are intended for particle selection from a gas. The concept of an impactor is illustrated in Fig. 5. In this case, a gas stream flows inside a bent cylindrical tube where the velocity of atoms or molecules varies due to the tube turns. Since nano- and microparticles are moving along straightforward trajectories, they attach to walls or are ejected from a flowing gas.

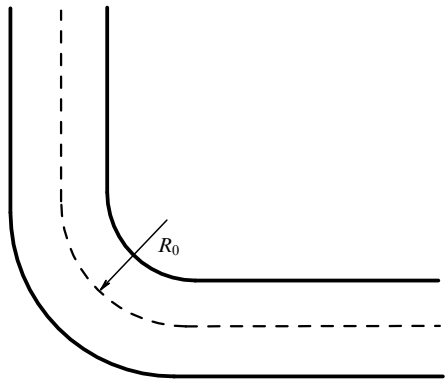

Figure 5. Gas flow along a tube.

4. Passing of a gas stream through an orifice

In considering a system consisting of a gas stream with clusters inside it, we assume a low cluster number density, so that clusters do not influence the gasdynamics of a gas flow. If parameters of a gas flow vary at small distances, clusters located there cannot come into equilibrium with the gas flow. Notably, if the flow rate varies during a small time compared to the relaxation time τ_{rel} according to formula (3.3), the equilibrium between clusters and a gas flow is violated in the course of variation of the flow rate. Therefore, cluster registration with determination of the velocity distribution function of clusters allows, in principle, finding the parameters of velocity variation for the gas stream.

Below, we shall consider this problem for the passage of a gas stream through an orifice into the region of low pressure. Let us analyze first the character of passage of a gasdynamic stream through an orifice irrespective of the cluster presence in this flowing gas. Assume for a gas flow with clusters that the orifice radius is small compared to the chamber radius, but is large compared to the mean free path of gas atoms.

Figure 6 shows the character of a gas passage through an orifice. For the laminar gas motion under consideration, the Reynolds number is not large and a gas moves along certain

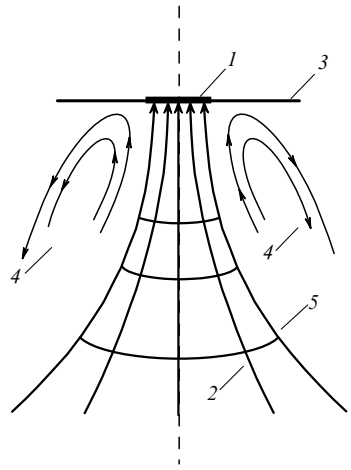

Figure 6. Character of passing a gas stream through a chamber orifice into the surrounding space: *1* — orifice, *2* — streamlines for an effluent flow, *3* — chamber boundary, *4* — vortices of a gas remaining inside the chamber, and *5* — boundary for an outgoing gas flow.

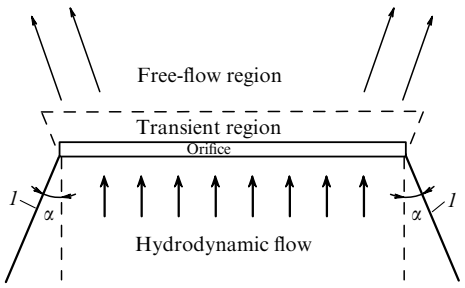

Figure 7. Passage of a gas flux through a chamber orifice; *1* — boundary streamline for the gas flow [12].

streamlines. Thus, a gas emerging from the chamber propagates along lines outgoing to infinity, whereas a gas remaining in the chamber flows along closed trajectories, and the gas velocities for these regions are identical at their boundary.

We first analyze the character of a gas stream passing through an orifice, based on considering the formation of an atomic beam as a result of irradiation of a metal surface by a focused laser beam [18–20]. Though this problem relates to a somewhat different process [21], the character of a beam production is identical for these cases. Indeed, as a result of vaporization of a metal surface, which is located in a vacuum or rarefied gas and is irradiated by a laser beam, an atomic vapor is formed near the surface with the semi-Maxwell velocity distribution function of atoms, i.e., evaporated atoms come into equilibrium with the surface and move outward from the surface. A beam of evaporated atoms is formed with a certain drift velocity and temperature at the distance from the surface equal to the mean free path of atoms, and beam parameters are connected with gas parameters inside the chamber ahead of the orifice due to the momentum and energy conservation laws.

In the case of a gas passage through an orifice, the character of this transition is given in Fig. 7. The energy conservation law then has the form

$$\frac{3}{2}\,T = \frac{1}{2}\,mc_{\rm s}^2(T_{\rm b}) + \frac{3}{2}\,T_{\rm b}\,, \tag{4.1}$$

where m is the mass of a gas atom, T is the gas temperature (hereinafter the temperature is expressed in energy units), $T_{\rm b}$ is the gas temperature in a beam, and $c_{\rm s}$ is the speed of sound, which is expressed through the gas temperature as $c_{\rm s} = (\gamma T/m)^{1/2} = (5T/3m)^{1/2}$. Since the speed of sound corresponds to the beam region, the gas temperature in the beam and in the moving gas before beam formation is given by

$$T_{\rm b} = \frac{9}{14}\,T = 0.64T\,. \tag{4.2}$$

From the equality of fluxes inside and outside the chamber at the orifice boundary, it follows that

$$\left(\frac{2T}{\pi m}\right)^{1/2} N = c_{\rm s}(T_{\rm b})N_{\rm b}\,, \tag{4.3}$$

where N is the atom number density ahead of an orifice, and $N_{\rm b}$ is the atom number density in the beam. From this, one can obtain the following relation between the atom number densities in a gas and in a beam:

$$N_{\rm b} = \sqrt{\frac{6T}{5\pi T_{\rm b}}}\,N = \sqrt{\frac{28}{15\pi}}\,N = 0.77N\,. \tag{4.4}$$

Note that relations (4.2) and (4.4) correspond to the infinity value of the rarefaction coefficient (2.2). Table 1 contains values of the parameters entering formula (4.4) for finite values of parameter (2.2) [22].

Table 1. Ratio of beam and gas parameters [22].

δ	$T_{\rm b}/T$	$N_{\rm b}/N$	References
∞	0.64	0.77	formulas (4.2) and (4.4)
6.3	0.7	0.3	[23]
1	0.8	0.6	[24]
1	0.8	0.6	[25]
10	0.85	0.75	[25]
1	0.85	0.75	[26]

Keeping to the schematic in Fig. 1, one can determine on the basis of simple measurements the drift velocity of gas atoms outflowing from an orifice. In order to do so, it is necessary to determine the discharge of gas inserted into the chamber (*1* in Fig. 1) and the gas pressure in it. Then, the gas consumption, i.e., the number of atoms inserted into the chamber per unit time (and, correspondingly, passed through an orifice per unit time) is $Q = \pi r^2 N v_{\rm g}$ under the assumption that the atom number densities near the orifice and inside the chamber are identical, and the atom velocity $v_{\rm g} = c_{\rm s}(T_{\rm b})$ in the orifice plane is independent of the distance to the orifice center ($c_{\rm s}$ is the speed of sound). Here, the atom number density N follows from the equation of state $N = p/T$ (p is the gas pressure, and T is the gas temperature).

Thus, one can find the drift velocity $v_{\rm dr}$ of a gas which outflows from an orifice on the basis of simple measurements and compare it with the speed of sound in the beam. In particular, Fig. 8 depicts the drift velocity of argon atoms, if argon escapes through an orifice into a vacuum, and the drift velocity is retrieved on the basis of measured argon consumption Q and the pressure p inside the chamber under the above assumption about the flux uniformity. The gas consumption unit 1 sccm corresponds to the consumption of 1 cm^3 of a standard gas (i.e., at the temperature 0 °C and pressure $p = 1$ atm) per minute, so that the gas flow measurement unit is 1 sccm $= 4.48 \times 10^{17}$ cm^{-3} s^{-1}.

Note that the speed of sound in argon at the temperature $T = 300$ K is $c_{\rm s}(T) = 3.2 \times 10^4$ cm s^{-1}. According to formula (4.2), the gas temperature in a beam is $T = 190$ K, which corresponds to the speed of sound $c_{\rm s}(T_{\rm b}) = 2.6 \times 10^4$ cm s^{-1}. This result relates to the limit $\delta = \infty$ and more or less corresponds to large values of argon consumption and orifice radii. For the limiting case of Fig. 8b, where the orifice radius is $r = 3$ mm and the gas consumption is $Q = 60$ sccm at a measured pressure $p = 60$ Pa in the chamber, one can obtain $N = 1.5 \times 10^{16}$ cm^{-3} for the number density of argon atoms in the chamber.

Since the gas-kinetic cross section for the collision of two argon atoms is $\sigma_{\rm g} = 3.7 \times 10^{-15}$ cm^2 [27], this corresponds to the mean free path $\lambda = 0.2$ mm of argon atoms and, correspondingly, a value of $\delta = 14$ is deduced for rarefaction coefficient (2.2). Since at this value of δ the beam velocity is equal to the speed of sound, the assumptions used are valid, evidently, for a gasdynamic beam.

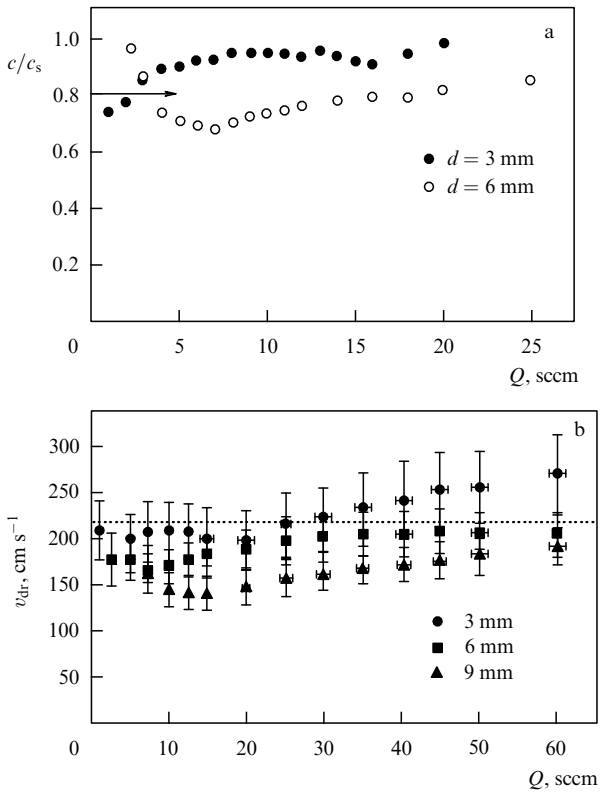

Figure 8. Drift velocity of argon atoms in a gas escaping through an orifice according to measurements (a) [4], and (b) [22]. The arrow in figure a and the dotted line in figure b correspond to the speed of sound $c_s(T_b)$ given by formulas (4.2)–(4.4); d — orifice diameter.

5. Cluster drift velocity in a gas flow

Let us insert a small number of nano-sized clusters into a gas flow in such a way that, on the one hand, the clusters do not influence the passage of the gas stream through an orifice and, on the other hand, the interactions between the clusters can be neglected, i.e., their behavior in the flowing gas is determined by cluster interaction with gas atoms only. Since a strong atom–cluster interaction takes place in a narrow region near the cluster surface, whose extent is on the order of atomic sizes, we may consider the scattering of atoms on clusters within the hard sphere model (see, for example, book [28]), and the diffusion cross section becomes $\sigma_0 = \pi r_0^2$ [29, 30], where r_0 is the cluster radius.

The cluster velocity will change in the vicinity of the orifice, together with the gas flow rate, on a scale comparable to the orifice radius. However, if the cluster transit time in this region is smaller or comparable to the cluster relaxation time τ_{rel} [formula (3.3)], an equilibrium of clusters with the gas flow is not achieved, i.e., the clusters pass through the orifice and propagate behind it with a velocity differing from the gas flow rate. Therefore, one can retrieve the character of acceleration of a gas flow ahead of an orifice on the basis of measurements of the velocity distribution function behind the orifice.

Considering this process from the standpoint of an experimental study, let us ascertain which parameters of a cluster beam may be obtained taking into account the measurement accuracy. These parameters follow from measurements of the velocity distribution function of clusters with the help of a mass spectral filter.

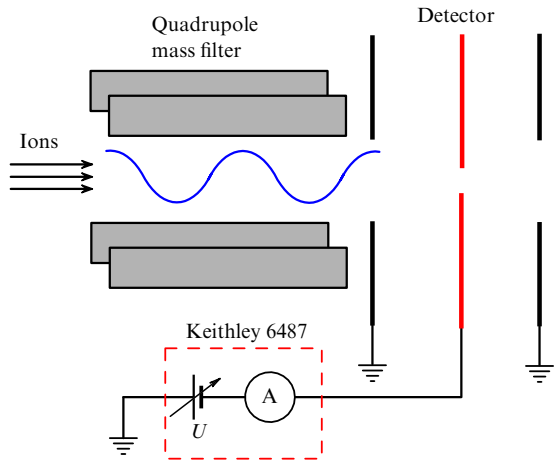

Figure 9. Measurement of the transverse velocity distribution function for charged clusters [35].

Figure 9 gives an example of such a mass filter (QMF-200 produced by Oxford Applied Research) and the principle of its operation. In this case, charged clusters are slowed down by a retarding potential U acting on a diaphragm. The cluster ions oscillate under the action of an alternating field induced across the gap and are selected in this way according to their mass. It is essential that the clusters be only singly charged or remain neutral under these conditions [9, 11, 31, 32]. The distribution function of cluster ions with a given energy eU and with a velocity v corresponding to this energy is given by [33, 34]

$$\frac{e^2}{M} f(v) = \frac{\mathrm{d}I(U)}{\mathrm{d}U} . \tag{5.1}$$

Figure 10 illustrates examples of the velocity distribution functions of clusters measured along the flow direction.

It is convenient to approximate the measured velocity distribution function of clusters after passage through the orifice by the expression

$$f(v) = C \exp\left[-\frac{M(v_\parallel - w)^2}{2T_\parallel} - \frac{Mv_\perp^2}{2T_\perp}\right] , \tag{5.2}$$

and the parameters of this distribution characterize the passage of a gas flow through an orifice. Here, C is a normalization factor, M is the cluster mass, w is the drift velocity of a cluster beam, $v_\parallel$, $v_\perp$ are the cluster velocities along the axis and perpendicular to it, respectively, and $T_\parallel$, $T_\perp$ are the cluster effective temperatures in these directions.

Being guided by the distribution function of clusters defined by formula (5.2), one can connect the parameters of this formula with the character of atom cluster collisions in the gas flux. For simplicity, we can model the gas flow near an orifice with a conical shape, as shown in Fig. 11. We consider below this simple chamber geometry as a model of the gas flow ahead of an orifice.

In what follows, an analysis of gas flow motion in a conical tube is considered [36]. Let us introduce the parameter ξ as

$$\xi = 1 + \frac{z \tan\alpha}{R} , \tag{5.3}$$

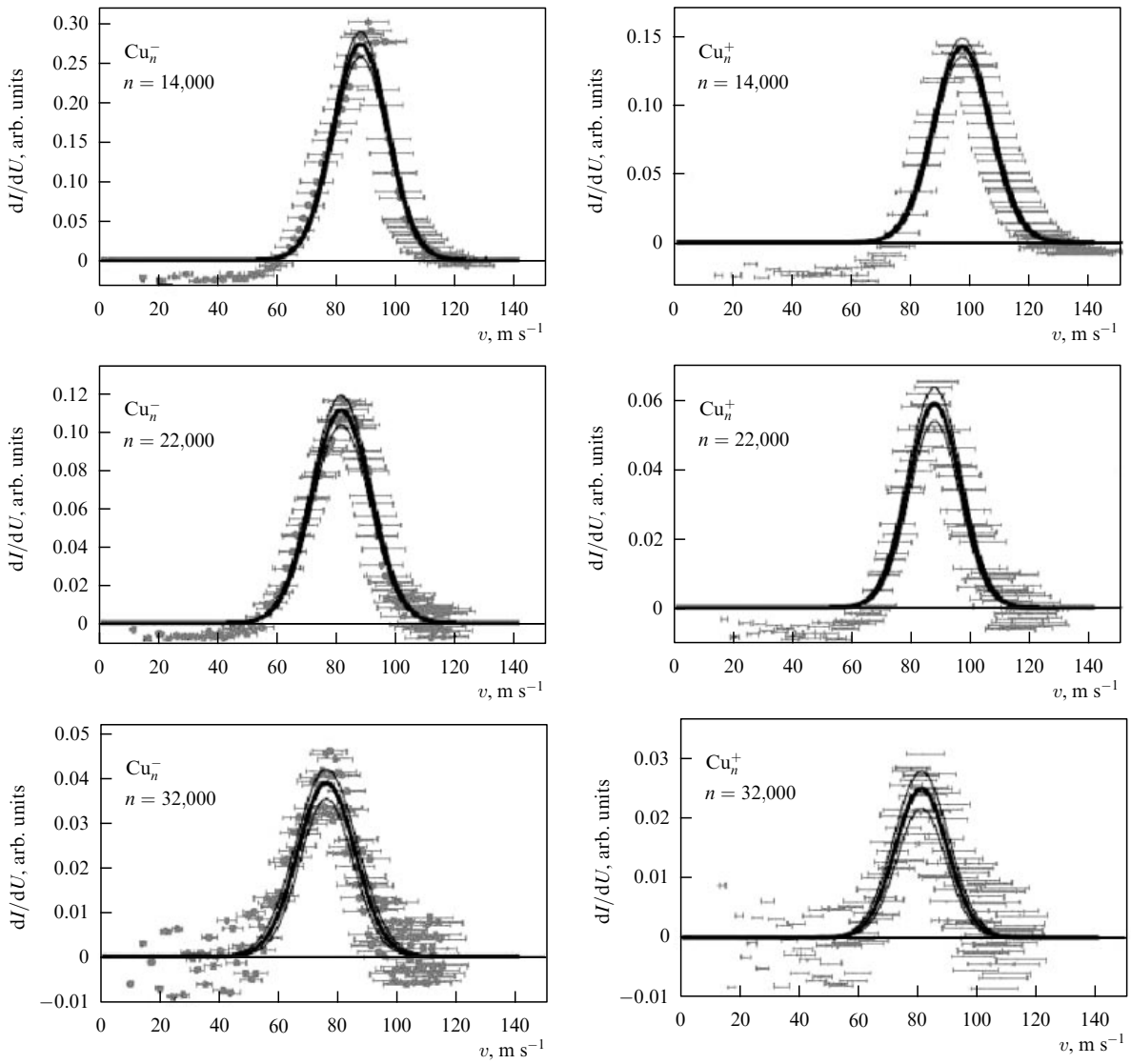

Figure 10. Velocity distribution function for positive and negative copper cluster ions which are attained by an argon flow under the following conditions: argon flow rate $Q = 15$ sccm, argon gas pressure $p = 19$ Pa, magnetron discharge power $P = 120$ W, and orifice radius $r = 3$ mm [35].

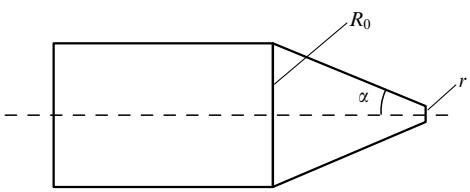

Figure 11. Geometry of a gas flow as motion in a cylinder with a conic end.

where z is the distance from the orifice for a given cross section, $R = r + z\tan\alpha$ is the tube radius in this cross section, and, from the law of conservation of a mass of the gas intersecting this cross section, we obtain for the flow velocity $v(z)$ at a distance z from the orifice in the form

$$v(z) = \frac{\mathrm{d}z}{\mathrm{d}t} = \frac{c_\mathrm{s} r^2}{(r + z\tan\alpha)^2} = \frac{c_\mathrm{s}}{\xi^2}\,, \tag{5.4}$$

where c_s is the flow velocity of a gas stream in the orifice plane. The solution of equation (5.4) leads to the following law of gas flow propagation:

$$\xi^3(t) = \frac{t_0 - t}{\tau_\mathrm{or}}\,, \qquad \tau_\mathrm{or} = \frac{r}{3c_\mathrm{s}\tan\alpha}\,. \tag{5.5}$$

This solution specifies the distance from the orifice for a given element of the gas flow if at the initial time moment the parameter ξ is small ($\xi \ll 1$), and then the solution is independent of the parameter t_0, or, in other words, $t_0 \gg \tau_\mathrm{or}$. A given element of the gas flow reaches the orifice at the time moment $t_0 - \tau_\mathrm{or}$, and its velocity $v(t)$ at time t equals

$$v(t) = c_\mathrm{s}\left(\frac{\tau_\mathrm{or}}{t_0 - t}\right)^{2/3}. \tag{5.6}$$

Let us determine now the cluster velocity w in a gas flow that is governed by the equation

$$\frac{\mathrm{d}w}{\mathrm{d}t} = \frac{v(t) - w}{\tau_\mathrm{rel}}\,. \tag{5.7}$$

In the limit of $w(t) \ll v(t)$, where clusters have no time to adapt to the gas flow velocity, we have the following estimate

of the cluster velocity w when the gas flow with clusters intersects the orifice plane:

$$w \sim c_s \left(\frac{\tau_{or}}{\tau_{rel}}\right)^{2/3}, \tag{5.8}$$

and this dependence of the drift cluster velocity on the process parameters takes place if the following criterion holds true when taking formula (5.5) into account:

$$\frac{\tau_{or}}{\tau_{rel}} \sim \frac{r}{c_s \tau_{rel} \tan\alpha} \ll 1\,. \tag{5.9}$$

The exact solution of equation (5.7) takes in this limit the following form [36]

$$w_0 = c_s (v\tau_{or})^{2/3} \Gamma\left(\frac{1}{3}\right) = 2.68 c_s \left(\frac{\tau_{or}}{\tau_{rel}}\right)^{2/3} = 1.3 c_s \left(\frac{r}{c_s \tan(\alpha)\,\tau_{rel}}\right)^{2/3}. \tag{5.10}$$

This drift velocity corresponds to the limit of the small ratio τ_{or}/τ_{rel} given by formula (5.9). Taking into account that the cluster drift velocity cannot exceed the velocity c_s of a gas flow, the cluster drift velocity w can be approximated in a wide range of parameters by the formula

$$w = \frac{w_0 c_s}{w_0 + c_s}\,, \tag{5.11}$$

which transforms into formula (5.10) in the limit of small drift velocities $w \ll c_s$, and is equal to the gas flow velocity c_s near the orifice in the case of fast relaxation of the cluster velocity.

Let us make a numerical estimation, being guided by the parameters of copper clusters in an argon flow, which were specified in Fig. 10. Copper clusters consist of $n = 1.4 \times 10^4$ atoms, on the average, corresponding to an average cluster radius $r_0 = 3.5$ nm. At a pressure of $p = 60$ Pa, which corresponds to the gas consumption $Q = 60$ sccm and the number density $N = 1.5 \times 10^{16}$ cm^{-3} of argon atoms, the reduced rate constant of relaxation process according to formula (3.3) is $k_{rel} = 2.2 \times 10^{-11}$ cm^3 s^{-1}, and the appropriate relaxation time $\tau_{rel} = 70$ μs. The required small ratio according to formula (5.9) is $r/(c_s\tau_{rel}) = 0.2$. This confirms the underlying assumption of the regime under consideration for the cluster drift in a gas flow. Experimental values of the cluster drift velocity as a function of gas consumption are presented in Fig. 12.

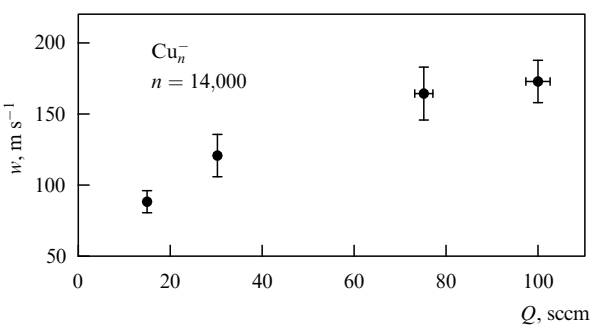

Figure 12. Dependence of the drift velocity of negatively charged copper clusters consisting of $n = 1.4 \times 10^4$ atoms on the argon flow rate at the orifice radius $r = 3.5$ mm [35].

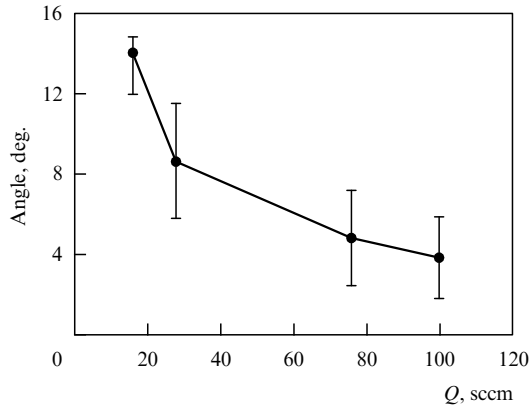

Figure 13. Dependence of the semi-cone angle on the gas flow rate Q as a result of modeling the gas streamlines by straight trajectories near an orifice using the data given in Fig. 12.

In the following, we consider a conical shape for the gas flow profile near an orifice. With the help of formulas (5.10) and (5.11) for the cluster drift velocity, we can retrieve the cone semi-angle α, being guided by the experimental data given in Fig. 12. Figure 13 contains the semi-cone angle dependence on the gas flow rate. Despite the large error bars at large flow rates, the following conclusions can be drawn from an analysis of the experimental data in Fig. 13. As the gas flow rate and, correspondingly, the number density of atoms increases, the region where the clusters gather drift velocity shifts closer to the orifice. Since this leads to a decrease in the effective angle for the gas flow motion according to the data given in Fig. 13, the gas streamlines tend to be parallel to the motion axis, i.e., they have the form displayed in Fig. 6.

Data for the cluster drift velocity given in Fig. 12 may be used to determine the streamlines of the gas flow which passes through an orifice under the above-mentioned conditions. Then, the number density of the clusters is relatively small, so they do not influence the gas propagation near a chamber orifice. Therefore, by modeling the gas stream passing through a given tube cross section by a conical flow shape, the cluster drift velocities can be determined on the basis of formulas (5.10) and (5.11) from the experimental data and the appropriate semi-cone angles α which are displayed in Fig. 13. Next, in the limit of $w(t) \ll v(t)$, equation (5.7) gives

$$\mathrm{d}z = \tau_{rel}\,\mathrm{d}w\,, \tag{5.12}$$

where the z-axis is perpendicular to the orifice plane. Assuming the angle α to be small (see Fig. 13), i.e., the flow is directed almost perpendicular to the orifice plane, we can find that the cluster drift velocity is mainly gathered at a distance $z \approx w\tau_{rel}$. Then, we find the effective semi-cone angle α in accordance with data presented in Fig. 13.

The parameters α and z obtained allow determining the boundary of a passing flow, so that a gas inside this region outflows from the chamber, whereas a gas outside this region remains in the chamber. Figure 14 represents streamlines for an argon flow, which were obtained on the basis of formulas (5.10)–(5.12).

The algorithm formulated above for the determination of the gas streamlines may be applied in the one-dimensional case if the gas pressure inside the chamber varies with a

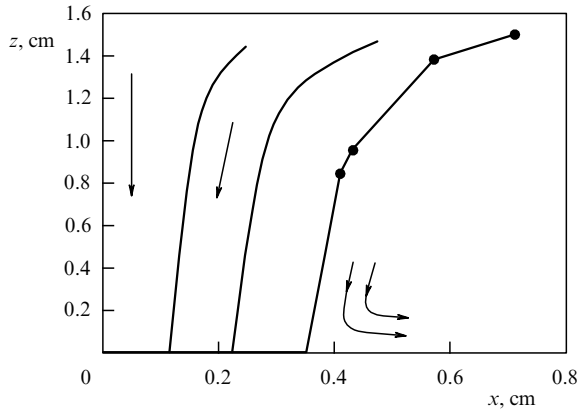

Figure 14. Gas streamlines for the right side of an argon flow which passes through an orifice with radius $r = 3.5$ mm under the conditions specified in Fig. 13.

variation of the gas flow rate and, simultaneously, the cluster drift velocity is fixed for a given gas consumption (or for a given gas pressure in the chamber).

Note that the laminar character of cluster motion in a gas flow is characterized by the Stokes number Stk, which is given by [37]

$$\mathrm{Stk} = \frac{\tau_{\mathrm{rel}} c_{\mathrm{s}}}{r_0}\,, \tag{5.13}$$

where τ_{rel} is the relaxation time for the cluster velocity to the gas flow velocity, c_{s} is the typical maximum velocity of the gas flow, and r_0 is the radius of a copper cluster. Using typical values of the parameters specified in Fig. 12, namely, a cluster radius of $r_0 = 5$ nm, and a velocity $c_{\mathrm{s}} = 2 \times 10^4$ cm s^{-1} of the gas passing through the orifice, we arrive at the relaxation time $\tau_{\mathrm{rel}} \approx 50$ μs of cluster motion for gas consumption $Q = 100$ sccm, which corresponds to a Stokes number of $\mathrm{Stk} \approx 2 \times 10^6$.

A large value of the Stokes number signifies the absence of perturbations near an orifice [38, 39]. In addition, in the case of laminar motion that takes place in the regime under consideration, the viscosity acts weakly on the gas motion [6, 40]. Hence, the motion of a gas is characterized by small Reynolds numbers [41, 42]

$$\mathrm{Re} = \frac{vr}{\nu}\,, \qquad \nu = \frac{\eta}{\rho}\,, \tag{5.14}$$

where η is the dynamic gas viscosity, ν is the kinematic gas viscosity, ρ is the gas density, R is the current flow radius, and v is the current velocity of a gas flow. Since gas stationarity requires the conservation of mass of a gas that flows through each tube cross section per unit time, we have $v(R)R^2 = v_{\mathrm{g}} r^2$, where v_{g} is the gas directed velocity near an orifice. This gives for the current Reynolds number

$$\mathrm{Re}\,(R) = \mathrm{Re}\,(r)\,\frac{r}{R}\,, \tag{5.15}$$

i.e., the maximum Reynolds number is attained near the orifice. For typical parameters of the gas flow under consideration ($Q = 60$ sccm and $r = 3$ mm), we have $\eta = 2.3 \times 10^{-4}$ g cm^{-1} s^{-1} and $\nu = 230$ cm^2 s^{-1} for the dynamic and kinematic argon viscosities, respectively, and the Reynolds number becomes $\mathrm{Re} \approx 30$, whereas the laminar gas motion is violated at higher Reynolds numbers, larger than $\mathrm{Re} \sim 10^4$ [43, 44].

6. Kinetics of cluster motion in a gas flow

The possibility of retrieving the streamlines of a gas flow on the basis of measured cluster drift velocities was shown in Section 5. The accuracy of this operation is restricted, because we model the boundary of a gas passing through an orifice by its conical shape, and change the current distance from the orifice plane with its average value. Nevertheless, we can determine streamlines for a gas flow passing through an orifice on the basis of the cluster drift velocity measured as a function of the number density of gas atoms (or the gas consumption) with a certain accuracy. This accuracy can be improved by using other measured parameters of the velocity distribution function of clusters at the exit.

Indeed, along with the cluster drift velocity w, the velocity distribution function (5.2) of clusters at the exit contains two additional parameters: the temperatures of the longitudinal and transverse cluster motion, $T_{\parallel}$ and $T_{\perp}$, respectively. These parameters may be determined from measured distribution functions of clusters over longitudinal velocities, as shown in Fig. 10, and also on the basis of cluster distributions over angles of divergence after passing through a chamber orifice. The small width of the velocity distribution function of clusters, as follows from Fig. 10, allows operating with the effective longitudinal temperature, i.e., with the velocity distribution function (5.2) at the exit behind the orifice. We discuss below the possibility of determining parameters of this distribution function on the basis of an analysis of cluster kinetics in a gas flow.

The basis of this consideration lies in the analysis of the kinetic equation for the cluster velocity distribution function $f(\mathbf{v}, t)$, which has the form

$$\frac{\partial f}{\partial t} = I_{\mathrm{col}}(f)\,. \tag{6.1}$$

Assuming the absence of external fields and nonuniformities, we include collisions of atoms with the clusters in the collision integral $I_{\mathrm{col}}(f)$ and take into account the variation of the gas flow velocity in the course of its approach to an orifice. Elastic atom–cluster collisions are included in the collision integral, so that it takes the form

$$I_{\mathrm{col}}(f) = \int \left[f(\mathbf{v}')\,\varphi(\mathbf{v}_1') - f(\mathbf{v})\,\varphi(\mathbf{v}_1)\right] g\,\mathrm{d}\sigma\,\mathrm{d}\mathbf{v}\,\mathrm{d}\mathbf{v}_1\,. \tag{6.2}$$

Here, $\mathbf{v}$, $\mathbf{v}'$ are cluster velocities before and after the collision, and $\mathbf{v}_1$, $\mathbf{v}_1'$ are atom velocities before and after the collision. In this case, the differential atom–cluster cross section as an element of the collision integral has the simple form within the framework of the liquid drop model for a cluster: $\mathrm{d}\sigma = \pi r_0^2\,\mathrm{d}\cos\vartheta = \sigma_0\,\mathrm{d}\cos\vartheta$, where r_0 is the cluster radius, σ_0 is the diffusion atom–cluster cross section, and ϑ is the scattering angle. Correspondingly, expressions for variation of the average cluster momentum $M\mathbf{v}$ and its energy $Mv^2/2$ are given by

$$\begin{aligned} I_{\mathbf{P}} &\equiv \int M\mathbf{v}\,I_{\mathrm{col}}(f)\,\mathrm{d}\mathbf{v} = \int g\mathbf{g}\,f(\mathbf{v})\,\varphi(\mathbf{v}_1)\,\mathrm{d}\mathbf{v}\,\mathrm{d}\mathbf{v}_1\,, \\ I_E &\equiv \int \frac{Mv^2}{2}\,I_{\mathrm{col}}(f)\,\mathrm{d}\mathbf{v} = \int \mathbf{V}\mathbf{g}g\,f(\mathbf{v})\,\varphi(\mathbf{v}_1)\,\mathrm{d}\mathbf{v}\,\mathrm{d}\mathbf{v}_1\,. \end{aligned} \tag{6.3}$$

Here, $\mathbf{g} = \mathbf{v}_1 - \mathbf{v}$ is the atom–cluster relative velocity, and $\mathbf{V} = (M\mathbf{v} + m\mathbf{v}_1)/M$ is the center-of-mass velocity for colliding particles. We made use of the fact that the cluster mass significantly exceeds the atomic mass, $M \gg m$, i.e., the cluster coordinate simultaneously coincides with the center of mass for a colliding atom and a cluster.

These quantities are used in equations for average cluster parameter distributions. Indeed, multiplying the kinetic equation by the cluster momentum $M\mathbf{v}$ and energy $Mv^2/2$, we obtain the following equations for average quantities after averaging over cluster and atom velocities [45, 46]:

$$M\,\frac{\mathrm{d}\mathbf{w}}{\mathrm{d}t} = m\sigma_0 N_\mathrm{a}\langle \mathbf{g}g\rangle\,, \qquad \frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = m\sigma_0 N_\mathrm{a}\langle \mathbf{V}\mathbf{g}g\rangle\,, \tag{6.4}$$

and the distribution functions of clusters and atoms used in equations (6.3) and (6.4) are given by expressions in the first approximation:

$$f(\mathbf{v}) = N_\mathrm{cl}\delta(\mathbf{v} - \mathbf{w})\,,$$
$$\varphi(\mathbf{v}_1) = N_\mathrm{a}\left(\frac{m}{2\pi T}\right)^{3/2} \exp\left[-\frac{m(\mathbf{v}_1 - \mathbf{w}_\mathrm{a})^2}{2T}\right], \tag{6.5}$$

where N_a, N_cl are the number densities of atoms and clusters, $\mathbf{w}$ is the cluster drift velocity, and $\mathbf{w}_\mathrm{a}$ is the average atomic velocity. Because of the criterion $M \gg m$, the above form of the cluster distribution function is also valid, when the following criterion is met [47]:

$$Mw^2 \gg T\,. \tag{6.6}$$

In particular, the extreme left point in Fig. 12, where we have a gas flow rate $Q = 16$ sccm, corresponds to an average cluster energy $Mw^2/2 = 24$ eV, which significantly exceeds the thermal cluster energy, i.e., criterion (6.6) holds true. Next, a Maxwell distribution for the atoms is assumed. Indeed, collisions of atoms with clusters have no influence on establishing the equilibrium between atoms. Assuming the variation length of the average atom velocity to be large compared to the mean free path of atoms, one can obtain a local thermodynamic equilibrium for atoms that leads to the Maxwell distribution function (6.5) over velocities, so we assume below the gas temperature to be constant as the gas stream accelerates in the vicinity of an orifice.

The first equation in Eqn (6.4) may be considered the Newton equation, where the friction force acting on the cluster is determined by its collisions with gas atoms [48], being directed perpendicular to the orifice plane. This gives

$$\mathbf{F} = \frac{m}{\lambda}\,\langle \mathbf{g}g\rangle\,, \tag{6.7}$$

where the mean free path of atoms is $\lambda = 1/(N_\mathrm{a}\sigma_0)$. Introducing an angle ϑ between vectors $\mathbf{w}$ and $\mathbf{v}_1$, we obtain for the right-hand side of the first equation in Eqn (6.4):

$$\langle g_z g\rangle = \left\langle (w - v_1\cos\vartheta)\sqrt{v_1^2 + w^2 - 2v_1 w\cos\vartheta}\,\right\rangle, \tag{6.8}$$

where averaging is taken over the distribution functions (6.5) for clusters and gas atoms. In the limit of $w \ll v_1$, we have

$$\langle g_z g\rangle = \left\langle (w - v_1\cos\vartheta)(v_1 - w\cos\vartheta)\right\rangle = \frac{8w}{3\sqrt{\pi}}\sqrt{\frac{2T}{m}}\,. \tag{6.9}$$

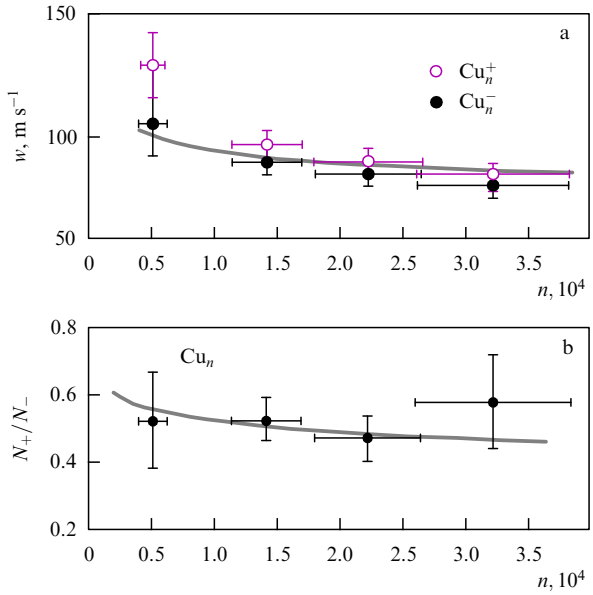

Figure 15. Drift velocities of positive and negative copper clusters (a) and the ratio of the number densities of positive and negative copper clusters (b) as functions of the number of cluster atoms [35]. The argon flow rate is $Q = 16$ sccm, and the orifice radius is $r = 3.5$ mm. (a) The solid line is obtained with the help of formulas (5.10) and (5.11). (b) The solid curve corresponds to establishing electron–ion equilibrium at an electron temperature of 0.2 eV.

As a result, the first equation in Eqn (6.4) agrees with equation (3.2), where the relaxation time is given by formula (3.3).

If criterion (6.6) holds true, we can obtain in the first approximation the expression for the center-of-mass velocity for colliding atom and cluster:

$$\mathbf{V} = \frac{M\mathbf{w} + m\mathbf{v}_1}{M + m} \approx \mathbf{w}\,. \tag{6.10}$$

This allows us to reduce the second equation in Eqn (6.4) to the form

$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = \frac{mw}{\lambda}\,\langle g_z g\rangle\,. \tag{6.11}$$

Dividing this equation by the first equation in Eqn (6.4), we obtain

$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}w} = Mw\,, \tag{6.12}$$

i.e., $\varepsilon = Mw^2/2$. As can be seen, in order to determine the cluster temperature, there is a need in the approximation based on a smallness of the expansion parameter w/v_1 for equation (6.8).

Thus, the determination of the longitudinal temperature in a cluster beam requires additional corrections to the kinetic equation compared with those considered above. Moreover, other corrections connected with the flow geometry and some other problems may be significant. As for the transverse temperature, it is connected with the flow direction in the transient region. On the basis of this analysis, one can formulate a general algorithm for the determination of streamlines during the passage of a gas flow through an orifice. In the first approximation, the measured drift velocity of clusters is used as a function of the number density of atoms (or the gas flow), as was exemplified in the construction of Fig. 15. In the next approximation, this

solution is taken as a basis, and corrections to it follow from a comparison between experimental and theoretical temperatures of a gas flow, depending on the number density of atoms.

7. Conclusion

The above theoretical and experimental analysis opens the prospects of using the cluster measurements to determine the evolution of a gas flow under certain conditions. The possibility of applying this method is demonstrated for the passage of a gas flow through an orifice. To achieve the goals, it is necessary to take advantage of the theory and experiment simultaneously in order to analyze various aspects of this process. Note that the streamlines of a gas flow may be found in a direct method by the addition of dust particles to the flow and making videos of that movement to see the streamlines. The use of nano-sized particles can provide a higher resolution and is based on other principles related to the nonequilibrium character of cluster motion in a gas flow.

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