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DERIVATION OF INITIAL STATES IN INVESTIGATION OF NUCLEATION BY THE THERMODIFFUSION-CHAMBER METHOD

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A method of deriving the dimensions and coordinates of new-phase nuclei (initial states) in investigating nucleation in spatially inhomogeneous systems is developed. The results of analyzing experimental data taking account of the possible influence of Brownian motion on the nucleation kinetics are given.

To study volume condensation (nucleation), thermodiffusional chambers are in increasing use. The basic aim of experimental investigations in this area is to find the dependence of the nucleation rate I on the degree of supersaturation S with a known temperature of the vapor–gas mixture. Unambiguous interpretation of the experimental results is difficult, however, because of two factors: first, the region of maximum supersaturation within which nuclei of new phase are formed is of finite size; second, the optical methods of recording new-phase particles used in the experimental investigations permit the recording of particles which are of the order of a micron in size, whereas the critical nuclei of new phase are of size $R \sim 10^{-9}$ m.

In connection with this, a method of deriving the initial states using experimental data on the parameters of the new-phase particles [3] is developed here on the basis of a mathematical model of the growth and motion of the new-phase particles forming in the thermodiffusional chamber [1, 2].

As shown by experiments, the interpretation of experimental data on the nucleation of vapor in the thermodiffusion chamber may be divided into three stages. These stages, which differ both in the depth of analysis and in the volume of experimental data required, will be described in sequence. The simplest is the first, in which minimal experimental data is required.

Stage 1 (Phenomenological)

Suppose that there is experimental information that new-phase nuclei form in the chamber with temperatures of the lower and upper plates T_1 and T_2 and ballast-gas pressure P and are able to grow, in these conditions, to dimensions permitting recording by optical methods. In this case, as shown in [2], it is necessary to plot graphs of the dimensionless quantity $\Delta\Phi(g^*(z))/kT(z)$, where $\Delta\Phi(g^*(z))$ is the work of critical-nucleus formation in conditions corresponding to the coordinate z.

Note that in the present work all the notation is analogous to that in [2]. In Fig. 1, the graph of the dimensionless work of critical-nuclei formation of dioctylphthalate

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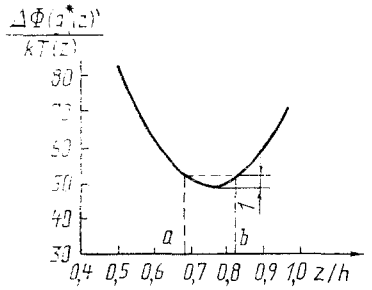

Fig. 1

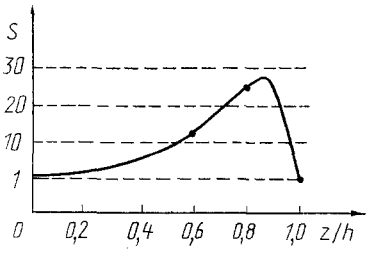

Fig. 2

Fig. 1. Dependence of the dimensionless work of formation of a critical new-phase nucleus on the coordinate of the point of nucleus formation, when $I \sim 1$ cm$^{-3}\cdot$sec^{-1}; $T_1 = 452$ K; $T_2 = 371$ K; $h = 2.67\cdot10^{-2}$ m.

Fig. 2. Variation in supersaturation S(z) within the chamber with steady operating conditions, for the same conditions as in Fig. 1.

(DOP) is shown. The minimum of this curve corresponds to the point with the coordinate $z/h = 0.75$. The points $z/h = a$ and $z/h = b$, for which the dimensionless work of nucleus formation differs by one from the minimal value define the region [a, b], within which it is necessary to take account of the spontaneous formation of new-phase nuclei. As is known, for spatially homogeneous systems [4, 5] $I \sim \exp(-\Delta\Phi(g^*)/kT)$; it may be expected that this dependence will basically be retained also for nucleation in spatially inhomogeneous systems [6].

To date, most investigations [7, 8] have been confined to determining the supersaturation profile $S(z) = n(z)/n_s(T(z))$, where $n(z)$ and $n_s(T(z))$ are the vapor density and saturated vapor density at temperature $T(z)$, respectively. It is assumed here that the new-phase nuclei are formed close to the maximum of S. It is evident from Fig. 2 that the maximum of S does not coincide with the minimum of the dimensionless work of critical-nucleus formation (this is confirmed by calculations for other cases). Two conclusions follow from this: 1) the maximum nucleation rate corresponds to a different temperature than that usually assumed [7, 8]; 2) the zone of the chamber where nucleation occurs is broader than previously thought. This noncoincidence of the extrema may possibly lead to difference in the value of the critical supersaturation found by the thermodiffusion-chamber method from values obtained by other methods (using a Wilson chamber, etc.) [8].

Thus, in the first stage, using experimental information on the nucleation rate, it is only possible to determine how I depends on the maximum degree of supersaturation or on the minimum of dimensionless work of nucleus formation, and to estimate the dimensions of the region where nucleation occurs. Note that neither $\Delta\Phi(g^*(z))/kT(z)$ nor S(z) depends on the ballast-gas pressure.

Stage 2 (Kinetic)

In the second stage in deriving the initial state, it is necessary to have additional information on the new-phase particles, in particular, that the particles are of radius R at height z_0 or to have the distribution function over the radius $f(R|z_0)$. Note that, in the conditions of a thermodiffusional chamber, the particle velocity may practically be used instead of its radius [2], since there is a unique relation between the particle velocity and radius. It is well known that it is considerably simpler to measure the particle velocity than its radius. In addition, in the second stage, it is also necessary to know the ballast-gas pressure P, which has a significant influence on the growth and motion of new-phase particles forming in the chamber.

The mathematical model of particle growth and motion in a thermodiffusional chamber developed in [1, 2] takes the form

$$\frac{dx}{dt} = v; \tag{1}$$

$$\frac{d(Mv)}{dt} = -Mg + F_{TP} + F_R; \tag{2}$$

TABLE 1. Experimental Data on the Parameters of the Distribution of New-Phase Particles over the Chamber Height

Helium pressure $P \cdot 10^{-3}$, Pa	Coordinate z/h of distribution function of new-phase particles over the height on visualization		
	lower boundary	maximum	upper boundary
14,1	0,8	0,87	0,965
7,3	0,82	0,89	0,99
2,9	0,835	0,92	1
1,82	0,83	0,925	1

$$\frac{dR}{dt} = L(n(z=x) - n_s(T(z=x))), \tag{3}$$

where x, v, R are the coordinate, velocity, and radius of the particle, respectively. The density n(z) and temperature T(z) fields are determined with the necessary accuracy from steady solutions of the diffusion and heat-conduction equations. Note that the thermophoretic force F_{TP} and the resistance force F_R depend on the Knudsen number Kn_g, and the mass-transfer coefficient L depends on Kn_v [1, 2].

Since Eqs. (1)-(3) constitute a nonlinear system of three differential equations of first order in the time derivatives, the initial state of the new-phase particles which form may be derived by inverting the time $t \to -t$ and solving the system [9]. The initial values chosen here are the experimental values of the particle coordinate x, its radius R, and the velocity v. The particle velocity v may practically always [2] be calculated in the quasi-steady approximation, and then to investigate a system of two differential equations. The experimental data for DOP obtained by Smolik are used as the initial data.

Table 1 gives the experimental data on the distribution function of new-phase particles over the height of the chamber at the instant of visualization obtained by photography in a laser knife. The nucleation rate $I \sim 1$ cm$^{-3}\cdot$sec^{-1}, $T_1 = 462$ K, $T_2 = 371$ K. Helium is used as the ballast gas.

Trajectories on the (R, z) plane obtained as a result of integrating Eqs. (1)-(3) are shown in Fig. 3. As established in [2], the visualization radius for DOP particles is 4.5 μm. Curve 1 describes the trajectory of particles making a contribution to the maximum of the experimentally observable distribution function of the new-phase particles on visualization. Curves 2 and 3 are the particle trajectories recorded, respectively, at the lower and upper boundaries of the distribution function of new-phase particles with respect to the height on visualization. It is interesting to note that kinetic calculation at a ballast-gas pressure of $1.4\cdot10^4$ Pa and above completely agrees with the earlier thermodynamic calculation (in the first stage). With reduction in ballast-gas pressure, as a result of analyzing the experimental data, an interesting result is obtained: the coordinate of maximum nucleation rate coincides with the minimum of dimensionless work of nucleus formation, but the width of the region within which particle formation occurs is markedly reduced. This is evidently associated with the influence of Brownian motion of the new-phase nucleus on the nucleation kinetics [6], which increaes with increase in the Brownian diffusion coefficient D_B of the new-phase particles. It is known that $D_B \sim 1/P$ in free-molecular conditions [10]. Note that there is a close mathematical analogy between the nucleation kinetics in a spatially inhomogeneous system [6] and the kinetics of binary nucleation, appearing in an identical structure of the kinetic equation and the presence of a saddle point [11, 12].

The trajectory in Eq. (4) describes the growth and motion of a new-phase particle formed at the point z/h = 0.75 with a ballast-gas pressure of $1.4\cdot10^5$ Pa. As shown by the calculations, increase in ballast-gas pressure means that more and more new-phase particles are unable to reach the visualization radius in the time available. In other words, an "effect" of decrease in nucleation rate with increase in ballast-gas pressure is experimentally observed. Of course, the specific value of the ballast-gas pressure at which these effects begin to appear depends on many factors, but they are all taken into account in the mathematical model developed in [1, 2].

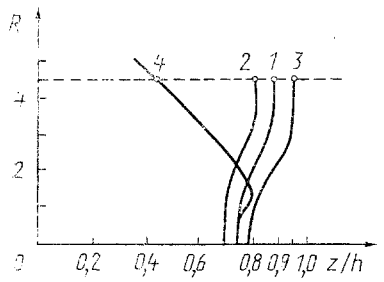

Fig. 3. Trajectory of motion of new-phase particles on the (R, z) plane; T_1 = 462 K, T_2 = 371 K, h = $2.67 \cdot 10^{-2}$ m: 1-3) P = $1.4 \cdot 10^4$ Pa, solution of (1)-(3) in inverse time ($t \to -t$); 4) helium pressure P = $1.4 \cdot 10^5$ Pa, solution in "forward" time. R, μm.

Calculations also show that a 10% spread in determining the particle radius leads to a 3% spread in determining the coordinate of particle nucleation. However, this is the case if the experimental radius is less than the free-fall radius $\overline{R}$ [2]; particles with radius less than $\overline{R}$ tend to the upper plate under the influence of the thermophoretic force. If the radius of the new-phase particle is greater than the free-fall radius $\overline{R}$ at the time of measurement, there are considerably stronger requirements on the accuracy of measuring the radius, in view of the characteristics of particle growth and motion noted in [1]. Small spread in determining the particle parameters will lead to large errors in deriving the initial states, as a result of the nonlinearity of the model employed. The physical reason for this is that, when $R > \overline{R}$, as a rule, there is a shift from free-molecular to diffusional conditions of particle growth.

Stage 3

Investigations with several measurements along the particle trajectory correspond to the third stage of deriving the initial state of new-phase particles. For example, at time t_1, coordinate x_1 and radius R_1 are measured; at time t_2, correspondingly, x_2 and R_2; and so on. It is evident that the use of additional information offers the possibility of parametric identification of the mathematical model. In particular, by specifying the data at time t_1 as the initial conditions and then solving the equations of the mathematical model, the fitting factors may be found by minimizing the square of the deviation of the solution obtained at time t_2. Unfortunately, such experimental data are not available at present.

CONCLUSIONS

1. The expediency of using the quantity $\Delta\Phi(g^*(z))/kT(z)$ in analyzing experiments in a thermodiffusion chamber has been shown. Analysis of Smolik's experimental data confirms that nucleation occurs close to the minimum of the dimensionless work of formation of a new-phase nucleus.

2. It is found that it is most expedient to perform experiments at ballast-gas pressures such that the free-fall radius $\overline{R}$ of the new-phase particles [1] is a few microns. In this case, the role of errors in measuring the particle radius is considerably reduced.

3. The extreme importance of conducting experiments with the same values of T_1 and T_2 but ballast-gas pressures differing by approximately an order of magnitude is established. In this case, the use of experimental data and model calculations on the growth and motion of new-phase particles [1, 2] permits the isolation of the kinetic effects due to nucleation and the subsequent growth of the nuclei to sizes for which optical methods may be used.

4. The use of several successive measurements of the parameters of the new-phase particles (the dependence of the particle velocity or radius on its position in the chamber) is proposed in experimental investigations; this offers the possibility of parametric identification of the mathematical model and, in particular, determination of the effective condensation and accommodation coefficients.

NOTATION

$g^*(z)$, number of molecules in the critical nucleus formed at the point z; k, Boltzmann constant; T, temperature; $M = (4\pi R^3/3)\rho_l$, mass of new-phase particle; ρ_l, its density; g = 9.8 m/sec^2; $Kn_g = \lambda_g/R$; $Kn_v = \lambda_v/R$; the approximate mean free path lengths λ_g and λ_v were defined in [1, 2].

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DIFFUSIONAL MASS TRANSFER IN LIQUID MIXTURES

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The general form of the equations for determining the flow relations in liquid mixtures is obtained. A closed calculation algorithm and an experimental method of holographic interferometry are developed for the identification of the binary-diffusion coefficients. A ternary mixture is investigated by the method of molecular dynamics.

Equation for Determining Flow Relations in Liquid Mixtures

It is known that any closed nonequilibrium macroscopic system passes to a state of statistical equilibrium in the course of its relaxation time. This state of the system is described by an N-particle Gibbs distribution function [1]. For the large canonical ensemble of a ν-component system, it takes the form

$$F_0^N = A \exp\left[-\left(E - \sum_{\alpha=1}^{\nu} \mu_\alpha N_\alpha\right)/KT\right],$$

where A is a normalization factor; μ_α, N_α are the chemical potential and number of particles of component α.

However, in practice, it is necessary to consider the system through times comparable with, or even less than, the relaxation time. In this case, its description may be constructed, as suggested in [2], by reducing the number of parameters characterizing the nonequilibrium macrosystem in the course of relaxation.

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