A SIMILARITY LAW FOR HOMOGENEOUS CONDENSATION IN FREE CO_2 JETS

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Introduction

As is known, physical processes occurring in a given gas jet which is expanding into a vacuum from a sonic nozzle are governed completely by three parameters: the pressure p_0, the temperature T_0 in the prechamber, and the diameter d_* of the nozzle critical section. A similarity law for CO_2 condensation in a free jet from sonic nozzles of different diameter is studied in this paper at the constant temperature $T_0 = 300°K$ (except cases where this is especially stipulated).

The number of molecule collisions after a gas expanding into a vacuum reaches the state of saturation governing the process of new phase formation may be inadequate to the formation of a critical nucleus. Hence, the possibility of describing the condensation process in such a "rapid" gas expansion within the framework of the classical theory of condensation is not obvious. The question of the applicability of the classical theory arose in investigations of homogeneous condensation in jets.

It has been shown experimentally in a number of papers that the complex $p_0 d_*^{\beta}|_{T_0} = \text{const}$ (where $0.5 < \beta < 1$) is generalizing for the position of the maximum of a dimer ionic signal [1], the dimer molar fraction [2], and the given mean cluster size [3].

The limiting process in the classical theory of homogeneous nucleation is critical nucleus formation by means of binary collisions. As is known, the physical processes occurring in a jet and governed by binary molecule collisions, translational–translational, translational–rotational, and translational–vibrational energy exchanges are generalized by the complex $p_0 d_*|_{T_0} = \text{const}$, corresponding to the constancy of the total number of binary collisions in the stream. Since the total number of ternary collisions in the stream is $\sim p_0 d_*^{0.5}|_{T_0}$, the authors of [1-3], without presenting any arguments, consider the generalization of experimental results by the complex $p_0 d_*^{\beta}|_{T_0} = \text{const} (\beta < 1)$ to be associated with the limiting stage of the condensation process governed by the mechanism of three-particle dimer formation and not considered in classical theory (apparently by analogy with the above-mentioned processes governed by binary collisions).

The aim of this paper is to show that the generalization of experimental results by such a complex can be explained even within the framework of the theory of condensation without considering three-particle collisions as a limiting stage of the process.

§1. Experiment

Experiments studying the condensation in a free CO_2 jet from a sonic nozzle were carried out in a three-section molecular-beam generator by the Kantrowitz–Grey scheme with cryogenic pumping. The experiments were to measure the intensity and composition of the molecular beam sorted from a free jet. A description of the generator and a discussion of the questions associated with extraction of the molecular beam are presented in [4].

A closed ionization lamp with output orifice Ø 3 mm was used as the intensity detector and a monopolar mass spectrometer with an entrance diaphragm Ø 2.5 mm as the density detector. The measurement method and transducer calibration are described in [5]. The carbon dioxide gas used in the experiment was subjected to multiple vacuum purification. The quantity of impurities is <0.01%.

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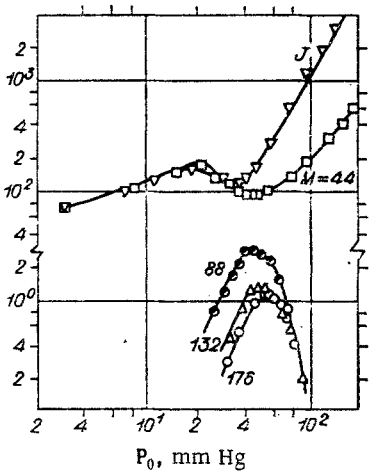

Fig. 1

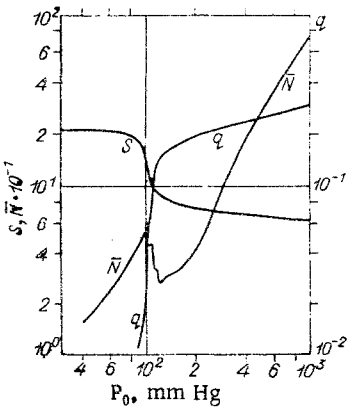

Fig. 2

The quantities p_0, T_0, d_* were measured with around 2% error; the error of the absolute intensity measurements does not exceed 20% and of the density, 40%. Reproducibility of the results is within 5%.

Typical dependences of the total intensity J and the ionic signals of the density sensor (in provisional units) on p_0 are shown in Fig. 1. The intensity and density curves are superposed for small p_0 in the absence of condensation. The conditions for the experiment were as follows: $d_* = 5.0$ mm, $T_0 = 234°K$, nozzle–skimmer spacing in nozzle diameters $\bar{x} = 50$, conical skimmer diameter $d_S = 1.9$ mm, collimator diameter 3 mm, skimmer–detector spacing 890 mm.

For a decrease in T_0 and an increase in d_*, the monomer intensity and density minimum as well as the maximums of the n dimensions (n = 2, 3, 4) shift toward lower p_0. The nature of the dependences obtained does not vary (with the accuracy of the experiment) as T_0, d_*, and d_S change.

It turns out that the positions of the minimums of the intensity curves in the coordinates p_0–T_0 and p_0–d_* are generalized by the complexes

$$p_0 T_0^{-4,45}|_{d_*} = \text{const}, \quad p_0 d_*^{0,6}|_{T_0} = \text{const}$$

as T_0 changes from 234° to 300°K and d_* from 1.9 to 5.0 mm. The experiments showed that the position of the minimum on the $J = J(p_0)$ curves depends weakly on the nozzle–skimmer spacing even in the domain of noticeable jet interaction with the skimmer. This affords a foundation for assuming that the position of the minimum of the $J = J(p_0)$ curves is determined substantially by the condensation process in the jet.

§2. Flow Analysis on the Jet Axis in the Presence of Condensation

The method of analyzing the flow in a free CO_2 jet behind a sonic nozzle in the presence of homogeneous condensation in the jet is elucidated in [6]. The analysis is based on the classical theory of nucleation [7]. The initial system of gasdynamic equations for an inviscid gas flow, as well as the equations describing the condensation kinetics, has the form

$$\rho u a = \text{const}; \tag{2.1}$$

$$\rho u du + dp = 0; \tag{2.2}$$

$$\varkappa RT/(\varkappa - 1) + u^2/2 - Lq = \varkappa RT_0/(\varkappa - 1); \tag{2.3}$$

$$p = \rho RT(1 - q); \tag{2.4}$$

$$I = [(p/kT)^2(2\sigma\mu/\pi N_A)^{1/2}/\rho_l] \exp\left(-4\pi r_*^2\sigma/3kT\right); \tag{2.5}$$

$$r_* = 2\sigma/\rho_l RT \ln [p/p_\infty(T)]; \tag{2.6}$$

$$dr/dt = (\alpha p/\rho_l)[1/(2\pi RT)^{1/2} - 1/(2\pi RT_l)^{1/2}], \tag{2.7}$$

where u, ρ are the velocity and density, respectively, of the gas-condensate mixture; p is the gas pressure; T is the gas temperature; q is the mass fraction of condensate; a is the stream-tube area, L is the specific heat of vaporization; $\varkappa$ is the ratio of the specific

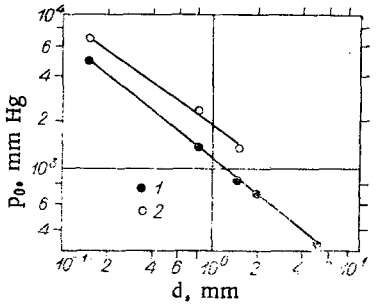

Fig. 3

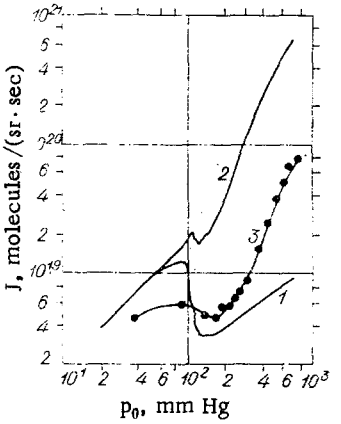

Fig. 4

heats for the gas; σ is the surface-tension factor; I is the rate of nucleation; r_* is the radius of the critical nucleus; N_A is the Avogadro number; μ is the molecular weight of the gas; ρ_ζ is the fluid density; $p_\infty(T)$ is the saturated vapor pressure above the plane surface at the temperature T; α is the condensation factor; and r is the drop radius.

It was assumed that the condensate is in a liquid phase and the drop temperature T_ζ equals the saturation temperature corresponding to the gas pressure. Thermodynamic values of CO_2 presented in [6, 8] were used in the computations.

The area of the stream tube a along the jet axis was given without taking account of the influence of condensation, i.e., that which would hold for isentropic expansion of a gas with $\varkappa = 1.4$. Two-dimensional computations showed that the error thus introduced in the condensate parameter is negligible. The system of equations for given p_0, T_0, d_* was solved numerically [6].

Results of the computation were used to determine the characteristics of the molecular beam sorted out of the condensing gas stream.

§3. Molecular-Beam Intensity

As computations showed, the variance in the condensate-particle (cluster) size distribution function $(\bar{r}^2 - \bar{r}^{-2})^{1/2}$ is less than 10% of the value of $\bar{r}$; hence, it was assumed in the calculation of the molecular-beam intensity that all the clusters have the same mean radius $\bar{r}$ or (in a conversion to the quantity of molecules per cluster) $\bar{N}$. It was assumed that the velocity distribution of both the gas molecules (monomers) and the clusters in the plane of the skimmer is described by an isotropic Maxwell distribution function with the same temperature T. This means that the velocity ratio for the clusters is $(\bar{N})^{1/2}$ times greater than for monomers. The exact expressions for the contribution to the beam intensity J by the monomer J_1 and cluster J_c intensities, obtained under the assumption that collisions do not occur in the beam, are based on the results of [9] and are presented in [6].

In the approximation $S \gg 1$, $\bar{N}S^2\varphi^2 \ll 1$, where $S = u(m/2kT)^{1/2}$ is the velocity ratio for monomers in the skimmer plane, φ is half the angle at which the skimmer is seen from the detector, and the expressions mentioned become simply

$$J_1 = (\rho u)_s \varphi^2 (1 - q) S^2; \tag{3.1}$$

$$J_c = (\rho u)_s \varphi^2 q \bar{N} S^2; \tag{3.2}$$

$$J = J_1 + J_c = (\rho u)_s \varphi^2 S^2 (1 - q + q\bar{N}), \tag{3.3}$$

where $(\rho u)_s$ is the value of the quantity ρu in the skimmer plane. As is seen from (3.3), when $q\bar{N} \gg 1$ almost all the beam molecules are united into a cluster.

It should be noted that for sufficiently large $\bar{N}$ the expression (3.2) overestimates J_c as compared with the exact value. Expressions (3.1)-(3.3) are convenient for analysis; however, the results presented here for a computation of the intensities have been obtained by exact formulas.

§4. Discussion of the Results

Results of computing the condensate fraction, the velocity ratio, and the mean cluster size ($d_* = 1.91$ mm, $x/d_* = 134$) are represented in Fig. 2.

The condensate fraction discloses a sharp growth at $p_0 \approx 100$ mm Hg; extraction of the heat of condensation thus results in an essential diminution in the velocity ratio. As p_0 rises further, the quantities q and S vary sufficiently weakly and the mean cluster size increases $\sim p_0^{1.5}$. Such a nature of the dependence $\bar{N}(p_0)$ for large p_0 is in agreement with experiment [3]. Reasons for the nonmonotonic behavior of $\bar{N}(p_0)$ are still unclear.

Theoretical and experimental values of p_0 as a function of the nozzle-exit diameter needed for the clusters in the far flow field to consist of 500 molecules on the average (points 1 and 2, respectively) are shown in Fig. 3.

A comparison of the curves presented in Fig. 3 permits us to speak about the qualitative agreement between the results of the computation and experiment. Computations of the stream velocity u at a large distance from the nozzle as a function of p_0 were analyzed; as for the case of the experimentally measured monomer velocities in [1], a rise in the computed velocity is noted from the beginning of condensation as p_0 rises because of the transition in the directed velocity of the heat of condensation with stream broadening.

Dependences of the monomer intensity 1 and the total intensity 2 of p_0, computed by using the quantities q, S, $\bar{N}$ for $d_* = 1.91$ mm, $x/d_* = 134$, $d_s = 4.11$ mm are shown in Fig. 4 (curve 3 is experiment).

The monomer intensity has a deep minimum due to a decrease in velocity ratio. The minimum of the total beam intensity is expressed much more weakly since the decrease in S is compensated by an increase in the condensate fraction. The sharp growth in $J(p_0)$ behind the minimum point is due to the fact that the beam consists primarily of clusters here. Since the quantities q and S vary weakly in this domain of p_0, $\bar{N} \sim p_0^{1.5}$, $(\rho u)_s \sim p_0$, we have, according to (3.3), $J \sim (\rho u)_s q \bar{N} \sim p_0^{2.5}$, as is indeed observed.

Since the theoretical and experimental curves agree qualitatively, it can be asserted that the behavior of the beam intensity behind the maximum point of the curves $J(p_0)$, which is observed in both our experiments and those of others ([1], for instance), is due to the condensation process in the jet and is caused by the above-mentioned reasons.

The computed dependences $q(p_0)$ are shown in Fig. 5 for $x/d_* = 500$ with different d_* [curves 1-3: $d_* = 0.1$; 1.91 and 4.97 mm], as are also the equilibrium value of the condensate fraction [curve 4: $d_* = \infty$], which was calculated under the assumption that all the subsequent states will lie on the phase-transition curve after the expanding gas has reached saturation. It is seen that the nature of the curve $q(p_0)$ is identical for all d_*: An abrupt change in the derivative $(\partial q/\partial p_0)_{d_* T_0}$ occurs for a certain p_0. As is seen from the curves presented in Figs. 4 and 5, a minimum in the intensity, if realized on the computed curves $J(p_0)$ for this same p_0, and the fraction of condensate are approximately identical and equal to ~12-15%. For larger p_0 the condensate fraction approaches equilibrium asymptotically. This result is unexpected and means that, despite the representations being added to the present, for sufficiently large values of p_0 condensation in a free jet proceeds in an almost equilibrium manner.

The computed curves $p_0(d_*)$, corresponding to identical values of the condensate fraction in the far jet field, are shown in Fig. 6. The computed 1 and experimental 2 dependences $p_0(d_*)$, corresponding to the minimum intensity of the curves $J(p_0)$, are shown here. It is seen that the computation predicts the complex $p_0 d_*^{\beta} | T_0 = \text{const}$ ($\beta = 0.6$) generalizing the position of the minimum intensity which describes the experiment well. An analysis of the curves presented in Figs. 3 and 6 shows that the conditions needed to obtain a given mean cluster size (see Fig. 3) of the given condensate fraction (see Fig. 6) are generalized by the same complex ($\beta = 0.6$-0.7).

Generalization of the computed data by the complex $p_0 d_*^{\beta} | T_0 = \text{const}$ ($\beta < 1$) can be explained qualitatively as follows. An approximate analysis showed that the condensation process described by the system (2.1)-(2.7) is defined uniquely by the number of binary collisions of one molecule z in the stream after the gas has reached saturation:

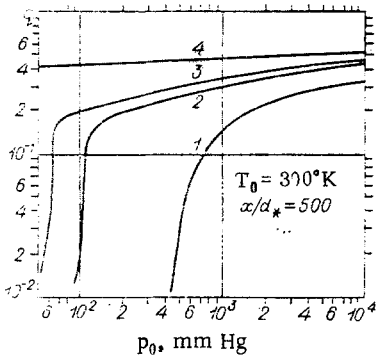

Fig. 5

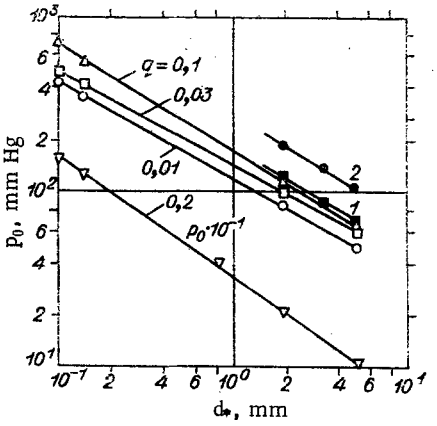

Fig. 6

$$z = \int_{x_1}^{\infty} \nu\,(dx/u) \sim d_* \int_{\bar{x}_1}^{\infty} \nu\,(d\bar{x}/u),$$

where ν is the frequency of the binary collisions at the point x; x_1 is a coordinate of the point where the gas reaches saturation, $\bar{x}_1 = x_1/d_*$. Since $\bar{x}_1$ is a decreasing function of p_0, $z \sim p_0^{\gamma} d_*$, where $\gamma > 1$ and depends for a given gas on p_0, T_0 and d_*, which results in the approximate complex $p_0 d_*^{1/\gamma} = \text{const}$ for $z = \text{const}$. Therefore, the power-law form of the generalizing complex $p_0 d_*^{\beta} | T_0 = \text{const}$ is a defined approximation, which is valid in some range of variation of the deceleration parameters.

As is seen from Fig. 6, the conditions needed to obtain a given condensate fraction are generalized by complexes with several different exponents β depending on the condensate fraction.

On the above basis, it can be asserted that classical theory yields a qualitatively true description of the homogeneous condensation process during rapid gas expansion. Therefore, a theory which does not consider any collisions except binary yields a similarity law for CO_2 condensation during free expansion in a vacuum which agrees with that obtained experimentally. Hence, the postulate of a number of authors about the governing role of three-particle collisions in the process of homogeneous gas condensation is doubtful.

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