SOVIET PHYSICS JETP VOLUME 32, NUMBER 4 APRIL 1971

KINETICS OF FORMATION OF PORES FROM A SUPERSATURATED SOLUTION OF VACANCIES

Yu. V. MIKHAILOVA and L. A. MAKSIMOV

Submitted May 7, 1970

Zh. Eksp. Teor. Fiz. 59, 1368–1377 (October, 1970)

The kinetic equation describing the motion of the dimensions of a pore in space, is solved under the condition that at the initial instant of time all the vacancies are in the gaseous phase. During the first stage, so long as the supersaturation remains unchanged, the distribution of the pores by dimensions has the form of a stationary distribution with a constant flux, which is cut off at a dimension that is large compared with the critical dimension, and which increases with time. During the second stage the supersaturation decreases. Then the number of pores practically remains unchanged and the critical dimension gradually overtakes the maximum pore dimension. Estimates of the characteristic times of the process are presented.

1. INTRODUCTION

In a solid under the influence of neutron bombardment, a large number of vacancies and interstitial atoms are produced. The latter have relatively large mobility and rapidly emerge to the surface or annihilate with the vacancies. In thermal annealing, when the mobility of the vacancies becomes noticeable, and the concentration is still higher than the thermal equilibrium value, clusters of vacancies are produced in the form of multivacancies and pores.

We consider in this paper the kinetics of the condensation of vacancies, using the following formulation: at $t = 0$ there are only elementary vacancies, and it is required to describe the time evolution of the process. It is assumed in addition that the supersaturation by the vacancies is not too large. Such an assumption makes it possible to simplify the calculations and to delineate distinctly the main stages of the process. We propose to treat the problem of condensation of a strongly supersaturated system in a separate article.

The formation of pores (multivacancies) is a particular case of a first-order phase transition far from the critical point, when the metastable phase can be regarded as a rarefied gas, and the stable phase is precipitated in the form of drops or pores. Classical examples of such transitions are the condensation of vapor in air and precipitation in a supersaturated solution. Having in mind the deep analogy between these processes, we shall use henceforth the terminology of the classical processes, identifying the vacancies with molecules and the pores with drops.

The process of condensation has three stages. The first stage is characterized by intense decomposition of the supersaturated solution (vapor) and formation of nuclei of a new phase (drops, grains, pores). At this stage drops whose dimensions exceed the critical value are produced through fluctuations. The calculation of the steady-state flux in dimension space, corresponding to this process, has been the subject of most papers on condensation kinetics.[1-6] At this stage, our problem is to determine the time-dependent distribution function of the multivacancies by dimensions. The probabilities of evaporation and absorption of one vacancy by a multivacancy of a given dimension will be assumed known and we shall not dwell on the details of the calculation, confining ourselves only to model representations concerning these quantities. During the first stage, the total number of molecules in the liquid phase (volume) is small compared with the total number of molecules (vacancies) and the supersaturation is practically constant.

The second stage sets in when the volume becomes comparable with the total number of molecules and the supersaturation begins to drop. This stage is characterized by the fact that most drops have a supercritical dimension, and their number if practically constant. The volume increases mainly because the drops grow. For this stage we obtain the time dependence of the supersaturation and of the multivacancy dimension distribution function.

During the next, third stage, when most of the supersaturated vapor (vacancies) has already been consumed in the formation of nuclei (of multivacancies), the main role is played by the growth of large drops at the expense of dissolution of small ones (coalescence). The theory of coalescence has been constructed by I. M. Lifshitz and V. V. Slezov.[7] We can add nothing that is essentially new concerning this stage.

2. CONSTRUCTION OF MODEL

The time variation of the density N_n of multivacancies containing n elementary vacancies is described by the equation

$$\frac{\partial N}{\partial t} = -\frac{\partial}{\partial n}\left[IN - \frac{\partial}{\partial n}(QN) \right] \tag{2.1}$$

in which the term IN is the average flux of multivacancies in the space of numbers n. I is equal to the difference between the evaporation probability Q and the probability of absorption of an elementary vacancy. This difference is determined by the diffusion flux of the vapor of vacancies from the surface of the pore, which is assumed to be spherical:

$$I = 4\pi RDN_1^s\left(\frac{R_s}{R} - \frac{R_s}{R_c}\right). \tag{2.2}$$

Here R is the radius of the pore, D is the diffusion coefficient, and N_1^S the equilibrium concentration of the vacancies. The quantity $R_S = 2\alpha v/T$ (α is the surface-tension coefficient and v - the specific volume of the vacancies in the pore) determines the dependence of the density of vapor in equilibrium with the drop on the drop radius (at $R \gg R_S$):

$$N_1(R) = N_1^s(1 + R_s/R). \tag{2.3}$$

The critical radius of the drop R_c is determined by the density of the supersaturated vacancy vapor

$$N_1 = N_1^s(1 + R_s/R_c), \quad R_c \gg R_s. \tag{2.4}$$

The last term in (2.1) is of fluctuation origin and indicates a tendency towards equalization of the concentrations when the absorption and evaporation probabilities P and Q are close to each other:

$$P = Q - I, \quad Q = 4\pi R^2 c N_1^s(R). \tag{2.5}$$

Here c is a quantity of the order of the thermal velocity of the vacancy vapor ($c \approx a/\tau$, a is the lattice period, and $1/\tau$ is the frequency of the transfer of vacancies from one site to another).

It can be shown that the partial differential equation (2.1) can be used to describe the kinetics of condensation of drops whose dimensions are large compared with

$$R_i = (R_s v)^{1/4}. \tag{2.6}$$

In the present paper we consider the case of weak supersaturation, so that

$$R_c \gg R_i. \tag{2.7}$$

In this case the drops whose dimensions are smaller than R_i play a minor role, since within a very short time on the order of

$$t_i \approx (R_i/a)^3/Q(R_i) \tag{2.8}$$

there is established a local equilibrium between these drops; this equilibrium is subsequently not violated. Bearing this in mind, we shall solve Eq. (2.1) with the initial condition ($t = t_i$)

$$\begin{gathered} N_1 = N_1^s(1 + \Delta(0)), \\ N_n = 0, \quad n > n_i = {}^4/_3 \pi R_i^3/v \end{gathered} \tag{2.9}$$

and with the boundary condition

$$N_{n_i} = \text{const}, \quad t > t_i. \tag{2.10}$$

We are interested in times that are large compared with t_i, and in multivacancies whose dimensions are large compared with n_i. We shall therefore formally refer the initial condition to the instant t = 0, and the boundary condition to n = 0.

Finally, if there is no external source for the supersaturation of the vacancy vapor and the times in question are short enough to be able to neglect the emergence of the vacancies to the surface of the crystal, then the total number of vacancies both in the free state and in the form of pores should be regarded as specified by:

$$N_1 + \sum_{n \geq 2} n N_n = \text{const}. \tag{2.11}$$

3. KINETICS AT A SMALL CONSTANT SUPERSATURATION (INITIAL STAGE OF CONDENSATION)

The detailed form of (2.1) is

$$\frac{\partial N}{\partial t} = \frac{v}{4\pi R^2} \frac{\partial}{\partial R} \left[4\pi R D N_1^s \left(\frac{R_s}{R} - \frac{R_s}{R_c} \right) N + \frac{v}{4\pi R^2} \frac{\partial}{\partial R} (4\pi R^2 c N_1^s N) \right]. \tag{3.1}$$

We introduce "natural" measurement units:

$$\begin{gathered} \rho = R/R_k, \quad \sigma = \rho^2/2, \quad \tau = tvDR_sN_1^s/R_k^3, \\ 1 + \Delta = N_1/N_1^s, \quad x = R_c/R_k, \quad \Delta = R_s/R_k x, \\ g = N\rho \frac{2\sqrt{2}}{3} (4\pi/vR_k^3)^2/N_1^s, \quad R_k = vc/4\pi D R_s. \end{gathered} \tag{3.2}$$

In the new notation, the complete system of equations (3.1) and (2.11) has the simplest form

$$\begin{gathered} \frac{\partial g}{\partial t} = -\frac{\partial}{\partial \sigma} \left[\left(\frac{1}{x} - \frac{1}{\rho} \right) g - \frac{\partial g}{\partial \sigma} \right], \\ \Delta(0) = \Delta + V, \quad V = \int_0^\infty d\sigma \sigma^{3/2} g. \end{gathered} \tag{3.3}$$

Bearing in mind the remarks of the preceding section, we shall pay no attention to the fact that Eq. (3.3), strictly speaking, is not valid near zero.

The kinetic equation (3.3) can be regarded as a continuity equation in the space of the pore surfaces. The flux

$$j = \left(\frac{1}{x} - \frac{1}{\rho} \right) g - \frac{\partial g}{\partial \sigma} \tag{3.4}$$

consists of a hydrodynamic part with "velocity" $1/x - 1/\rho$ and a diffusion part with a diffusion coefficient equal to unity.

The static solution of the kinetic equation (3.3) corresponds to zero flux

$$j = 0; \quad g_x = b \exp\left[-\rho + (\rho^2/2x)\right]. \tag{3.5}$$

If the supersaturation value Δ is negative ($x < 0$), then the function g_x specifies the distribution of the "heterophase fluctuations" of the unsaturated vapor,[4] if $\Delta = 0$ then the function g_∞ specifies the thermodynamic-equilibrium distribution of the drops by dimensions in the saturated vapor

$$g_\infty = be^{-\rho}. \tag{3.6}$$

A similar distribution in the pure saturated vapor takes the form of the Boltzmann distribution connected with the surface energy of the drop.[4] The distribution (3.6) for vapor in a medium reflects the fact that the minimum work necessary to produce in the vapor a quasi-stationary state of a drop includes additional energy of the diffusion vapor cloud with increased partial pressure. Formula (3.6) casts no doubts on the expression (2.3), since it is derived by considering a vapor in equilibrium with the drop, and in this case the partial pressure does not depend on the distance to the drop, and there is no diffusion cloud.

The total number N_1^S of molecules in the liquid phase, per unit volume and per unit density, is equal, for a uniform distribution, to

$$V_\infty = \int_0^\infty d\sigma\, \sigma^{3/2} g_\infty = 6\sqrt{2} b. \tag{3.7}$$

Since for saturated vapor the fraction of molecules in the drops is small compared with the number of molecules in the free state, $V_\infty \ll 1$ and consequently $b \ll 1$. Obviously, a system in the state (2.9) is supersaturated only if $\Delta(0) > V_\infty$. We shall henceforth use the parameter b as a boundary condition for the nonequilibrium distribution function (see the remarks following (2.10)):

$$g|_{\rho=0} = b. \tag{3.8}$$

If $\Delta > 0$ ($x > 0$), the distribution (3.5) is close to the equilibrium distribution (3.6) for $\rho \ll x$, reaches a minimum when $\rho = x$, and increases without limit for $\rho > x$.

In solving the system (3.3) with the initial condition

$$g|_{t=0} = 0 \tag{3.9}$$

the supersaturation is practically constant so long as the number of molecules in the liquid phase is small compared with the total number of molecules (initial stage of condensation):

$$V \ll \Delta(0). \tag{3.10}$$

If the initial supersaturation is large, so that $\Delta(0) \gg V_\infty$ (but $\Delta(0) \ll 1$), then the first stage with constant supersaturation is well prolonged and is of interest in itself.

The main idea of solving the problem of condensation during this stage lies in the fact that the rate of establishment of local equilibrium between the number of drops of close dimensions, characterized by a unity diffusion coefficient, greatly exceeds the "hydrodynamic rate" of change of distribution after local equilibrium has been established. It is therefore natural to assume that the solution of the problem will be a local equilibrium distribution cut off at a certain value $\rho = y$ that depends on time.

Let us find the formal distribution G, which is a local equilibrium one at all values of ρ, and which is finite at infinity. Such a distribution is the stationary (x = const) solution of the kinetic equation (3.3). Putting in (3.4) $j = j_x$ = const, we get

$$j = (1/x - 1/\rho)G - \partial G/\partial\sigma;$$
$$G = g_x(1-\varphi), \quad \varphi = \int_0 d\sigma\, j g_x^{-1}. \tag{3.11}$$

This distribution is finite at infinity if

$$\varphi(\infty) = \int_0^\infty d\sigma\, j g_x^{-1} = 1. \tag{3.12}$$

By the saddle-point method we obtain

$$j = j_x = \frac{1}{\sqrt{2\pi x^3}} g_x(x) = \frac{b}{\sqrt{2\pi x^3}} \exp\left[-\frac{x}{2}\right]. \tag{3.13}$$

The function G decreases monotonically with increasing ρ:

$$G = \begin{cases} g_x(\rho), & \rho < x - \sqrt{x}, \\ {}^1/_2 g_x(x)\,[1 - (\rho - x)/\sqrt{\pi x}], & \rho \approx x, \\ j(1/x - 1/\rho)^{-1} \to xj, & \rho > x + \sqrt{x}. \end{cases} \tag{3.14}$$

The lower expression is obtained directly from the definition of the flux (3.11), in which it is necessary to neglect the diffusion term, which is small when $\rho \gg x$.

The behavior of the function G is a reflection of the fact that the system of supersaturated vapor is stable against fluctuations in the formation of the drops (pores) whose dimensions are smaller than critical, and therefore when $\rho \ll x$ the distribution G coincides with the equilibrium distribution. The system of supersaturated vapor is unstable with respect to drops of supercritical size. Large drops increase with an overwhelming fraction of the probability.

We seek the solution of the kinetic equation (3.3) the form

$$g = G\psi. \tag{3.15}$$

Substituting (3.15) in the kinetic equation (3.3), we obtain

$$\frac{\partial\psi}{\partial\tau} = -u\frac{\partial\psi}{\partial\sigma} + \frac{\partial^2\psi}{\partial\sigma^2}, \quad \psi|_{\tau=0} = 0, \quad \psi|_{\rho=0} = 1, \tag{3.16}$$

$u = j - G^{-1}\partial G/\partial\sigma$ is the hydrodynamic velocity and is always positive in this equation:

$$u = \frac{2j}{G} + \left(\frac{1}{\rho} - \frac{1}{x}\right) = \frac{1}{x}\begin{cases} x/\rho - 1, & \rho < x - \sqrt{x} \\ 4/\sqrt{2\pi x} + (4/\pi - 1)(\rho - x)/x, & \rho \approx x \\ 1 - x/\rho \to 1. & \rho > x + \sqrt{x} \end{cases} \tag{3.17}$$

It is more convenient to solve (3.16) relative to $\psi = \partial\psi/\partial\tau$:

$$\frac{\partial\dot\psi}{\partial\tau} = -u\frac{\partial\dot\psi}{\partial\sigma} + \frac{\partial^2\dot\psi}{\partial\sigma^2}, \quad \dot\psi|_{\sigma=0} = \delta(\tau), \quad \dot\psi|_{\tau=0} = 0. \tag{3.18}$$

In the zeroth approximation we neglect in (3.18) the term with the second derivative

$$\frac{\partial\dot\psi}{\partial\tau} = -u\frac{\partial\dot\psi}{\partial\sigma}, \quad \dot\psi = \delta(\tau - T). \tag{3.19}$$

The function $T(\rho)$ is a solution of the equation

$$\frac{dT}{d\sigma} = \frac{1}{u}, \quad T|_{\sigma=0} = 0, \quad T = \int_0^\sigma \frac{d\sigma'}{u}. \tag{3.20}$$

We obtain a more accurate solution by replacing (3.18) with

$$\frac{\partial\dot\psi}{\partial\tau} = \chi\frac{\partial^2\dot\psi}{\partial z^2}, \quad z = T - \tau,$$
$$\chi = u^{-2}|_{z=0}, \quad s = \int_0^\tau \chi\, d\tau'. \tag{3.21}$$

It is easy to verify that the conditions for the applicability of the solution (3.21)

$$T \gg \sqrt{s}, \quad \sqrt{s}\, du/dT \ll u, \tag{3.22}$$

have been satisfied. The first inequality shows that the zeroth approximation describes correctly the behavior of the function ψ. We see that the variation of the distribution function with time is described approximately by the formula

$$g = G\Theta(\tau - \tilde{T}(\rho)) = G\Theta(y - \rho), \quad T(y) = \tau,$$
$$\Theta(y) = \begin{cases} 0, y < 0, \\ 1, y > 0. \end{cases} \tag{3.23}$$

Thus, at a constant supersaturation the kinetics of the process of condensation is such that at any instant of time the distribution is in local equilibrium everywhere except in a narrow vicinity of the front $\rho = y$, and the region $(0, y)$ is filled while the region (y, ∞) is empty.

Let us write out the explicit form of the function responsible for the motion of the front:

$$T(\rho)=\begin{cases} x^3\left[\ln\dfrac{x}{x-\rho}-\rho/x-\dfrac{1}{2}\dfrac{\rho^2}{x^2}\right], & \rho<x-\sqrt{x},\\ {}^1\!/_2x^3\ln x, & \rho=x-\sqrt{x},\\ {}^1\!/_2x^3(\ln x+\sqrt{2\pi}), & \rho=x+\sqrt{x},\\ x\sigma^{-}, & \rho\gg x. \end{cases} \tag{3.24}$$

We note that according to (3.23) nuclei of critical dimension are produced within a time

$$t_L=x_0{}^3\ln x_0,\quad x_0=x|_{t=0}. \tag{3.25}$$

Let us find the time dependence of the supersaturation at small values of time. Substituting (3.23) in the conservation law (3.3) we get

$$\Delta(0)=\Delta+\int\limits_0^{\sigma_y}d\sigma\,\sigma^{3/2}G,\quad \sigma_y=y^2/2. \tag{3.26}$$

Let us estimate the integral

$$V(\sigma)=\int\limits_0^{\sigma}d\sigma\,\sigma^{3/2}G,\quad \sigma\gg x^2/2. \tag{3.27}$$

When ρ increases from zero to $\sqrt{x}$, this integral reaches rapidly a value V_∞. The region from $\sqrt{x}$ to x adds very little. With further increase of ρ, the function G tends to a constant value and

$$V=V_\infty+(\sigma_y/\sigma_M)^{5/2}\Delta(0),$$
$$\Delta(0)\left(\frac{1}{\sigma_M}\right)^{5/2}=\frac{2}{5}x_0j_{x_0}. \tag{3.28}$$

It is clear from (3.28) that so long as the states with $\sigma\approx\sigma_M$ remain unfilled, saturation is practically constant. Since according to (3.23) $\sigma_y=\tau/x$ when $y\gg x$, we obtain from (3.26) for small values of time

$$x_0/x=1-(\tau/\tau_M)^{5/2},\quad \tau_M=x_0\sigma_M, \tag{3.29}$$

where τ_M determines the duration of the initial stage. We emphasize that the supersaturation begins to change when the lion's share of the molecules in the liquid phase are in drops with supercritical dimensions, and the distribution of the latter is approximately constant up to $\rho=y(y\gg x)$.

4. KINETICS AT VARIABLE SUPERSATURATION (SECOND AND THIRD STAGES OF CONDENSATION)

In the course of time, the number of vacancies (molecules) V in the condensed state increases approaching the value $\Delta(0)$. The concentration of the molecules in the free state then decreases and the critical dimension becomes a monotonically increasing function of time, thereby greatly complicating the problem. However, so long as the times are not too large, the main final result of the preceding section, namely that most drops (pores) have dimensions larger than the critical, remains in force. Such drops grow monotonically with a hydrodynamic rate $u=1/x$ and fluctuations are of no importance for them. The kinetic equation (3.3) then degenerates into the simple equation

$$\frac{\partial g}{\partial\tau}=-\frac{\partial}{\partial\sigma}\left(\frac{g}{x}\right), \tag{4.1}$$

according to which the function g is an arbitrary function of one argument

$$g=g(\sigma-\sigma_y(\tau)),\quad \sigma_y=\int\limits_0^{\tau}\frac{d\tau}{x(\tau)}. \tag{4.2}$$

The form of this function is determined, first, by the initial condition (at $\tau=\tau_0$ we have $x_0^3\ll\tau_0\ll\tau_M$), and it is natural to choose as the initial condition the distribution of the large drops (3.23), obtained in the preceding section:

$$g(\tau=\tau_0)=\begin{cases} x_0j_{x_0}, & \sigma<\sigma_y(\tau)\\ 0, & \sigma>\sigma_y(\tau) \end{cases}. \tag{4.3}$$

Second, the form of the solution of (4.1) is determined from the boundary condition, i.e., from the distribution of the drops whose dimensions are relatively close to critical. For small dimensions, the distribution of the multivacancies is close to $G(\rho, x(\tau))$. Indeed, the function G satisfying the Eq. (3.11) describes well the solution of the kinetic equation (3.3) far from the front, if the left side of this equation (3.3) is small compared with any term on the right-hand side of this equation. In particular, it is necessary to satisfy the inequality

$$\left|\frac{\partial^2G}{\partial\sigma^2}\right|\gg\left|\frac{\partial G}{\partial\tau}\right|=\left|\frac{\partial G}{\partial x}\frac{dx}{d\tau}\right|. \tag{4.4}$$

Substituting in this inequality the function (3.14), we find that the inequality (4.4) is satisfied for all the dimensions smaller than or of the order of critical, if

$$dx/d\tau\ll 1/x^3. \tag{4.5}$$

Assuming the condition (4.5) to be satisfied, we can assume as the boundary condition for (4.2)

$$g=[xj_x]_{x=x(\tau)}\quad\text{as}\quad\sigma\to 0. \tag{4.6}$$

Thus, we find that the distribution of the drops (pores) of large dimension for variable supersaturation is given by

$$g=\begin{cases} [xj_x]_{x=x(\tau')}, & \sigma<\sigma_y(\tau),\\ 0, & \sigma>\sigma_y(\tau), \end{cases} \tag{4.7}$$

and the delayed instant of time τ' is determined from the equation

$$\sigma_y(\tau)-\sigma=\sigma_y(\tau');\quad \sigma=\int\limits_{\tau'}^{\tau}\frac{d\tau}{x}. \tag{4.8}$$

Inclusion of the second derivative in (4.1) shows that the width of the front is equal to $\sqrt{\tau}$.[1] The flux j_x at the critical point drops exponentially with increasing x, and therefore the main part of the drops is concentrated in the region near the front, their number being practically constant.

The dependence of the critical dimension on time is obtained by substituting the obtained distribution (4.7) in the conservation law (3.3):

$$1=\frac{x_0}{x}+\frac{5}{2}\left(\frac{1}{\sigma_M}\right)^{5/2}\int\limits_0^{\sigma_y}d\sigma\,\sigma^{3/2}\exp[x_0-x(\tau')]. \tag{4.9}$$

So long as x is close to its initial value, Eq. (4.9) does not differ from (3.28). At large values of the time, Eq. (4.9) takes the form

$$1=\frac{x_0}{x}+\left(C\frac{\sigma_y}{\sigma_M}\right)^{3/2};\quad \tau\gg\tau_M, \tag{4.10}$$

---

[1] The more accurate expression for Eq. (4.7) is

$$g(\tau,\sigma)=\int\limits_0^{\tau}d\tau' j_{x(\tau')}\frac{1}{\sqrt{4\pi(\tau-\tau')}}\exp\left[-\frac{1}{4(\tau-\tau')}\left(\sigma-\int\limits_{\tau'}^{\tau}\frac{d\tau}{x}\right)^2\right].$$

where C is a number of the order of unity.

Substituting here the expression for σ_y in terms of x (see (4.2)), we get

$$x = x_0 \exp\left({}^3/_2 C\tau / \tau_M\right). \tag{4.11}$$

Thus, the supersaturation decreases exponentially with a half life of the order of τ_M. The front grows in this case very slowly. The volume $\sigma_y^{3/2}$ of the pores (drops) increases in accordance with (4.11) only by a factor of two when the critical dimension changes from the value $2x_0$ to very large dimensions (when $x_0/x \ll 1$).

The preceding analysis was based on the assumption (4.5) and on the condition $y \gg x$. These inequalities cease to be valid in times of the order of

$$\tau_P = \tau_M \ln \tau_M. \tag{4.12}$$

The violation of the inequality (4.5) is immaterial, since it only leads to the result that in the region of drops whose dimensions are close to critical there is not enough time for the establishment of a state of the same type as in the case of constant supersaturation. However, during this stage only an insignificant number of particles is present in this region, and the lack of information concerning these particles is of no importance.

Violation of the inequality $y \gg x$ makes Eq. (4.10) incorrect. Indeed, this equation virtually implies that the number of supercritical drops is constant. When the critical dimension x catches up with the frontal point, then the dimensions of a certain fraction of the drops of the main group become subcritical, and these drops begin to evaporate intensively so that their number decreases rapidly. At this instant, a new stage of the process begins, during which the ratio y/x exceeds only insignificantly unity, and remains at approximately the same level. Since the exact equation of motion of the front is

$$d\sigma_y / d\tau = 1/x - 1/y \tag{4.13}$$

we get from the condition y/x = const

$$y = {}^3/_2 x, \qquad x^3 = {}^4/_9 \tau. \tag{4.14}$$

We have thus arrived at the coalescence process (4.14), which was analyzed in detail in [7]. This process is characterized by the fact that the critical dimension increases approximately like $t^{1/3}$, and the leading front of the distribution lies in the vicinity of 3x/2. We shall not consider this stage in the present paper.

In conclusion we present the characteristic times of the process: the time during which nuclei of critical dimensions are produced is

$$\tau_L \approx x_0{}^3 \ln x_0; \tag{4.15}$$

The time during which the critical dimension remains constant is

$$\tau_M \approx x_0{}^{4} \exp(x_0/5); \tag{4.16}$$

The time during which the critical dimension changes by a factor of two is

$$\tau_N \approx \tau_M; \tag{4.17}$$

The time of start of coalescence is

$$\tau_P \approx \tau_M \ln \tau_M. \tag{4.18}$$

The authors are sincerely grateful to I. M. Lifshitz and V. V. Slezov for a useful discussion that resulted in an appreciable revision of the present article, and to Yu. M. Kagan and V. V. Vasil'ev for interest in the work.

---

[1] H. Volmer, Kinetik der Phasenbildung, 1939.

[2] R. Becker and W. Doring, Ann. d. Phys., **24**, 719 (1935).

[3] Ya. B. Zel'dovich, Zh. Eksp. Teor. Fiz. **12**, 525 (1942).

[4] Ya. I. Frenkel', Statisticheskaya fizika (Statistical Physics), AN SSSR, 1948.

[5] Yu. Kagan, ZhFKh (Journal of Physical Chemistry) **34**, 92 (1960).

[6] V. I. Vladimirov and Sh. Kh. Khannakov, FMM **26**, 409 (1968).

[7] I. M. Lifshitz and V. V. Slezov, Zh. Eksp. Teor. Fiz. **35**, 479 (1958) [Sov. Phys.-JETP **8**, 331 (1959)].

Translated by J. G. Adashko
157