Condensed Matter Physics 2008, Vol. 11, No 4(56), pp. 597–613

On the kinetics of phase transformation of small particles in Kolmogorov's model

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Received May 16, 2007, in final form March 15, 2008

The classical Kolmogorov-Johnson-Mehl-Avrami (KJMA) theory is generalized to the case of a finite-size system. The problem of calculating the new-phase volume fraction in a spherical domain is solved within the framework of geometrical-probabilistic approach. The solutions are obtained for both homogeneous and heterogeneous nucleations. It is shown that the finiteness property results in a 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, i.e. a slowing down of the transformation process takes place. The obtained results can be used, in particular, for controlling the crystallization kinetics in amorphous powders.

Key words: *KJMA theory, volume fraction, nucleation, Avrami exponent*

PACS: *05.70.Fh, 68.55.Ac, 81.15.Aa*

1. Introduction

The kinetics of a phase transformation process in infinite space is described by the well-known expression of Kolmogorov [1] for the volume fraction $X_{\mathrm{K}}(t)$ of the material transformed:

$$X_{\mathrm{K}}(t) = 1 - \exp\left[-\int_0^t I(t')V(t',t)\mathrm{d}t'\right], \tag{1}$$

where $V(t',t)$ is the volume at time t of the nucleus appearing at time t'; $I(t)$ is the nucleation rate. For the spherical shape of nuclei, $V(t',t) = (4\pi/3)R^3(t',t)$, $R(t',t) = \int_{t'}^{t} u(\tau)\mathrm{d}\tau$, where $R(t',t)$ is the radius of a nucleus, $u(t)$ is its growth velocity. This expression was also derived by Johnson, Mehl and Avrami [2,3] with the use of a different approach at constant values of I and u.

Under the restrictions of Kolmogorov's model [1], or the K-model [4] (these restrictions are considered in detail in this monograph), the KJMA expression is exact in the case of an infinite system. In practice, the fulfillment of the inequality $\overline{L} \ll R_0$ is required for its validity, where R_0 is the size of the system considered, $\overline{L}$ is the mean grain size. This inequality is satisfied in many cases, and the KJMA formula is widely used for the analysis of experimental data. However, in the case of a system of sufficiently small size and at certain values of nucleation and growth rates, the deviation of the volume fraction $X(t)$ from $X_{\mathrm{K}}(t)$ is possible. In particular, such a situation can occur in the process of crystallization of a liquid drop or a small amorphous ball, especially at the temperature at which the nucleation rate is small while the growth velocity is large.

Therefore, consideration of the problem of calculating the new-phase volume fraction in a finite system and derivation of the criteria for the applicability of the KJMA expression are of interest. Until recently, the inclusion of finite-size effects into the KJMA theory was performed mainly for thin films [5–8]. In reference [5], the time cone method is used for this purpose. In reference [7], the anisotropy of nuclei (ellipsoids) is also included in this problem. The detailed calculation of transformation kinetics in thin films for a spherical shape of nuclei is given in reference [8].

In the present report, a rigorous solution of this problem is presented for a spherical domain. The cases of both homogeneous and heterogeneous nucleations are considered. The time dependence of the volume fraction $X(t)$ is shown to differ qualitatively from that in infinite space; therefore, it cannot be derived from the latter, equation (1), by the use of correction factors. The obtained dependencies $X(t)$ are in qualitative agreement with the corresponding results of reference [8]. The solution is obtained with the help of the critical region method which was earlier applied by the author to solving other problems of calculating the volume fractions [9,10].

2. Calculating the volume fraction in a spherical domain. Homogeneous nucleation

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

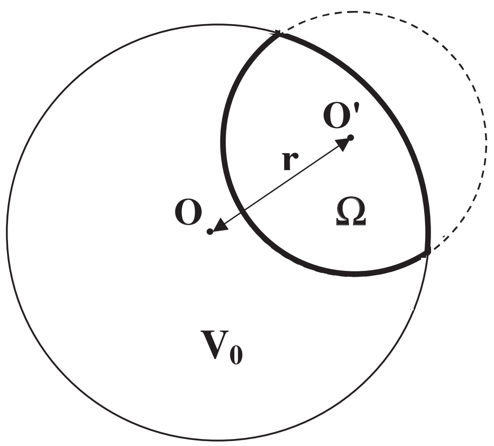

Figure 1. The domain and the critical region for the point O'. The critical region part of volume $\Omega(r\,;t',t) = v(r\,;t',t)$ is marked out.

Take at random the point O' in the domain. Let it be at a distance r from the centre of the domain which is the point O (figure 1). We find the probability $Q(r,t)$ that the point O' will be non-transformed at time t. Let us specify the critical region for the point O' – the sphere of radius $R(t',t)$. At time t', the boundary of this region moves at the velocity $u(t')$, so that in the time interval $0 \leqslant t' \leqslant t$ its radius decreases from the greatest value $R(0,t) \equiv R_m(t)$ up to $R(t,t) \equiv 0$. In order for the point O' to be non-transformed, it is necessary and sufficient that no centre of a new phase should be formed within the critical region in the time interval $0 \leqslant t' \leqslant t$. The probability of this event is [1]

$$Q(r,t) = \exp\left[-Y(r,t)\right]. \tag{2}$$

In the case of infinite space, the function Y does not depend on r and has the following form [1]:

$$Y(t) = \int_0^t I(t')V(t',t)\mathrm{d}t', \tag{3}$$

where $V(t',t) = (4\pi/3)R^3(t',t)$ is the critical region volume at time t'.

In the considered case, the new-phase centres can appear only within the domain. At the same time, in general, only a part of the critical region for the point O' lies within this domain. Let us denote the volume of this part by $\Omega(r\,; t',t)$ (figure 1). 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:

$$Y(r,t) = \int_0^t I(t')\Omega(r\,; t',t)\mathrm{d}t'. \tag{4}$$

The volume fraction $Q(t)$ of the material non-transformed at time t is the probability for the point O' to fall in the non-transformed part of the domain:

$$Q(t) = \frac{1}{V_0}\int_0^{R_0} Q(r,t)(4\pi r^2)\mathrm{d}r, \tag{5}$$

accordingly, the volume fraction of the material transformed is $X(t) = 1 - Q(t)$.

Furthermore, the problem is how to find an 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 the spacing between centres h, the volume of the second sphere lying within the first sphere is equal to

$$v(r_1,r_2;h) = \pi\left\{\frac{2}{3}\left(r_1^3+r_2^3\right) + \frac{1}{12}h^3 - \frac{1}{2}h\left(r_1^2+r_2^2\right) - \frac{1}{4}\frac{\left(r_1^2-r_2^2\right)^2}{h}\right\}. \tag{6}$$

Determine the times t_1 and t_2 by the equations

$$R_m(t_1) = R_0\,, \qquad R_m(t_2) = 2R_0\,. \tag{7}$$

The following three cases with respect to time t arise.

1) $R_m(t) < R_0$: $t < t_1$

Let us determine the distance r_0 by the equality

$$r_0 = R_0 - R_m\,. \tag{8}$$

At $0 \leqslant r \leqslant r_0$, the critical region lies entirely within the domain in the whole time interval $0 \leqslant t' \leqslant t$; accordingly, $\Omega(r\,; t',t) = V(t',t)$. Let us determine the time $t_m(r,t)$ by the equation

$$R(t_m,t) = R_0 - r. \tag{9}$$

At $r_0 < r \leqslant R_0$ the critical region lies partially within 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 $t_m \leqslant t' \leqslant t$ the critical region is entirely within the domain; hence, $\Omega(r\,;t',t) = V(t',t)$. Thus,

$$Y_1(r,t) = \begin{cases} \int_0^t I(t')V(t',t)\mathrm{d}t' \,, & 0 \leqslant r \leqslant r_0 \,, \\ \int_0^{t_m(r,t)} I(t')v(r\,;t',t)\mathrm{d}t' + \int_{t_m(r,t)}^t I(t')V(t',t)\mathrm{d}t' \,, & r_0 < r \leqslant R_0 \,; \end{cases} \tag{10}$$

2) $R_0 \leqslant R_m(t) \leqslant 2R_0$: $t_1 \leqslant t \leqslant t_2$

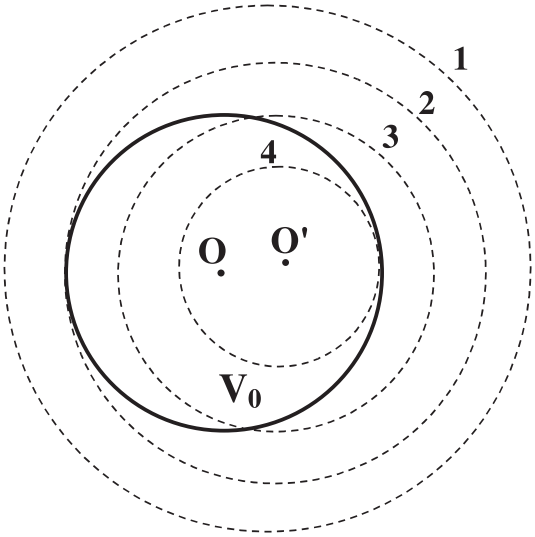

Figure 2. Positions of the critical region boundary at different times t': 1) $0 \leqslant t' < t'_m(r,t)$; 2) $t' = t'_m(r,t)$; 3) $t'_m(r,t) < t' < t_m(r,t)$ 4) $t' = t_m(r,t)$.

Let us determine the distance r'_0 by the equality

$$r'_0 = R_m - R_0 \,, \tag{11}$$

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

$$R(t'_m, t) = R_0 + r. \tag{12}$$

Consider the case $0 < r < r'_0$. In figure 2, 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 within 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 $r'_0 \leqslant r \leqslant R_0$ we have:

$$\Omega(r\,;t',t) = \begin{cases} v(r\,;t',t) \,, & 0 \leqslant t' < t_m(r,t), \\ V(t',t) \,, & t_m(r,t) \leqslant t' \leqslant t. \end{cases} \tag{13}$$

Thus,

$$Y_2(r,t) = \begin{cases} V_0 \int_0^{t'_m(r,t)} I(t')\mathrm{d}t' + \int_{t'_m(r,t)}^{t_m(r,t)} I(t')v(r\,;t',t)\mathrm{d}t' + \int_{t_m(r,t)}^t I(t')V(t',t)\mathrm{d}t' \,, \\ \qquad\qquad 0 \leqslant r < r'_0 \,, \\ \int_0^{t_m(r,t)} I(t')v(r\,;t',t)\mathrm{d}t' + \int_{t_m(r,t)}^t I(t')V(t',t)dt' \qquad r'_0 \leqslant r \leqslant R_0 \,; \end{cases} \tag{14}$$

3) $R_m(t) > 2R_0$: $t > t_2$

As it follows from the foregoing, in this case

$$\Omega(r\,;t',t) = \begin{cases} V_0\,, & 0 \leqslant t' \leqslant t'_m(r,t), \\ v(r\,;t',t)\,, & t'_m(r,t) < t' < t_m(r,t), \\ V(t',t)\,, & t_m(r,t) \leqslant t' \leqslant t \end{cases} \tag{15}$$

for arbitrary r-value. Accordingly,

$$\begin{aligned} Y_3(r,t) &= V_0 \int_0^{t'_m(r,t)} I(t')\mathrm{d}t' + \int_{t'_m(r,t)}^{t_m(r,t)} I(t')v(r;t',t)\mathrm{d}t' \\ &\quad + \int_{t_m(r,t)}^{t} I(t')V(t',t)\mathrm{d}t', 0 \leqslant r \leqslant R_0\,. \end{aligned} \tag{16}$$

The volume fraction of the material transformed in every case is

$$X_i(t) = 1 - \frac{1}{V_0}\int_0^{R_0} \mathrm{e}^{-Y_i(r,t)}(4\pi r^2)\mathrm{d}r\,,\quad i = 1,\ 2,\ 3. \tag{17}$$

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

$$X(t) = \eta(t_1 - t)X_1(t) + \eta(t_2 - t)\eta(t - t_1)X_2(t) + \eta(t - t_2)X_3(t)\,, \tag{18}$$

where $\eta(x)$ is the symmetric unit function [13].

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. The distinction will be only in determining $\Omega(r;t',t)$.

3. The case of constant nucleation and growth rates

In order to analyse 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 a 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 each case described above:

1) $\tau < 1$

$$Q_1(t) = (1-\tau)^3\,\mathrm{e}^{-\alpha\tau^4} + 3\int_{1-\tau}^{1} \mathrm{e}^{-\alpha\phi_1(x,\tau)}x^2\mathrm{d}x, \tag{19}$$

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) $1 \leqslant \tau \leqslant 2$

$$Q_2(\tau) = 3\left\{\int_0^{\tau-1} \mathrm{e}^{-\alpha\phi_2(x,\tau)}x^2\mathrm{d}x + \int_{\tau-1}^{1} \mathrm{e}^{-\alpha\phi_1(x,\tau)}x^2\mathrm{d}x\right\}, \tag{20}$$

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) $\tau > 2$

$$Q_3(\tau) = 3\int_0^1 \mathrm{e}^{-\alpha\phi_2(x,\tau)}x^2\mathrm{d}x. \tag{21}$$

The volume fraction of the material transformed is given by expression (18) 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:

$$X_\mathrm{K}(\tau) = 1 - \mathrm{e}^{-\alpha\tau^4}. \tag{22}$$

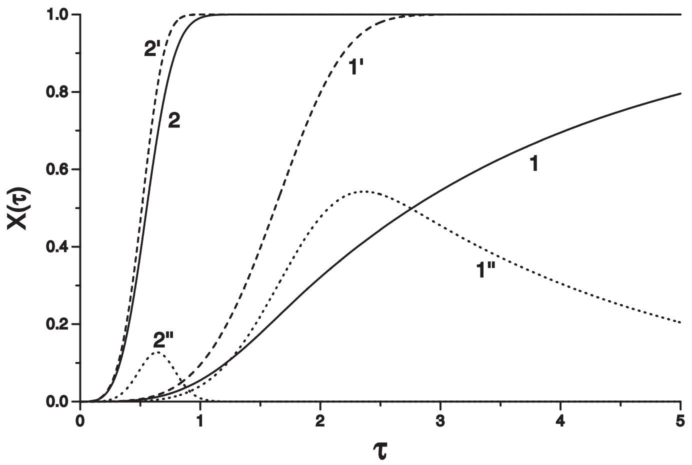

Figure 3. The volume fractions $X(\tau)$ (full lines), $X_\mathrm{K}(\tau)$ (dashed lines) and $\Delta X(\tau) = X_\mathrm{K}(\tau) - X(\tau)$ (dotted lines) in the process of homogeneous nucleation. The groups of curves (1, 1$'$, 1$''$) and (2, 2$'$, 2$''$) are for $\alpha = 0.1$ and $\alpha = 10$, respectively.

In figure 3, the dependence $X(\tau)$ at different values of α is shown in comparison with that given by expression (22) for infinite space. Also, the function $\Delta X(\tau) = X_\mathrm{K}(\tau) - X(\tau)$ that gives the error caused by the use of (22) 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 are as follows:

1) $\rho \geqslant 1$

$$Q_1(\rho) = \left(\frac{\rho-1}{\rho}\right)^3 \mathrm{e}^{-\beta} + \frac{3}{\rho^3}\int_{\rho-1}^{\rho} \mathrm{e}^{-\beta\psi_1(y,\rho)}y^2\mathrm{d}y\,, \tag{23}$$

where $\psi_1(y,\rho) = \sum_{=-1}^{4} P_k(\rho)y^k$: $P_{-1}(\rho) = (2/5)\rho^5 - (3/4)\rho^4 + (1/2)\rho^2 - 3/20$; $P_0(\rho) = -(3/2)\rho^4 + 2\rho^3 + 1/2$; $P_1(\rho) = 2\rho^3 - (3/2)\rho^2 - 1/2$; $P_2(\rho) = -\rho^2$; $P_3 = 1/4$; $P_4 = 1/10$.

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

$$Q_2(\rho) = \frac{3}{\rho^3}\left\{\int_0^{1-\rho} \mathrm{e}^{-\beta\psi_2(y,\rho)}y^2\mathrm{d}y + \int_{1-\rho}^{\rho} \mathrm{e}^{-\beta\psi_1(y,\rho)}y^2\mathrm{d}y\right\}, \tag{24}$$

where $\psi_2(y,\rho) = \sum_{=0}^{4} P_k(\rho)y^k$ 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) $0 < \rho \leqslant 1/2$

$$Q_3(\rho) = \frac{3}{\rho^3}\int_0^{\rho} \mathrm{e}^{-\beta\psi_2(y,\rho)}y^2\mathrm{d}y. \tag{25}$$

The volume fraction of the transformed material is

$$X(\rho) = \eta\left(\frac{1}{2}-\rho\right)X_3(\rho) + \eta\left(\rho-\frac{1}{2}\right)\eta\left(1-\rho\right)X_2(\rho) + \eta\left(\rho-1\right)X_1(\rho)\,, \tag{26}$$

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

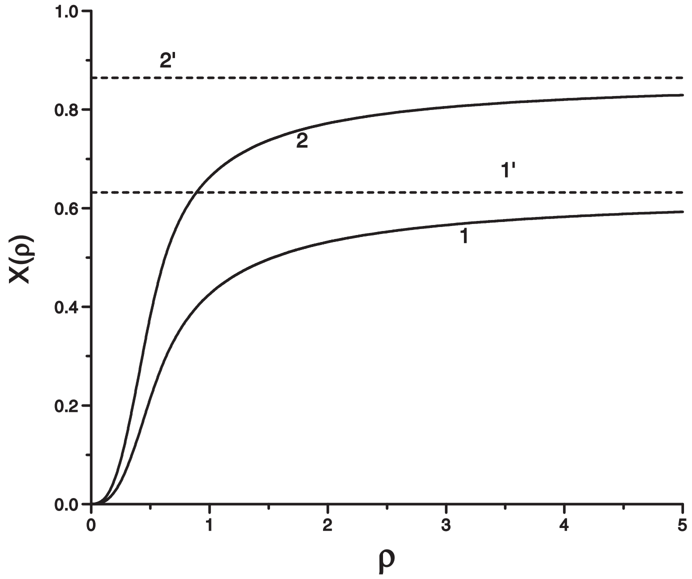

Figure 4. The volume fractions $X(\rho)$ (full lines) and $X_{\mathrm{K}}(\rho)$ (dashed lines) at fixed time. The pairs of curves (1, 1′) and (2, 2′) are for $\beta = 1$ and $\beta = 2$, respectively.

The KJMA formula in this notation is as follows

$$X_{\mathrm{K}}(\rho) = \exp(-\beta). \tag{27}$$

In figure 4, the dependence $X(\rho)$ is shown for different values of β.

4. 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 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 volume fraction on time is derived from the general solution of Section 2 with the use of a δ-shaped representation of the nucleation rate:

$$I(t') = n\delta_+(t'). \tag{28}$$

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 (6) and going to dimensionless variables, we obtain: $v(r_1, r_2; h) = V_0 f(x,\tau)$, where

$$f(x,\tau) = \frac{1}{2}\left(1+\tau^3\right) + \frac{1}{16}x^3 - \frac{3}{8}x\left(1+\tau^2\right) - \frac{3}{16}\frac{\left(1-\tau^2\right)^2}{x}\,. \tag{29}$$

The expressions for $Q_i(\tau)$ are as follows:
1) $\tau < 1$

$$Q_1^{(h)}(\tau) = (1-\tau)^3 \, \mathrm{e}^{-\gamma\tau^3} + 3\int_{1-\tau}^{1} \mathrm{e}^{-\gamma f(x,\tau)} x^2 \mathrm{d}x, \tag{30}$$

2) $1 \leqslant \tau \leqslant 2$

$$Q_2^{(h)}(\tau) = (\tau-1)^3 \, \mathrm{e}^{-\gamma} + 3\int_{\tau-1}^{1} \mathrm{e}^{-\gamma f(x,\tau)} x^2 \mathrm{d}x, \tag{31}$$

3) $\tau > 2$

$$Q_3^{(h)}(\tau) = \mathrm{e}^{-\gamma} \,. \tag{32}$$

The volume fraction $X^{(h)}(\tau)$ of the material transformed is given by expression (18) as before, while in the case of infinite space it is given by the following one:

$$X_{\mathrm{K}}^{(h)}(\tau) = 1 - \mathrm{e}^{-\gamma\tau^3} \,. \tag{33}$$

In figure 5, the dependencies $X^{(h)}(\tau)$ and $X_{\mathrm{K}}^{(h)}(\tau)$ together with $\Delta X^{(h)}(\tau) = X_{\mathrm{K}}^{(h)}(\tau) - X^{(h)}(\tau)$ are shown for different γ-values.

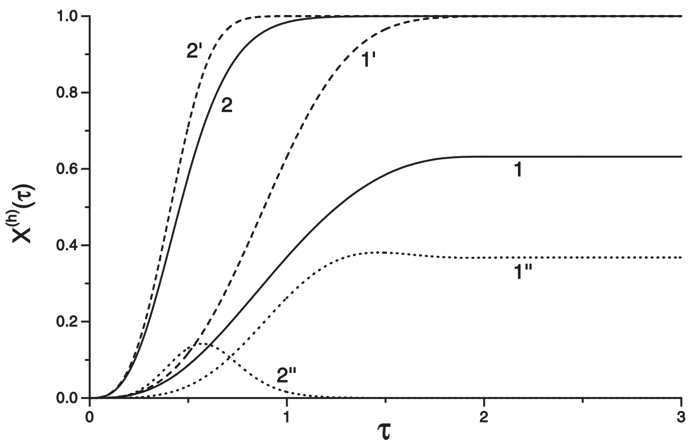

Figure 5. The volume fractions $X^{(h)}(\tau)$ (full lines), $X_{\mathrm{K}}^{(h)}(\tau)$ (dashed lines) and $\Delta X^{(h)}(\tau) = X_{\mathrm{K}}^{(h)}(\tau) - X^{(h)}(\tau)$ (dotted lines) in the first type of heterogeneous nucleation at $\gamma = 1$ (1, 1′, 1″) and $\gamma = 10$ (2, 2′, 2″).

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 the 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 of m particles being located within the volume Δv is

$$P_N(m) = C_N^m \left(\frac{\Delta v}{V_0}\right)^m \left[1 - \frac{\Delta v}{V_0}\right]^{N-m} . \tag{34}$$

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

$$P_N(0) = \left[1 - \frac{\Delta v}{V_0}\right]^N . \tag{35}$$

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 (35) replaces the expression (2) in the case given. For the three cases described above it is not difficult to get the following:

1) $\tau < 1$

$$Q_1^{(N)}(\tau) = (1-\tau)^3 \left[1-\tau^3\right]^N + 3\int_{1-\tau}^{1} \left[1 - f(x,\tau)\right]^N x^2 \mathrm{d}x \,, \tag{36}$$

were $f(x,\tau)$ is given by expression (29).

2) $1 \leqslant \tau \leqslant 2$

$$Q_2^{(N)}(\tau) = 3\int_{\tau-1}^{1} \left[1 - f(x,\tau)\right]^N x^2 \mathrm{d}x, \tag{37}$$

3) $\tau > 2$

$$Q_3^{(N)}(\tau) = 0. \tag{38}$$

The volume fraction of the transformed material is

$$X^{(N)}(\tau) = \eta(1-\tau)X_1(\tau) + \eta(\tau-1)\eta(2-\tau)X_2(\tau) + \eta(\tau-2). \tag{39}$$

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

$$X_c^{(1)}(\tau) = \eta(1-\tau)\tau^3 + \eta(\tau-1). \tag{40}$$

In figure 6, the dependence $X^{(N)}(\tau)$ for different N-values is shown.

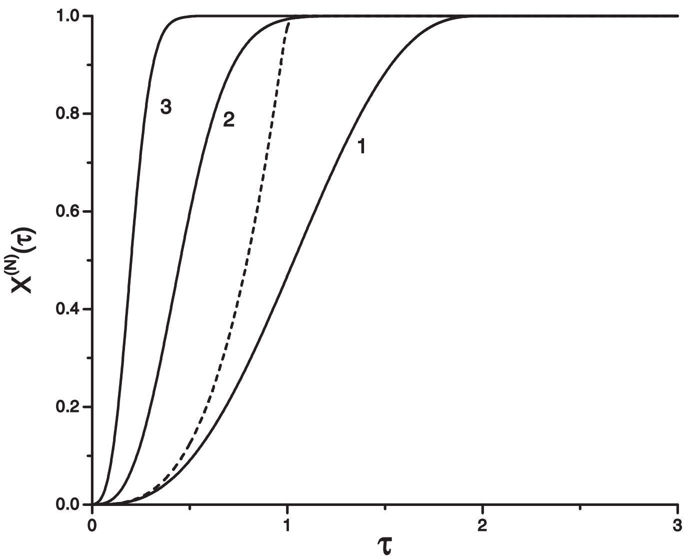

Figure 6. The volume fractions $X^{(N)}(\tau)$ in the second type of heterogeneous nucleation. The curves 1, 2, 3 correspond to $N = 1$, 10 and 100. The dashed line represents the dependence $X_c^{(1)}(\tau)$, equation (40).

5. Crystallization of a liquid drop

As illustrated in figure 3, the departure of $X(\tau)$ from $X_{\mathrm{K}}(\tau)$ increases with a decrease in α, which, in particular, corresponds to a decrease in R_0. The parameter α has the following meaning: $4\alpha = IV_0t^*$ is the mean number of centres formed in the domain during time t^*. For increasing α, the curves $X(\tau)$ and $X_{\mathrm{K}}(\tau)$ 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 process being completed 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 grain in the system in the final state is of the order of $(I/u)^{-1/4}$. Hence, we get another 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.

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 reference's [14,15], 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 planar interface) [12] may be presented in the following form [15]:

$$I(T) = 2N\nu\left(\frac{\sigma}{T}\right)^{1/2}\exp\left[-\frac{\Delta g + \Delta G_c(T)}{T}\right], \tag{41}$$

$$u(T) = a\nu\exp\left(-\frac{\Delta g}{T}\right)\left[1 - \exp\left(-\frac{\Delta\mu(T)}{T}\right)\right]. \tag{42}$$

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 (41) and (42) is as follows.

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

$$R_c(T) = \frac{2\sigma}{\Delta\mu(T)}a, \tag{43}$$

$$\Delta G_c(T) = \frac{16\pi}{3}\frac{\sigma^3}{\Delta\mu^2(T)}, \tag{44}$$

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 Spaepan [16]:

$$\Delta\mu(T) = \frac{2h_mT(1-T)}{1+T}, \tag{45}$$

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 [15] may be also used instead of (45).

The remainder of the parameters are as follows: $a = 2.26 \cdot 10^{-8}$ cm is the interatomic distance; $N = 8.7 \cdot 10^{22}$ cm^{-3} is the number of atoms in unit volume; $\nu = 10^{13}$ 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; $\sigma \simeq 0.43h_m$ [17].

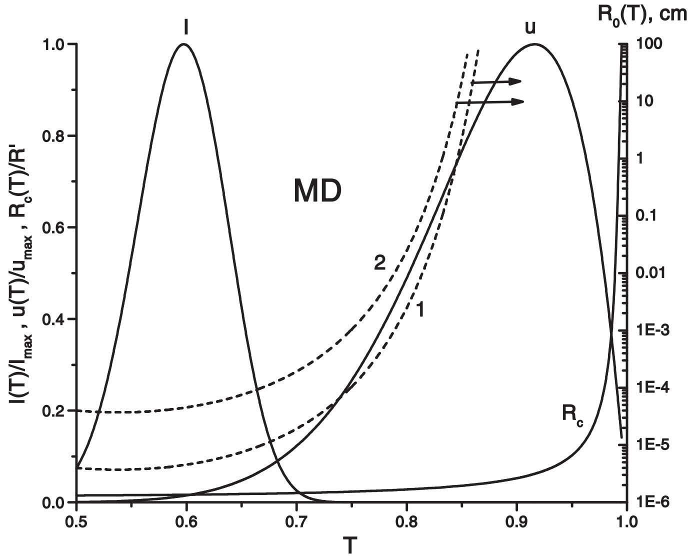

Figure 7. The temperature dependencies of the nucleation rate (I), the growth velocity (u) and the critical radius (R_c) – left Y-axis. Dashed lines represent the dependence (46) for $\alpha = 1$ (1) and $\alpha = 10^4$ (2) – right Y-axis. The region above the curve 2 is that of the MD regime. The marked deviations from the KJMA law occur in the region near and below the curve 1.

In figure 7, the temperature dependencies 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 a deeper supercooling than the latter. The critical radius decreases rather rapidly with a 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 [18–20]. Accordingly, the deviation from the KJMA law considered here occurs beyond this regime, when this condition is not satisfied.

Consider the following dependence:

$$R_0(T) = \alpha^{1/4}\bar{L}(T) = \left(\frac{\alpha u(T)}{I(T)}\right)^{1/4}. \tag{46}$$

For definiteness, let $\alpha = 1$ (in this case, the deviation from the KJMA law is distinct – see figure 3 – $\max(\Delta X(\tau)) \simeq 0.25$). Letting, as an example, $T \simeq 0.84$, we get, from

(41) and (42), $I(0.84) \simeq 16\ cm^{-3}s^{-1}$, $u(0.84) \simeq 0.23\ s^{-1}cm$, and it follows from (46) that $R_0 \simeq 0.34\ cm$, which is a macroscopic size. At the same time, $R_c(0.84) \simeq 6a \ll \bar{L}$.

In figure 7, the dependence (46) 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 7 (this is the dependence (46) 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.

6. Discussion

The expressions obtained above yield the volume-fraction value, $X(t)$, averaged over an ensemble of identical systems. 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 the probability for the volume fraction at time t to be in the interval $[X_i, X_i + \mathrm{d}X_i]$ is denoted by $p(X_i, t)$, then the mean value is

$$X(t) = \int_0^1 X_i p(X_i, t)\mathrm{d}X_i\,. \tag{47}$$

In terms of an ensemble of N_a systems, expression (47) is replaced by the following:

$$X(t) = \lim_{N_a\to\infty} X(N_a, t)\ , \qquad X(N_a, t) = \frac{1}{N_a}\sum_{i=1}^{N_a} X_i(t). \tag{48}$$

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, for the deviation $\delta(N_a, t)$ of the volume fraction $X(N_a, t)$ from its mean we have

$$\begin{aligned} \delta(N_a, t) &\equiv X(N_a, t) - X(t) = \frac{\sigma(t)}{\sqrt{N_a}}\chi(N_a, t)\ , \\ \chi(N_a, t) &\equiv \frac{1}{\sqrt{N_a}\sigma(t)}\sum_{i=1}^{N_a} \Delta X_i(t). \end{aligned} \tag{49}$$

According to Lyapunov's theorem [11], $\chi(N_a, t)$ has the normal distribution for $N_a \to \infty$, so the following estimate for the probability of the inequality $\chi(N_a, t) < \varepsilon$ is applicable for sufficiently large N_a:

$$p\{\chi(N_a, t) < \varepsilon\} \simeq \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\varepsilon} \mathrm{e}^{-(z^2/2)}\mathrm{d}z. \tag{50}$$

Hence, we find

$$p\{\delta(N_a, t) < \varepsilon\} \simeq \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\sqrt{N_a}\varepsilon/\sigma(t)} \mathrm{e}^{-(z^2/2)}\mathrm{d}z. \tag{51}$$

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 5).

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:

$$X^{(h)}(t) = \sum_{N=0}^{\infty} P(N) X^{(N)}(t)\,, \qquad P(N) = \frac{\gamma^N}{N!}\mathrm{e}^{-\gamma}. \tag{52}$$

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 $X^{(N)}(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N; t)$, at the location of the particles at the fixed points $\vec{r}_k$, over all $\vec{r}_k$. It is seen in figure 6 for the case $N = 1$ in what way this averaging changes the time dependence of the volume fraction (curves 1 and dashed). In particular, the transformation time t_f is doubled. This is due to the particle positions near the domain boundary being taken into account.

Consider some limiting cases of the expressions derived. At $\tau \to 0$ the addend in (19) has the following expansion in terms of τ: $3\tau - 3\tau^2 + \tau^3 + O(\tau^5)$. Accordingly, the volume fraction is

$$Q(\tau) = Q_1(\tau) = \mathrm{e}^{-\alpha\tau^4}\left[1 + O(\alpha\tau^5)\right]. \tag{53}$$

That is, we get the KJMA expression, as we should. 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' should lie at a distance greater than $R_m(t)$ from the domain boundary. In order to allow the volume $\Delta V = (4\pi/3)[R_0^3 - (R_0 - R_m)^3]$ of the boundary layer to be neglected, the condition $\Delta V/V_0 \ll 1$ or $R_m/R_0 \ll 1$ should be obeyed.

At $\tau > 2$ we have

$$Q(\tau) = Q_3(\tau) = J(\alpha)\mathrm{e}^{-4\alpha\tau} = J(\alpha)\mathrm{e}^{-IV_0 t}, \tag{54}$$

where

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

At $\alpha \to 0$, $J(\alpha) \to 1$. Thus, we get the following result: the time dependence of the volume fraction qualitatively differs from that in infinite space (it cannot be derived from the latter, equation (22), by the use of correction factors). That is, the Avrami exponent n_A decreases with time from 4 to 1. The Avrami exponent [3,12] is the slope of the tangent to the plot of $\ln(-\ln(1 - X(t)))$ against $\ln t$ (figures 8, 9). In other words, the finiteness of the domain leads to a slowing down of the transformation process in comparison with the

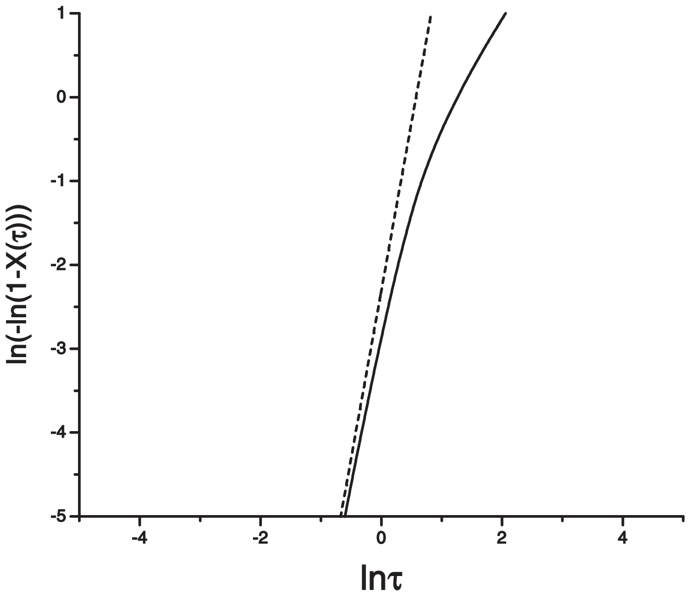

Figure 8. The function $\ln(-\ln(1-X(\tau)))$ versus $\ln\tau$ for the case of homogeneous nucleation with $\alpha = 0.1$. The dashed line is for $X_{\mathrm{K}}(\tau)$.

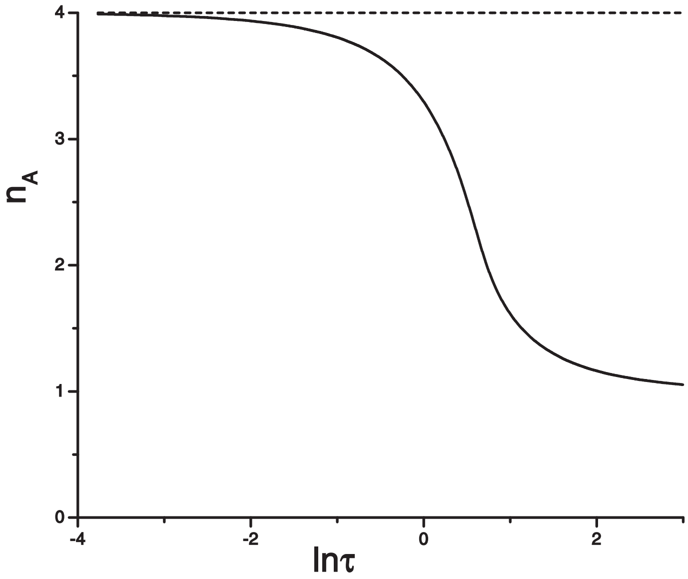

Figure 9. The dependence of the Avrami exponent n_A on $\ln\tau$ corresponding to figure 8.

nucleation in infinite space. It is not difficult to derive from (54) the following expression for $n_A(\xi)$, where $\xi \equiv \ln\tau$:

$$n_A(\xi) = \frac{1}{1 - z(\alpha)\exp(-\xi)}\,. \tag{55}$$

Here, $\xi > \ln 2$ and $z(\alpha) \equiv [\ln J(\alpha)]/4\alpha \simeq 1$.

Similarly, it is seen from (30)–(32) that the Avrami exponent decreases with time from 3 to 0 in the first variant of heterogeneous nucleation.

At $\rho \to 0$ we get from (25):

$$Q(\rho) = Q_3(\rho) = \mathrm{e}^{-4\beta\rho^3}\left[1 + O(\rho^4)\right]. \tag{56}$$

This is expression (54) 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 will appear in the domain by time t. This is a volume fraction at small R_0 and at large t, since averaging over r is not essential in this case.

In the case $\rho \to \infty$ we obtain from (23)

$$Q(\rho) = Q_1(\rho) = \mathrm{e}^{-\beta}. \tag{57}$$

That is, we have the KJMA expression $X_{\mathrm{K}}(t)$ again.

As is evident from the foregoing, the transformation time t_f is infinite in the case of homogeneous nucleation in a finite domain. Moreover, the finiteness of the domain leads to the slowing down of the transformation process in comparison with nucleation in infinite space. The transformation time is finite in the process of heterogeneous nucleation considered above, $t_f = 2t^*$, since all the centres appear at $t' = 0$. The meaning of this time in the context of the ensemble of N_a systems is as follows: at $t \geqslant t_f$ the volume fraction in each system is equal to either 1 or 0 with the probability equal to unity, for the number of particles $N \geqslant 1$ and $N = 0$, respectively. In a more general process of heterogeneous nucleation, where the centres appear at arbitrary times t', the transformation time is infinite.

The pattern shown in figure 7 is typical of the phenomena of crystallization and amorphization of a supercooled liquid. Amorphization is the result of nucleation and growth of non-crystalline nuclei – clusters [14,15]. Correspondingly, for this process, the dependencies in figure7 are shifted to the left and start at the melting temperature $\tilde{T}_m$ for the infinite cluster [14,15]. The pattern of figure 7 is apparently rather general which also arises in other cases of phase transformations with homogeneous nucleation rate. In reference [20], the KJMA model was applied to the description of the Ising lattice-gas kinetics at mesoscopic scales of length and time. An excellent agreement of these two models was demonstrated in two dimensions and for moderately strong fields. A metastable phase decay picture of reference[20] is similar to the one just considered. The magnetic field H plays the role of temperature in figure 7 (the temperature itself is a fixed parameter therein). A test of the KJMA picture was carried out in the MD regime. Equation (46) for $\alpha = 1$ limiting this regime is that for the dynamic spinodal (DSP) [20]. This equation determines the $R_0^{(\mathrm{DSP})}(H, T)$ dependence, so the noticeable deviations from the KJMA law should take place at the system sizes $R_0 \sim R_0^{(\mathrm{DSP})}$ and to a greater extent at $R_0 < R_0^{(\mathrm{DSP})}$. At the same time, these sizes may be still macroscopic, $1 \ll R_c \ll \bar{L} \sim R_0$, since $R_0^{(\mathrm{DSP})}$is large in the region of weak fields (which corresponds to slight supercooling in figure 7). In this case, expressions (19)–(21) for the volume fraction should be used instead of (22).

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Про кінетику фазового перетворення малих часток в моделі Колмогорова

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Отримано 16 травня 2007 р., в остаточному вигляді – 15 березня 2008 р.

Класична теорія Колмогорова-Джонсона-Мейла-Аврами узагальнюється на випадок обмеженої системи. У рамках геометрико-ймовірнісного підходу вирішується задача обчислення об'ємної частки нової фази в сферичній області. Одержано розв'язки для випадків гомогенної і гетерогенної нуклеації. Показано, що властивість обмеженості системи приводить до якісної відмінності часової залежності об'ємної частки від такої в необмеженому просторі: показник Аврами в процесі гомогенної нуклеації зменшується з часом від 4 до 1.

Ключові слова: *KJMA-теорія, об'ємна частка, науклеація, показник Аврами*

PACS: *05.70.Fh, 68.55.Ac, 81.15.Aa*