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On calculating volume fractions of competing phases

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Abstract. A method for calculating volume fractions of phases in a system with several simultaneously growing phases is proposed. Solutions of the problem for the spaces of dimensionalities 2 and 3 are obtained. The approximation of independent phases, in which the expressions for volume fractions have the simplest form, is considered. The high accuracy of this approximation is shown.

1. Introduction

The kinetics of a phase transformation process in the case of the formation of a single phase is described by the well-known expression of Kolmogorov [1] or Johnson, Mehl and Avrami (JMA) [2–4]:

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

where: $X(t)$ is the volume fraction of the new phase; $I(t)$ is the nucleation rate; $V(t',t)$ is the volume at time t of a freely growing nucleus formed at time t':

$$V(t',t) = gR^D(t',t) \qquad R(t',t) = \int_{t'}^t u(\tau)\,\mathrm{d}\tau. \tag{2}$$

Here, $u(t)$ is the growth rate of a nucleus, $R(t',t)$ is its radius; D is the dimensionality; g is a geometrical factor: $g = 2, \pi, 4\pi/3$ for $D = 1, 2, 3$, respectively.

In addition to such phase transformations, there can occur phase transformations proceeding via formation of two or more distinct phases simultaneously. One example of such a process is the solidification of supercooled liquid when it is accompanied by competitive formation of crystalline and amorphous phases. The hypothesis of availability of 'anticrystalline' clusters along with crystalline ones in a liquid and the role of the former in the vitrification process was proposed for the first time by Ubbelode [5]. The physical aspects of this phenomenon were considered in references [6–8], where a calculation of the liquid solidification kinetics taking into account the competitive formation of two or more phases was also carried out.

In this connection, the problem of calculating volume fractions of phases in similar systems, i.e. generalizing expression (1) to this case, is both of interest and topical. As distinct from the single-phase case, the specific difficulties connected with the difference in growth rates of phases arise here. In the present paper, a geometrical probability approach is developed for solving this problem. The expressions for volume fractions as

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well as more simple approximation-of-independent-phases (AIP) expressions are derived for dimensionalities $D = 2, 3$ in the framework of Kolmogorov's model [1, 4]. The analysis of the solution obtained leads to the conclusion that the AIP expressions provide high accuracy.

2. The single-phase case

In this section the description of the proposed method, which can be called the 'method of the critical region', is given for the case of single-phase transformation. That is, we shall derive expression (1) differently from references [1, 2].

Let us find the probability $\mathrm{d}X(t)$ that the point O taken at random will be transformed to the growing phase in the time interval $[t, t + \mathrm{d}t]$. To this end, the fulfilment of the following two conditions is necessary and sufficient: (a) the point O is not transformed before time t; (b) the new-phase nucleus able to 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 $Q(t)$ and $\mathrm{d}P(t)$ denote the probabilities of the first and second events, respectively. Let us consider the space-time scheme of the process which results in the fulfilment of both conditions.

We specify the region of radius $R(t', t)$ with the point O as its centre (the *critical region*). At time t' the region boundary is moving at the velocity $u(t')$, so the radius decreases from its greatest value $R(0, t)$ to $R(t, t) \equiv 0$. As this takes place, the fulfilment of condition (a) means that the appearance of new-phase centres in this region is not allowed within the time interval $0 \leqslant t' \leqslant t$. In reference [1], the function $Q(t)$ is calculated from this condition directly. On the other hand, $Q(t)$ can be calculated by using condition (b).

The critical centre appearing at t' must lie within a ring of width $\mathrm{d}R(t', t)$, $\mathrm{d}R(t', t) = (\partial R(t', t)/\partial t)\mathrm{d}t$, at the distance $R(t', t)$ from the point O. Consequently, the probability of its appearance is

$$\mathrm{d}P(t', t) = I(t')\,\mathrm{d}t'\,\dot{V}(t', t)\,\mathrm{d}t \tag{3}$$

where $\dot{V}(t', t) \equiv \partial V(t', t)/\partial t$.

The probability for the critical centre to appear within the time interval $0 \leqslant t' \leqslant t$ is obtained by integration of (3) with respect to t':

$$\mathrm{d}P(t) = \left(\int_0^t I(t')\dot{V}(t', t)\,\mathrm{d}t'\right)\mathrm{d}t. \tag{4}$$

Thus, the simultaneous fulfilment of conditions (a) and (b) yields the following equality for $\mathrm{d}X(t)$:

$$\mathrm{d}X(t) = Q(t)\left(\int_0^t I(t')\dot{V}(t', t)\,\mathrm{d}t'\right)\mathrm{d}t. \tag{5}$$

It is easily seen that $X(t) = 1 - Q(t)$. Therefore, expression (5) is a differential equation for $X(t)$. The solution of this equation with respect to the initial condition $X(0) = 0$ is expression (1). According to the geometrical definition of probability [9], $X(t)$ yields the fraction of the material transformed ($Q(t)$ is the fraction of the initial phase).

3. The case of several phases

In the case of a system with a number of new phases greater than one, we also assume the fulfilment of the initial premises of Kolmogorov's model [1, 4] for every phase. One of the restrictions of this model concerns the shape of the nuclei. Though it may be an arbitrary convex shape, all the nuclei must be geometrically similar to each other and have the same

orientation. The linear size $R(t', t)$ of a nucleus is defined arbitrarily; the geometrical factor g depends on this definition. The particular case of a spherical shape is used here for simplicity. Considering the case of another shape merely involves redetermining g. Thus, the results obtained below pertain equally to the case of an arbitrary shape of the nuclei permitted by Kolmogorov's model.

At first, we consider the two-phase case. Let two phases labelled below by indices 1 and 2 grow in the initial phase. The nucleation rates of the two phases are $I_i(t)$ and the growth rates are $u_i(t)$ $(i = 1, 2)$ under the condition $u_2(t) > u_1(t)$ for all t. We find the probability $\mathrm{d}X_1(t)$ $(\mathrm{d}X_2(t))$ that an arbitrary point O is transformed to phase 1 (2) in the time interval $[t, t + \mathrm{d}t]$.

Generalizing the single-phase case, we specify two regions: 1 and 2 of radii $R_1(t', t)$ and $R_2(t', t)$, respectively, with the point O as the centre (figure 1):

$$R_i(t', t) = \int_{t'}^{t} u_i(\tau)\,\mathrm{d}\tau. \tag{6}$$

The ring of width $\Delta R(t', t) = R_2(t', t) - R_1(t', t)$ between the boundaries of regions 1 and 2 will be called region 1–2.

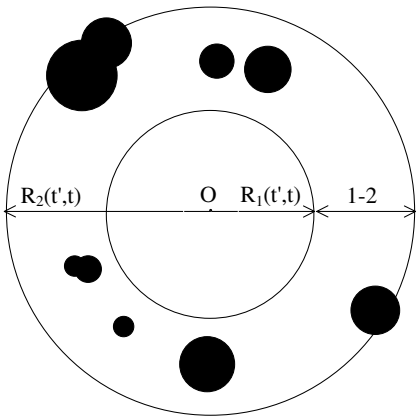

Figure 1. The critical regions in the two-phase problem. The nuclei 1 in region 1–2 are shown by black circles.

Let us consider conditions (a) and (b) with respect to phase 1. In order that the point O be transformed in the time interval $[t, t + \mathrm{d}t]$ by phase 1, it is necessary and sufficient that the following conditions should be satisfied: (a) it is not transformed to any phase before time t (the probability of this event is $Q(t)$); (b) the critical centre 1 appears at any time t', $0 \leqslant t' \leqslant t$.

The fulfilment of condition (a) means that the appearance of centres 1 in region 1 is excluded within the interval $0 \leqslant t' \leqslant t$. At the same time, they may appear outside region 1 without any restrictions, since they will not reach the point O by time t (figure 1). In addition, the appearance of centres 2 in region 2 is excluded.

The fulfilment of condition (b) implies that a centre 1 must appear at the region-1 boundary at some time t'. The probability of this event is given by expression (4). Therefore, the equation for $X_1(t)$ is

$$\mathrm{d}X_1(t)/\mathrm{d}t = Q(t)\int_0^t I_1(t')\dot{V}_1(t', t)\,\mathrm{d}t'. \tag{7}$$

With respect to phase 2, condition (a) remains the same. Therefore, we consider condition (b) only. If there were no nuclei 1 in region 1–2, this condition would give equation (7) with

the replacement of index 1 with 2 for the fraction of phase 2. However, the availability of nuclei 1 here results in only a part of the ring of volume $\mathrm{d}V_2(t', t)$ being accessible for the appearance of the critical centre 2. Consequently, we have the following expression for the probability of its appearance:

$$\mathrm{d}P_2(t) = \left(\int_0^t I_2(t') \dot{V}_2(t', t) q^{(1)}(t', t)\, \mathrm{d}t' \right) \mathrm{d}t \tag{8}$$

where $q^{(1)}(t', t)$ is the probability that the point on the region-2 boundary at which the critical centre 2 appears at time t' lies in the untransformed material.

Accordingly, the expression for the volume fraction of the second phase is

$$\mathrm{d}X_2(t)/\mathrm{d}t = Q(t) \int_0^t I_2(t') \dot{V}_2(t', t) q^{(1)}(t', t)\, \mathrm{d}t'. \tag{9}$$

Integration of the set of equations (9) and (10), in view of the fact that $Q = 1 - (X_1 + X_2)$, yields the desired volume fractions:

$$Q(t) = \exp\left[- \int_0^t I_1(t') V_1(t', t)\, \mathrm{d}t' - \int_0^t \mathrm{d}\tau \int_0^\tau \mathrm{d}t'\, I_2(t') \dot{V}_2(t', \tau) q^{(1)}(t', \tau) \right] \tag{10}$$

$$X_1(t) = \int_0^t \mathrm{d}\tau\, Q(\tau) \int_0^\tau \mathrm{d}t'\, I_1(t') \dot{V}_1(t', \tau) \tag{11}$$

$$X_2(t) = \int_0^t \mathrm{d}\tau\, Q(\tau) \int_0^\tau \mathrm{d}t'\, I_2(t') \dot{V}_2(t', \tau) q^{(1)}(t', \tau). \tag{12}$$

Passing on to the case of $n > 2$ phases, $u_n(t) > u_{n-1}(t) > \cdots > u_1(t)$, we add the regions $3, 4, \ldots, n$ of radii $R_i(t', t)$, equation (6), in figure 1. Condition (a) results in the scenario that centres i may appear outside region i only. Consequently, there are nuclei $1, 2, \ldots, i-1$ in the ring $(i-1)$–i between the boundaries of the regions $i-1$ and i, so only the part $q^{(i-1)}(t', t)$ of the volume $\mathrm{d}V_i(t', t)$ is accessible for the appearance of the critical centre i. Thus, the equation for the phase-i volume fraction is

$$\mathrm{d}X_i(t)/\mathrm{d}t = Q(t) \int_0^t I_i(t') \dot{V}_i(t', t) q^{(i-1)}(t', t)\, \mathrm{d}t' \tag{13}$$

where $i = 1, 2, \ldots, n$ and $q^{(0)} \equiv 1$.

Hence, the following expressions for volume fractions of phases are obtained:

$$\begin{aligned} Q(t) &= \exp\left[- \int_0^t I_1(t') V_1(t', t)\, \mathrm{d}t' - \sum_{i=2}^{n} \int_0^t \mathrm{d}\tau \int_0^\tau \mathrm{d}t'\, I_i(t') \dot{V}_i(t', \tau) q^{(i-1)}(t', \tau) \right] \\ X_i(t) &= \int_0^t \mathrm{d}\tau\, Q(\tau) \int_0^\tau \mathrm{d}t'\, I_i(t') \dot{V}_i(t', \tau) q^{(i-1)}(t', \tau). \end{aligned} \tag{14}$$

4. Calculation of the functions $q^{(i)}(t', t)$

In order to derive the expression for $q^{(1)}(t', t)$, we use the geometrical constructions shown in figure 2. The problem is that of how to find the probability that an arbitrary point O' taken on the circumference of the ring of radius $R_2(t', t)$ is untransformed. This event must take place satisfying the previously stated condition, i.e. the point O is also not transformed before time t. Thus, we have for the point O' a single-phase problem modified by the additional condition. Let us specify a region $1'$ of radius $R_1(t'', t')$, $0 < t'' < t'$, with the point O' as the centre. In order that the above-stated event take place, the appearance of centres 1 must be excluded in this region within the time interval $0 \leqslant t'' \leqslant t'$. The additional condition already excludes the

appearance of these centres in region 1, i.e. in the region of radius $R_1(t'', t)$ with the point O as the centre. Consequently, we must take into account only the part of region $1'$ lying outside region 1. Let $v(t'', t', t)$ denote the volume of this part (figure 2). We consider for $D = 3$ two overlapping spheres of radii r_1, r_2 and with the centre separation h. It is not difficult to derive the following expression for the volume of the part of the second sphere lying outside the first one:

$$\Omega(r_1, r_2; h) = \pi \left[\frac{2}{3}(r_2^3 - r_1^3) - \frac{1}{12}h^3 + \frac{1}{2}h(r_1^2 + r_2^2) + \frac{1}{4}\frac{(r_1^2 - r_2^2)^2}{h} \right] \tag{15}$$

where $r_1 > r_2$ and $r_1 - r_2 \leqslant h \leqslant r_1 + r_2$.

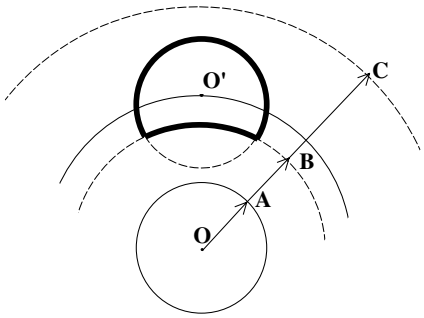

Figure 2. The calculation of $q^{(1)}(t', t)$. Full and dashed lines are the boundaries of regions at times t' and $t'' < t'$, respectively: $|OA| = R_1(t', t)$, $|OB| = R_1(t'', t)$, $|OO'| = R_2(t', t)$, $|OC| = R_2(t'', t)$. The region of volume $v(t'', t', t)$, equation (16), is marked out.

We find $v(t'', t', t)$ from the following formula:

$$v(t'', t', t) = \Omega[R_1(t'', t), R_1(t'', t'); R_2(t', t)]. \tag{16}$$

Now we obtain $q^{(1)}(t', t)$ using result (1) from the single-phase problem:

$$q^{(1)}(t', t) = \exp\left[-\int_0^{t'} I_1(t'')v(t'', t', t)\, \mathrm{d}t'' \right]. \tag{17}$$

Overlapping of regions 1 and $1'$ takes place if $r_1 + r_2 > h$; that is,

$$R_1(t'', t) + R_1(t'', t') > R_2(t', t) \tag{18}$$

and begins at the time t_c' determined by the equation

$$R_1(0, t) + R_1(0, t_c') = R_2(t_c', t). \tag{19}$$

In the time interval $0 < t' < t_c'$, as long as the radius $R_1(0, t')$ is small enough, these regions do not overlap. At $t' > t_c'$ the regions overlap in the time interval $0 < t'' < t_c''$, and then the overlap disappears, since the boundaries of these regions move at the velocity $u_1(t'')$, i.e. the radii $R_1(t'', t')$ and $R_1(t'', t)$ decrease with this velocity. The time t_c'' is determined by the following expression:

$$R_1(t_c'', t) + R_1(t_c'', t') = R_2(t', t). \tag{20}$$

For the constant growth rates u_k, equation (19) has the form

$$u_1 t + u_1 t_c' = u_2(t - t_c') \tag{21}$$

from which we have

$$t_c' = t\frac{u_2 - u_1}{u_2 + u_1} \equiv t\frac{1 - \alpha}{1 + \alpha} \qquad \alpha \equiv \frac{u_1}{u_2}. \tag{22}$$

In the limiting case $u_1 \ll u_2$ ($\alpha \ll 1$), we get $t_c' \approx t$. Therefore, the overlap is absent over almost the whole interval $0 < t' < t$, and $v(t'', t', t) = V_1(t'', t')$. In this case, $q^{(1)}$ is a function of t' only, and expression (10) becomes simpler:

$$Q(t) = \exp\left[-\int_0^t I_1(t')V_1(t', t)\,\mathrm{d}t' - \int_0^t I_2(t')V_2(t', t)q^{(1)}(t')\,\mathrm{d}t'\right]. \tag{23}$$

The functions $q^{(i)}(t', t)$ for $i > 1$ are calculated similarly. So, $q^{(2)}(t', t)$ is the fraction of the material untransformed at the distance $R_3(t', t)$ from the point O. Since there are nuclei of the first and second phases in region 2–3, we use for its calculation the result (10) from the two-phase problem in view of the correlation with the point O described above:

$$q^{(2)}(t', t) = \exp\left[-\int_0^{t'} I_1(t'')v_1(t'', t', t)\,\mathrm{d}t'' - \int_0^{t'} \mathrm{d}\tau \int_0^{\tau} \mathrm{d}t''\, I_2(t'')\frac{\partial v_2(t'', \tau, t)}{\partial \tau}q^{(1)}(t'', \tau)\right] \tag{24}$$

where

$$\begin{aligned} v_1(t'', t', t) &= \Omega[R_1(t'', t), R_1(t'', t'); R_3(t', t)] \\ v_2(t'', t', t) &= \Omega[R_2(t'', t), R_2(t'', t'); R_3(t', t)]. \end{aligned} \tag{25}$$

5. Approximation of independent phases

As is evident from the foregoing, the calculation of the functions $q^{(i)}(t', t)$ is a rather cumbersome procedure. It is desirable therefore to derive approximate but simpler expressions for volume fractions. Let us consider the simplest approximation among the possible ones. If we neglect the availability of the phases between the boundaries of regions $(i-1)$ and i, i.e. put $q^{(i-1)} = 1, i = 2, \ldots, n$, then the equations for the volume fractions become identical:

$$\mathrm{d}X_i^0(t)/\mathrm{d}t = Q^0(t)\int_0^t I_i(t')\dot{V}_i(t', t)\,\mathrm{d}t' \qquad i = 1, \ldots, n \tag{26}$$

whence we get

$$Q^0(t) = \exp\left[-\sum_{i=1}^n \int_0^t I_i(t')V_i(t', t)\,\mathrm{d}t'\right] \tag{27}$$

$$X_i^0(t) = \int_0^t \mathrm{d}\tau\; Q^0(\tau)\int_0^{\tau} \mathrm{d}t'\, I_i(t')\dot{V}_i(t', \tau). \tag{28}$$

In the case of constant nucleation and growth rates, the integrals are easily calculated:

$$Q^0(t) = \exp\left[-\left(\sum_{i=1}^n k_i\right)t^{D+1}\right] \tag{29}$$

$$X_i^0(t) = \left[k_i \Big/ \left(\sum_{i=1}^n k_i\right)\right]\left\{1 - \exp\left[-\left(\sum_{i=1}^n k_i\right)t^{D+1}\right]\right\} \tag{30}$$

where $k_i \equiv (g/(D+1))I_i u_i^D$.

In this approximation, all the phases are equivalent despite the difference in growth rates; there is no correlation between them. Equation (26) for the fraction of phase i has the same form as equation (5) in the single-phase case. Also, expression (27) for the fraction of the material untransformed has the form of a product of similar quantities: $Q_i^0 = \exp(-Y_i(t))$,

for each phase in the appropriate single-phase problem ($Y_i(t)$ is the integral in (27)). For these reasons, the given approximation can be called the 'approximation of independent phases'.

Furthermore, the problem is that of estimating the error yielded by the AIP. First, we shall establish some inequalities. If the functions $q^{(i)}(t', t)$ are calculated in the AIP with substitution of $V_j(t'', t')$ for $v_j(t'', t', t)$ in them, they have the following simple form:

$$q^{(i)}(t') = \exp\left[-\sum_{j=1}^{i}\int_0^{t'} I_j(t'')V_j(t'', t')\,\mathrm{d}t''\right]. \tag{31}$$

The values of volume fractions calculated using formulae (14) and (13) with the exact functions, $q^{(i)}(t', t)$, and the approximate ones, $q^{(i)}(t')$, equation (31), are designated below by $Q^{ex}(t)$, $X_i^{ex}(t)$ and $Q^{ap}(t)$, $X_i^{ap}(t)$, respectively. So, the expression for $Q^{ap}(t)$ is

$$Q^{ap}(t) = Q^0(t)\exp\left[\sum_{i=2}^{n}\int_0^{t} I_i(t')V_i(t', t)(1 - q^{(i-1)}(t'))\,\mathrm{d}t'\right]. \tag{32}$$

Then the following inequalities hold:

$$Q^0(t) < Q^{ex}(t) < Q^{ap}(t) \tag{33}$$

$$X_1^0(t) < X_1^{ex}(t) < X_1^{ap}(t). \tag{34}$$

We shall carry out assessments at constant nucleation and growth rates. First, we consider the two-phase case. In this case, expression (32) becomes

$$Q^{ap}(t) = \exp[-(k_1 + k_2)t^{D+1} + \varphi^{(1)}(t)] \tag{35}$$

where

$$\varphi^{(1)}(t) = (D + 1)k_2\int_0^{t}(t - t')^D\left[1 - \exp(-k_1 t'^{D+1})\right]\,\mathrm{d}t'.$$

The function $\varphi^{(1)}(t)$ determines the distinction between $Q^{ap}(t)$ and $Q^0(t)$. The expansion of $\varphi^{(1)}(t)$ in terms of t is

$$\varphi^{(1)}(t) = \frac{k_1k_2}{A}t^{2(D+1)} - \frac{k_1^2k_2}{B}t^{3(D+1)} \pm \cdots \tag{36}$$

where $A = 20$ and 70, $B = 168$ and 990 for $D = 2$ and 3, respectively.

The difference $\Delta Q(t) = Q^{ap}(t) - Q^0(t)$ is

$$\Delta Q(t) = \exp(-(k_1 + k_2)t^{D+1})[\exp(\varphi^{(1)}(t)) - 1]. \tag{37}$$

Let us note that $\Delta Q(t) < \exp(-k_1t^{D+1})$, since $\phi^{(1)}(t) < k_2t^{D+1}$. Hence it follows that $\Delta Q(t)$ tends to zero at large t. Also, $\Delta Q(0) = 0$. Therefore, the function $\Delta Q(t)$ is not monotonic; it has a maximum. In order to estimate its maximal value, $\Delta Q_{\max}$, we replace it by the simpler function $\Delta Q(\xi)$, using two terms of expansion (36):

$$\Delta Q(\xi) = (a\xi^2 - b\xi^3)\exp(-\xi) \qquad \xi = (k_1 + k_2)t^{D+1} \tag{38}$$

where $a = X_1^0X_2^0/A$, $b = (X_1^0)^2X_2^0/B$ and $X_i^0 = k_i/(k_1 + k_2)$ is the volume fraction of phase i in the AIP in the final state ($t = \infty$).

The highest possible values of the factors a and b are the following: $\max(a) = 1/4A$ (at $X_1^0 = X_2^0 = 1/2$), $\max(b) = 4/27B$ (at $X_1^0 = 2/3$, $X_2^0 = 1/3$). These are small quantities even for two dimensions. The substitution of $\Delta Q(\xi)$ for $\Delta Q(t)$ is justified by the smallness of a, b. Thus, $\max(\Delta Q(\xi)) < 4a\mathrm{e}^{-2} \leqslant \mathrm{e}^{-2}/A$, so we have the following inequality:

$$\Delta Q_{\max} < \varepsilon = \mathrm{e}^{-2}/A. \tag{39}$$

Here, $\varepsilon \approx 7 \times 10^{-3}$ and 2×10^{-3} for $D = 2$ and 3, respectively.

We also evaluate the correction to the first-phase volume fraction calculated in the AIP in the final state:

$$X_1^{ap} = (D+1)k_1 \int_0^\infty t^D \exp\left[-(k_1+k_2)t^{D+1} + \frac{k_1k_2}{A}t^{2(D+1)} - \frac{k_1^2k_2}{B}t^{3(D+1)}\right] \mathrm{d}t. \tag{40}$$

After changing t to ξ, we have

$$X_1^{ap} = X_1^0 \int_0^\infty \mathrm{e}^{-\xi + a\xi^2 - b\xi^3}\, \mathrm{d}\xi. \tag{41}$$

In view of the smallness of the factors a and b, this integral can be replaced with the following one:

$$X_1^{ap} = X_1^0 \int_0^\infty \mathrm{e}^{-\xi}(1 + a\xi^2 - b\xi^3)\, \mathrm{d}\xi = X_1^0(1+\delta) \tag{42}$$

where $\delta = 2a - 6b$.

The evaluation for δ is $\delta < 2a \leqslant 1/2A$.

The estimate obtained, $\varepsilon, \delta \ll 1$, together with inequalities (33), (34), shows that the exact values of the volume fractions in a two-phase system practically do not differ from those calculated in the AIP.

Passing on to the case of n phases, it is easy to write down the expression for $Q^{ap}(t)$:

$$Q^{ap}(t) = \exp\left[-\left(\sum_{i=1}^n k_i\right)t^{(D+1)} + \phi^{(n-1)}(t)\right] \tag{43}$$

$$\phi^{(n-1)}(t) = (D+1)\int_0^t (t-t')^D \{k_2[1 - \mathrm{e}^{-k_1 t'^{D+1}}] + k_3[1 - \mathrm{e}^{-(k_1+k_2)t'^{D+1}}] + \cdots + k_n[1 - \mathrm{e}^{-(\sum_{i=1}^{n-1} k_i)t'^{D+1}}]\}\, \mathrm{d}t'. \tag{44}$$

The expansion of $\varphi^{(n-1)}(t)$ in a series is

$$\varphi^{(n-1)}(t) = \frac{k_1k_2 + (k_1+k_2)k_3 + \cdots + (k_1+\cdots+k_{n-1})k_n}{A}t^{2(D+1)} - \frac{k_1^2k_2 + (k_1+k_2)^2k_3 + \cdots + (k_1+\cdots+k_{n-1})^2k_n}{B}t^{3(D+1)} \pm \cdots. \tag{45}$$

Repeating the procedure of assessments described above, we change the variable t to $\xi = (k_1 + k_2 + \cdots + k_n)t^{D+1}$. Accordingly, the factors a and b have the following forms now:

$$\begin{aligned} a &= f_A(X_1^0, \ldots, X_n^0)/A \qquad b = f_B(X_1^0, \ldots, X_n^0)/B \\ f_A &= X_1^0X_2^0 + (X_1^0 + X_2^0)X_3^0 + \cdots + (X_1^0 + \cdots + X_{n-1}^0)X_n^0 \\ f_B &= (X_1^0)^2X_2^0 + (X_1^0 + X_2^0)^2X_3^0 + \cdots + (X_1^0 + \cdots + X_{n-1}^0)^2X_n^0. \end{aligned} \tag{46}$$

It is not difficult to derive $\max(f_A(X_1^0, \ldots, X_n^0)) = (n-1)/2n < 1/2$. Therefore, $a < 1/2A$, and the above-stated evaluations apply with ε and δ twice as large as those for the two-phase case.

Thus, the difference between the exact values of the volume fractions and those obtained in the AIP may be thought of as negligible for a system with an arbitrary number of phases also.

Returning to the case of time-dependent nucleation and growth rates, we note the following fact. The expansions of the functions

$$Y_i(t) = \int_0^t I_i(t')V_i(t', t)\, \mathrm{d}t'$$

and

$$\tilde{Y}_i(t) = \int_0^t I_i(t')V_i(t', t)\left[1 - q^{(i-1)}(t')\right] \mathrm{d}t'$$

in terms of t begin at t^{D+1} and $t^{2(D+1)}$, respectively. Therefore, the case given does not differ fundamentally from the one considered.

6. Discussion

The main results of the present paper are the expressions for the volume fractions of competing phases as well as providing the justification for using the AIP. Also, the proposed geometrical probability method itself may be useful for solving other problems related to calculation of volume fractions.

Notice that the problem given can also be solved in the framework of either the Kolmogorov [1] or the Johnson and Mehl [2] approach. The latter is more descriptive, since it deals with nuclei of phases immediately. Therefore, it is of interest to consider the solution (10)–(14) in the context of this approach.

Two basic assumptions are used by Johnson and Mehl: (1) the colliding nuclei can intergrow without changing shape and (2) the new centres can appear over the whole volume of a system including in the already transformed volume (fictitious centres). It is significant that in the single-phase case, these assumptions do not distort the pattern of the actual process. At the same time, the spatial homogeneity of distribution of the nuclei which results from these assumptions essentially simplifies solving the problem. Hence, expression (1) is exact. In the case of two competing phases ($u_2 > u_1$), assumption (2) distorts the actual picture: the fictitious nuclei of the faster-growing phase located inside the slower-growing one go out into the untransformed region with time and contribute to the incrementing of the amount of material transformed (see figure 3(a)). The AIP expressions do not take into account this effect and consequently give an excessive fraction of the faster-growing phase. At the same time, expressions (10)–(14) take this effect into account: the factor $q^{(i-1)}(t', t)$ removes the contribution of fictitious centres to the volume fraction of phase i. This can be shown directly

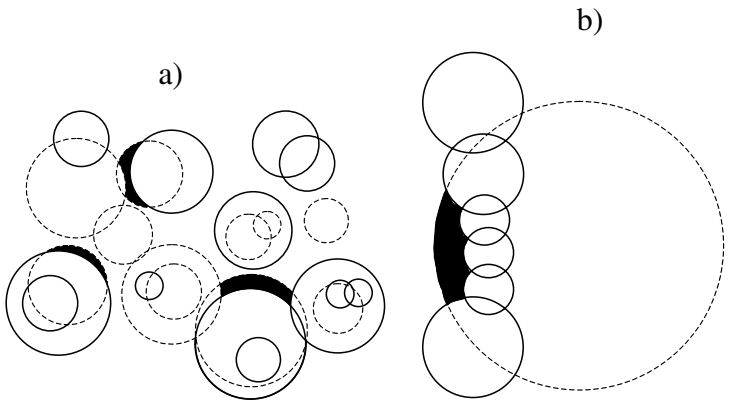

Figure 3. The typical configurations of nuclei in the Johnson–Mehl approach in the two-phase case. Nuclei 1 and 2 are shown by full and dashed lines, respectively. (a) The black pieces represent the contribution of fictitious nuclei to the incrementing of the real volume. (b) The 'obstructive' configuration: nucleus 2 passes through the continuous chain of nuclei 1 and contributes to the incrementing of the real volume (the black piece).

by deriving these expressions in the Johnson–Mehl approach reformulated in terms of the theory of probability. However, this is beyond the scope of the present paper. This may also be seen from the following reasoning. Expression (32) for $n = 2$ (or, what amounts to the same thing, expression (23)) may be rewritten as

$$Q^{ap}(t) = \exp\{-Y_1(t) - [Y_2(t) - \varphi^{(1)}(t)]\} \tag{47}$$

where

$$\phi^{(1)}(t) = \int_0^t I_2(t')x_1(t')V_2(t', t)\,\mathrm{d}t' \qquad x_1(t') = 1 - q^{(1)}(t').$$

$Y_i(t)$ is the 'extended' volume of phase i in the JMA approach [2, 3]; that is, the total volume of spheres of the ith kind. $x_1(t)$ is the volume fraction of phase 1 in a single-phase case. The product $\mathrm{d}p_2(t') = I_2(t')x_1(t')\,\mathrm{d}t'$ is the probability of the fictitious centre 2 appearing in $\mathrm{d}t'$. If we use the exact function $q^{(1)}(t', t)$ instead of $q^{(1)}(t')$, then $\mathrm{d}p_2(t')$ is the probability of the appearance in $\mathrm{d}t'$ of the fictitious centre 2 which contributes at time t to the incrementing of the real volume. So, the function $\varphi^{(1)}(t)$ is the extended volume of fictitious nuclei 2 which is subtracted in (47) from the total extended volume of phase 2.

Some comments concerning the model used here should be made for the example of two phases. Calculating the function $q^{(1)}(t', t)$ implies that the phase-2 centre appearing on the region-2 boundary reaches the point O at time t with probability equal to unity, in spite of the presence of phase-1 nuclei in region 1–2 (black circles in figure 1). That is, these nuclei do not prevent the critical centre from reaching the point O; its growth is not obstructed and not retarded. The role of the phase-1 nuclei is just to occupy part of the volume. Such a situation is a consequence of the model used and corresponds to the actual picture except some special configurations of nuclei described below. Firstly, in the $D = 2$ space (and, to a greater extent, for $D = 3$), there is the possibility of enveloping a nucleus 1 by a nucleus 2 with consequent enclosure of the former. Secondly, in view of the restriction on the shape of the nucleus which is used here (the shape remains spherical all the time), the process of enveloping may be replaced by that of intergrowth of nuclei 1 and 2. Thus we have the following picture in the context of the Johnson–Mehl approach. There are two kinds of sphere, each with its own nucleation and growth rates. They arise throughout the system and intergrow after impingement (figure 3(a)). The volume fraction of every kind of grain which is obtained in this process is given by the solution presented. This is the direct extension of the Kolmogorov–Johnson–Mehl–Avrami model to the two-phase case and seems to be a reasonable approach to this problem.

The analysis of the solution performed shows that the influence of fictitious centres is negligible. It should be noted that all the assessments were made generally—that is, independently of the relations between either nucleation or growth rates. The result is expressed only in terms of combinations of these quantities, X_i^0. In figure 4, the dependence of the volume fractions in the two-phase case for $D = 2$ is shown via the dimensionless variable $\xi = (k_1 + k_2)t^3$:

$$Q^0(\xi) = \exp(-\xi) \tag{48}$$

$$Q^{ap}(\xi) = \exp(-\xi + \varphi^{(1)}(\xi)) \tag{49}$$

$$\phi^{(1)}(\xi) = 3X_2^0\xi \int_0^1 (1 - y^2)[1 - \mathrm{e}^{-X_1^0\xi y^3}]\,\mathrm{d}y = a\xi^2 - b\xi^3 \pm \cdots \tag{50}$$

$$X_1^0(\xi) = X_1^0[1 - \mathrm{e}^{-\xi}] \tag{51}$$

$$X_1^{ap}(\xi) = X_1^0 \int_0^\xi Q^{ap}(\xi')\,\mathrm{d}\xi' \tag{52}$$

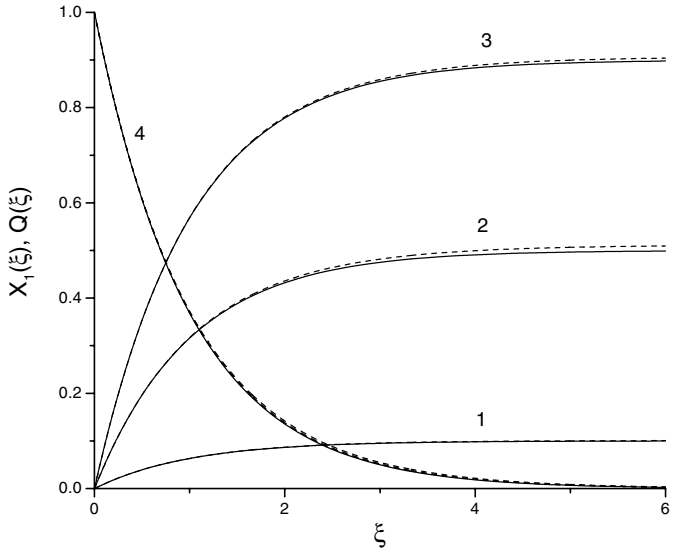

Figure 4. The volume fractions $X_1^0(\xi)$ (full lines 1–3), $X_1^{ap}(\xi)$ (dashed lines 1–3), $Q^0(\xi)$ (full line 4) and $Q^{ap}(\xi)$ (dashed line 4). Curves 1, 2 and 3 correspond to $X_1^0(\infty) = 0.1$, 0.5 and 0.9. In the case of $Q^{ap}(\xi)$, the curves corresponding to these values of $X_1^0(\infty)$ are not distinct at the present scale.

where $X_i^0 \equiv X_i^0(\infty)$ and $X_1^0 + X_2^0 = 1$.

In figure 5, the following functions are shown:

$$\Delta Q(\xi) = Q^{ap}(\xi) - Q^0(\xi)$$

$$\Delta X_1(\xi) = X_1^{ap}(\xi) - X_1^0(\xi)$$

$$\Delta X_2(\xi) \equiv X_2^0(\xi) - X_2^{ap}(\xi) = \Delta Q(\xi) + \Delta X_1(\xi).$$

As was stated above, passing from X_i^0, Q^0 to X_i^{ap}, Q^{ap} corresponds to removing fictitious nuclei 2. From this it follows that $\Delta Q(\xi)$ is the volume fraction of black pieces in figure 3(a). As the overlap of spheres increases at a late stage of the process, the black pieces gradually disappear ($\Delta Q(\xi) \to 0$). $\Delta X_1(\xi)$ is the volume fraction of the parts of nuclei 1 which are covered by the fictitious nuclei in figure 3(a) and contribute to $X_1(\xi)$ after removing the latter. As to the case of n phases, we can write similarly

$$s(\xi) \equiv \sum_{i=2}^{n} \Delta X_i(\xi) = \Delta Q(\xi) + \Delta X_1(\xi)$$

$$\Delta X_i(\xi) \equiv X_i^0(\xi) - X_i^{ap}(\xi) > 0 \qquad \text{for } i = 2, \ldots, n$$

The following estimates are obtained:

$$\Delta X_i(\xi) < s(\xi) \leqslant \Delta Q_{\max} + \Delta X_1(\infty)$$

In the final state, $\xi \to \infty$, $s = \Delta X_1$.

As is evident from figures 4 and 5, the dependences $Q^{ap}(\xi)$ and $Q^0(\xi)$ as well as $X_1^{ap}(\xi)$ and $X_1^0(\xi)$ practically coincide, and the corresponding functions $\Delta Q(\xi)$ and $\Delta X_2(\xi)$ are negligibly small even for $D = 2$ which is in agreement with the analytical assessments made above. For $D = 3$, the error yielded by use of the AIP is still smaller, because of the smaller

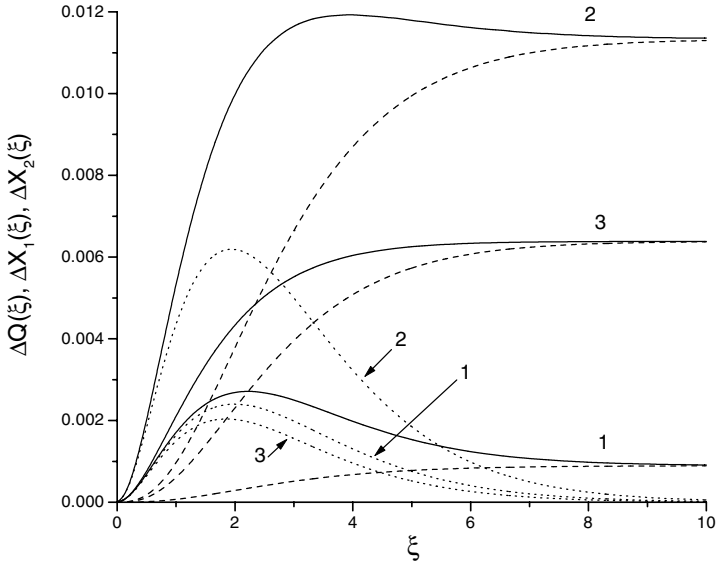

Figure 5. The errors yielded by use of the AIP: $\Delta Q(\xi)$ (dotted lines), $\Delta X_1(\xi)$ (dashed lines) and $\Delta X_2(\xi)$ (full lines). The curves 1–3 correspond to the same values of $X_1^0(\infty)$ as in figure 4.

value of a. The error is maximal at $X_1^0 = X_2^0 = 1/2$, since the coefficient a is maximal at these values.

The effect of fictitious nuclei cannot reveal itself for two reasons. Firstly, it develops over time sufficiently slowly. This fact is reflected by the characteristic form of the function $\phi^{(1)}$. Its expansion, equation (50), starts at ξ^2; the coefficient a is small. Also, this is an oscillating series, converging rapidly enough. Secondly, at the late stage of the process, $\xi > 1$, the growth of the fictitious nuclei is inhibited because of the impingements on other nuclei (figure 3(a)).

The error yielded by using the AIP does not increase substantially with increase in the number of phases, n. The increase of the error is obviously due to the increase in the number of types of fictitious centre: the centres with $i > 1$ inside phase 1, the centres with $i > 2$ inside phase 2 etc. However, as before, the impingements of nuclei suppress the development of this effect.

This reasoning suggests that generalization of the applicability of the AIP expressions to other cases which are beyond the scope of the model considered is possible. That is, if any effect sufficiently slowly developing with time is present in a system, the AIP expressions are expected to be good approximations for the volume fractions. Let us consider two examples of such geometrical effects relating to interaction between nuclei of different phases.

The first of them is present in the model considered but not taken into account by the solution given: a nucleus 2 passes through a continuous chain consisting of nuclei 1 and contributes to the incrementing of the real volume (figure 3(b)). This effect is obviously like that of fictitious nuclei but manifests itself much more weakly than the latter for two reasons. Firstly, the centre 2 is not inside a nucleus 1 of the chain but outside it. Secondly, the probability of formation of such specific configurations is very small (for $D = 3$, there must be a two-dimensional layer consisting of nuclei 1 instead of the chain). Taking into account such 'obstructive' configurations in figure 1 would lead to a slight decrease of $q^{(i)}$. On the other hand, the approximations as regards $q^{(i)}$ made in deriving Q^{ap}, X_i^{ap} also decrease these quantities. Thus this effect may be thought of as taken into account by the expressions for Q^{ap}

and X_i^{ap} automatically, in view of its smallness.

The second effect is beyond the scope of the model considered but it may be present in a real system. On a nucleus 2 enveloping a nucleus 1, the shape of the former near the interface between these nuclei may deviate from spherical (figure 6). Rigorous analysis of this phenomenon must of course include the physical mechanisms of growth. However, we consider this process here purely mathematically, likening the growth of a nucleus to the propagation of a spherical wave. Then this deviation is due to the difference in growth rates of phases 1 and 2. It develops when the common point C (figure 6(a)) of the interface enters the region of 'geometrical shadow' with respect to the centre 2, O_2; that is, it becomes located beyond the point of tangency, T (similarly, the front of a spherical wave is distorted beyond the screen located on its path). It is seen from the definition of this effect itself that it develops at the late stage when the overlaps of spheres take place to a great extent. In turn, the impingements of nuclei at this stage will inhibit this process. Consequently, this effect is expected to also be small. Let us consider schematically what form of analytical dependence describes it.

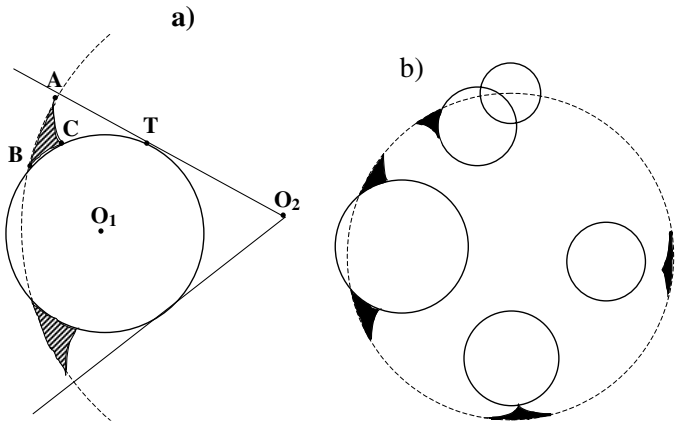

Figure 6. Enveloping of nucleus 1 (full) by nucleus 2 (dashed). The nucleus 2 shape, AC, deviates from the spherical one, AB. (b) The special example of distortion of the shape of nucleus 2 due to the effect of the enveloping. The shaded (a) and black (b) pieces are not taken into account by the AIP expressions.

For simplicity, we consider the case of heterogeneous nucleation when the centres of both phases are formed at $t' = 0$ with densities n_1 and n_2. The condition of tangency at time t has the form $r^2 = (u_1^2 + u_2^2)t^2$, where $r = |O_1O_2|$ (figure 6(a)). In order that the nucleus 2 be 'undisturbed' at time t, it is necessary that no centres 1 should be in the region of radius r with the point O_2 as the centre. The probability of this event is $q(t) = \exp(-n_1 V_r(t))$, where $V_r(t)$ is the volume of this region. Thus, $n_2 q(t)$ 'undisturbed' spheres of volume $V_2(t)$ and $n_2[1 - q(t)]$ spheres of volume less than $V_2(t)$ are present in unit volume of a system at time t. The volume of the latter is a random quantity. Denote its mean value by $\bar{V}(t) = V_2(t) - \Delta V(t)$. The extended volume of spheres 2 in the JMA approach is

$$Y_2(t) = n_2\{q(t)V_2(t) + [1 - q(t)]\bar{V}(t)\} = n_2\{V_2(t) - [1 - q(t)]\,\Delta V(t)\}. \tag{53}$$

Hence, we obtain the following expression for the volume fraction of the untransformed material:

$$Q(t) = Q^0(t)\exp[\psi(t)] \qquad \psi(t) \equiv n_2\,\Delta V(t)[1 - \mathrm{e}^{-n_1 V_r(t)}] \tag{54a}$$

where $Q^0(t) = \exp[-n_1 V_1(t) - n_2 V_2(t)]$ is the AIP expression.

Consider the case of $D = 2$. Introduce the dimensionless variable

$$\xi = \pi(n_1 u_1^2 + n_2 u_2^2)t^2$$

and the notation $\kappa(\xi) \equiv \Delta V(\xi)/V_2(\xi)$, $\gamma \equiv n_1/n_2$. Then expression (53) turns into the following:

$$Q(\xi) = \exp[-\xi + \psi(\xi)] \qquad \psi(\xi) = \kappa(\xi)X_2^0\xi[1 - \mathrm{e}^{-(X_1^0+\gamma X_2^0)\xi}] \qquad (54b)$$

where

$$X_i^0 = n_i u_i^2/(n_1 u_1^2 + n_2 u_2^2).$$

The exact form of the function $\Delta V(t)$ is unknown (this is the mean volume of the black pieces in figure 6(b)). It would appear reasonable that it is small in comparison with $V_2(t)$, with the result that $\kappa(\xi)$ is rather a small quantity—possibly, $\kappa \ll 1$. Thus the influence of the function $\psi(\xi)$ on $Q(\xi)$ is negligible, and the AIP expressions yield the values of the volume fractions with high accuracy.

Acknowledgment

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