Validity of Avrami's kinetics for random and nonrandom distributions of germs

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Up to now, the time dependence of the volume fraction during a first-order phase transition has been often described by Avrami's model, in which nucleation is assumed to occur randomly in the infinite volume. In this paper we present a computer simulation of the phase transition in order to verify the validity of Avrami's kinetics in the cases of random and nonrandom distribution of germ nuclei. Our results indicate that Avrami's kinetics is the correct solution, provided the distribution of nuclei is random and the extended volume is computed by including the so-called *phantom* nuclei. It is also shown that the general solution in the form of a functional of the extended volumes is appropriate for both nucleus distributions. [S0163-1829(96)07426-7]

INTRODUCTION

Phase transitions represent one of the most important topics in materials science, since they are usually encountered in the production cycle of materials. The kinetics of these transitions play a fundamental role in the definition of the microstructure and, therefore, of the mechanical properties of the final product. The time dependence of the volume fraction of the new phase is generally described by Avrami's theory[1,2] which has also been successful in describing crystallization, polymerization, and surface reconstruction kinetics.[3–7] In the framework of Avrami's model, the phase transition is assumed to occur by nucleation and growth. The former takes place at random in the infinite volume.[1,2] In particular the new phase fills up the whole volume of the original phase through nuclei which start growing at preexisting germs distributed in the volume. When nucleation occurs at a preexisting distribution of germs, it is usually called heterogeneous nucleation process.[8] With the term ''germ'' we refer to a preexisting site, of null size, which, once ''lighted,'' gives rise to a growing nucleus.

In his papers Avrami provides the solution of the kinetic problem once the heterogeneous nucleation and the particle growth laws have been established. It is worth noticing that by this model no information about the morphology of the system during the transition is accessible. On the other hand, this kind of information is accessible by computer simulations which, in turn, are becoming a very useful tool in this scientific field.[6,9,10] Nevertheless, to the best of the authors' knowledge no computer simulations, aimed at verifying Avrami's kinetics, have been reported in the literature. We do believe that this kind of computation is needed to verify two fundamental and delicate issues regarding (i) the extension of the relationship between the extended and the nonoverlapping volumes of single nuclei also in the case of infinitesimal increments[2] and (ii) the necessity of including phantom nuclei in the computation of the extended volume, in order to obtain the analytic expression of the phase-transition kinetics. With reference to point (ii) we underline that Avrami's prescription of considering *phantom nuclei* to get the correct kinetics is by no means a trivial issue. As a matter of fact two papers have been recently dedicated to the problem of phantoms, i.e., whether they have to be included in the computation of the extended volume or not.[11,12] In Ref. 11 the noncorrectness of Avrami's prescription [point (ii)] was claimed, and an alternative kinetics has been derived not considering the phantom nuclei in the evaluation of the extended volume.

In this paper we present a computer simulation of the phase transition according to Avrami's model. Simulations were performed in the case of both *random* and *nonrandom* distributions of germs. Our results show that Avrami's conclusions are correct and his general solution in the form of a functional correctly describes the kinetics for both random and non-random germ arrangements. The paper is organized as follows: the first section is devoted to summarizing the main results of Avrami's model; in the second section, after giving a brief description of the computer program, simulations under different nucleation conditions for random and nonrandom distributions of germs are reported and discussed.

RESULTS AND DISCUSSION

A. Avrami's model

To set the ground for the results described in this paper, a brief summary of the most salient points of Avrami's theory, which dates back to 1939–40, is indispensable.

It is necessary to give some definitions. The word ''extended'' denotes the fraction of the transformed volume each nucleus would have if its growth were not impeded by the impingement upon other nuclei. Several regions of the ex-

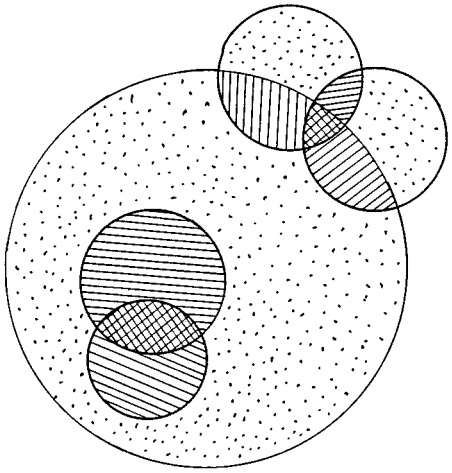

FIG. 1. Pictorial view of the nuclei arrangement. Dotted areas indicate V_1', i.e., the transformed volume of the nonoverlapping regions. Single hatched areas indicate the V_2' regions and double hatched areas indicate the V_3' regions. In the figure two overlapped phantom nuclei are also shown. In Avrami's model the phantom germs are allowed to grow (dN_p/dt) becoming phantom nuclei. It is evident that they do not contribute to the transformed volume, although they contribute to the V_m'. They have to be considered so as to restore the complete randomness of the germ distribution.

tended volume can be identified (see Fig. 1), namely the following: (i) the *single nucleus* regions corresponding to the nonoverlapping portion of the extended volume. This volume is denoted by V_1' (ii) the *double nucleus* regions, defined by the overlap of two nuclei. This volume is indicated by V_2' and (iii) the *triple nucleus* regions are identified as the portion of the extended volume resulting from the overlap of three nuclei. This volume is indicated by V_3'.

Higher order volumes, V_m', are identified in a similar way. Since a region (for the sake of simplicity we omitted the adjective overlapped) of a certain order grows at the expense of regions of lower order, it is possible to define the extended volume of order k. It represents the volume which the region of order k would have if regions of higher order did not overlap it. On the basis of geometrical considerations, the following relation holds between the extended and the overlapped volumes $V_{k\,\mathrm{ex}}$ and V_m', respectively:

$$V_{k\ \mathrm{ex}}(t)=\sum_{m=k}^{\infty}\binom{m}{k}V_m'. \tag{1}$$

Regarding the transformed volume (kinetics), always through geometrical considerations, Avrami found the following equation:

$$V(t)=\sum_{m=1}^{\infty}(-)^{m+1}V_{m\ \mathrm{ex}}(t). \tag{2}$$

At this point two considerations are required: the first is that Avrami's theory is independent of the space dimension and of the shape of the nuclei; the second is that the formal solution (2), due to its complexity, is useless for getting meaningful information from real kinetics.

Nevertheless, as Avrami demonstrated,[2] and we will show shortly, Eq. (2) can be simplified when the random distribution of germs is taken into account. In order to do that the fundamental concept of *phantom* germs (or phantom nuclei) was introduced by Avrami. Those are all the germs which are captured by the growing new phase (see Fig. 1). The ''capture'' of germs, as modeled in Ref. 2, led to the following expression for the actual nucleation rate:

$$\frac{dN_a}{dt}=[1-V(t)]\,\frac{dN_p}{dt} \tag{3}$$

where $V(t)$ is the fraction of transformed volume at running time t and dN_p/dt is the nucleation rate one would have in the absence of germ capture by the transformed volume, that is including the *phantom germs* (Fig. 1). In Eq. (3) the subscripts ''*a*'' and ''*p*'' stand for ''actual'' and ''including phantoms,'' respectively. Although the buried nuclei do not contribute to the transformed volume, $V(t)$, Avrami proposed to take them into account in calculating the $V_{1\,\mathrm{ex}}$ in order to restore the complete randomness of the system.[2] Under this assumption, the ratio between the nonoverlapping portion of the volume and the extended one reads, on the average,

$$\frac{V_1'(t)}{V_{1\ \mathrm{ex}}(t)}=1-V(t), \tag{4}$$

where

$$V_{1\ \mathrm{ex}}(t)=\int_0^t\frac{dN_p}{dz}\,v_{1\ \mathrm{ex}}(t,z)dz, \tag{5}$$

in which $v_{1\,\mathrm{ex}}(t,z)$ is the extended volume, at time t, of a single nucleus which starts growing at time $z<t$. $V_{1\,\mathrm{ex}}(t)$ is the extended volume with the inclusion of the phantom nuclei. Moreover, Avrami assumed Eq. (4) to hold even in the case of infinitesimal increments dV_1' and $dV_{1\,\mathrm{ex}}$, that is

$$\frac{dV_1'(t)}{dV_{1\ \mathrm{ex}}(t)}=1-V(t). \tag{6}$$

Since the increment of the nonoverlapping volume is equal to the increment of the transformed one, Eq. (6) becomes

$$\frac{dV(t)}{1-V(t)}=dV_{1\ \mathrm{ex}}(t). \tag{7}$$

Integration of Eq. (7) gives

$$V(t)=1-e^{-V_{1\ \mathrm{ex}}(t)}. \tag{8}$$

Equation (8) is simpler than Eq. (2) and it is *Avrami's formula*. In the case of a random distribution of germs, Avrami's formula should be equal to the series expansion reported in Eq. (2). We point out, once again, that the $V_{1\,\mathrm{ex}}$ in Eq. (8) is given by Eq. (5), explicitly including phantom nuclei.

Avrami's formula can be also derived by considering the ratio between the increments of the nonoverlapping portion of the nucleus and the extended one. For a single actual nucleus with ''birth time'' z, the ratio between the increments of the nonoverlapping portion of the nucleus (v') and the extended one ($v_{1\,\mathrm{ex}}$) is *assumed* to be given by[2]

$$\frac{\partial_t v'(t,z)}{\partial_t v_{1\ \mathrm{ex}}(t,z)} = \frac{1-V(t)}{1-V(z)}, \tag{9}$$

where the volume increments are in the time interval t and $t+dt$. By summing in Eq. (9) on the population of actual nuclei, we get

$$d\int_0^t v'(t,z)\left[\frac{dN_a}{dz}\right]dz = [1-V(t)]d\int_0^t \frac{v_{1\ \mathrm{ex}}(t,z)}{1-V(z)}\left[\frac{dN_a}{dz}\right]dz. \tag{10}$$

Since the increment of the nonoverlapping volume is equal to the increment of the transformed volume, Eq. (10) reads

$$\begin{aligned} dV(t) &= [1-V(t)]d\int_0^t v_{1\ \mathrm{ex}}(t,z)\left[\frac{dN_p}{dz}\right]dz \\ &= [1-V(t)]dV_{1\ \mathrm{ex}}(t), \end{aligned} \tag{11}$$

where use of Eq. (3) has been made. The integration of Eq. (11) leads to Eq. (8).

It is worth noting that, because of the cancellation of the $[1-V(z)]$ terms in Eq. (10), the $V_{1\,\mathrm{ex}}$ quantity includes the contribution of the phantom nuclei. Moreover, we point out that Avrami used two definitions for the extended volume: in the first one (1939) the extended volume did not contain the phantom contribution whereas in the second work (1940) it did. Nevertheless Eqs. (1) and (2) still remain valid for both definitions; obviously the V'_m (as well as the $V_{k\ \mathrm{ex}}$) are numerically different in both cases.

B. Computer program and results

The program has been written for two-dimensional (2D) and 3D transitions. For the sake of simplicity in what follows we will refer only to the two-dimensional case. The transition takes place in a square lattice made up of $n\times n$ points. In this matrix N_0 points, from which the phase transition could start, are chosen. These ''labeled'' points represent Avrami's ''*germ nuclei.*''

Following Avrami's assumptions, the number of nuclei (including phantoms) which start growing per unit time, at time z, is given by $\Delta N_p = N_0 b\exp(-bz)\Delta z$. The nucleus radius grows according to $R(t,z)=\alpha(t-z)^q$, where α, q are constants and t is the actual time whereas z is the time at which a particular nucleus start growing. Points at a distance less or equal than $R(t,z)$ (around the growing nucleus) change from ''0'' (which indicates the untransformed surfaces) to ''1.'' In the case of superposition of two or more nuclei, the points of the overlapped region are labeled with a number equal to the number of superpositions. In our program a number of superpositions as large as 20 was used. It is worth underlining that in order to preserve the random hypothesis, the germs buried by a growing nucleus are allowed to grow as well.

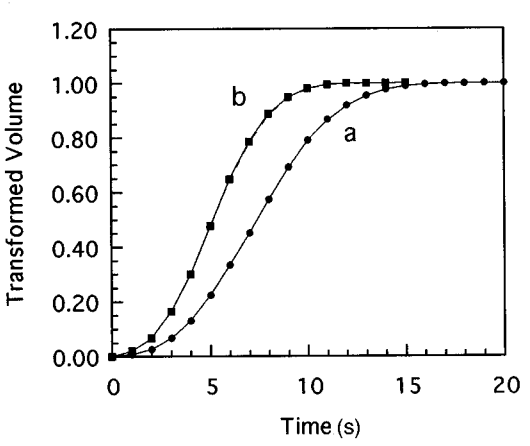

FIG. 2. The fractions of transformed volume $V(t)$, $A(t)$ (dots), and $B(t)$ (full line) are reported as a function of time for the case C1. Simulation parameters for curve a are $\alpha=1\ \mathrm{s}^{-1}$, $q=1$, $b=0.1\ \mathrm{s}^{-1}$, $N_0=2500$, and $n=400$; for curve b are $\alpha=1\ \mathrm{s}^{-1}$, $q=1$, $b=0.1\ \mathrm{s}^{-1}$, $N_0=10\,000$, and $n=500$. The $A(t)$ kinetics coincides with the $V(t)$ one. See text for the definition of $A(t)$ and $B(t)$. The $V_{1\ \mathrm{ex}}$ volume in the $B(t)$ function is computed including phantoms.

As previously stated, we used a $n\times n$ square lattice although Avrami's theory is for a phase transition occurring on an infinite surface. For this purpose we used the well known Born–Van Karman boundary conditions. However, by running the program without the boundary conditions (the growth is stopped at the border of the lattice) no substantial differences between the two simulations were observed, indicating that border effects are irrelevant.

The program outputs are the transformed surface, $V(t)$, consisting of all the points which, at time t, are labeled with any number different from zero; the overlapped surfaces, $V'_i(t)$, for $i=1$–20 which is given by all the points labeled with i; the $V_{k\ \mathrm{ex}}$ quantity that was computed by using Eq. 1. From these quantities the additional outputs $A(t)=\Sigma_{m=1}^{N_0}(-)^{m+1}V_{m\ \mathrm{ex}}(t)$ and $B(t)=1-\exp(-V_{1\ \mathrm{ex}})$ were calculated.

Two cases have been considered with reference to the randomness of the nucleation process: (i) germs nuclei are randomly distributed in the space. Therefore the choice of nucleus for growth can be sequential: case C1; (ii) germs nuclei are ordered to form a square sublattice. The germs which start growing in time interval $t,t+dt$ are randomly chosen in the sublattice: case C2.

The simulations performed in cases C1 and C2 are reported in Figs. 2 and 3. As expected in both cases the $A(t)$ output coincides with $V(t)$, whereas $B(t)$ is equal to $V(t)$ only for the case C1. The extended volumes were computed, on the basis of Eq. (1), by using the overlapped volumes, V'_m. The simulation takes into account regions with at most 20 superpositions. In Fig. 4 we report the evolution of the overlapped regions, V'_m (m runs from 1 to 20), as a function of time for the kinetics of Fig. 2 (curve a). It can be seen that 99% of the transformed phase has already occurred when V'_{13} starts growing. Therefore the evaluation of $V_{1\ \mathrm{ex}}(t)$ is, in

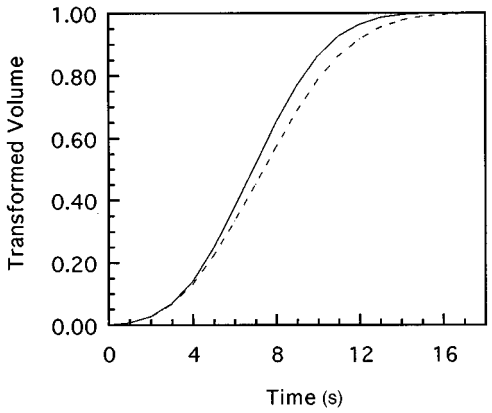

FIG. 3. The fractions of transformed volume $V(t)$, $A(t)$ (full line), and $B(t)$ (dashed line) are reported as a function of time for the case C2. Simulation parameters are the same as in Fig. 2(a) The $A(t)$ kinetics coincides with the $V(t)$ one. See text for the definition of $A(t)$ and $B(t)$. The $V_{1\,\mathrm{ex}}$ volume in the $B(t)$ function is computed including phantoms.

practice, exact. In the simulations reported in Figs. 2 and 3 the $V_{1\,\mathrm{ex}}$ term in the $B(t)$ expression was computed by including phantoms.

Referring to the case C1, it is worth remembering that in Ref. 2 Avrami showed that all the important quantities of the kinetics can be expressed in terms of the $V_{1\,\mathrm{ex}}$. As an example, the following equation:

$$V'_m = \frac{V_{1\ \mathrm{ex}}}{m!}\, e^{-V_{1\ \mathrm{ex}}}, \tag{12}$$

states that at any time the overlapped volumes are distributed according to Poisson's formula. The simplest way to check

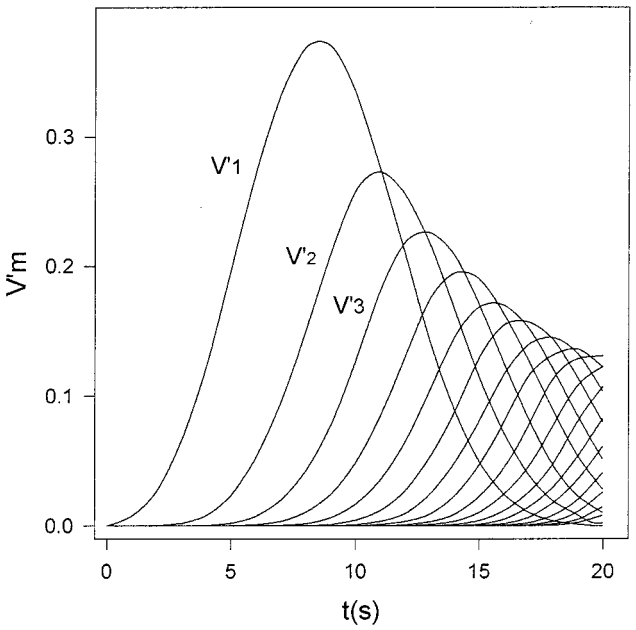

FIG. 4. Time dependence of the extension of the overlapped regions V'_m up to $m=20$. The computation refers to the simulation reported in Fig. 2(a).

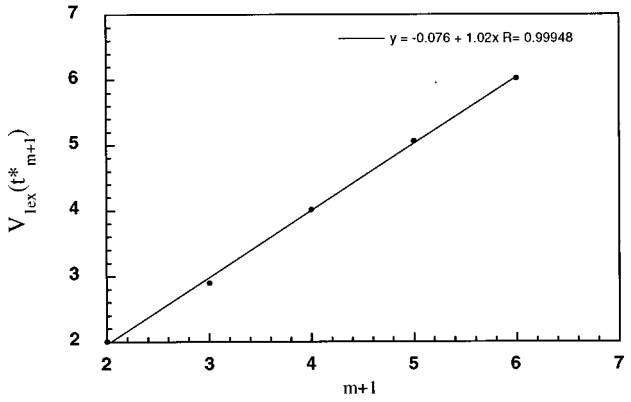

FIG. 5. Plot of $V_{1\ \mathrm{ex}}(t^*_{m+1})$ versus $(m+1)$ (dots). The selected time t^* is obtained from Fig. 4 for $V'_m = V'_{m+1}$. The full line is a linear best fit; quantitative result of the fit is also reported.

whether Eq. (12) is satisfied or not is to consider the selected times t^* for which $V'_m = V'_{m+1}$, since in this case Eq. (12) implies $V_{1\ \mathrm{ex}}\,(t^*_{m+1}) = m+1$. In Fig. 5 we report the $V_{1\ \mathrm{ex}}$ (t^*_{m+1}) extracted by the computer simulation as a function of $(m+1)$. The obtained straight line definitely demonstrates the correctness of Eq. (12).

The simulations of case (i) show that Avrami's expression [Eq. (8)] is the correct solution of the phase transition problem for a random distribution of germs. On the other hand, in the case C2, where the germs are not distributed at random, Eq. (8) does not work anymore as also pointed out by Martin.[9]

An accurate study about the effect of the impingement geometry on the kinetics of the phase transition was undertaken by Price[10] through computer simulations. In his simulations all germs start growing at the same time, namely $dN_p/dt \propto \delta(t)$ (δ being Dirac's delta function), so that no phantom nuclei are present. This is the main difference between our simulations and those of Price.[10] It is worth underlining that Price considered only ordered distributions of germs, so that his simulations fulfill the case C2 of the present paper. Our results for C2 are in complete agreement with the simulations of Ref. 10, which show discrepancies between Avrami's formula and the real kinetics. However, such a discrepancy was attributed in Ref. 10 to the modeling of the impingement process Avrami proposed in Ref. 2, whereas, in the present work, simulations for the case C1 indicate those discrepancies as due to the lack of randomness.

Another issue which deserves to be discussed is the necessity of including phantom clusters for obtaining the exact solution of the kinetics. For this purpose we computed the $B(t)$ function evaluating $V_{1\ \mathrm{ex}}$ *without* the contribution of phantoms, from now on indicated with $V^a_{1\ \mathrm{ex}}$. We still used Eq. (1) which holds also in this case. The results are shown in Fig. 6(a) for the case C1. The dots are the $V(t)$; the full line (dashed line) is the $B(t)$ function including (not including) the contribution of phantoms. In order to reduce the stochastic error the curves have been obtained by averaging over five runs in which just as many seeds, for generating the pseudorandom sequence, have been employed. The error bar has not been reported because its magnitude is within the

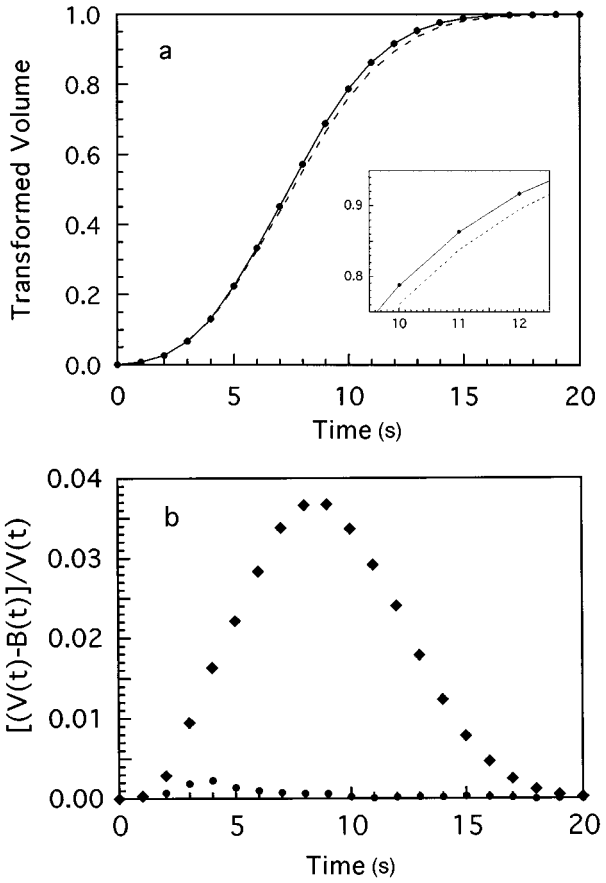

FIG. 6. The time dependence of the transformed fractions $V(t)$ (full points) and $B(t)$ with (without) phantoms, for the case C1, are reported in panel (a) as full line (dashed line). In panel (b) the relative difference $[V(t)-B(t)]/V(t)$ is shown for both inclusion (circle) and noninclusion (diamond) of phantoms. All the curves were obtained by averaging over five outputs. The parameters are $\alpha=1\ \mathrm{s}^{-1}$, $q=1$, $b=0.1\ \mathrm{s}^{-1}$, $N_0=10\,000$, and $n=800$.

symbol size. In Fig. 6(b) the relative differences $[(V-B$ (including ph.))$/V]$ and $[(V-B$ (without ph.))$/V]$ are reported as a function of time. We stress that while the included-phantom relative difference approaches zero averaging over a higher and higher number of runs, the nonphantom included difference remains practically constant (4%) whatever number of runs is employed in the average. These results suggest that the displacement between the $B(t)$ kinetics computed without phantoms and the $V(t)$ kinetics is actually due to a systematic error originating by the exclusion of phantoms from the $V_{1\,\mathrm{ex}}$ computation. Therefore, for the case C1, $V(t)=B(t)=1-\exp(-V_{1\,\mathrm{ex}})$ only holds whether phantoms are taken into account in the $V_{1\,\mathrm{ex}}$ evaluation.

In the frame of Avrami's theory, as we have previously demonstrated, the inclusion of phantom nuclei in $V_{1\,\mathrm{ex}}$ is indispensable to get the right kinetics. However, one could wonder whether it is possible to find the solution of the kinetic problem in the form of a functional $V[V^a_{1\,\mathrm{ex}}]$. This question has been the subject of two recent works,[11,12] where the authors proposed, in substitution of Eq. (8) the following kinetics:

$$V(t)=\kappa\int_0^t I(z)(t-z)^n[1-V(z)]^2dz, \tag{13}$$

where $I(z)$ is the nucleation rate, V is the transformed volume, κ is an appropriate constant, and $(t-z)^n$ stems from the time dependence of the radius growth law with $n>1$. Unfortunately, this equation hardly can be employed for describing phase transitions kinetics, due to its peculiar asymptotic behavior. As a matter of fact, when t approaches infinity the transformed fraction diverges with a power law of time whatever the nucleation rate function is. The first and the second derivatives of Eq. (13) are

$$\frac{dV}{dt}=n\kappa\int_0^t I(z)(t-z)^{n-1}[1-V(z)]^2dz, \tag{14}$$

$$\frac{d^2V}{dt^2}=n(n-1)\kappa\int_0^t I(z)(t-z)^{n-2}[1-V(z)]^2dz \quad \text{for } n\neq 1. \tag{15}$$

Both the integrands are positive defined. As a consequence the first and the second derivatives are always positive so that the following conclusions can be achieved: (i) $V(t)$ diverges as a function of time since $\dot{V}(\infty)>0$; (ii) no flex point occurs in the $V(t)$ kinetics because $\ddot{V}(t)\neq 0\,\forall t$.

As far as we know the only physical case for which the above-mentioned functional can be found is when all germs start growing simultaneously.[10] This is a trivial case in that $dN_p/dt=dN_a/dt=(N_0/V_0)\,\delta(t)$, V_0 being the whole volume and, consequently, phantom nuclei do not exist at all. In this case $V^a_{1\,\mathrm{ex}}=\int_0^t dN_a/dx\,v_{1\,ex}(t,x)dx$ and by considering $v_{1\,\mathrm{ex}}(t,x)=\beta(t-x)^3$, β being constant, Eq. (8) gives

$$V[V^a_{1\,\mathrm{ex}}]=V\left[\frac{N_0}{V_0}\,v_{1\,\mathrm{ex}}(t)\right]=1-e^{-(N_0/V_0)\beta t^3}, \tag{16}$$

which is the well-known stretched exponential form widely used in the literature. If kinetics were expressed in the form $V[V^a_{1\,\mathrm{ex}}]$ it would be pretty appealing, since they would be given as a function of the actual nucleation rate and microscopic growth law of the nucleus, that is through quantities experimentally accessible.[13]

CONCLUSIONS

A study on the validity of Avrami's model has been presented on the ground of computer simulations. Our results indicate that Avrami's formula is the correct solution of the phase transition problem, provided the distribution of germs is random and the contribution of phantoms to the $V_{1\,\mathrm{ex}}$ is taken into account. Once the condition of randomness is relaxed, Avrami's formula does not hold anymore. As a consequence, in the random case, the ratio between the infinitesimal increments of the volumes of the nonoverlapping region to the extended one is equal to the fraction of untransformed volume.

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