MOTION AND GROWTH OF NEW-PHASE PARTICLES FORMED IN A THERMODIFFUSION CHAMBER

J. Vitovec, N. V. Pavlyukevich, I. Smolik, and
S. P. Fisenko

UDC 546.423

The correlation between the growth and motion of new-phase particles in a thermodiffusion chamber is theoretically investigated. The results are compared with experimental data.

Thermodiffusion chambers [1, 2] (Fig. 1) are widely used at present to study homogeneous condensation (nucleation). The basic aim of such research is to find experimental dependences of the nucleation rate I on the degree of supersaturation S at a known temperature. However, two factors interfere with the unique interpretation of the experimental results: first, the finite size of the region of maximums supersaturation within which the nuclei are formed; and second, the use of optical methods of recording the new-phase particles in the experiments, permitting the recording of particles of dimensions no less than a few microns, whereas the critical new-phase nuclei are of size $\sim 10^{-9}$ m; of course, the new-phase particle, as it grows, moves away from the point at which it is formed, under the action of gravity, thermophoresis, and Brownian motion.

In a thermodiffusion chamber (Fig. 1), the material being investigated evaporates from plate I, and condenses at plate II. Evaporation occurs in a helium atmosphere; the partial pressure of helium P is considerably greater than the partial pressure of the vapor, $T_1 > T_2$, and the choice of $\Delta T = T_1 - T_2$ and P is such that the density of the gas mixture consisting of helium and dioctylphthalate vapor at plate I is greater than the density of the mixture around the upper plate II. The density of dioctylphthalate vapor is considerably higher close to plate I than at plate II, which more than compensates for the temperature reduction in heium density around plate I. In the experiments, the temperature gradient is approximately 25 deg/cm, and the helium pressure varies in the range 10^3-$1.5 \cdot 10^4$ Pa. Close to plate II, at a height of around 0.9 h, there is a maximum of the supersaturation S, in the vicinity of which new-phase nuclei are formed.

In the thermodiffusion chambers, transport processes in the gas and disperse phases are related. However, at low rates of nucleation I, it may be assumed that the new-phase particles grow in a supersaturation field determined solely by transport processes in the gas phase. This assumption holds if $\ell \ll D(n_s(T_1) - n_s(T_2))/h^2$.

The density, temperature, and supersaturation fields in a thermodiffusion chamber have been much investigated; see, for example, [3, 4] and the literature cited there. In these studies, diffusion, heat conduction, thermodiffusion, and nonideality of the gas mixture have been taken into account.

Since growth and motion of new-phase particles in low-intensity phase transformation are considered below, simplification of the system of interrelated equations is possible. If thermodiffusion is neglected and it is assumed that $uh/D \ll 1$, the steady distributions of the density n(z) and temperature T(z) will be close to linear, i.e., may be determined from the solution of the equations

$$\nabla^2 n(z) = 0, \qquad (1)$$

$$\nabla^2 T(z) = 0 \qquad (2)$$

with boundary conditions

A. V. Lykov Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR, Minsk. Institute of Theoretical Principles of Chemical Processes, Czechoslovak Academy of Sciences, Prague. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 56, No. 6, pp. 936-942, June, 1989. Original article submitted February 8, 1988.

0022-0841/89/5606-0648$12.50

$$n(0) = n_s(T_1), \quad n(h) = n_s(T_2), \tag{3}$$

$$T(0) = T_1, \quad T(h) = T_2. \tag{4}$$

The degree of supersaturation $S = n(z)/n_s(T(z))$ is calculated by the model in Eqs. (1)-(4) for dioctylphthalate (DOP), used in the experiments. The temperature values of the plates are taken to be close to the experimental values: $T_1 = 452$ K, $T_2 = 354$ K. At these temperatures, the condition of small nucleation rate holds.

In spatially homogeneous systems, the state with maximum supersaturation corresponds to the minimum work of formation of a new-phase nucleus and hence the maximum rate of nucleation [5-7]. In inhonogeneous systems, when $n = n(z)$ and $T = T(z)$, the quantity $\Delta\Phi(g^*(z))/kT(z)$ more accurately characterizes the nucleation rate than the degree of supersaturation $S(z)$. In particular, the coordinate of minimum work of nucleus formation in the thermodiffusion chamber (Fig. 2) does not coincide with the coordinate of maximum supersaturation, which is $z/h = 0.9$. This may expediently be used in analyzing experimental data on the nucleation kinetics in inhomogeneous systems.

The points $z/h = a$ and $z/h = b$ (Fig. 2), for which the reduced work of nucleus formation differs from the minimum value by unity, define the region $[a, b]$, within which the spontaneous formation of new-phase nuclei must be taken into account. For DOP, $b - a \cong 0.12h$.

As follows from Zel'dovich–Frenkel theory, the nucleation rate is of the same order of magnitude within the region where the reduced work differs by no more than unity. In describing the flow of vapor–gas mixture in the chamber, no account is taken of kinetic effects – in particular, the jumps in temperature and concentration at the plate surface, the magnitude of which depends on the Knudsen number and the velocity of gas-mixture flow u [8].

In the given conditions, in which the Knudsen number – defined as the ratio of the free path length to h – and the evaporation rate are small, these effects may be neglected. However, in analyzing the growth of new-phase particles, the role of attenuation of the medium is significant, since the Knudsen number – defined here as the ratio of the mean free path length to the particle radius – may vary over broad limits.

The approximate mean free path lengths of helium λ_g and vapor λ_v molecules are now determined, taking into account that the partial pressure of helium is much greater than the partial pressure of the vapor [9, 10]

$$\lambda_g = \frac{1}{\sqrt{2}\pi\sigma_g^2 n_g}, \tag{5}$$

$$\lambda_v = \frac{1}{\sqrt{1 + \frac{m_v}{m_g}}\, n_g \pi \sigma_{vg}^2}, \tag{6}$$

where n_g is the number of helium molecules per unit volume; m_v, σ_v and m_g, σ_g are, respectively, the mass and diameter of vapor and helium molecules; $\sigma_{vg}^2 = (\sigma_v + \sigma_g)^2/4$. In accordance with Eqs. (5) and (6), two Knudsen numbers may be introduced $Kn_g = \lambda_g/R$, $Kn_v = \lambda_v/R$.

Knowing the vapor-density and temperature fields inside the chamber according to Eqs. (1)-(4), the motion and growth of the new-phase particle inside the chamber may be calculated. Suppose that x, v, R are, respectively, the center-of-mass coordinate of the particle, its velocity, and its radius. The system of equations describing the evolution of the new-phase nucleus takes the form

$$\frac{dx}{dt} = \mathrm{v}, \tag{7}$$

$$\frac{d(M\mathrm{v})}{dt} = -Mg + F_{\text{тф}} + F_R, \tag{8}$$

$$\frac{dR}{dt} = L[n - n_s(T(z = x))], \tag{9}$$

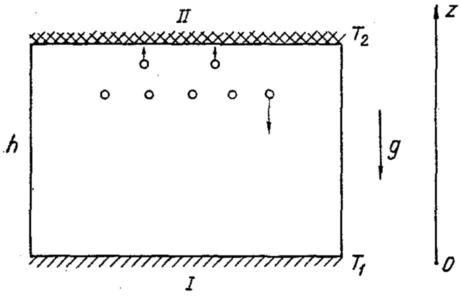

Fig. 1

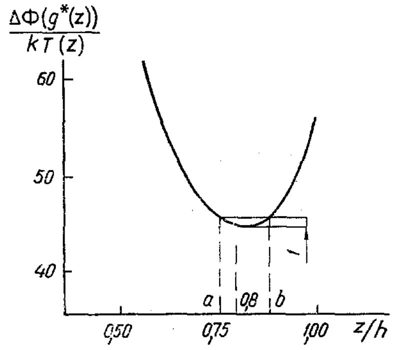

Fig. 2

Fig. 1. General form of thermodiffusion chamber.

Fig. 2. Dependence of the reduced work of formation of a critical new-phase nucleus on the coordinate of the point of nucleus formation.

where $M = (4\pi/3)R^3\rho_L$ is the particle mass.

The initial conditions are

$$x(0)=x_0,\quad \mathbf{v}(0)=\mathbf{v}_0,\quad R(0)=R_{cr}(x_0). \tag{10}$$

Note that $R_{cr}(x_0)$ means that, initially, the radius of the new-phase nucleus is taken to be equal to the radius of the critical nucleus [5] for the conditions corresponding to the point x_0.

Since $R_{cr} \sim 10^{-9}$ m, all the interaction processes between the nucleus and the vapor–gas mixture in practically any conditions are of free-molecular type in this case (Kn_g, $Kn_v \gg 1$). With growth of the new-phase particle, the Knudsen number decreases, and may become much less than unity. Interpolational expressions for the thermophoretic force F_{tp} and resistance force F_R valid over the whole range of Kn_g were given in [11]. Because the expressions used in the numerical calculations are so unwieldy, they are not given here.

Expressions for L are known from aerosol physics in two limiting conditions: $Kn_v \ll 1$ and $Kn_v \gg 1$. An interpolational expression for L with correct asymptotes when $Kn_v \gg 1$ and $Kn_v \ll 1$ is obtained using the relation

$$\frac{1}{L}=\frac{1}{L_c}+\frac{1}{L_F}, \tag{11}$$

where $L_F=\frac{1}{\rho_L}\sqrt{\frac{mkT}{2\pi}}=L$ in free-molecular conditions; $L_c = Dm/\rho_L R = L$ in continuum conditions. Adopting the approximate expression $D = (\beta/4)\lambda_v\tilde{v}$ for the diffusion coefficient [9], where $\tilde{v} = \sqrt{(8kT/\pi m)}$ and β is a fitting parameter, it follows from Eq. (11) that

$$L=\frac{1}{\rho_L}\sqrt{\frac{mkT}{2\pi}}\,\frac{1}{1+\frac{1}{\beta\,\mathrm{Kn}_v}}. \tag{12}$$

The physical meaning of L is that it is the mass-transfer coefficient divided by the DOP density in the condensed phase.

Note, in passing, that the best agreement between calculation and experiment is obtained with $\beta = 1.55$.

The next step is to analyze the solution of the system in Eqs. (7)-(9) with the initial conditions in Eq. (10).

The behavior of all the new-phase particles formed inside the thermodiffusion chamber may be divided into two classes. Particles of both classes move toward the upper plate initially under the action of thermophoresis. Particles belonging to the first class are

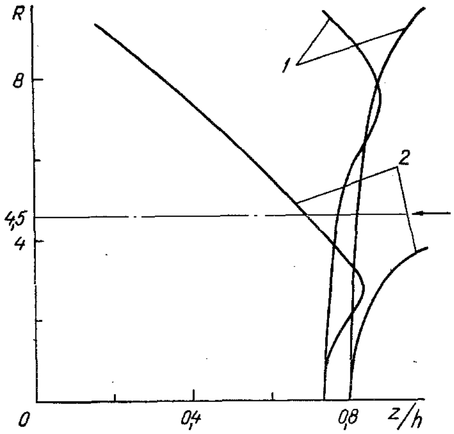

Fig. 3. Trajectories of the motion of new-phase particles in the (R, z) plane: 1) helium pressure 10^3 Pa; 2) $1.5 \cdot 10^4$ Pa. R, μm.

able to grow to a definite size — to so-called free-fall radius $\bar{R}$ — and then change their direction of motion under the action of gravity. Particles of the second class are unable to grow to size $\bar{R}$ and reach plate II. The free-fall radius $\bar{R}$ is determined from the condition (v = 0)

$$Mg = F_{tp}. \tag{13}$$

Using [11], the approximate expression for F_{tp} is now written

$$F_{tp} = -\frac{KR6\pi\eta^2\nabla Tk}{m_g P}, \tag{14}$$

where K is the constant of thermophoresis (in particular, $K \sim 1$ and $Kn_g \ll 1$). Substituting Eq. (14) into Eq. (13) gives

$$\bar{R} = \sqrt{\frac{9\eta^2\nabla TKk}{2m_g\rho_L gP}}. \tag{15}$$

For the conditions of the thermodiffusion chamber, using the thermophysical parameters of helium, it is found that

$$\bar{R} = 2{,}34 \cdot 10^{-6} P^{-1/2} (\nabla T)^{1/2} K^{1/2}.$$

In particular, $\bar{R}$ = 15, 5, and 4 μm for P = 10^3, $8 \cdot 10^3$, and $1.5 \cdot 10^4$ Pa in the case of DOP. In experiments at a helium pressure of $8 \cdot 10^3$ Pa, particles moving upward and downward are visually observed, an at a helium pressure in the chamber of $1.5 \cdot 10^4$ Pa only particles moving downward are seen. Comparing these experimental data with the calculation of the free-fall radii, it may be concluded that DOP drops with $R \geq 4.5$ μm are observed visually. The experimental method and the thermodiffusion chamber were described in detail in [3].

Other conditions being equal, the possibility that a new-phase particle will grow to size R depends on the coordinates of particle nucleation. Particle trajectories are shown in Fig. 3. As is evident from Fig. 3, particles formed in the region $z/h \geq 0.8$ belong to the second class. At a pressure P = 10^3 Pa or less, particles moving both downward and upward will be observed visually in this section of the thermodiffusion chamber.

The number of new-phase particles with the same trajectory in the R, z plane is directly proportional to the nucleation rate $I(x_0)$, where x_0 is the coordinate of the point of particle nucleation. In steady conditions, particles of different sizes will be found at the same height in the thermodiffusion chamber. Using the above considerations and the data in Figs. 2 and 3, the size distribution function of the particles may be plotted.

The quasi-steady velocity v of a new-phase particle when $Kn_g < 1$ and $R > \bar{R}$ is now found, by equating the gravitational force and the resistance force and neglecting thermophoresis

$$v = \frac{2\rho_L R^2}{9\eta}. \tag{16}$$

In these conditions, $Kn_V << 1$, and it follows from Eqs. (7) and (9) that

$$\frac{dR}{dx} = \frac{L(n-n_s)}{v} \sim \frac{n-n_s}{PR^3}. \tag{17}$$

It follows from Eq. (17) that the slope of the curves in Fig. 3 is inversely proportional to the helium pressure in the system. Calculations are also undertaken for thermodiffusion chambers in which the hot plate is at the top. In this case, gravity and thermophoresis act in the same direction. It is shown that, for the same values of supersaturation and helium pressure as above, no new-phase particles should be observed. The new-phase particles formed in these conditions move considerably more rapidly and are unable to reach a radius $R \sim 4.5$ µm before they reach the cold plate. The minimum of the reduced work of nucleus formation has the coordinate $z/h = 0.2$.

The results of numerical investigation show that, in the system described by Eqs. (7)-(10), there are processes with three characteristic time scales differing by several orders of magnitude. The fastest is the establishment of a quasi-steady velocity of motion of particles of the given radius; for micronic particles, this time is no greater than 10^{-7} sec. If $Kn_V > 1$, the second most rapid process is growth of the nuclei in free-molecular conditions. In this case, as is well known, the radius varies in proportion to the time ($R \sim t$). The slowest process in these conditions is motion of the new-phase particle within the thermodiffusion chamber. If $Kn_V < 1$, however – this condition holds when $R \geq 4$ µm for $P = 10^3$ Pa and when $R \geq 0.1$ µm for $P = 1.5 \cdot 10^4$ Pa), particle growth is much slower, and the law of variation in radius takes a different form: $R \sim \sqrt{t}$. In these conditions, particle growth becomes the slowest process.

NOTATION

$\Delta\Phi(g^*(z))$, work of formation of critical nucleus at point z; $g^*(z)$, critical size; F_{tp}, thermophoretic force; F_R, resistance force; ρ_L, density of new phase; D, mutual diffusion coefficient; η, viscosity of helium; h, chamber height; R, particle radius; g, acceleration due to gravity. Thermophysical parameters of DOP: molecular weight 390.56 kg/km; molecular diameter 10.12 Å; saturated vapor pressure in the range 290-490 K; $\log P_{eq} = 12.185459 - 4223.559/(T - 47.493)$. Indices: s, saturated vapor; g, helium; v, vapor; c, continuum conditions; F, free-molecular conditions.

LITERATURE CITED

1. P. P. Wegener and P. Mirabel, Naturwiss., 74, No. 3, 111-119 (1987).
2. A. G. Amelin, Theoretical Principles of Cloud Formation on Condensation [in Russian], Leningrad (1972).
3. I. Smolik and J. Vitovec, J. Aerosol. Sci., 13, No. 6, 587-596 (1982).
4. V. N. Chukanov and A. P. Kuligin, Teplofiz. Vys. Temp., 25, No. 1, 70-78 (1987).
5. Ya. I. Frenkel', Kinetic Theory of Liquids [in Russian], Moscow–Leningrad (1975).
6. Ya. B. Zel'dovich, Zh. Éksp. Teor. Fiz., 12, No. 11-12, 525-538 (1942).
7. E. M. Lifschitz and L. P. Pitaevskii, Physical Kinetics [in Russian], Moscow (1979).
8. N. V. Pavlyukevich, G. E. Gorelik, V. V. Levdanskii, et al., Physical Kinetics and Transport Processes in Phase Transformations [in Russian], Minsk (1980).
9. P. P. Wagner, Aerosol Growth by Condensation, Springer (1982).
10. M. N. Kogan, Dynamics of Rarefied Gas [in Russian], Moscow (1967).
11. L. Talbot, R. K. Cheng, R. W. Scefer, and D. R. Willis, J. Fluid Mech., 101, No. 4, 737-758 (1980).