On the theory of phase transformations with position-dependent nucleation rates

N V Alekseechkin

'Kharkov Institute of Physics and Technology' National Science Centre,
Akademicheskaya Street 1, Kharkov 61108, Ukraine

E-mail: n.alex@kipt.kharkov.ua

Abstract
An expression for the phase volume fraction in a system with a position-dependent nucleation rate is derived in the framework of the geometrical-probabilistic approach. As examples of such systems, the following cases are considered: (1) nucleation on surfaces, on curves and at points; (2) nucleation on a finite domain. The volume fractions are derived for both time-dependent nucleation rate and time-dependent growth velocity for the following systems: (a) a planar layer with nucleation on the mid-plane, an infinitely long cylinder with nucleation on the axis and a sphere with nucleation at the centre; (b) random planes, straight lines and points in infinite space; (c) a spherical domain. The equivalence of the processes of homogeneous nucleation and nucleation at points is established. The solutions for both homogeneous and heterogeneous nucleations are obtained for case (c). It is shown that the finiteness property results in the qualitative distinction of the volume-fraction time dependence from that in infinite space: the Avrami exponent in the process of homogeneous nucleation decreases with time from 4 to 1.

1. Introduction

The probabilistic phenomenological approach to the description of a phase transformation process is based on the notion of centres of a new phase appearing, around which the accretion of the substance proceeds at some rate. Correspondingly, two functions are used: the nucleation rate $I(t)$ of the new-phase centres and their growth velocity $u(t)$. The aim is to derive the temporal characteristics of the process, such as: the volume fraction $X(t)$ of the new phase, the size distribution function of the nuclei and the perimeter (in 2D) or the area (in 3D) of the grain boundaries.

The acceptance of a hypothesis regarding the nucleation-and-growth pattern constitutes the initial premise of the phenomenological model. Justification of the premises accepted is carried out in the corresponding field where this model is used, e.g. crystallography. The purpose of the phenomenological theory is the development of methods for deriving final results starting from these premises.

The starting points of Kolmogorov's model [1, 2] are the following.

(1) The volume in which a phase transformation process proceeds is infinite. Practically, this implies that $\bar{L} \ll R_0$, where $\bar{L}$ is the mean nucleus size, R_0 is the system size.
(2) The nucleation rate may depend on time, but does not depend on coordinates. The probability of the new-phase centre appearing in volume V in dt' is equal to $I(t')V\,dt'$.
(3) The initial size R_c of a nucleus is equal to zero. Practically, this implies that $R_c \ll \bar{L}$.
(4) The uniformity of the growth rate: all of the nuclei at time t grow at the same linear velocity $u(t)$. Thus, for example, the growth velocity of a nucleus cannot be a function of its radius, i.e. depend on the appearance time t'. More precisely, the growth law allowed is formulated in reference [1] as follows. The accretion of substance around the new-phase centre proceeds with the linear rate

$$\tilde{u}(t, \vec{n}) = u(t)c(\vec{n}) \tag{1}$$

where $\vec{n}$ is a unit vector directed outwards from this centre; the function $c(\vec{n}) \equiv c(\theta, \phi)$ is such that the extreme points of the vectors of length $c(\vec{n})$ drawn from the origin in all of the directions $\vec{n}$ form a convex surface. Thus, though the growth rate is allowed to depend on direction, this dependence must be the same at every point.
(5) From this fact, the restriction on the shape of nuclei follows: the principle of geometrical similarity as regards the shape of nuclei. It may be an arbitrary convex shape, but all of the nuclei must be geometrically similar to each other and have the same orientation in the space.

From (1), the size of a nucleus in the direction $\vec{n}$ is

$$\tilde{R}_{\vec{n}}(t', t) = R(t', t)c(\vec{n}) \tag{2}$$

where

$$R(t', t) = \int_{t'}^{t} u(\tau)\,d\tau$$

is the radius of a spherical nucleus. The increment of the nucleus volume in dt in the direction $\vec{n}$ is equal to $d\tilde{V}_{\vec{n}}(t', t) = R^2(t', t)\,dR(t', t)\,c^3(\vec{n})\,d\Omega$, where $d\Omega = \sin\theta\,d\theta\,d\phi$ is the solid-angle element. Hence, the volume of a nucleus at t is $\tilde{V}(t', t) = V(t', t)c^3$, where

$$c^3 = \frac{1}{4\pi}\int_{\Omega} c^3(\vec{n})\,d\Omega \tag{3}$$

and $V(t', t) = (4\pi/3)R^3(t', t)$ is the volume of a spherical nucleus. Setting $g \equiv (4\pi/3)c^3$, we obtain $\tilde{V}(t', t) = gR^3(t', t)$, where g is the shape constant.

As regards the interaction of nuclei during the growth process, two main types may be singled out [2].

(1) When two nuclei collide, the growth of each of them is stopped in the direction of the collision front, but continued in an ordinary way into the untransformed region. As a result, a boundary is formed between these nuclei and a structure consisting of a set of grains of irregular shape is obtained in the final state.
(2) Two colliding nuclei coalesce as two droplets into one nucleus of larger size.

The KJMA theory [1, 3, 4] deals with the first type only; the models with droplet interaction are not included in this theory.

In view of the fact that the KJMA theory describes a process at the formal mathematical level, the fields of its application are diverse and not restricted to problems in crystallography. Examples of applications are presented, in particular, in the recent work [5], where an extensive literature relating to this theory is also given. Other examples are presented in reference [2]:

models of active biological media; models of forming foams; statistical models in the evolutional theory of populations; models of forming clouds; generally, models of propagation of signals of arbitrary nature which originate from the disturbance sources appearing randomly.

In the present paper, the extension of the KJMA theory to the case of position-dependent nucleation rate, as well as to finite systems, is carried out. In other words, the first and second restrictions on the KJMA model from the list above are removed. To do this, the critical region method is used. Earlier it was applied by the author to the problem of calculating volume fractions of competing phases [6]. It should be pointed out that the critical region concept itself was introduced by Kolmogorov in reference [1], though no specific term for this region is used therein. The result of Kolmogorov's approach can be formulated in the following form: the probability for an arbitrary point O′ of a system to remain untransformed at time t is

$$Q(t) = \exp[-Y(t)] \qquad \text{where } Y(t) = \int_0^t I(t')\tilde{V}(t', t)\,\mathrm{d}t'. \tag{4}$$

In other words, this is the probability that no centre of a new phase appears inside the critical region ($\tilde{V}(t', t)$ is its volume at t').

In the case of a position-dependent nucleation rate, expression (4) must be replaced by the following one:

$$Q(\vec{r}_0, t) = \exp[-Y(\vec{r}_0, t)] \tag{5}$$

where $\vec{r}_0$ is the radius vector of the point O′.

The functions $Y(t)$ and $Y(\vec{r}_0, t)$, calculated according to the algorithm of reference [1], are expressed in terms of an integral over the critical region. So, for the problem considered here, $Y(\vec{r}_0, t)$ must have the following form:

$$Y(\vec{r}_0, t) = \int_{t_0}^t \mathrm{d}t' \int_{\tilde{V}(t', t)} I_{\vec{r}_0}(\vec{r}', t')\,\mathrm{d}^3\vec{r}'. \tag{6}$$

In the case of several competing phases [6] with nuclei of spherical shape, the following expression may be written for the kth phase:

$$Y_k(t) = \int_0^t \mathrm{d}t' \int_0^{R_k(t', t)} I_k(t')q^{(k-1)}(t', r)(4\pi r^2)\,\mathrm{d}r \tag{7}$$

where $q^{(k-1)}(t', r)$ is the untransformed part of the critical region for the kth phase [6].

In this sense, the case (4) of $Y(t)$ may be thought of as the simplest one. Thus, the method of Kolmogorov is a 'differential' method with respect to time, but an 'integral' method with respect to the spatial variable. That is, the finite quantity $\tilde{V}(t', t)$ is used in deriving expressions (4), (5).

The proposed method differs from Kolmogorov's one in that it is a 'differential' method with respect to both time and the spatial variables: the differential of $V(t', t)$ is used for deriving the volume-fraction expression. As a result, the solution is expressed in terms of integrals over the time variables only, which is convenient for analysis of the dependences obtained [6]. Therefore, this method, as a 'finer' instrument for calculating volume fractions, is more effective in some cases. In particular, this advantage manifests itself in solving the present problem: it is natural to operate with $\mathrm{d}V$ rather than V in the case of a position-dependent nucleation rate.

In those problems where this distinction between the two approaches is not significant and the probabilistic reasoning is like that of reference [1], the use of the result (5) of Kolmogorov's approach permits one to get the solution in the shortest way (see sections 3 and 5).

The following two special cases of systems with non-homogeneous nucleation rates are significant for applications.

(1) Nucleation on different i-dimensional objects, $i < 3$: surfaces, lines and points (the nucleation rate may be represented as a δ-function of the coordinates).
(2) Nucleation on a finite domain G. The nucleation rate at the point $A(\vec{r})$ of the space has the form of a step function:

$$I(\vec{r}, t) = \begin{cases} I_0(\vec{r}, t) & A(\vec{r}) \in G \\ 0 & A(\vec{r}) \notin G. \end{cases}$$

In a simpler case, I_0 does not depend on $\vec{r}$.

This paper is organized as follows. In section 2, the general expression for the volume fraction for a position-dependent nucleation rate is derived. In section 3, the expressions for volume fractions of an infinite plate with nucleation on the mid-plane, an infinite cylinder with nucleation on the axis and a sphere with nucleation at the centre are obtained. The problem of calculating volume fractions when the nucleation occurs on planes, straight lines and at points randomly distributed in infinite space is solved in section 4. Sections 5–7 are devoted to calculating the volume fraction in a spherical domain. A discussion of the results is given in section 8.

2. Calculating the volume fraction in the case of a position-dependent nucleation rate

Let us introduce the frame of reference with the point O as the origin (figure 1). We seek the probability $\mathrm{d}X(t)$ that the point $\mathrm{O}'(\vec{r}_0)$ randomly chosen in the system will be transformed in the time interval $[t, t + \mathrm{d}t]$. In order for this event take place, it is necessary and sufficient to have the fulfilment of the following two conditions:

(1) the point O is not transformed before time t;
(2) the new-phase nucleus that can transform the point O' in the time interval $[t, t + \mathrm{d}t]$ appears at any time t', $0 \leqslant t' \leqslant t$; we call this nucleus a critical one.

Let $Q(\vec{r}_0, t)$ and $\mathrm{d}Y(\vec{r}_0, t)$ denote the probabilities of the first and second events, respectively. We deal with nuclei of spherical shape below. The case of an arbitrary shape permitted by Kolmogorov's model can be considered similarly without difficulties of principle. Consider the space-time scheme of the process which results in the fulfilment of both conditions.
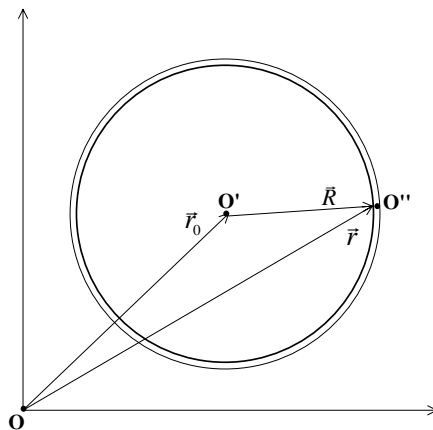
Figure 1. The framework used to derive the expression for the volume fraction in the case of a position-dependent nucleation rate.

Let us specify the spherical region of radius $R(t', t)$ with the point O′ as the centre—the critical region. At time t' the region boundary is moving towards the centre at the velocity $u(t')$, so the radius decreases from its greatest value $R(0, t) \equiv R_m(t)$ to $R(t, t) = 0$. As this happens, the fulfilment of condition (1) implies that the appearance of the new-phase nuclei is forbidden within this region in the time interval $0 \leqslant t' \leqslant t$. In reference [1], the function $Q(t)$ is calculated from this condition directly. In the present approach, condition (2) is used for its calculation.

The critical centre appearing at t' must lie inside the spherical layer of thickness $dR(t', t) = (\partial R(t', t)/\partial t)\, dt$ at the distance $R(t', t)$ from the point O′. Let it appear in the volume element $dV(\vec{r})$ in the neighbourhood of the point $O''(\vec{r})$ (figure 1). This nucleation process is not Poissonian with respect to either t or $\vec{r}$ since the nucleation rate depends on these variables; i.e. the property of stationarity [7] of this process is not satisfied. However, we assume the fulfilment of the remaining two properties of a Poisson process:

(a) the probability of the appearance of a centre in the four-dimensional volume element $dt'\, dV(\vec{r})$ is equal to $dP_{\vec{r}} = I(\vec{r}, t')\, dt'\, dV(\vec{r})$, and the probability of the appearance of more than one centre is an infinitesimally small quantity in comparison with it;

(b) the numbers of centres appearing in two disjoint volumes are independent quantities.

In order to get the probability $dP_{\vec{r}_0}(t', t)$ of the appearance of a critical centre at t', we must integrate $dP_{\vec{r}}$ over the critical region boundary. To this end, let us introduce the spherical frame of reference with the point O′ as the origin. The coordinates of the point O″ are $(R(t', t), \theta, \phi)$ where $R(t', t) = |\vec{r} - \vec{r}_0|$. The volume element $dV(\vec{r})$ is equal to $dV(t', t)\, d\Omega/4\pi$ where $dV(t', t) = 4\pi R^2(t', t)\, dR(t', t)$. The nucleation rate in this frame of reference is $I(\vec{r}, t') \equiv I_{\vec{r}_0}(\vec{R}, t') = I_{\vec{r}_0}(R(t', t), \theta, \phi; t')$ (the dependence of quantities on $\vec{r}_0$ is indicated below by an index). We introduce the following notation:

$$J_{\vec{r}_0}(t', t) = \frac{1}{4\pi} \int_\Omega d\Omega\, I_{\vec{r}_0}(R(t', t), \theta, \phi; t') \tag{8}$$

where the integration is over the whole solid angle.

In the case of an arbitrary nucleus shape permitted by Kolmogorov's model, the critical region obviously has the same shape and orientation as the nuclei. In this case, the radius vector $\vec{R}(t, t)$ has the length given by (2) in the direction $\vec{n}$, so $I(\vec{r}, t') = I_{\vec{r}_0}(R(t', t)c(\vec{n}), \theta, \phi; t')$, $d\tilde{V}_{\vec{n}}(t', t) = (1/4\pi)\, dV(t', t)\, c^3(\vec{n})\, d\Omega$ and the expression for $J_{\vec{r}_0}(t', t)$ is the following:

$$J_{\vec{r}_0}(t', t) = \frac{1}{4\pi} \int_\Omega I_{\vec{r}_0}(R(t', t)c(\vec{n}), \theta, \phi; t')c^3(\vec{n})\, d\Omega. \tag{9}$$

The critical nucleus appearing at O″ must have the same orientation as the critical region, so at time t (when it arrives at the point O), it will be a copy of the latter at t'.

Thus, we have, for the desired probability $dP_{\vec{r}_0}(t', t)$,

$$dP_{\vec{r}_0}(t', t) = J_{\vec{r}_0}(t', t)\, dt'\, dV(t', t). \tag{10}$$

The probability $dY_{\vec{r}_0}(t)$ of the critical centre appearing in the time interval $0 \leqslant t' \leqslant t$ is obtained by integrating (10) over t':

$$dY_{\vec{r}_0}(t) = \left\{ \int_0^t dt'\, J_{\vec{r}_0}(t', t) \frac{\partial V(t', t)}{\partial t} \right\} dt. \tag{11}$$

Thus, the simultaneous fulfilment of conditions (1) and (2) leads to the following equality for $dX_{\vec{r}_0}(t)$:

$$dX_{\vec{r}_0}(t) = Q_{\vec{r}_0}(t)\, dY_{\vec{r}_0}(t). \tag{12}$$

Since $X_{\vec{r}_0}(t) = 1 - Q_{\vec{r}_0}(t)$, expression (12) is a differential equation for $X_{\vec{r}_0}(t)$. Its solution with respect to the initial condition $X_{\vec{r}_0}(t_0) = 0$ is

$$X_{\vec{r}_0}(t) = 1 - \exp[-Y_{\vec{r}_0}(t)] \tag{13}$$

where

$$Y_{\vec{r}_0}(t) = \int_{t_0}^{t} d\tau \int_{0}^{\tau} dt' \, J_{\vec{r}_0}(t', \tau) \frac{\partial V(t', \tau)}{\partial \tau}.$$

The function $X_{\vec{r}_0}(t)$ is the probability that the point O′ is transformed at time t under the condition that it is located in the volume element $d^3\vec{r}_0$. The probability of the latter event is $d^3\vec{r}_0/V_0$, where V_0 is the volume of the system considered. The probability $X(t)$ for the point O′ to be transformed under the condition that it will appear somewhere in the system, or the probability of the point O′ falling in the transformed part of the system, is

$$X(t) = \frac{1}{V_0} \int_{V_0} X_{\vec{r}_0}(t) \, d^3\vec{r}_0 \tag{14}$$

where the integration is over the system volume.

Expression (14) is the desired volume fraction of the material transformed according to the geometrical definition of probability [7]. If the system is infinite, then expression (14) is regarded as the limit at $V_0 \to \infty$. However, it is important that finite domains naturally obey this expression. Thus, the expressions obtained may also be regarded as a generalization of expression (4) to the case of a finite domain. Even though the nucleation rate inside the domain does not depend on $\vec{r}$, the function $X_{\vec{r}_0}(t)$ depends on $\vec{r}_0$. The reason for this is that generally only a part of the critical region for the point O′ lies inside the domain. The size of this part depends on $\vec{r}_0$. This is shown in more detail in section 5 through the procedure of calculating the volume fraction in a spherical domain.

3. Nucleation on plane, on a straight line, at a point

We shall use the indices s, l, c for a plane, a straight line and a point, respectively. Let the plane considered be the yz-plane of the Cartesian frame of reference. Also, the straight line is the z-axis and the point is the origin (the point O). The volume nucleation rate may be represented in every case as follows:

$$I_v^{(i)}(\vec{r}, t) = \begin{cases} I_s(t)\delta(x) & i = s \\ I_l(t)\delta(x)\delta(y) & i = l \\ I_c(t)\delta(x)\delta(y)\delta(z) & i = c \end{cases} \tag{15}$$

where $I_i(t)$, $i = s, l, c$, are the specific nucleation rates: I_s (I_l) is the number of centres appearing on unit area (length) per unit time, I_c is the probability of the centre appearing at the point per unit time.

If the plane is in the middle of a plate of thickness $\varepsilon_s = 2L$, the straight line is the axis of a cylinder with cross-sectional area $\varepsilon_l = \pi L^2 \equiv s$ and the point is the centre of a sphere of volume $\varepsilon_c = (4\pi/3)L^3 \equiv v_c$, then the mean volume nucleation rate for every case is

$$\bar{I}_v^{(i)}(t) = \varepsilon_i^{-1} \int_{\varepsilon_i} I_v^{(i)}(\vec{r}, t) \, d\varepsilon_i$$

or

$$\bar{I}_v^{(s)}(t) = \sigma I_s(t) \qquad \bar{I}_v^{(l)}(t) = \lambda I_l(t) \qquad \bar{I}_v^{(c)}(t) = n I_c(t) \tag{16}$$

where $\sigma = (2L)^{-1}$ is the mean area in unit volume, $\lambda = s^{-1}$ is the mean length in unit volume and $n = v_c^{-1}$ is the mean number of points in unit volume.

Without loss of generality, let us take the point O' on the x-axis at the distance r_0 from the origin. As the angle θ of the spherical frame of reference with the point O' as the origin, we take the angle formed by the vector $\vec{R}$ with the negative x-axis. The angle ϕ is in the yz-plane. Then the components of the radius vector $\vec{r}$ are $x = r_0 - R(t', t)\cos\theta$, $y = R(t', t)\sin\theta\sin\phi$, $z = R(t', t)\sin\theta\cos\phi$. Substituting these values into (15) and following the computational scheme of section 1, we shall derive the desired result (see the appendix). However, it is simpler to get the result by the critical region method immediately.

The critical region for the point O' at time t' is the sphere of radius $R(t', t)$. Either the part of the plane of area $S_{r_0}(t', t) = \pi[R^2(t', t) - r_0^2]$ (the part of the straight line of length $l_{r_0}(t', t) = 2[R^2(t', t) - r_0^2]^{1/2}$) or the point may be located inside it. Let us define the time $t_m(t, r_0)$ by the equation

$$R(t_m, t) = r_0. \tag{17}$$

At $t' > t_m$ the object considered is outside the critical region.

In order for the point O' to be untransformed at time t, the new-phase centre is forbidden to appear in the time interval $0 \leqslant t' \leqslant t_m(t, r_0)$ on the circle of area $S_{r_0}(t', t)$, on the segment of length $l_{r_0}(t', t)$, at the point O. The probabilities $Q_{r_0}^{(i)}(t)$ of these events can be calculated by the method of reference [1]; the result is obvious:

$$Q_{r_0}^{(i)}(t) = \exp\left[-\int_0^{t_m(t, r_0)} I_i(t')\zeta_{r_0}^{(i)}(t', t)\,\mathrm{d}t'\right] \qquad r_0 < R_m(t) \tag{18}$$

where

$$\zeta_{r_0}^{(i)}(t', t) = \begin{cases} S_{r_0}(t', t) & i = s \\ l_{r_0}(t', t) & i = l \\ 1 & i = c \end{cases}$$

and

$$Q_{r_0}^{(i)}(t) = 1 \qquad r_0 > R_m(t) \tag{19}$$

since in this case the object is outside the critical region at all t' (equation (17) has no solution).

This is the form of expression (5) in this case. The advantage of the 'shortened' form of the critical region method is even more apparent in the case of nucleation on a surface (line) of arbitrary form. Evidently the result is analogous to (18):

$$Q_{\vec{r}_0}^{(i)}(t) = \begin{cases} \begin{cases} \exp\left[-\int_0^{t_m(t, p)} I_s(t')S_{\vec{r}_0}(t', t)\,\mathrm{d}t'\right] & i = s \\ \exp\left[-\int_0^{t_m(t, p)} I_l(t')l_{\vec{r}_0}(t', t)\,\mathrm{d}t'\right] & i = l \end{cases} & p(\vec{r}_0) < R_m(t) \\ 1 & p(\vec{r}_0) > R_m(t) \end{cases} \tag{20}$$

where $S_{\vec{r}_0}(t', t)$ is the area of the surface part ($l_{\vec{r}_0}(t', t)$ is the length of the line part) enclosed by the critical region at time t'; $p(\vec{r}_0)$ is the shortest distance from the point O' to the surface (line). At $t' > t_m(t, p)$ the object remains outside the critical region. In the given case, the quantities depend on all of the coordinates of the point O', which is denoted by the index $\vec{r}_0$.

To get the fraction of the material of the plate transformed, we integrate the function $X_{r_0}^{(s)}(t) = 1 - Q_{r_0}^{(s)}(t)$ over r_0 according to (14):

$$X^{(s)}(t) = 2\int_0^L X_{r_0}^{(s)}(t)\,\frac{\mathrm{d}r_0}{2L}. \tag{21}$$

Denote by t^* the time at which the nucleus appearing at $t' = 0$ reaches the plate boundary: $R_m(t^*) = L$. At $t < t^*$ $(R_m(t) < L)$ this integral, in view of (19), reduces to the following one:

$$X_1^{(s)}(t) = 2\sigma \int_0^{R_m(t)} X_{r_0}^{(s)}(t) \, dr_0 = 2\sigma R_m(t) \int_0^1 X_\xi^{(s)}(t) \, d\xi \qquad \xi = r_0/R_m. \tag{22}$$

At $t > t^*$, we use expression (21) itself for the volume fraction, which can also be represented as

$$X_2^{(s)}(t) = \int_0^1 X_\kappa^{(s)}(t) \, d\kappa \qquad \kappa = r_0/L. \tag{23}$$

Finally, we obtain

$$X^{(s)}(t) = \eta(t^* - t) X_1^{(s)}(t) + \eta(t - t^*) X_2^{(s)}(t) \tag{24}$$

where $\eta(x)$ is the symmetric unit function [8].

The same expression applies for the volume fractions of the cylinder and sphere. We have for the cylinder

$$X_1^{(l)}(t) = \int_0^{R_m(t)} X_{r_0}^{(l)}(t) \frac{2\pi r_0 \, dr_0}{s} = 2\pi \lambda R_m^2(t) \int_0^1 X_\xi^{(l)}(t) \xi \, d\xi \tag{25}$$

$$X_2^{(l)}(t) = 2 \int_0^1 X_\kappa^{(l)}(t) \kappa \, d\kappa \tag{26}$$

and for the sphere

$$X_1^{(c)}(t) = \int_0^{R_m(t)} X_{r_0}^{(c)}(t) \frac{4\pi r_0^2 \, dr_0}{v} = 4\pi n R_m^3(t) \int_0^1 X_\xi^{(c)}(t) \xi^2 \, d\xi \tag{27}$$

$$X_2^{(c)}(t) = 3 \int_0^1 X_\kappa^{(c)}(t) \kappa^2 \, d\kappa. \tag{28}$$

At constant nucleation and growth rates, the integrals in the latter case are evaluated yielding the following explicit time dependence:

$$X_1^{(c)}(t) = \frac{6}{(I_c t^*)^3} \left\{ \frac{(I_c t)^3}{6} - \frac{(I_c t)^2}{2} + I_c t - 1 + e^{-I_c t} \right\} \tag{29}$$

$$X_2^{(c)}(t) = 1 - \frac{6 e^{-I_c(t-t^*)}}{(I_c t^*)^3} \left\{ \frac{(I_c t^*)^2}{2} - I_c t^* + 1 - e^{-I_c t^*} \right\} \tag{30}$$

where

$$t^* = L/u$$

Expression (24), with (29) and (30), gives the mean volume fraction of the sphere at time t. The true fraction $X_{tr}^{(c)}(t) = V(t', t)/v$ is a random quantity due to the randomness of the appearance time t'. The volume fraction (24) is obtained as a result of averaging $X_{tr}^{(c)}(t)$ using the function $I_c \exp(-I_c t')$ which is the distribution function of the appearance time. Thus,

$$X_1^{(c)}(t) = \int_0^t V(t', t) I_v(t') \, dt' \qquad (t < t^*)$$

$$X_2^{(c)}(t) = \int_0^{t-t^*} v I_v(t') \, dt' + \int_{t-t^*}^t V(t', t) I_v(t') \, dt' \qquad (t > t^*) \tag{31}$$

where $I_v(t') = n I_c \exp(-I_c t')$. It is easy to establish that these expressions yield (29) and (30).

The transformation time t_f is infinite in this simple finite system. This fact is a clear consequence of the randomness of the appearance time t'. The mean transformation time is $\bar{t}_f = I_c^{-1} + t^*$. In the limiting case $I_c \to \infty$, t_f is obviously finite and equal to t^*.

4. Nucleation on random planes, on straight lines, at points; another derivation of Kolmogorov's formula

In view of generality of the approach used we shall carry out consideration for these three cases simultaneously.

Let either planes (straight lines) or points be distributed randomly in an infinite system. For deriving the volume fractions of the material transformed at nucleation on these objects, we use the critical region method again. We choose at random a point O′ in the system and seek the probability $Q^{(i)}(t)$ that it will be untransformed at time t. The critical region for the point O′ at time $t' = 0$ is a sphere of radius $R_m(t)$. Let it either be intersected by N planes (straight lines) or include N points. Denote by r_k the distance from point O′ to the kth object, $k = 1, \ldots, N$. The probability $q_N^{(i)}(\{r_k\}, t)$ for the point O′ to be untransformed at time t at the given N and realization of the set $\{r_k\} = \{r_1, r_2, \ldots, r_N\}$ is a product of the probabilities (18):

$$q_N^{(i)}(\{r_k\}, t) = \prod_{k=1}^{N} Q_{r_k}^{(i)}(t) = \prod_{k=1}^{N} \exp\left[-\int_0^{t_m(t,r_k)} I_i(t')\zeta_{r_k}^{(i)}(t', t)\, \mathrm{d}t' \right] \qquad i = s, l, c. \qquad (32)$$

The desired function $Q^{(i)}(t)$ is obtained by averaging $q_N^{(i)}(\{r_k\}, t)$ over all r_k-values and N:

$$Q^{(i)}(t) = \sum_{N=0}^{\infty} P^{(i)}(N) \int_0^{R_m(t)} \cdots \int_0^{R_m(t)} q_N^{(i)}(\{r_k\}, t) f^{(i)}(r_1, \ldots, r_N)\, \mathrm{d}r_1 \cdots \mathrm{d}r_N \qquad (33)$$

where $f^{(i)}(\{r_k\})$ is the distribution function of the set $\{r_k\}$, $P^{(i)}(N)$ is the probability of the given N.

In order to deduce the expression for $f^{(i)}(\{r_k\})$, we first choose the parametric space for every kind of object. In the case of points, the parametric space is the coordinate space itself: the point is determined by the coordinates (r, θ, ϕ); the volume element is $\mathrm{d}v = r^2 \sin\theta\, \mathrm{d}r\, \mathrm{d}\theta\, \mathrm{d}\phi$. We assume that the points are distributed according to the Poisson law: the probability for the point to be in the volume element $\mathrm{d}v$ is equal to $\gamma_c\, \mathrm{d}v$ and does not depend on either volume element shape or position. We divide the volume $V_m(t) = (4\pi/3)R_m^3(t)$ of the critical region into layers of thickness $\mathrm{d}r$; $\mathrm{d}v(r) = 4\pi r^2\, \mathrm{d}r$. Further, we use the following property of the Poisson process [7]: the probability of the kth point being in the volume element $\mathrm{d}v_k$ under the condition that there are N points in the whole volume $V_m(t)$ is equal to $\mathrm{d}v_k/V_m$ (the distribution over volume is uniform). Going from v_k to r_k, we find that the probability for the kth point to be at the distances $[r_k, r_k + \mathrm{d}r_k]$ is equal to $4\pi r_k^2\, \mathrm{d}r_k/V_m$. Also, all of the distances r_k are independent quantities. Consequently,

$$f^{(c)}(\{r_k\}) = \prod_{k=1}^{N} f^{(c)}(r_k) \qquad (34)$$

where $f^{(c)}(r_k) = 3r_k^2/R_m^3$.

A plane is uniquely determined by two angles θ, ϕ and the length r_k of the perpendicular to it from the point O′. The measure element for planes in the parametric space (r, θ, ϕ) is $\mathrm{d}E^{(s)} = \sin\theta\, \mathrm{d}r\, \mathrm{d}\theta\, \mathrm{d}\phi$ [9]. We also assume the Poisson distribution for planes: the probability for a plane to be in the 'volume' element $\mathrm{d}E^{(s)}$ is $\gamma_s\, \mathrm{d}E^{(s)}$. Further, we similarly derive expression (34) with $f^{(s)}(r_k) = 1/R_m$ for the set $\{r_k\}$ distribution.

Let us determine a straight line by its direction θ, ϕ and the polar coordinates r, β of the intersection point of this line with the plane perpendicular to it and passing through the point O′. Thus, the measure element is $\mathrm{d}E^{(l)} = r\, \mathrm{d}r\, \mathrm{d}\beta\, \mathrm{d}\Omega$, and for the Poisson distribution of straight lines (with the parameter γ_l), the probability for the kth line to be at the distances $[r_k, r_k + \mathrm{d}r_k]$ from the point O′ is $f^{(l)}(r_k)\, \mathrm{d}r_k = 2r_k\, \mathrm{d}r_k/R_m^2$.

Returning now to expression (33) we see that the N-dimensional integral is equal to $w_i^N(t)$, where

$$w_i(t) = \int_0^{R_m(t)} Q_r^{(i)}(t) f^{(i)}(r) \, \mathrm{d}r. \tag{35}$$

Averaging using $P^{(i)}(N) = \alpha_i^N \exp(-\alpha_i)/N!$ yields

$$Q^{(i)}(t) = \sum_{N=0}^{\infty} \frac{\alpha_i^N}{N!} \mathrm{e}^{-\alpha_i} w_i^N = \mathrm{e}^{-\alpha_i(t)(1-w_i(t))}. \tag{36}$$

We determine the parameter α_i for every kind of object. For points: $\alpha_c = \bar{N} = V_m(t)n$. For planes, we express α_s in terms of σ. The area S_r of the plane part located inside the critical region is equal to $\pi(R_m^2 - r^2)$. Its mean value is

$$\bar{S}_r = \pi \int_0^{R_m(t)} (R_m^2 - r^2) \frac{\mathrm{d}r}{R_m} = \frac{2}{3} \pi R_m^2.$$

The mean area in unit volume is $\sigma = \bar{S}_r \bar{N}/V_m = \bar{S}_r \alpha_s/V_m = \alpha_s/2R_m$, from which

$$\alpha_s = 2\sigma R_m. \tag{37}$$

Similarly, it is easy to get for straight lines

$$\alpha_l = \pi \lambda R_m^2. \tag{38}$$

Substituting the α_i-values obtained into (36), we find the fraction of the material transformed for every case:

$$X^{(i)}(t) = 1 - \exp(-X_1^{(i)}(t)) \tag{39}$$

where the $X_1^{(i)}(t)$ are given by expressions (22), (25) and (27).

Consider in greater detail the case of nucleation at points. Expression (39) for this case has the following form:

$$X^{(c)}(t) = 1 - \exp\left\{-4\pi n \int_0^{R_m(t)} \left[1 - \exp\left(-\int_0^{t_m(t,r)} I_c(t') \, \mathrm{d}t'\right)\right] r^2 \, \mathrm{d}r\right\}. \tag{40}$$

Let us introduce the function $\bar{I}_v(t)$ via the equality

$$\bar{I}_v(t) = nI_c(t) \exp\left[-\int_0^t I_c(t') \, \mathrm{d}t'\right]. \tag{41}$$

Its integral is

$$n_0(t) = \int_0^t \bar{I}_v(t') \, \mathrm{d}t' = n \left\{1 - \exp\left[-\int_0^t I_c(t') \, \mathrm{d}t'\right]\right\}. \tag{42}$$

It is easily seen that the exponent in (40) is expressible in terms of $\bar{I}_v(t)$ as follows:

$$X^{(c)}(t) = 1 - \exp\left\{-4\pi \int_0^{R_m(t)} r^2 \, \mathrm{d}r \int_0^{t_m(t,r)} \bar{I}_v(t') \, \mathrm{d}t'\right\}. \tag{43}$$

Changing the order of integration here, we obtain nothing more nor less than the formula of Kolmogorov:

$$X^{(c)}(t) = 1 - \exp\left\{-\int_0^t \bar{I}_v(t') V(t', t) \, \mathrm{d}t'\right\} \tag{44}$$

from where it is seen that the function $\bar{I}_v(t')$ has the meaning of the mean volume nucleation rate. This can be proved as follows.

In the case of nucleation at points, the volume nucleation rate may be represented as

$$I_v(\vec{r}, t) = I_c(t) \sum_{k=1}^{N_f(t)} \delta(\vec{r} - \vec{r}_k) \tag{45}$$

where $\vec{r}_k$ is the position vector of the kth point in any frame of reference, $N_f(t)$ is the number of 'non-activated' points in the system (e.g. those points at which the nucleation has not occurred by time t). We assume the volume V_0 of the system to be large enough but finite and containing N_0 points. The number N_f is a random quantity distributed according to the binomial law

$$P(N_f) = C_{N_0}^{N_f} \phi(t)^{N_f} [1 - \phi(t)]^{N_0 - N_f}$$

where

$$\phi(t) = \exp\left[-\int_0^t I_c(t')\, dt'\right]$$

is the probability for the point to be 'non-activated' by time t. Hence, we find $\bar{N}_f(t) = N_0\phi(t)$, so the averaging of $I_v(\vec{r}, t)$, expression (45), over N_f and volume at $V_0 \to \infty$ yields $\bar{I}_v(t) = I_c(t)n\phi(t)$, i.e. expression (41).

In the limiting case of large values of $I_c(t)$, the function $\bar{I}_v(t)$ has a δ-shaped form: $\bar{I}_v(t) = n\delta_+(t)$, so expression (44) describes the case where all of the centres appear at $t' = 0$:

$$X(t) = 1 - \exp[-nV_m(t)]. \tag{46}$$

Expression (44) shows that the process of nucleation at points can be regarded as the process of homogeneous nucleation with the appropriate nucleation rate (41). The reverse statement is also true: the process of homogeneous nucleation with the nucleation rate $I_v(t)$ may be represented as the process of nucleation at points. The corresponding specific nucleation rate $I_c(t)$ is easily derived from (41):

$$I_c(t) = I_v(t) \Big/ \left(n - \int_0^t I_v(t')\, dt'\right) = \frac{I_v(t)}{n - n_0(t)}. \tag{47}$$

The parameter n remains arbitrary under the single condition $n > n_0(t)$. Thus, the reverse representation is not unique: expression (47) describes a family of curves corresponding to different n-values. Two different situations are possible: $n_0(t)$ is either finite or infinite for $t \to \infty$.

Consider the latter case by examining the simplest example of $I_v = \text{constant} = a$. In this case,

$$I_c(t) = \frac{a}{n - at}. \tag{48}$$

The number of centres appearing by time t, $n_0(t) = at$, increases with time infinitely. Hence, the parameter n must also be infinite. However, there is no contradiction here. The number $n_0(t)$ can be represented as a sum: $n_0(t) = n_0^{(r)}(t) + n_0^{(f)}(t)$, where

$$n_0^{(r)}(t) = \int_0^t I_v(t')Q(t')\, dt' \qquad n_0^{(f)}(t) = \int_0^t I_v(t')X(t')\, dt'. \tag{49}$$

$n_0^{(r)}(t)$ is the number of actual centres, i.e. appearing in the untransformed volume; $n_0^{(f)}(t)$ is the number of centres appearing in the volume which is already transformed. The latter are nothing but the fictitious centres, or 'phantoms', in the JMA approach. Their number increases infinitely in the case of constant nucleation rate ($n_0^{(r)}(t)$ is always finite). The divergence occurs because formally the transformation time t_f is infinite. Actually, it may of course be chosen finite and determined by the equality $Q(t_f) = Q_{\min}$, where $Q_{\min}$ is the minimal value of the

volume fraction observed experimentally. Then the process is considered in the time interval $0 < t < t_f$, and some $n > a t_f$ may be taken as the n-value in (48).

The established equivalence of the processes of homogeneous nucleation and nucleation at points shows that the Avrami and Johnson–Mehl approaches are not alternative to each other [2], but reduce to each other by means of relations (41) and (47), respectively.

Consider the limiting cases for planes. If the exponent in $Q_{r_0}^{(s)}(t)$, expression (18), is small (small nucleation and growth rates, small times), then expression (22) changes to the following one:

$$X_1^{(s)}(t) = 2\pi\sigma \int_0^{R_m(t)} dr_0 \int_0^{t_m(t,r_0)} dt'\, I_s(t') \left[R^2(t', t) - r_0^2 \right]. \tag{50}$$

Changing the order of integration here, we get

$$X_1^{(s)}(t) = \int_0^t dt'\, \bar{I}_v(t') V(t', t) \qquad \bar{I}_v(t') = \sigma I_s(t'). \tag{51}$$

In the case of a large value of the exponent,

$$X_1^{(s)}(t) = 2\sigma R_m(t). \tag{52}$$

Corresponding limiting cases for the system of random planes are obtained by substituting (51) and (52) into (39). The expression $X^{(s)}(t) = 1 - \exp[-2\sigma R_m(t)]$ may be treated as the volume fraction of infinite planar 'nuclei' formed at $t' = 0$.

One fact related to the one-dimensional asymptote (52) of the volume fraction is worthy of notice, which applies in the case of competitive formation on the plane of two or more different phases. Let two phases with nucleation and growth rates $I_{s,k}(t)$ and $u_k(t)$, $k = 1, 2$, $u_2(t) > u_1(t)$, be formed simultaneously. As was shown in reference [6], the approximation of independent phases may be used in the given case for calculating the fractions of these phases. Thus, we have

$$Q_{r_0}^{(s)}(t) = \exp[-Y_{r_0,1}(t) - Y_{r_0,2}(t)] \tag{53}$$

where

$$Y_{r_0,k}(t) = \begin{cases} \displaystyle\int_0^{t_{m,k}(t,r_0)} I_{s,k}(t') S_{r_0,k}(t', t)\, dt' & r_0 < R_{m,k}(t) \\ 0 & r_0 > R_{m,k}(t). \end{cases}$$

The total volume fraction $X^{(s)}(t)$ of the material transformed is obtained by integration of the expression $1 - Q_{r_0}^{(s)}(t)$ over r_0:

$$X^{(s)}(t) = 2\sigma R_{m,1}(t) \left\{ \int_0^1 \left[1 - e^{-Y_{\xi,1}(t) - Y_{\xi,2}(t)} \right] d\xi + \int_1^{R_{m,2}/R_{m,1}} \left[1 - e^{-Y_{\xi,2}(t)} \right] d\xi \right\} \tag{54}$$

where $\xi \equiv r_0/R_{m,1}$, $t < t^*$; t^* is determined by the equality $R_{m,2}(t^*) = L$.

In the limiting case of large values of $Y_{\xi,2}(t)$, we have

$$X^{(s)}(t) = 2\sigma R_{m,2}(t). \tag{55}$$

Thus, the phase transformation process is governed by the second (fast-growing) phase. Grains of the first (slow-growing) phase are 'immured' inside the layer of the second one and cannot contribute to the incrementing of the transformed volume.

5. Calculating the volume fraction in a spherical domain; homogeneous nucleation

Consider the process of phase transformation of the spherical domain of volume $V_0 = (4\pi/3)R_0^3$ for homogeneous nucleation inside it of new-phase centres with the nucleation rate $I(t)$ and growth velocity $u(t)$. Let the nuclei have spherical shape.

Take at random the point O′ in the domain. Let it be at distance r from the centre of the domain which is the point O (figure 2). We seek the probability $Q(r, t)$ that the point O′ will be untransformed at time t. Let us specify the critical region for the point O′—the sphere of radius $R(t', t)$. In order for the point O′ to be untransformed, it is necessary and sufficient that no centre of a new phase is formed inside the critical region in the time interval $0 \leqslant t' \leqslant t$. The probability of this event is given by expression (5), in which the variable r instead of vector $\vec{r}_0$ will be used below.
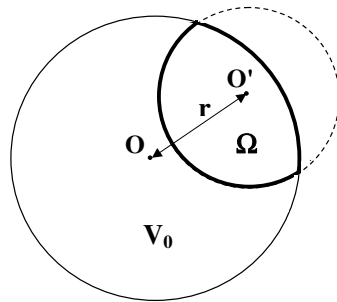
Figure 2. The domain and the critical region for the point O′. The critical region part of the volume $\Omega(r; t', t) = v(r; t', t)$ is marked out.

The new-phase centres can appear only inside the domain. At the same time, in general, only a part of the critical region for the point O′ lies inside this domain. Denote by $\Omega(r; t', t)$ the volume of this part (figure 2). Hence, calculating the probability $Q(r, t)$, we must take $\Omega(r; t', t)$ instead of $V(t', t)$. Accordingly, the expression for $Y(r, t)$ has the following form:

$$Y(r, t) = \int_0^t I(t')\Omega(r; t', t)\, \mathrm{d}t'. \tag{56}$$

The volume fraction $Q(t)$ of the material untransformed at time t is the probability for the point O′ to fall in the untransformed part of the domain:

$$Q(t) = \frac{1}{V_0} \int_0^{R_0} Q(r, t)(4\pi r^2)\, \mathrm{d}r. \tag{57}$$

Furthermore, the problem is that of how to find the explicit form of the function $\Omega(r; t', t)$ depending on t, t' and r. For this purpose the following expression will be used. For two overlapping spheres of radii r_1, r_2 and spacing between centres h, the volume of the part of the second sphere lying inside the first sphere is equal to

$$v(r_1, r_2; h) = \pi \left\{ \frac{2}{3}(r_1^3 + r_2^3) + \frac{1}{12}h^3 - \frac{1}{2}h(r_1^2 + r_2^2) - \frac{1}{4}\frac{(r_1^2 - r_2^2)^2}{h} \right\}. \tag{58}$$

Determine the times t_1 and t_2 by the equations

$$R_m(t_1) = R_0 \qquad R_m(t_2) = 2R_0. \tag{59}$$

The following three cases with respect to time t arise.

(1) $R_m(t) < R_0$: $t < t_1$. Determine the distance l_0 by the equality

$$l_0 = R_0 - R_m. \tag{60}$$

For $0 \leqslant r \leqslant l_0$ the critical region lies entirely inside the domain over the whole time interval $0 \leqslant t' \leqslant t$; accordingly, $\Omega(r; t', t) = V(t', t)$. Determine the time $t_m(r, t)$ by the equation

$$R(t_m, t) = R_0 - r. \tag{61}$$

At $l_0 < r \leqslant R_0$ the critical region lies partially inside the domain in the interval $0 \leqslant t' < t_m(r, t)$; accordingly, $\Omega(r; t', t) = v(R_0, R(t', t); r) \equiv v(r; t', t)$. Further, in the interval $t_m(r, t) \leqslant t' \leqslant t$ the critical region is entirely in the domain; hence, $\Omega(r; t', t) = V(t', t)$. Thus,

$$Y_1(r, t) = \begin{cases} \displaystyle\int_0^t I(t') V(t', t)\, \mathrm{d}t' & 0 \leqslant r \leqslant l_0 \\ \displaystyle\int_0^{t_m(r,t)} I(t') v(r; t', t)\, \mathrm{d}t' + \int_{t_m(r,t)}^t I(t') V(t', t)\, \mathrm{d}t' & l_0 < r \leqslant R_0. \end{cases} \tag{62}$$

(2) $R_0 \leqslant R_m(t) \leqslant 2R_0$: $t_1 \leqslant t \leqslant t_2$. Determine the distance l_0' by the equality

$$l_0' = R_m - R_0 \tag{63}$$

and the time $t_m'(r, t)$ by the equation

$$R(t_m', t) = R_0 + r. \tag{64}$$

Consider the case $0 < r < l_0'$. In figure 3, the positions of the critical region boundary are shown for this case at different times t'. In the time interval $0 \leqslant t' \leqslant t_m'(r, t)$ the domain lies entirely inside the critical region; accordingly, $\Omega(r; t', t) = V_0$. In the interval $t_m'(r, t) < t' \leqslant t_m(r, t)$, $\Omega(r; t', t) = v(r; t', t)$. And in the remaining interval $t_m(r, t) < t' \leqslant t$, $\Omega(r; t', t) = V(t', t)$. At $l_0' \leqslant r \leqslant R_0$ we have

$$\Omega(r; t', t) = \begin{cases} v(r; t', t) & 0 \leqslant t' < t_m(r, t) \\ V(t', t) & t_m(r, t) \leqslant t' \leqslant t. \end{cases} \tag{65}$$
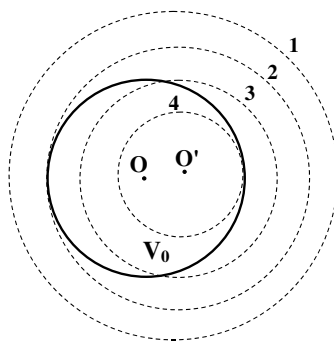
Figure 3. Positions of the critical region boundary at different times t': (1) $0 \leqslant t' < t_m'(r, t)$; (2) $t' = t_m'(r, t)$; (3) $t_m'(r, t) < t' < t_m(r, t)$; (4) $t' = t_m(r, t)$.

Thus,

$$Y_2(r, t) = \begin{cases} V_0 \displaystyle\int_0^{t_m'(r,t)} I(t')\,\mathrm{d}t' + \displaystyle\int_{t_m'(r,t)}^{t_m(r,t)} I(t')v(r;t',t)\,\mathrm{d}t' \\[1.5em] \quad + \displaystyle\int_{t_m(r,t)}^{t} I(t')V(t',t)\,\mathrm{d}t' & 0 \leqslant r < l_0' \\[1.5em] \displaystyle\int_0^{t_m(r,t)} I(t')v(r;t',t)\,\mathrm{d}t' + \displaystyle\int_{t_m(r,t)}^{t} I(t')V(t',t)\,\mathrm{d}t' & l_0' \leqslant r \leqslant R_0. \end{cases} \quad (66)$$

(3) $R_m(t) > 2R_0$: $t > t_2$. As follows from the foregoing, in this case

$$\Omega(r; t', t) = \begin{cases} V_0 & 0 \leqslant t' \leqslant t_m'(r,t) \\ v(r; t', t) & t_m'(r,t) < t' < t_m(r,t) \\ V(t', t) & t_m(r,t) \leqslant t' \leqslant t \end{cases} \quad (67)$$

for arbitrary r-value. Accordingly,

$$Y_3(r, t) = V_0 \int_0^{t_m'(r,t)} I(t')\,\mathrm{d}t' + \int_{t_m'(r,t)}^{t_m(r,t)} I(t')v(r;t',t)\,\mathrm{d}t'$$

$$+ \int_{t_m(r,t)}^{t} I(t')V(t',t)\,\mathrm{d}t' \qquad 0 \leqslant r \leqslant R_0. \quad (68)$$

The volume fraction of the material transformed in every case is

$$X_i(t) = 1 - \frac{1}{V_0} \int_0^{R_0} \mathrm{e}^{-Y_i(r,t)}(4\pi r^2)\,\mathrm{d}r \qquad i = 1, 2, 3. \quad (69)$$

The volume fraction at any time t is given by the following expression:

$$X(t) = \eta(t_1 - t)X_1(t) + \eta(t_2 - t)\eta(t - t_1)X_2(t) + \eta(t - t_2)X_3(t) \quad (70)$$

where $\eta(x)$ is the symmetric unit function [8].

The case of arbitrary shape of the domain as well as arbitrary nucleus shape permitted by Kolmogorov's model can be considered in a similar way, following the procedure described above.

6. The case of constant nucleation and growth rates

For analysis of the effect of the finiteness of the system on the rate of a phase transformation process, we consider the case of time-independent nucleation and growth rates. First, we study the time dependence of the volume fraction at fixed value of R_0. Let us introduce the following dimensionless variables: time $\tau = ut/R_0 = t/t^*$, $t^* = R_0/u$, distance $x = r/R_0$ and the parameter $\alpha = (\pi/3)(I/u)R_0^4$. The calculation of integrals in the expressions for Y_i yields the following expressions for the volume fraction of the initial phase for every case described above:

(1) $\tau < 1$:

$$Q_1(\tau) = (1 - \tau)^3 \mathrm{e}^{-\alpha\tau^4} + 3 \int_{1-\tau}^{1} \mathrm{e}^{-\alpha\phi_1(x,\tau)} x^2\,\mathrm{d}x \quad (71)$$

where

$$\phi_1(x, \tau) = \sum_{k=-1}^{4} P_k(\tau)x^k$$

and the coefficients $P_k(\tau)$ are as follows:

$$P_{-1}(\tau) = -(3/20)\tau^5 + (1/2)\tau^3 - (3/4)\tau + 2/5$$
$$P_0(\tau) = (1/2)\tau^4 + 2\tau - 3/2$$
$$P_1(\tau) = -(1/2)\tau^3 - (3/2)\tau + 2$$
$$P_2 = -1$$
$$P_3(\tau) = (1/4)\tau$$
$$P_4 = 1/10.$$

(2) $1 \leqslant \tau \leqslant 2$:

$$Q_2(\tau) = 3\left\{\int_0^{\tau-1} e^{-\alpha\phi_2(x,\tau)}x^2\,dx + \int_{\tau-1}^1 e^{-\alpha\phi_1(x,\tau)}x^2\,dx\right\} \tag{72}$$

where

$$\phi_2(x,\tau) = \sum_{k=0}^4 P_k(\tau)x^k$$

and

$$P_0(\tau) = 4\tau - 3$$
$$P_1 = 0$$
$$P_2 = -2$$
$$P_3 = 0$$
$$P_4 = 1/5.$$

(3) $\tau > 2$:

$$Q_3(\tau) = 3\int_0^1 e^{-\alpha\phi_2(x,\tau)}x^2\,dx. \tag{73}$$

The volume fraction of the material transformed is given by expression (70) with the replacements $t \to \tau$, $t_1 \to \tau_1 = 1$, $t_2 \to \tau_2 = 2$. The KJMA expression in this notation has the following form:

$$X_K(\tau) = 1 - e^{-\alpha\tau^4}. \tag{74}$$

In figure 4, the dependence $X(\tau)$ at different values of α is shown in comparison with that given by expression (74) for infinite space. Also, the function $\Delta X(\tau) = X_K(\tau) - X(\tau)$ giving the error yielded by use of (74) is presented.

Furthermore, consider the dependence of the volume fraction on radius R_0 of the domain at fixed time. To this end, let us introduce the following dimensionless quantities: radius $\rho = R_0/ut$, distance $y = r/ut$ and the parameter $\beta = (\pi/3)Iu^3t^4$. The expressions for the volume fraction $Q_i(\rho)$ of the initial phase in three cases described above have the following forms:

(1) $\rho \geqslant 1$:

$$Q_1(\rho) = \left(\frac{\rho-1}{\rho}\right)^3 e^{-\beta} + \frac{3}{\rho^3}\int_{\rho-1}^\rho e^{-\beta\psi_1(y,\rho)}y^2\,dy \tag{75}$$

where

$$\psi_1(y,\rho) = \sum_{k=-1}^4 P_k(\rho)y^k$$
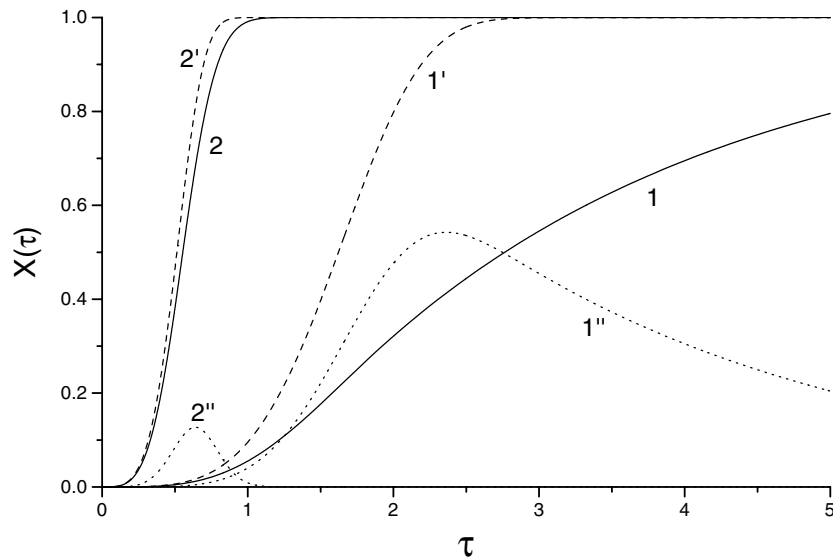
Figure 4. The volume fractions $X(\tau)$ (full lines), $X_K(\tau)$ (dashed lines) and $\Delta X(\tau) = X_K(\tau) - X(\tau)$ (dotted lines) in the process of homogeneous nucleation. The groups of curves $(1, 1', 1'')$ and $(2, 2', 2'')$ are for $\alpha = 0.1$ and $\alpha = 10$, respectively.

and

$$P_{-1}(\rho) = (2/5)\rho^5 - (3/4)\rho^4 + (1/2)\rho^2 - 3/20$$
$$P_0(\rho) = -(3/2)\rho^4 + 2\rho^3 + 1/2$$
$$P_1(\rho) = 2\rho^3 - (3/2)\rho^2 - 1/2$$
$$P_2(\rho) = -\rho^2$$
$$P_3 = 1/4$$
$$P_4 = 1/10.$$

(2) $1/2 < \rho < 1$:

$$Q_2(\rho) = \frac{3}{\rho^3} \left\{ \int_0^{1-\rho} e^{-\beta \psi_2(y,\rho)} y^2 \, dy + \int_{1-\rho}^{\rho} e^{-\beta \psi_1(y,\rho)} y^2 \, dy \right\} \tag{76}$$

where

$$\psi_2(y, \rho) = \sum_{k=0}^{4} P_k(\rho) y^k$$

and

$$P_0(\rho) = -3\rho^4 + 4\rho^3$$
$$P_1 = 0$$
$$P_2(\rho) = -2\rho^3$$
$$P_3 = 0$$
$$P_4 = 1/5.$$

(3) $0 < \rho \leqslant 1/2$:

$$Q_3(\rho) = \frac{3}{\rho^3} \int_0^{\rho} e^{-\beta \psi_2(y,\rho)} y^2 \, dy. \tag{77}$$
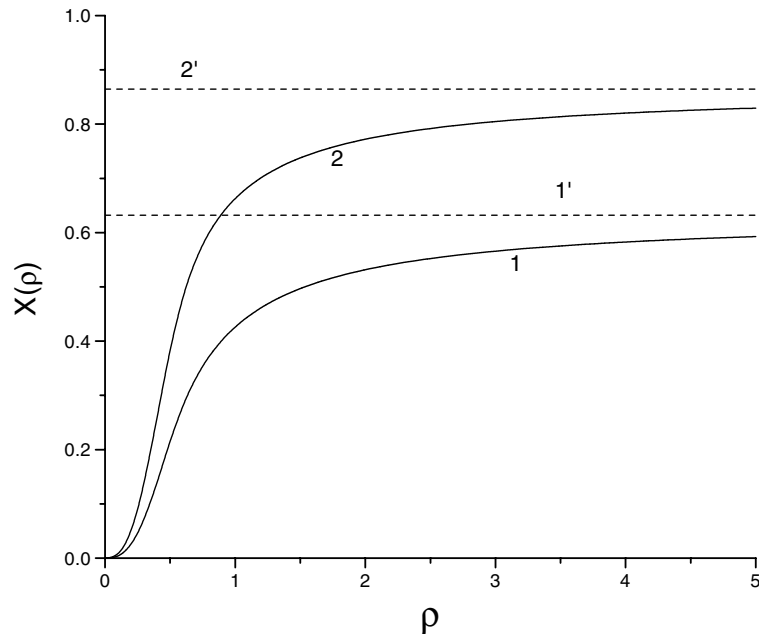
The volume fraction of the transformed material is

$$X(\rho) = \eta\left(\frac{1}{2} - \rho\right)X_3(\rho) + \eta\left(\rho - \frac{1}{2}\right)\eta(1 - \rho)X_2(\rho) + \eta(\rho - 1)X_1(\rho) \tag{78}$$

where $X_i(\rho) = 1 - Q_i(\rho)$.

The KJMA formula in this notation has the form

$$X_K(\rho) = \exp(-\beta). \tag{79}$$

In figure 5, the dependence $X(\rho)$ is shown for different values of β.

Figure 5. The volume fractions $X(\rho)$ (full lines) and $X_K(\rho)$ (dashed lines) at fixed time. The pairs of curves $(1, 1')$ and $(2, 2')$ are for $\beta = 1$ and $\beta = 2$, respectively.

Consider some limiting cases of the expressions derived. At $\tau \to 0$ the addend in (71) has the following expansion in terms of τ: $3\tau - 3\tau^2 + \tau^3 + O(\tau^5)$. Accordingly, the volume fraction is

$$Q(\tau) = Q_1(\tau) = e^{-\alpha\tau^4}\left[1 + O(\alpha\tau^5)\right]. \tag{80}$$

That is, we get the KJMA expression, as we must. Small τ-values correspond to small times and large R_0. The condition $\tau \ll 1$ ($R_m \ll R_0$) has the following meaning. It is proposed in deriving the expression for the volume fraction in reference [1] that the point O' lies at a distance greater than $R_m(t)$ from the domain boundary. To allow neglect of the volume $\Delta V = (4\pi/3)[R_0^3 - (R_0 - R_m)^3]$ of the boundary layer, the condition $\Delta V/V_0 \ll 1$ or $R_m/R_0 \ll 1$ must be obeyed.

At $\tau > 2$ we have

$$Q(\tau) = Q_3(\tau) = J(\alpha)e^{-4\alpha\tau} = J(\alpha)e^{-IV_0t} \tag{81}$$

where

$$J(\alpha) \equiv 3\int_0^1 e^{\alpha(3+2x^2-x^4/5)}x^2\,\mathrm{d}x.$$

At $\alpha \to 0$, $J(\alpha) \to 1$. Thus, we get the following result: the time dependence of the volume fraction differs qualitatively from that in infinite space (it cannot therefore be derived from the latter, equation (74), by use of correction factors). That is, the Avrami exponent n_A decreases with time from 4 to 1. The Avrami exponent [4, 13] is the slope of the tangent to the plot of $\ln(-\ln(1 - X(t)))$ against $\ln t$ (figures 6, 7). In other words, the finiteness of the domain leads to a slowing down of the transformation process in comparison with the nucleation in infinite space. The fact that the dependence $n_A(\tau)$ reaches unity not at $\tau = 2$ but later is due to the presence of the factor $J(\alpha)$. It is not difficult to derive from (81) the following expression for $n_A(\xi)$, where $\xi \equiv \ln \tau$:

$$n_A(\xi) = \frac{1}{1 - z(\alpha)\exp(-\xi)}. \tag{82}$$

Here, $\xi > \ln 2$ and $z(\alpha) \equiv [\ln J(\alpha)]/4\alpha \simeq 1$.
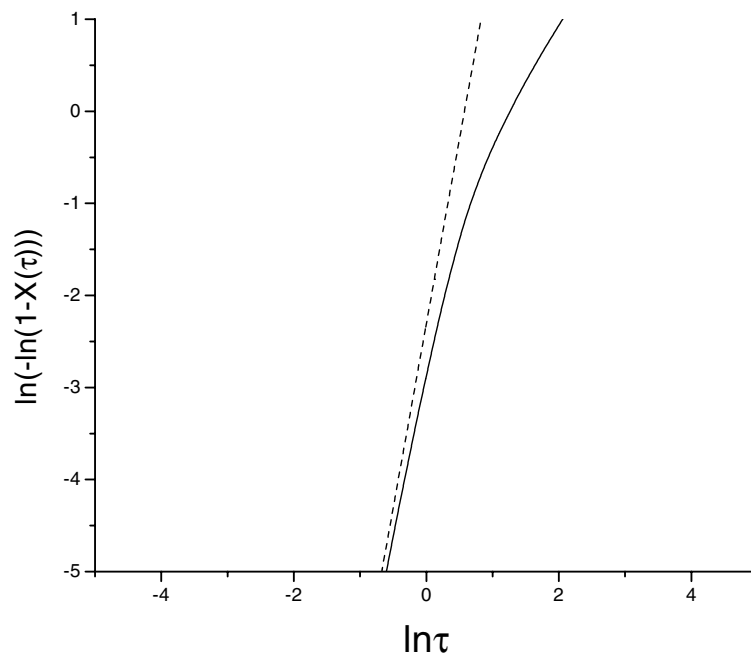
Figure 6. The function $\ln(-\ln(1 - X(\tau)))$ versus $\ln \tau$ for the case of homogeneous nucleation with $\alpha = 0.1$. The dashed line is for $X_K(\tau)$.

At $\rho \to 0$ we get from (77)

$$Q(\rho) = Q_3(\rho) = e^{-4\beta\rho^3}\left[1 + O(\rho^4)\right]. \tag{83}$$

This is expression (81) again, with $J(\alpha) = 1$ ($\alpha \to 0$ at $\rho \to 0$). The function $Q(t) = \exp(-IV_0 t)$ is the probability that no centre of a new phase appears in the domain by time t. This is a volume fraction at small R_0 and large t, since averaging over r is not essential in this case.

In the case $\rho \to \infty$ we obtain from (75)

$$Q(\rho) = Q_1(\rho) = e^{-\beta}. \tag{84}$$

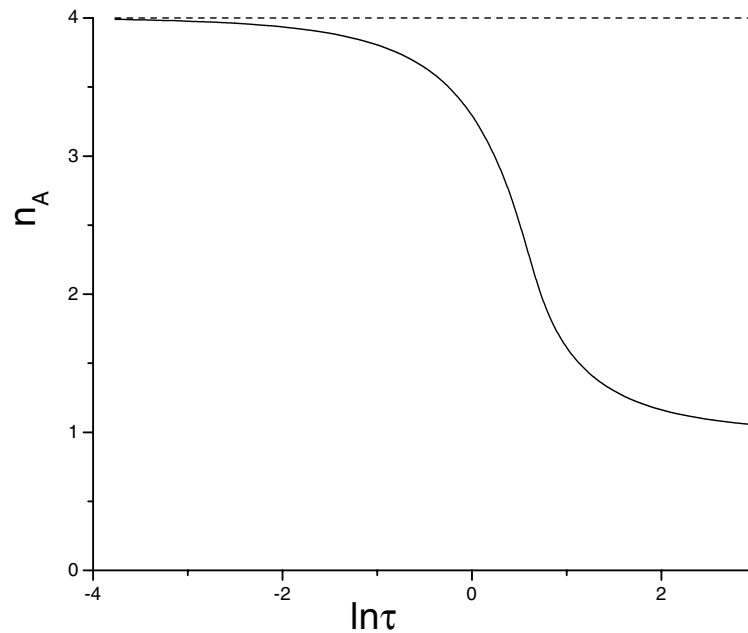That is, we have the KJMA expression for $X_K(t)$ again.

Figure 7. The dependence of the Avrami exponent n_A on $\ln \tau$ corresponding to figure 6.

7. Heterogeneous nucleation

Let us derive the expression for the volume fraction in the case of nucleation at fixed points randomly distributed over the domain (for example, on foreign particles) under the condition that all of the new-phase centres appear at $t' = 0$. Two variants of the problem are possible. In the first one, the points are distributed with the mean density n; their number in the domain is a random quantity. For this case, the dependence of the volume fraction on time is derived from the general solution of section 5 with the use of a δ-shaped representation of the nucleation rate:

$$I(t') = n\delta_+(t').$$ (85)

We use the dimensionless variables τ and x as well as the parameter $\gamma = nV_0 = (4\pi/3)nR_0^3$ which is the mean number of particles in the domain. Substituting $r_1 = R_0$, $r_2 = R_m(t)$ and $h = r$ into expression (58) and going to dimensionless variables, we obtain

$$v(r_1, r_2; h) = V_0 f(x, \tau)$$

where

$$f(x, \tau) = \frac{1}{2}(1 + \tau^3) + \frac{1}{16}x^3 - \frac{3}{8}x(1 + \tau^2) - \frac{3}{16}\frac{(1 - \tau^2)^2}{x}.$$ (86)

The expressions for $Q_i(\tau)$ are the following:

(1) $\tau < 1$:

$$Q_1^{(h)}(\tau) = (1 - \tau)^3 e^{-\gamma\tau^3} + 3\int_{1-\tau}^{1} e^{-\gamma f(x,\tau)}x^2 \, dx.$$ (87)

(2) $1 \leqslant \tau \leqslant 2$:

$$Q_2^{(h)}(\tau) = (\tau - 1)^3 e^{-\gamma} + 3\int_{\tau-1}^{1} e^{-\gamma f(x,\tau)}x^2 \, dx.$$ (88)

(3) $\tau > 2$:
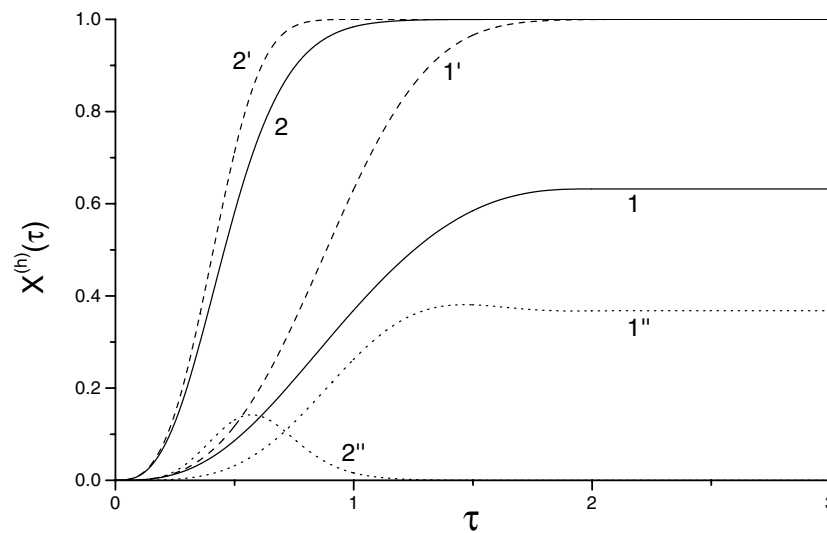
$$Q_3^{(h)}(\tau) = \mathrm{e}^{-\gamma}. \tag{89}$$

The volume fraction $X^{(h)}(\tau)$ of the material transformed is given by expression (70) as before, while in the case of infinite space it is given by the following one:

$$X_K^{(h)}(\tau) = 1 - \mathrm{e}^{-\gamma \tau^3}. \tag{90}$$

In figure 8, the dependences $X^{(h)}(\tau)$ and $X_K^{(h)}(\tau)$ together with

$$\Delta X^{(h)}(\tau) = X_K^{(h)}(\tau) - X^{(h)}(\tau)$$

are shown for different γ-values.

Figure 8. The volume fractions $X^{(h)}(\tau)$ (full lines), $X_K^{(h)}(\tau)$ (dashed lines) and $\Delta X^{(h)}(\tau) = X_K^{(h)}(\tau) - X^{(h)}(\tau)$ (dotted lines) in the first type of heterogeneous nucleation at $\gamma = 1$ (1, 1′, 1″) and $\gamma = 10$ (2, 2′, 2″).

It is seen from (87)–(89) that the Avrami exponent decreases with time from 3 to 0.

In the second variant of heterogeneous nucleation, the number N of particles in the domain is fixed. We assume a uniform distribution of particles over volume: the probability for any particle to be in the volume Δv is equal to $\Delta v / V_0$ and does not depend on either the shape or position of this volume. In this case, the binomial distribution applies: the probability that m particles are located inside the volume Δv is

$$P_N(m) = C_N^m \left(\frac{\Delta v}{V_0} \right)^m \left[1 - \frac{\Delta v}{V_0} \right]^{N-m}. \tag{91}$$

In particular, the probability that there are no particles inside the volume Δv is equal to

$$P_N(0) = \left[1 - \frac{\Delta v}{V_0} \right]^N. \tag{92}$$

Setting $\Delta v = \Omega(t, r)$, $\Omega(t, r)$ is equal to either $V_m(t)$ or $v(R_0, R_m(t); r)$ or V_0; we see that expression (92) replaces expression (5) in the case given. It is not difficult to get for the three cases described above:

(1) $\tau < 1$:

$$Q_1^{(N)}(\tau) = (1 - \tau)^3 \left[1 - \tau^3\right]^N + 3 \int_{1-\tau}^{1} [1 - f(x, \tau)]^N x^2 \, dx \tag{93}$$

where $f(x, \tau)$ is given by expression (86).

(2) $1 \leqslant \tau \leqslant 2$:

$$Q_2^{(N)}(\tau) = 3 \int_{\tau-1}^{1} [1 - f(x, \tau)]^N x^2 \, dx. \tag{94}$$

(3) $\tau > 2$:
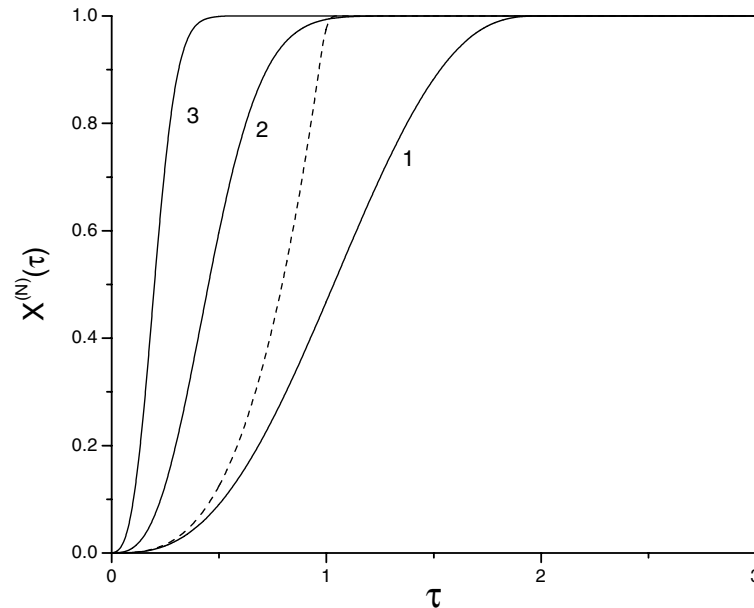
$$Q_3^{(N)}(\tau) = 0. \tag{95}$$

The volume fraction of the transformed material is

$$X^{(N)}(\tau) = \eta(1 - \tau)X_1(\tau) + \eta(\tau - 1)\eta(2 - \tau)X_2(\tau) + \eta(\tau - 2). \tag{96}$$

In the case $N = 1$, where the nucleation occurs at the centre of the domain,

$$X_c^{(1)}(\tau) = \eta(1 - \tau)\tau^3 + \eta(\tau - 1). \tag{97}$$

In figure 9, the dependence $X^{(N)}(\tau)$ for different N-values is shown.

Figure 9. The volume fractions $X^{(N)}(\tau)$ in the second type of heterogeneous nucleation. The curves 1, 2, 3 correspond to $N = 1, 10$ and 100. The dashed line represents the dependence $X_c^{(1)}(\tau)$, equation (97).

8. Discussion

As follows from the foregoing, the geometrical-probabilistic approach, in the form of the critical region method, is effective in solving different problems involved in calculating volume fractions. Also, the undoubted advantage of this approach is the rigour: the results are consequences of the initial premises.

Some comments concerning the subject of section 4 should be made. Nucleation at random points was considered for the first time by Avrami [4], who believed that phase transformation generally follows this scenario. Nucleation on random planes and straight lines was considered by Cahn [10] as applied to the problem of nucleation on grain boundaries and edges. The consideration was in the framework of the JMA approach and expressions for the volume fractions at constant nucleation and growth rates were obtained.

However, this approach, which is also called the mean-field approximation, is intuitive but not rigorous mathematically. It can yield both exact and approximate results. An example of the former is Kolmogorov's formula which is also obtained in the JMA approach. As an example of the latter case, the volume fractions of competing phases may be considered: the JMA approach yields approximate expressions for them [6]. This was the reason for reconsidering the expressions of reference [10]. The derivation of these expressions performed in the present paper supports the results of reference [10]: expressions (39) at constant nucleation and growth rates go into those obtained by Cahn. As is clear from the theory of section 3, the exactness of the mean-field approach in this problem is a consequence of the Poisson distribution law for the objects. This kind of distribution is frequently found in physical systems. However, cases of inhomogeneous distribution of the objects are also possible. For example, the points (the particles on which nucleation occurs) may be non-uniformly distributed over a volume for various reasons (γ_c depending on $\vec{r}$). These cases can also be considered in the framework of the theory of sections 3 and 1 in view of the corresponding modifications. In particular, the function $Q^{(i)}(t)$ calculated by the critical region method according to the scheme of section 3 will depend on the radius vector $\vec{r}_0$ of the point O′ in any frame of reference, so expression (14) must be used for calculating the volume fraction. The detailed consideration of these cases is beyond the scope of this paper.

The expressions obtained in sections 5–7 yield the volume-fraction value, $X(t)$, averaged over an ensemble of identical systems (see also the similar remark at the end of section 3). The volume-fraction value, $X_i(t)$, in the individual system is obviously a random quantity, since it is a result of the realization of the random process. If we denote by $p(X_i, t)$ the probability for the volume fraction at time t to be in the interval $[X_i, X_i + dX_i]$, then the mean value is

$$X(t) = \int_0^1 X_i p(X_i, t) \, dX_i. \tag{98}$$

In terms of an ensemble of N_a systems, expression (98) is replaced by the following:

$$X(t) = \lim_{N_a \to \infty} X(N_a, t) \qquad X(N_a, t) = \frac{1}{N_a} \sum_{i=1}^{N_a} X_i(t). \tag{99}$$

Let $\Delta X_i(t) \equiv X_i(t) - X(t)$ be the deviation from the mean value and let $\sigma(t) \equiv M\{[X_i(t) - X(t)]^2\}$ be the variance. Then we have for the deviation $\delta(N_a, t)$ of the volume fraction $X(N_a, t)$ from its mean

$$\delta(N_a, t) \equiv X(N_a, t) - X(t) = \frac{\sigma(t)}{\sqrt{N_a}} \chi(N_a, t) \tag{100}$$

where

$$\chi(N_a, t) \equiv \frac{1}{\sqrt{N_a}\sigma(t)} \sum_{i=1}^{N_a} \Delta X_i(t).$$

According to Lyapunov's theorem [7], $\chi(N_a, t)$ has the normal distribution for $N_a \to \infty$, so the following estimate for the probability of the inequality $\chi(N_a, t) < \varepsilon$ applies for sufficiently large N_a:

$$p\{\chi(N_a, t) < \varepsilon\} \simeq \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\varepsilon} e^{-(z^2/2)} \, dz. \tag{101}$$

Hence, we find

$$p\left\{\delta(N_a, t) < \varepsilon\right\} \simeq \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\sqrt{N_a}\varepsilon/\sigma(t)} \mathrm{e}^{-(z^2/2)}\, \mathrm{d}z. \tag{102}$$

The right-hand side of this equality is practically equal to unity at

$$\sqrt{N_a}\varepsilon/\sigma(t) \simeq 3.$$

Hence, for the given accuracy ε, the corresponding value of N_a is about $(3\sigma(t)/\varepsilon)^2$.

The two variants of heterogeneous nucleation considered above may correspond to the following experimental conditions in the case of crystallization of liquid drops. In the first variant, the drop is extracted at random from the bulk of a liquid in which the foreign particles are distributed with the mean density n. In this case, the number of particles in the drop is random including zero. The latter case leads to the final value of $X^{(h)}(\tau)$ being less than unity (figure 8).

In the second variant of heterogeneous nucleation, it is known that there are N particles in the drop. Evidently, the expressions for $X^{(h)}(t)$ may be obtained by averaging the expressions for $X^{(N)}(t)$ over all N:

$$X^{(h)}(t) = \sum_{N=0}^{\infty} P(N) X^{(N)}(t) \qquad P(N) = \frac{\gamma^N}{N!}\mathrm{e}^{-\gamma}. \tag{103}$$

In particular, at $t > 2t^* \equiv t_f$, $X^{(N)}(t) = 1$ at $N \geqslant 1$ and $X^{(0)} = 0$. Consequently,

$$X^{(h)}(t > t_f) = \sum_{N=1}^{\infty} P(N) = 1 - \mathrm{e}^{-\gamma}.$$

In turn, the expressions for $X^{(N)}(t)$ may be obtained by averaging the volume fraction $X^{(N)}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_k; t)$, at the location of the particles at the fixed points $\vec{r}_k$, over all $\vec{r}_k$. It is seen from figure 9 for the example $N = 1$ how such averaging changes the time dependence of the volume fraction. In particular, the transformation time t_f is doubled. This is due to taking into account the particle positions near the domain boundary.

As illustrated in figure 4, the departure of $X(\tau)$ from $X_K(\tau)$ increases with decrease in α, which, in particular, corresponds to decrease in R_0. The parameter α has the following meaning: $4\alpha = IV_0 t^*$ is the mean number of centres formed in the domain during time t^*. For increasing α the curves $X(\tau)$ and $X_K(\tau)$ come closer together in the sense of numerical values, but the qualitative distinction between them remains. However, this distinction can no longer be detected experimentally at sufficiently large α, since the phase transformation is finished ($X(\tau) \to 1$) at small τ, so the process is described with great accuracy by the KJMA expression over the whole time interval. The condition of the completion of the process may be formulated as $\alpha\tau_f^4 \simeq 1$, where τ_f is the transformation time. It is not difficult to derive that the mean linear size $\bar{L}$ of a nucleus in the system in the final state is of order $(I/u)^{-1/4}$. Hence, we get one more representation for α: $\alpha \simeq (R_0/\bar{L})^4$. For τ_f, we have $\tau_f \simeq \bar{L}/R_0$. Consequently, the condition for applicability of the KJMA expression with respect to the α-values, $\alpha \gg 1$, becomes $R_0/\bar{L} \gg 1$. It is easy to show that the condition $\gamma \gg 1$ for the applicability of the KJMA expression to the first type of heterogeneous nucleation is reduced to the same inequality.

In conclusion, let us consider the conditions under which the deviation from the KJMA law takes place, by looking at the example of a metastable (supercooled) liquid crystallization. In references [11, 12], the kinetics of crystallization and amorphization of $Pd_{82}Si_{18}$ alloy was described. The values of the parameters included in the expressions given below are taken from these works. The expression for the nucleation rate of the crystalline nuclei and that for

their growth velocity (for the approximation of a planar interface) [13] may be represented in the following form [12]:

$$I(T) = 2Nv\left(\frac{\sigma}{T}\right)^{1/2}\exp\left[-\frac{\Delta g + \Delta G_c(T)}{T}\right] \tag{104}$$

$$u(T) = av\exp\left(-\frac{\Delta g}{T}\right)\left[1 - \exp\left(-\frac{\Delta\mu(T)}{T}\right)\right]. \tag{105}$$

Hereafter, all the quantities with energy dimensions are reduced to kT_m, k is the Boltzmann constant, T_m is the melting temperature. Accordingly, the temperature T is dimensionless (in units of T_m); $T_m = 1$. The meaning of the quantities in (104) and (105) is as follows.

$\Delta G_c(T)$ is the work done in achieving critical size ($R_c(T)$) nucleus formation:

$$R_c(T) = \frac{2\sigma}{\Delta\mu(T)}a \tag{106}$$

$$\Delta G_c(T) = \frac{16\pi}{3}\frac{\sigma^3}{\Delta\mu^2(T)} \tag{107}$$

where $\sigma \equiv \sigma'a^2/kT_m$ (σ' is the surface tension on the crystal–liquid interface); $\Delta\mu(T)$ is the difference in chemical potential of atoms in the two phases. There are different approximations for this significant function, e.g. the expression of Thomson and Spaepen [14]:

$$\Delta\mu(T) = \frac{2h_m T(1 - T)}{1 + T} \tag{108}$$

where $h_m = 0.92$ is the heat of melting per atom. The expansion of $\Delta\mu(T)$ in terms of T in the vicinity of T_m [12] also may be used instead of (108).

The remainder of the parameters are as follows: $a = 2.26 \times 10^{-8}$ cm is the interatomic distance; $N = 8.7 \times 10^{22}$ cm^{-3} is the number of atoms in unit volume; $v = 10^{13}$ s^{-1} is the frequency of atom vibrations; $\Delta g = 10$ (this corresponds to about 1 eV) is the energy of activation of atom jumps; $\sigma \simeq 0.43h_m$ [15].

In figure 10, the temperature dependences of the nucleation rate, growth velocity and critical radius are shown on the same scales ($I_{\max} \simeq 10^{19}$ cm^{-3} s^{-1} and $u_{\max} \simeq 0.3$ cm s^{-1} are the maximal values of $I(T)$ and $u(T)$; $R' = R_c(0.995) \simeq 172a$). The characteristic feature of this figure is that the maxima of $I(T)$ and $u(T)$ are separated: the former is located at deeper supercooling than the latter. The critical radius decreases rather rapidly with decrease in temperature. The nucleation rate becomes appreciable when the critical radius becomes small (this corresponds to the fact that the probability of large fluctuations is vanishingly small). At the same time, the nucleation rate remains small enough up to some temperature. Thus, there is a temperature interval in which the values of the parameter α are sufficiently small for macroscopic values of the system size R_0. Notice that the condition $\alpha \simeq (R_0/\bar{L})^4 \gg 1$ considered above corresponds to the multidroplets (MD) regime [5, 16, 17]. Accordingly, the deviation from the KJMA law considered here occurs beyond this regime, when this condition is not satisfied.

Consider the following dependence:

$$R_0(T) = \alpha^{1/4}\bar{L}(T) = \left(\frac{\alpha u(T)}{I(T)}\right)^{1/4}. \tag{109}$$

For definiteness, let $\alpha = 1$ (in this case, the deviation from the KJMA law is distinct—see figure 4—$\max(\Delta X(\tau)) \simeq 0.25$). Letting, as an example, $T \simeq 0.84$, we get, from (104) and (105), $I(0.84) \simeq 16$ cm^{-3} s^{-1}, $u(0.84) \simeq 0.23$ s^{-1} cm, and it follows from (109) that $R_0 \simeq 0.34$ cm, which is a macroscopic size. At the same time, $R_c(0.84) \simeq 6a \ll \bar{L}$.
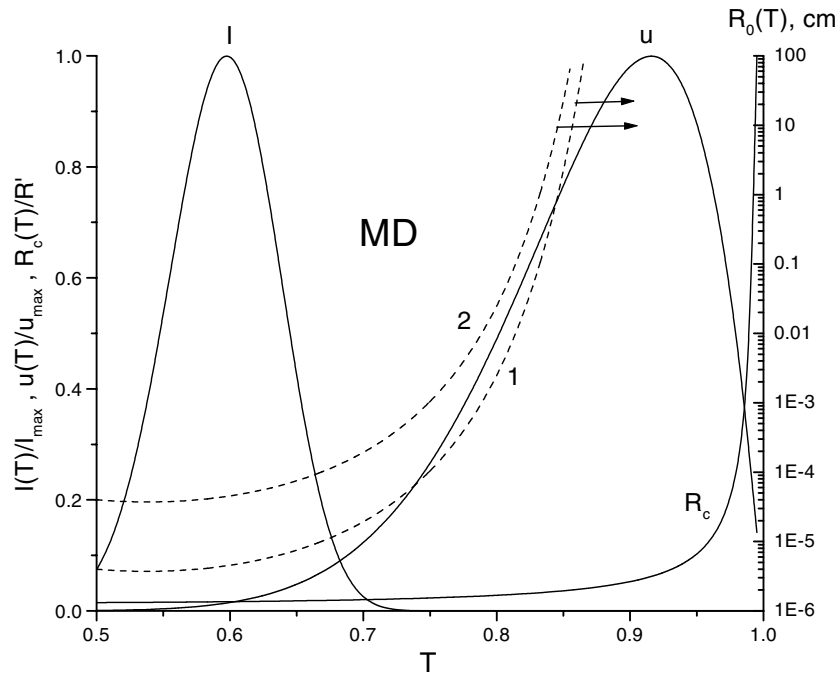
Figure 10. The temperature dependences of the nucleation rate (I), the growth velocity (u) and the critical radius (R_c)—left Y-axis. Dashed lines represent the dependence (109) for $\alpha = 1$ (1) and $\alpha = 10^4$ (2)—right Y-axis. The region above the curve 2 is that of the MD regime. The marked deviations from the KJMA law occur in the region near and below the curve 1.

In figure 10, the dependence (109) for $\alpha = 1$ is shown by dashed line 1. The deviation from the KJMA law at some temperature may be observed for sizes R_0 near this curve and below it. If we assume $\alpha = 10^4$ ($R_0/\bar{L} = 10$, $\max(\Delta X(\tau)) \simeq 0.02$) as the lowest limit of α for the MD regime, then this regime is operative for all temperatures in the region above curve 2 in figure 10 (this is the dependence (109) for $\alpha = 10^4$). It should be noted that the condition $R_c \ll \bar{L}$ is satisfied here down to the deepest supercooling ($\bar{L}(0.6)/R_c(0.6) \simeq 70$), though, as a rule, such supercooling is not achievable in practice.

The pattern shown in figure 10 is typical for the phenomena of crystallization and amorphization of a supercooled liquid. It is apparently rather general and also arises in other cases of phase transformations with homogeneous nucleation rate. In reference [5], the KJMA model was applied to the description of the Ising lattice-gas kinetics at mesoscopic scales of length and time. The excellent agreement between these two models was demonstrated in two dimensions and for moderately strong fields. The metastable phase decay picture of reference [5] is similar to that just considered. The magnetic field H plays the role of the temperature in figure 10 (the temperature itself is a fixed parameter therein). A test of the KJMA picture was carried out in the MD regime. Equation (109) for $\alpha = 1$ limiting this regime is that for the dynamic spinodal (DSP) [5]. This equation determines the $R_0^{(DSP)}(H, T)$ dependence, so the noticeable deviations from the KJMA law should occur at system sizes $R_0 \sim R_0^{(DSP)}$ and to a greater extent at $R_0 < R_0^{(DSP)}$. At the same time, these sizes may be still macroscopic, $1 \ll R_c \ll \bar{L} \sim R_0$, since $R_0^{(DSP)}$ is large in the region of weak fields (which corresponds to slight supercooling in figure 10). As all of these conditions are fulfilled, expressions (71)–(73) for the volume fraction should be used instead of (74).

Appendix

In the case of nucleation on a plane, expression (8) has the following form:

$$J_{r_0}^{(s)}(t', t) = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \, \sin\theta \, I_s(t') \delta(r_0 - R(t', t) \cos\theta). \tag{A.1}$$

In order to integrate over θ, we use the following property of the δ-function:

$$\delta(x(\theta)) = \frac{1}{|dx/d\theta|} \Bigg|_{\theta=\theta_0} \delta(\theta - \theta_0)$$

where θ_0 is the root of the equation

$$r_0 - R(t', t) \cos\theta = 0. \tag{A.2}$$

This equation is valid only at $R(t', t) \geq r_0$. Hence, the maximal value of t' which is denoted by $t_m(t, r_0)$ is determined by equation (17). At $t_m < t' < t$, $J_{r_0}(t', t) = 0$. We shall take this fact into account with the help of the asymmetric unit function $\eta_-(x)$ [8].

As a result of integration of (A.1), we get

$$J_{r_0}^{(s)}(t', t) = \frac{I_s(t') \eta_-(R(t', t) - r_0)}{2R(t', t)}. \tag{A.3}$$

For nucleation on a straight line and at a point, we have respectively

$$\begin{aligned} J_{r_0}^{(l)}(t', t) &= \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \, \sin\theta \, I_l(t') \delta(r_0 - R(t', t) \cos\theta) \delta(R \sin\theta \sin\phi) \\ &= \frac{I_l(t') \eta_-(R(t', t) - r_0)}{2\pi R^2(t', t) \sin\theta_0} \end{aligned} \tag{A.4}$$

$$\begin{aligned} J_{r_0}^{(c)}(t', t) &= \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \, \sin\theta \, I_c(t') \delta(r_0 - R(t', t) \cos\theta) \delta(R \sin\theta \sin\phi) \\ &\quad \times \delta(R \sin\theta \cos\phi) \\ &= \frac{2 I_c(t') \eta_-(R(t', t) - r_0) \delta(R \sin\theta_0)}{4\pi R^2(t', t) \sin\theta_0}. \end{aligned} \tag{A.5}$$

Substituting $\sin\theta_0 = \sqrt{R^2 - r_0^2}/R$ into (A.5), we find

$$\frac{2\delta(R \sin\theta_0)}{\sin\theta_0} = 2\delta(R - r_0) \eta_-(R - r_0) \, dR = \delta_+(R - r_0) \, dR = d\eta_+(R - r_0).$$

Substituting the $J_{r_0}^{(i)}$-values into (10), we obtain

$$dP_i(t', t) = I_i(t') \eta_-(R - r_0) \, dt' \, d\zeta_{r_0}^{(i)}(t', t) \tag{A.6}$$

where $\zeta_{r_0}^{(i)}(t', t)$ is given by (18); in the case of points, we put $\zeta_{r_0}^{(c)}(t', t) = \eta_+(R(t', t) - r_0)$.

Thus, we have the following expression for $Y_{r_0}^{(i)}(t)$:

$$Y_{r_0}^{(i)}(t) = \int_{t_0}^t d\tau \int_0^{t_m(\tau, r_0)} dt' \, I_i(t') \frac{\partial \zeta_{r_0}^{(i)}(t', \tau)}{d\tau} \tag{A.7}$$

Changing the order of integration here, we get finally

$$Y_{r_0}^{(i)}(t) = \begin{cases} \displaystyle\int_0^{t_m(t, r_0)} dt' \, I_i(t') \zeta_{r_0}^{(i)}(t', t) & r_0 < R_m(t) \\ 0 & r_0 > R_m(t). \end{cases} \tag{A.8}$$

References

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