DYNAMICS OF THE FORMATION OF AN AEROSOL FROM SUPERSATURATED STEAM

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The process of homogeneous formation of a condensed phase is traditionally regarded as a two-stage process: the emergence of nucleation centers and their further growth in the supersaturated vapor. It is tacitly assumed that the spectrum of dimensions of the condensate particles is determined by the first stage — the formation of nucleation centers. In actuality, however, the initial size distribution of the particles may be substantially distorted because the rate of mass exchange depends on the curvature of the surface and because the Thompson critical dimension r_{cr} is variable. When the vapor is no longer supersaturated, the value of r_{cr} increases, and the fine aerosol particles may go over into the region of subcritical dimensions, with subsequent evaporation. This leads to a reduction in the calculated aerosol concentration; the reduction may be misinterpreted as being the result of coagulation. We should point out at once that this study deals with aerosols in whose formation the coagulation process is not decisive. Naturally, the process of reduction of the calculated particle concentration cannot be investigated within the framework of a monodisperse approximation. Moreover, we shall show that this also cannot be done within the framework of the widely used model which takes account of the distribution function by introducing its first four moments.

1. Applicability of Moment Equations. The model, as is known, is based on the approximate solution of the kinetic equation for the particle-size distribution function $f(r, t)$ [1]

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial r}(\dot{r} f) = \delta(r - r_{cr}) J, \tag{1.1}$$

where $\dot{r}$ is the rate of growth of the particles; J is the rate of nucleation center formation, calculated, for example, by the Frenkel–Zel'dovich formula; δ is the Dirac delta function.

Equation (1.1) is obtained from the Fokker–Planck equation by disregarding the diffusion term and introducing a source which takes account of the nucleation. The four-moment approximation [2] was obtained on the assumption of a free-molecule regime of particle growth, without taking account of the effect of the curvature of the particle surface ($\dot{r}$ independent of r). It is also assumed that there are no particles of subcritical dimensions ($r < r_{cr}$). Following [2], we multiply Eq. (1.1) by r^n and integrate from r_{cr} to ∞; introducing the following notation for the moments of the distribution function:

$$\Omega_n = \int\limits_{r_{cr}}^{\infty} r^n f dr \quad (n = 0, 1, 2 \ldots),$$

we find

$$\frac{d\Omega_n}{dt} = \int\limits_{r_{cr}}^{\infty} r^n \frac{\partial f}{\partial t} dr - r_{cr}^n f(r_{cr}) \frac{dr_{cr}}{dt},$$

$$\int\limits_{r_{cr}}^{\infty} r^n \frac{\partial}{\partial r}(\dot{r} f) dr = -r_{cr}^n f(r_{cr}) \dot{r}(r_{cr}) - n \int\limits_{r_{cr}}^{\infty} \dot{r} r^{n-1} f dr,$$

where it is assumed that $r^n f(r) \to 0$ as $r \to \infty$.

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Thus, from (1.1) we have

$$\frac{d\Omega_n}{dt} = n \int_{r_{\text{cr}}}^{\infty} \dot{r} r^{n-1} f dr + J r_{\text{cr}}^n + r_{\text{cr}}^n \left[\dot{r}(r_{\text{cr}}) - \frac{dr_{\text{cr}}}{dt}\right] f(r_{\text{cr}}). \qquad (1.2)$$

In [2-5] the last term on the right side of (1.2) is absent for some reason. Perhaps there was a mistake due to an unfortunate choice of notation: $\dot{r}(r_{cr}) \equiv \dot{r}_{cr}$ and $dr_{cr}/dt \equiv \dot{r}_{cr}$; the terms in square brackets cancel each other out. In actuality, however, they are very different; dr_{cr}/dt is the rate of growth of the critical dimension, i.e., a quantity arising out of the variation of supersaturation in the system, while $\dot{r}(r_{cr})$ is the rate of growth of the particles of critical size. In general, by the definition of critical dimension, $\dot{r}(r_{cr})$ is equal to zero; however, in this model, which does not take account of the fluctuation processes when $r \approx r_{cr}$, the assumption that $\dot{r}(r_{cr}) \neq 0$ is necessary. The "lost" term on the right side of (1.2) has a theoretical impact on the applicability of the moment equations used in [2-5], since the presence of $f(r_{cr})$ in these equations requires a knowledge of the whole distribution function in the calculations.

Let us try to determine when these equations may nevertheless be used. To do this, we write the kinetic equation (1.1) without particles of subcritical size:

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial r}(\dot{r} f) = 0, \quad r \in]r_{\text{cr}}, \infty[. \qquad (1.3)$$

Then we must have the boundary condition for $r = r_{cr}$:

$$\left[\dot{r}(r_{\text{cr}}) - \frac{dr_{\text{cr}}}{dt}\right] f(r_{\text{cr}}) = J \quad \text{for} \quad \dot{r}(r_{\text{cr}}) - \frac{dr_{\text{cr}}}{dt} > 0.$$

The last expression is the relative velocity of "motion" of the particles (in the space of dimensions) in terms of the movable left-hand boundary of the region in which Eq. (1.3) is given; the product on the left side of the boundary condition is obviously the flux of particles through the boundary. As in [1], we assume that the formation of new particles of subcritical size takes place as the result of nucleation. For $\dot{r} - dr_{cr}/dt < 0$ the formulation of the boundary condition for $r = r_{cr}$ for the first-order equation (1.3) is incorrect.

Integrating (1.3) multiplied by r^n, we obtain (for $\dot{r} = \text{const}(r)$)

$$\frac{d\Omega_n}{dt} = n\dot{r}\Omega_{n-1} + \begin{cases} J r_{\text{cr}}^n & \text{for} \quad \dot{r} - \dfrac{dr_{\text{cr}}}{dt} > 0, \\ r_{\text{cr}}^n \left(\dot{r} - \dfrac{dr_{\text{cr}}}{dt}\right) f(r_{\text{cr}}) & \text{for} \quad \dot{r} - \dfrac{dr_{\text{cr}}}{dt} < 0. \end{cases} \qquad (1.4)$$

The moment equations of [2-5] coincide with (1.4) when $\dot{r} - dr_{cr}/dt > 0$, and in this case it is correct to use them. The case $\dot{r} - dr_{cr}/dt < 0$ corresponds to a condition of evaporation ($\dot{r} < 0$, $dr_{cr}/dt = 0$) or rapid growth of r_{cr} (the critical dimension "overtakes" the distribution function). The question that naturally arises is this: Which parameter of the aerosol determines the sign of the difference $\dot{r} - dr_{cr}/dt$ and what is the region of its values for which the moment equations may be used?

First we shall consider the case of free-molecule growth of the particles:

$$\sigma^* dr/d\tau_f = S - p_r/p_\infty. \qquad (1.5)$$

Here $\sigma^* = \dfrac{2\sigma m}{r_1 \rho k T}$; $d\tau_f = \dfrac{\alpha\sigma^* p_\infty}{\rho r_1}\sqrt{\dfrac{m}{2\pi k T}}\, dt$; r is the dimension of a particle of condensate, referred to the "molecular" dimension r_1 ($4\pi r_1^3\rho/3 = m$); m is the mass of a molecule; ρ is the density of the condensate; σ is its surface tension; T is the temperature (the same for the gaseous and condensed phases); α is the evaporation coefficient; $p_\infty(T)$ is the saturated vapor pressure above a plane surface; on the other hand, the pressure of the vapors near the surface of a particle is determined by taking account of their curvature:

$$p_r = p_\infty \exp(\sigma^*/r). \qquad (1.6)$$

The supersaturation S in the system is expressed in terms of the critical dimension:

$$S = \exp(\sigma^*/r_{cr}). \qquad (1.7)$$

Let us analyze the processes in the aerosol after the formation of nucleation centers, when the supersaturation is no longer high ($S \sim 1$). As can be seen from (1.7), in this case we must have $r_{cr} \gg \sigma^*$ (the value of σ^* for most substances is several units or tens). Using the expansion for exp in (1.6), (1.7), we find from (1.5) that

$$dr/d\tau_f = 1/r_{cr} - 1/r. \qquad (1.8)$$

Suppose that at the initial moment all the $r \gg r_{cr}$, which is usually the case after the formation of nucleation centers is completed. Then the growth rate $dr/d\tau_f$ (1.8) for particles of different dimensions will be nearly the same, and we can analyze the formation of the aerosol in the monodisperse approximation. If at time τ_f the total number of molecules per unit volume of aerosol is $N_V(\tau_f)$ and the number of condensate particles is n, then the supersaturation will be $S = (N_V - nr^3)/N_\infty$. Hence, taking account of (1.7), for $r_{cr} \gg \sigma^*$ we have

$$nr^3 = N_V - N_\infty - \sigma^* N_\infty / r_{cr}. \qquad (1.9)$$

For the system of equations (1.8), (1.9) an approximate solution $r(\tau_f)$ can be constructed by the method of successive approximations. Taking account of the fact that $\sigma^* N_\infty / r_{cr} \ll N_\infty$, we take as the first approximation

$$nr^3 = N_V - N_\infty = N,$$

where $N(\tau_f)$ is the number of molecules in the condensate if we assume phase equilibrium in the system.

Expressing r from this and substituting into (1.8), we find

$$1/r_{cr} = (1/3)n^{-1/3}N^{-2/3}dN/d\tau_f + (n/N)^{1/3}. \qquad (1.10)$$

Using this expression in (1.9), we can find the next approximation for r, and so on. If the higher derivatives $d^kN/d\tau_f^k$ are small, this process converges very rapidly, and even the first approximation is quite acceptable for our calculated analysis. The ratio $r/r_{cr} = 1 + (1/3)n^{-2/3} N^{-1/3}dN/d\tau_f$ obviously characterizes the "distance" between the dimensions of the particles and the critical dimension. As $r/r_{cr} \to 1$, this distance becomes small, and if we take account of the finite (nonzero) dispersion of the distribution function, the critical dimension "overtakes" the dimensions of the particles. Since n = const (for $r > r_{cr}$ the number of particles in the system remains unchanged), it is the value of $N^{-1/3}dN/d\tau_f$ that will be decisive. If it tends to zero, then $r_{cr} \to r$; if it has a nonzero value (although one that depends on τ_f), r_{cr} will not catch up with r. The form of the function $N(\tau_f)$ for which the boundary between the two regimes has the simplest appearance can be found from the condition

$$N^{-1/3}dN/d\tau_f = \text{const}, \quad \text{i.e. } N = \text{const}\,\tau_f^{3/2}; \qquad (1.11)$$

this is in fact a function of the external mass source (or sink). Let us now consider systems for which a relation of the form $N = N_0\tau_f^\nu$ holds. From (1.11) it follows that for values of

$\nu < 3/2$ the critical dimension "overtakes" the dimensions of the particles. From (1.10) we have

$$1/r_{cr} = N^{-1/3}\left(\frac{\nu}{3} n^{-1/3}\tau_f^{\nu/3-1} + n^{1/3}\tau_f^{-\nu/3}\right).$$

If $\nu > 3/2$, then $\nu/3 - 1 > -\nu/3$, and therefore for large values of τ_f

$$r_{cr} \approx \frac{3}{\nu}(N_0 n)^{1/3}\tau_f^{1-\nu/3}.$$

From this we can see the second boundary for ν: for $3/2 < \nu < 3$ the critical dimension increases but does not "overtake" the particle dimensions; for $\nu = 3$ it remains unchanged, i.e., the supersaturation does not decrease; and for $\nu > 3$ the supersaturation in the system increases. This last statement indicates that the rate at which supersaturation comes about is so high that condensation on the existing nuclei does not ensure removal of the excess vapor; nucleation centers are formed continuously. Thus, the boundary for the unconditional applicability of the moment equations is $\nu \geq 3/2$; in all other cases they may be used only at the stage before the critical dimension has "overtaken" the distribution function. This is the stage to which the calculations of [2-5] are restricted. We can recommend an a posteriori estimate of the applicability of the moment equations: estimating particle dimension from the mathematical expectation and variance of the distribution function the minimum and comparing it with the critical dimension.

For a continuous regime of growth of condensate particles, we can carry out a similar analysis and distinguish the boundary values of ν. From the equation of diffusion growth of a particle

$$\frac{dr}{dt} = \frac{mD}{r_1^2\rho kTr}(p - p_r)$$

in a manner similar to (1.8), we obtain

$$\frac{dr}{d\tau_c} = \frac{1}{r}\left(\frac{1}{r_{cr}} - \frac{1}{r}\right), \quad d\tau_c = \frac{m\sigma^* D p_\infty}{r_1^2\rho kT}dt.$$

The analysis shows that for the relation $N = N_0\tau_c^\nu$ when $\nu < 1$ the critical dimension overtakes the particle dimensions, for $1 < \nu < 3/2$ it increases but does not catch up with r, and for $\nu > 3/2$ it is impossible to remove the supersaturation by condensation on the existing particles, so that r_{cr} decreases. It should be noted that the boundary for the removal of supersaturation in the free-molecule regime of growth is $\nu < 3$; therefore, when supersaturation is produced at a rate $\nu \in (3/2, 3)$ in the system after the formation of the nucleation centers, we have free-molecule growth of the centers and the supersaturation drops. However, as the particles increase in size, their regime of growth changes to a continuous regime which does not ensure removal of the vapors. Therefore the supersaturation increases once again, and we may have repeated formation of particles through nucleation. As a result, we obtain a bimodal or even polymodal aerosol.

The investigation we carried out relates to sufficiently large values of τ, and in this sense it is asymptotic ($S \to 1$); it does not enable us to consider the stage of nucleation-center formation and the immediately following stage of particle growth. We therefore carried out an additional numerical investigation of the process of condensation in an aerosol.

2. Numerical Investigation. The basis of this investigation is the chain of Becker-Döhring kinetic equations

$$\frac{dn_i}{dt} = \frac{c_{i-1}n_{i-1}}{1+\delta_{2i}} - (c_i + a_i)n_i + a_{i+1}n_{i+1}, \quad i = 2, 3 \ldots, \qquad (2.1)$$
$$n_1 = N_V - \sum_2^\infty in_i,$$

where n_i is the concentration of particles containing i molecules; c_i is the frequency of attachment and a_i is the frequency of detachment of vapor molecules; these are calculated from the well-known formulas:

$$c_i = \omega_i n_1, \quad a_i = \frac{\omega_i p_\infty}{kT} \exp\left(\frac{\sigma^*}{i^{1/3}}\right), \quad \omega_i = \alpha r_1^2 i^{2/3} \sqrt{\frac{8\pi kT}{m}};$$

the denominator of the first term on the right side of (2.1) (where δ_{2i} is the Kronecker delta) enables us to make sure that molecules in binary collisions are not counted twice.

We consider the isothermal process; then after the introduction of the dimensionless variables $S_i = \frac{n_i kT}{p_\infty}$, $\tau = \alpha r_1^2 p_\infty \sqrt{\frac{8\pi}{mkT}}\, t$ the system (2.1) takes the following form

$$\frac{dS_i}{d\tau} = (i-1)^{2/3} \frac{SS_{i-1}}{1+\delta_{2i}} - i^{2/3}\left(S + a_i^*\right) S_i + (i+1)^{2/3} a_{i+1}^* S_{i+1}, \quad (2.2)$$
$$S = S_V - \sum_2^\infty iS_i,$$

where $a_i^* = \exp\left(\frac{\sigma^*}{i^{1/3}}\right)$.

The initial conditions are: for all $i \geqslant 2$ we have $S_i = 0$ (there is no condensate); the quantity S_V varies with time according to the law $S_V = S_{V_0} + S_\tau \tau^\nu$. In its complete form the system (2.2) can be used for numerical calculation on computers only for small values of i ($i < 10^4$); we are interested in much larger values ($i \sim 10^{10}$–10^{15}). A direct solution of (2.2) for such values of i is impossible, but we do not need one; for sufficiently smooth distribution functions it is possible to aggregatize the system, i.e., to separate the particles into classes. The equations (2.1) for i = 3, 4, ... can be written in the form

$$dn_i/dt = g_i - g_{i+1}, \; g_i = c_{i-1} n_{i-1} - a_i n_i,$$

where g_i is the flux of particles in the space of dimensions. Then the number of particles containing between j and l molecules will be $n_{jl} = \sum_j^l n_i$ and can be determined from the equation

$$dn_{jl}/dt = g_j - g_{l+1}. \quad (2.3)$$

The expressions for the flux g_i are selected in accordance with the sign of the difference $(c_{i-1} - a_i)$:

$$g_i^- = c_{i-1}(n_{i-1} - n_i) + (c_{i-1} - a_i)\, n_i \approx -c_{i-1}\frac{\partial n}{\partial i} + (c_{i-1} - a_i)\, n_{il},$$
$$g_i^+ = a_i(n_{i-1} - n_i) + (c_{i-1} - a_i)\, n_{i-1} \approx -a_i\frac{\partial n}{\partial i} + (c_{i-1} - a_i)\, n_{ji},$$

and the quantity $\partial n/\partial i$ is is approximated in terms of n_{ji} and n_{il}. It is found that for values of $i < i_{cr}$ the diffusion coefficient in the space of dimensions is equal to c_{i-1}, while for $i > i_{cr}$ it is equal to a_i. The first value of the diffusion coefficient, c_{i-1}, was used in the subcritical region by Zel'dovich in deriving the formula for the rate of nucleation; in [1] Bakhanov used for the diffusion coefficient the expression $(c_{i-1} + a_i)/2$, which follows from the symmetric difference scheme he adopted. However, this cannot be considered satisfactory, since when $c \to 0$, the solution of the kinetic equation with such a diffusion coefficient differs greatly from the solution of the system (2.1).

The aggregatized system of equations (2.3) was solved by a rigidly stable numerical method. The most characteristic results of the calculations are shown in Figs. 1 and 2 ($\sigma^* = 10$, $S_{V_0} = 0$, $S_\tau = 1$). In Fig. 1a we show for different values of ν (ν = 1, 3 on curves 1, 3) the variation of the critical dimension r_{cr} and the average-mass dimension $\bar{r}$ of the particles in the aerosol; $r_{cr} = \sigma^*/\ln S$ is shown by the solid curves, and $\bar{r} = \left(\sum_2^\infty i^{4/3} S_i\right)\left(\sum_2^\infty iS_i\right)^{-1}$

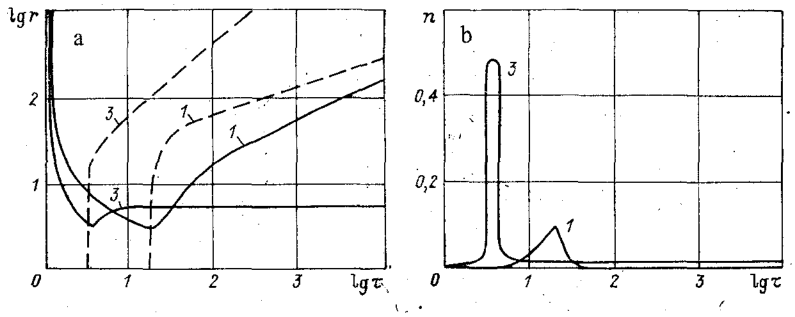

Fig. 1

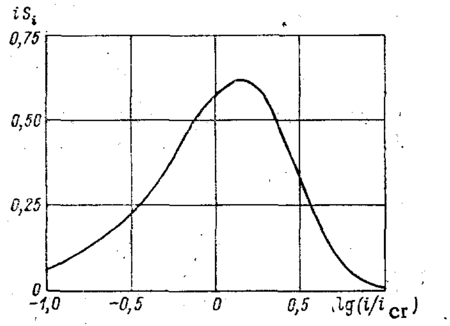

Fig. 2

by the dashed curves. The figure makes it clear how the critical dimension for the value ν = 1 (< 3/2) "overtakes" the average-mass dimension, while for $\nu = 3$ it does not change after the formation of nucleation centers. Figure 1b illustrates the influence of these processes on the calculated concentration of particles $n = \sum_{2}^{\infty} n_i = N_\infty \sum_{2}^{\infty} S_i$: in the first case ($\nu = 1$) after the stage of nucleation-center formation is completed, the number of particles in the aerosol decreases monotonically (because the smaller particles evaporate), but in the second case ($\nu = 3$) it remains constant. Figure 2 indicates that for values of $\nu < 3/2$ a large proportion of the aerosol particles may be in the subcritical region ($i < i_{cr}$); this figure shows the distribution of condensate particles according to size ($\nu = 1$, $\tau > 10^3$).

The calculation also showed that when $\nu < 3/2$, the rate of growth of the critical dimension for large values of τ is practically independent of ν. Moreover, if the distribution function is plotted logarithmically against time it does not change its shape but is displaced along the log i axis, i.e., there exists an asymptotic solution of the problem of condensation growth of a polydisperse aerosol.

3. Asymptotic Solution. Thus, our analytic and numerical investigations have shown that when $\nu < 3/2$ (for a free-molecule regime of particle growth) the critical dimension "overtakes" the distribution function. Smaller particles become subcritical and begin to evaporate, i.e., the total number of particles in the aerosol decreases. In order to ensure in this case the supersaturation is removed, the dimensions of the remaining particles must increase more rapidly than $\tau_f^{\nu/3}$. As the critical dimension approaches the value of r corresponding to the maximum of the distribution function, the number of particles going into the subcritical region per unit of time increases; consequently the rate of growth of the remaining particles increases even more. However, it cannot exceed the limit $r \sim \tau_f^{1/2}$, since for this value r_{cr} no longer "overtakes" r. As a result, r_{cr} and the aerosol particles increase like $\tau_f^{1/2} + o(\tau_f^{1/2})$.

This argument is only qualitative and is open to many objections. In what follows, however, we shall show that for $\nu < 3/2$, r_{cr} does in fact behave asymptotically like $\sqrt{\tau_f}$, and so do the average dimensions of the aerosol particles. Moreover, it is found that there exists an asymptotic form of the particle-size distribution function which depends only on a single parameter of the initial distribution function. We write the kinetic equation for the distribution function, using the expression for $dr/d\tau_f$ (1.8):

$$\frac{\partial f}{\partial \tau_f} + \frac{\partial}{\partial r}\left[\left(\frac{1}{r_{cr}} - \frac{1}{r}\right) f\right] = 0. \tag{3.1}$$

We assume that there exists a maximum particle dimension r_m such that $f(r) = 0$ when $r > r_m$. Such an assumption is valid for all real systems. In the variables $z = r/r_m$, $d\eta = d\tau_f/r_m^2$ Eq. (3.1) takes the form

$$\frac{\partial f}{\partial \eta} + \frac{\partial}{\partial z}\left[\left(b - \frac{1}{z}\right) f\right] - z(b-1)\frac{\partial f}{\partial z} = 0. \tag{3.2}$$

Here $b = r_m/r_{cr}$, and for $dr_m/d\tau_f$ we again use the expression (1.8). After introducing the new function

$$\varphi(z, \eta) = f\left[(b-1)z - b + \frac{1}{z}\right] \exp\left(\int\limits_0^\eta (b-1)\, d\eta\right)$$

into Eq. (3.2), we obtain

$$\frac{\partial \varphi}{\partial \eta} - \left[(b-1)z - b + \frac{1}{z}\right]\frac{\partial \varphi}{\partial z} + \frac{1-z}{(b-1)z - b + \frac{1}{z}}\frac{db}{d\eta}\varphi = 0. \tag{3.3}$$

As in the analysis of the system (1.8), (1.9), we use successive approximations. As our initial approximation, we take φ when $b = \text{const}$; the last term on the left in (3.3) then vanishes:

$$\frac{\partial \varphi}{\partial \eta} - \frac{z-1}{z}[(b-1)z - 1]\frac{\partial \varphi}{\partial z} = 0. \tag{3.4}$$

The equation of characteristics for (3.4) can be integrated; taking account of the fact that for large τ_f the values of $b \in [0, 2]$, we write the integral

$$(1-z)[1-(b-1)z]^{1/(1-b)} = C\exp[(2-b)\eta]. \tag{3.5}$$

For $\eta = 0$ we have

$$C = (1-z_0)[1-(b-1)z_0]^{1/(1-b)}. \tag{3.6}$$

An analysis of (3.5), (3.6) shows that the characteristic with $z_0 = 1$ is $z = 1$, while the characteristics with $z_0 < 1$ arrive at the point $z = 0$ at time $\eta = \ln C/(b-2)$, corresponding to the total evaporation of a particle with initial dimension z_0. Consequently, for large values of η the particle-size distribution is determined only by the largest particles of the initial aerosol, i.e., by particles for which $z_0 \lesssim 1$. In this case for C (3.6) we can use the expansion

$$C \approx (1-z_0)(2-b)^{1/(1-b)}. \tag{3.7}$$

Eliminating the the constant C between the equations (3.5) and (3.7), we find

$$1 - z_0 = (1-z)\left[\frac{2-b}{1-(b-1)z}\right]^{1/(b-1)} \exp[(b-2)\eta]. \tag{3.8}$$

Along the characteristic $\varphi(z, \eta) = \varphi_0[z_0(z, \eta)]$.

Suppose that the initial distribution function $f(z, 0)$ has in a neighborhood of $z = 1$ the form

$$f(z, 0) = f(z_0) = A(1-z_0)^\gamma,$$

i.e., at the point $z_0 = 1$ it takes on a nonzero value (for $\gamma = 0$) or tends to 0 at a different rate ($\gamma \neq 0$). Then from the definition of $\varphi(z, \eta)$, we have

$$\varphi_0(z_0) = A(1 - z_0)^{\gamma+1}[1/z_0 - b + 1] \approx A(2 - b)(1 - z_0)^{\gamma+1},$$

$$f(z, \eta) = \frac{A(2 - b)(1 - z_0)^{\gamma+1} z}{(1 - z)[1 - (b - 1)z]} \exp\left(-\int_0^{\eta} (b - 1)\, d\eta\right). \tag{3.9}$$

After substituting the value of $(1 - z_0)$ from (3.8) into (3.9), we obtain an asymptotic expression for $f(z, \eta)$:

$$f(z, \eta) = \psi(z, b)\left[2(b - 1)\tau_f + r_{m0}^2\right]^{\varkappa}, \quad \varkappa = \frac{(b - 2)(\gamma + 1)}{2(b - 1)} - \frac{1}{2}. \tag{3.10}$$

Here we have taken account of the fact that for $b = \text{const}$ it follows from $dr_m/d\tau_f = (b - 1)/r_m$ that

$$r_m^2 = 2(b - 1)\tau_f + r_{m0}^2, \quad \eta = \frac{1}{2(b - 1)} \ln\left[2(b - 1)\tau_f + r_{m0}^2\right].$$

The equation of material balance for the aerosol (1.9) in the nonmonodisperse case takes the form

$$\int_0^{r_m} f(r, \tau_f)\, r^3 dr = N_V - N_\infty - \frac{\sigma^* N_\infty}{r_{cr}}. \tag{3.11}$$

Substituting the relation (3.10) into the integral (3.11), we obtain

$$r_m^4 \int_0^1 f(z, \tau_f)\, z^3 dz = \left[2(b - 1)\tau_f + r_{m0}^2\right]^{\varkappa+2} \int_0^1 \psi(z, b)\, z^3 dz \approx N. \tag{3.12}$$

The last integral is independent of τ_f. For the sake of simplicity, we set $r_m \gg r_{m0}$, and from (3.12) we find for the case $N = N_0\tau_f^{\nu}$ that

$$\varkappa + 2 = \nu, \; b = 1 + (\gamma + 1)/(\gamma + 1 + 3 - 2\nu). \tag{3.13}$$

The asymptotic expression (3.9) for the distribution function $f(z, \tau_f)$ takes the form

$$f(z, \tau_f) = B_f \tau_f^{\nu-2} \frac{z(1 - z)^{\gamma}}{[1 - (b - 1)z]^{\gamma+5-2\nu}}, \tag{3.14}$$

where $B_f = A[2(b - 1)]^{\nu-2}(2 - b)^{\gamma+5-2\nu} = \text{const}(\tau_f, z)$. The second approximation for φ can be found as follows. If in (3.11) we do not disregard the terms $\sigma^* N_\infty / r_{cr}$, then the value b_2 determined from (3.12) will be time-dependent. Since $\sigma^* N_\infty/(r_{cr}N) \to 0$ for large values of τ_f, the term which must be added to the value of b found in the first approximation will be small. After substituting the value $b_2(\tau_f)$ found in this way into (3.3), we look for the second approximation φ_2. As τ_f increases, $\varphi_2 \to \varphi$. We can convince ourselves of this, for example, by expanding the left sides of (3.12) in a series in b in a neighborhood of the first approximation, determining the additive term $\Delta b(\tau_f)$ from this, and substituting it into (3.3). For the analysis it is quite possible to use a simple first approximation. Summing up our discussion thus far, we can say that we have proved the asymptotic convergence of the initial distribution function to the function (3.14), which depends only on the behavior of the initial function near $r = r_m$. For sufficiently large values of τ_f the maximum dimension increases according to the law $r_m = \sqrt{2(b - 1)\tau_f}$, and when there are no sources of vapor ($\nu = 0$), we have a more exact formula:

$$r_m = \sqrt{2(b - 1)\tau_f + r_{m0}^2}. \tag{3.15}$$

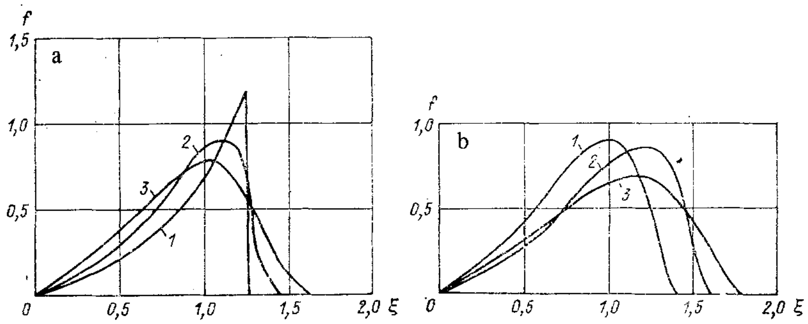

Fig. 3

Since $r_{cr} = r_m/b$, it follows that $r_{\text{cr}} \approx \sqrt{\frac{b-1}{b^2} 2\tau_f} \sim \tau_f^{1/2}$; the quantity $\sigma^* N_\infty / r_{cr} N$ when $N_\infty =$ const will approach 0 if $\nu > -1/2$. This last condition is the lower boundary for the existence of an asymptotic solution. The fact that the region of existence extends to negative values of ν is of some interest, since it indicates the existence of evaporation regimes (N decreases as time increases) for which the aerosol particles nevertheless grow.

Figure 3 shows the asymptotic distribution functions for $\gamma = 0$, 1, and 2 (curves 1-3, respectively) when $\nu = 0$ (Fig. 3a) and for $\nu = -0.5$, 0.5, and 1 (curves 1-3, respectively) when $\gamma = 2$ (Fig. 3b). The graphs show the normalized functions plotted against the coordinate $\xi = r/r_{cr} = bz$; the value $\xi = 1$ corresponds to the critical dimension. It can be seen that a large number of particles have subcritical dimensions; in most cases the maximum of the distribution function is also near $r = r_{cr}$.

From (3.14) we can also obtain the rate of growth of the average particle dimension.

To see this, we note that by the definition of average,

$$r_{ik}^{i-k} = \frac{\int\limits_0^{r_m} f(r, \tau_f)\, r^i dr}{\int\limits_0^{r_m} f(r, \tau_f)\, r^k dr} = \frac{r_m^{i+1}}{r_m^{k+1}} \frac{\int\limits_0^1 f(z, \tau_f)\, z^i dz}{\int\limits_0^1 f(z, \tau_f)\, z^k dz} = r_m^{i-k} L_i / L_k,$$

where

$$L_i = \int\limits_0^1 \frac{z^{i+1} (1-z)^\gamma\, dz}{[1-(b-1)z]^{\gamma+5-2\nu}} = \text{const}\,(\tau_f).$$

Therefore $r_{ik}(\tau_f) = C_{ik} r_m(\tau_f)$.

For a continuous regime of condensate particle growth we can carry out an analogous construction. In this case the kinetic equation

$$\frac{\partial f}{\partial \tau_c} + \frac{\partial}{\partial r}\left[\left(\frac{1}{r_{\text{cr}}} - \frac{1}{r}\right)\frac{f}{r}\right] = 0 \tag{3.16}$$

in the variables

$$\varphi = f\left[(b-1)z - \frac{b}{z} + \frac{1}{z^2}\right] \exp\left(\int\limits_0^\eta (b-1)\, d\eta\right), \quad z = \frac{r}{r_m}, \quad d\eta = \frac{d\tau_c}{r_m^3}$$

takes the following form for the first approximation to φ :

$$\frac{\partial \varphi}{\partial \eta} - \frac{z-1}{z^2}[(b-1)z^2 + (b-1)z - 1]\frac{\partial \varphi}{\partial z} = 0.$$

From this, after some transformations analogous to (3.5)-(3.14), we find

$$f(z, \tau_c) = B_c \tau_c^{\nu-4/3} z^2 (1-z)^\gamma (z-z_1)^{h_1(\gamma+1)-1} (z-z_2)^{h_2(\gamma+1)-1} \tag{3.17}$$

where $h_1 = z_1^2 (z_2 - 1)/(z_1 - z_2)$; $h_2 = z_2^2 (z_1 - 1)/(z_2 - z_1)$; $z_{1,2}$ are the roots of the equation $z^2 + z - 1/(b-1) = 0$; $b = 1 + (\gamma + 1)/(2(\gamma + 1) + 3 - 3\nu)$. Here $r_m = [3(b-1)\tau_c + r_{mo}^3]^{1/3}$, and the critical and average particle dimensions also behave in this way. An asymptotic solution exists for $-1/3 < \nu < 1$.

4. Comparison with Experimental Results.

We shall now consider some results which may be useful in practice. Thus, for aerosols formed through homogeneous nucleation, the values of γ may be very large. For very large values of γ the distribution functions (3.14) and (3.17) will tend, respectively, to

$$f_f \to B_f \tau_f^{\nu-2} \xi (2-\xi)^{2\nu-5} \exp\left[\frac{2(2\nu-3)}{2-\xi}\right]; \tag{4.1}$$

$$f_c \to B_c \tau_c^{\nu-4/3} \xi^2 \left[(\xi+3)^{5\nu-11}(2\xi-3)^{4\nu-7}\right]^{1/3} \exp\left[\frac{3(\nu-1)}{3-2\xi}\right]. \tag{4.2}$$

Here we again use the variable $\xi = r/r_{cr}$, as being more convenient for practical use and being determinable from the aerosol spectrum with greater accuracy. This can be seen if we multiply (3.1) and (3.16) by r^3 and integrate from 0 to ∞; in a manner analogous to (1.4), we obtain

$$d\Omega_3/d\tau_f = 3(\Omega_2/r_{cr} - \Omega_1), \quad d\Omega_3/d\tau_c = 3(\Omega_1/r_{cr} - \Omega_0).$$

If in the experiment the analysis of the disperse state of the aerosol was preceded by a period during which its mass remained almost unchanged (i.e., $d\Omega_3/d\tau \approx 0$), then $r_{cr} = r_{21}$ for free-molecule particle growth and $r_{cr} = r_{10}$ for continuous growth; therefore the value of r_{cr} can be determined with good accuracy. Since the formation of aerosols of nonvolatile compounds takes place at high temperatures, while the disperse analysis in most cases is carried out at room temperature, it follows that for applicability of asymptotic formulas we must have $\nu < 3/2$ (or $\nu < 1$) during the cooling period as well. The asymptotic distribution functions were found to be representable as the product of two functions: One of these depends only on time, while the other depends only on z. Therefore the normalized distribution function depends only on z, and when it is plotted logarithmically as $f(\ln r) = f(\ln z + \ln r_m)$, it remains unchanged in shape as time increases, simply shifting along the ln r axis.

The functions we have obtained are characterized by low dispersion (see Fig. 3); the maximum dimension is about 1.5-2 times the average dimension. On the other hand, dimension spectra actually observed have a much greater dispersion. This difference may perhaps be explained as follows. In most cases the temperature of the different parts of the volume in which the condensation takes place is nonuniform; the aerosol formation often takes place during the process of cooling of the suspension, i.e., when there is a temperature gradient in it. The dimensionless times τ_f and τ_c are proportional to the quantity p_∞, which is a sharply varying function of temperature: $p_\infty = p^* \exp(-l/RT)$ (where l is the heat of phase transition).

Suppose that the two parts of the volume have a temperature difference $T' - T'' = \Delta T$; then

$$p'_\infty = p''_\infty \exp\left(\frac{l\Delta T}{RT^2}\right), \quad \frac{r'_m}{r''_m} = \sqrt{\frac{\tau'_f}{\tau''_f}} = \exp\left(\frac{l\Delta T}{2RT^2}\right).$$

The complete distribution function is the sum of the distributions f' and f", which when plotted on log paper will be displaced from each other by a distance $l\Delta T/(2RT^2)$. If the density of the aerosol-particle suspension is the same throughout the volume, its colder regions will contain $[-3l\Delta T/(2RT^2)]$ times as many particles and will make the main contribution to the complete particle-size distribution function. When the suspension cools by giving up heat to the external environment (the wall of the vessel), the regions that are decisive (for the calculated concentration) will be those near the wall. In the first approximation, near the wall we may assume that $\partial T/\partial x = \text{const}$; then for the complete distribution function we can write (to within a constant factor) the following expression:

$$f(\ln \xi) = \int_0^\infty f(\ln \xi - \ln q)\, q^{-3} d \ln q, \tag{4.3}$$

where $\ln q = l(T - T_s)/(2RT_s^2)$, T_s is the wall temperature. This integral represents the summation of the calculated concentration of particles over the regions with different temperatures. Since there are few particles in the regions that have been heated more, the upper

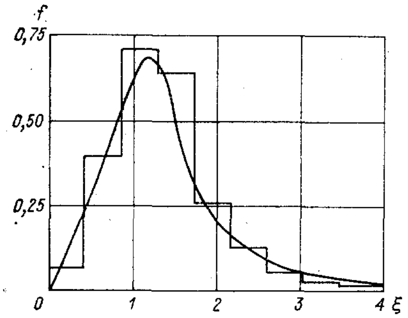

Fig. 4

limit extends to infinity. Substituting f_f from (4.1) into (4.3), we obtain

$$f(\xi)=\int_{q_0}^{\infty}\frac{\xi}{q}\left(2-\frac{\xi}{q}\right)^{2\nu-5}\exp\left[\frac{2(2\nu-3)}{2-\frac{\xi}{q}}\right]\frac{dq}{q^4}. \qquad (4.4)$$

Here $q_0 = 1$ for $\xi < 2$ and $q_0 = \xi/2$ for $\xi > 2$. For $\nu = 0$ it is possible to integrate (4.4):

$$f(\xi)=\begin{cases}\frac{1}{\xi^2}[2-(9u^3+9u^2+6u+2)\exp(-3u)], & \xi<2,\\ \frac{2}{\xi^3}, & \xi\geqslant 2,\end{cases} \qquad (4.5)$$

where $u = \xi/(2 - \xi)$.

The distribution function (4.5) corresponds to the formation of an aerosol during the process of cooling due to heat exchange with the external environment; there are no vapor sources. Such a case was realized, in particular, in the experiments of [6]; the suspension of oxide particles formed as the result of the combustion of magnesium powder became cooled when it moved in the reaction tube. Since the particle temperature was lower than the melting point of the oxide, there was no coagulation (this is confirmed by the fact that the aerosol contained only single crystals). In Fig. 4 the distribution function $f(\xi)$ of (4.5) is compared with the histogram* constructed from the results of the experiments in [6]; this scale factor in the transition from the experimental value of r to the dimensionless variable ξ was so chosen as to make maxima coincide.

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*The authors of [6] were kind enough to give us their results on the dispersity of the aerosol.