Original Article

Computer simulation in 3D of a phase transformation nucleated by simple sequential inhibition process

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Abstract

Analytical and numerical models of nucleation and growth transformations usually suppose that nuclei are located uniform randomly, i.e., according to a Poisson point process, within the matrix. Nonetheless, nucleation might be prevented or made more difficult if a new nucleus tries to form very close to another already existent nucleus. In these circumstances, it is better to locate the nuclei according to a point process in which there is an exclusion zone around each nucleus. The 3D Sequential point process is a convenient point process to model such a situation. By changing the nuclei density, the Sequential point process can generate arrangements of nuclei in space with distinct characteristics. In this work, we compare 3D computer simulations with nuclei generated by the Sequential point process with nuclei generated by a Poisson point process. Stereological parameters, as well as the correction function (obtained from the two-point correlation function), characterize the progress of the transformation. The 3D Sequential point process can produce a range of outcomes. Transformation kinetics behavior changes from close to a transformation nucleated according to a homogeneous Poisson point process to a transformation close to a periodic arrangement of nuclei.

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1. Introduction

Formal or global kinetics is a branch of solid-state transformations theory that deals with nucleation and growth in a phenomenological way. Formal kinetics does not directly employ physical models of the nucleation and growth mechanisms. Instead, formal kinetics “prescribes” how nucleation and growth take place. For example, in the pioneering work of Johnson-Mehl, Avrami, and Kolmogorov, JMAK [1–3], they supposed that nuclei were uniform randomly located in space and the transformed regions grew with a spherical shape and a constant velocity. They obtained two well-known expressions, each for a different nucleation rate. In the most simple case, the site-saturation case, nucleation would take place early in the transformation, and no nucleation would occur subsequently. By contrast, in the constant nucleation rate case, a constant number of nuclei per unit of time per unit of volume would appear. Site-saturated nucleation assumption, which

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we adopt in this paper, results in the well-known expression given below in Section 2.3. JMAK theory applies to nuclei uniformly randomly located in space. JMAK theory was extended in subsequent papers. As an example, in 1956, Cahn [4] proposed an analytical model to describe the transformation nucleated on the grain boundaries.

More recent work by Rios and Villa [5–7] revisited, generalized, and obtained new results based on these earlier works. Rios and Villa [5] used modern mathematical methods belonging to Stochastic Geometry. For example, Rios and Villa [5] replaced the concept of “uniform randomly” located nuclei by nuclei located in space according to a homogeneous or heterogeneous Poisson point process.

As seen above, previous work, so far, has modeled either Poisson point process nucleation or situations in which nucleation takes place in “clusters” [4,7]. To the best of our knowledge, there are no models for the situation in which the nuclei remain uniformly located in 3D space, but they are not located in space according to a Poisson point process. Our previous work deals with 2D nucleation only [8,9].

We could find only one experimental work by Sudbrack et al. [10] that experimentally proved that their nucleation, although uniform, was not in agreement with a Poisson point process. Sudbrack et al. [10] experimentally determined the pair correlation function from the centers of their transformed regions on a planar section. Their pair correlation function was consistent with each nucleus having an “exclusion zone” or “nucleus-free zone” around it in their Ni-Cr-Al superalloy.

We believe that there are two main reasons for this scarcity of experimental work on this subject. The first reason is that nucleation on grain boundaries is evident from the microstructural examination. By contrast, when the nuclei remain uniform, it might not be immediately apparent from the microstructure that nucleation departed from a Poisson point process. The second reason is that most experimental papers on transformation kinetics report only the volume fraction transformed as a function of time. Some of them also report the interfacial area density between transformed and untransformed region. However, very few experimental papers make other measurements, such as the contiguity or the two-point correlation function, which could throw more light on the location of the nuclei. Therefore, the deviation from a Poisson point process could remain undetected.

Returning to the exclusion zone found by Sudbrack et al. [10], it is reasonable to suppose that a decrease in nucleation probability around a nucleus may cause it. For example, consider an alloy A-B supersaturated in B from which precipitate rich in B nucleates. As soon as a critical nucleus forms and starts to grow, the concentration of B will drop near the growing precipitate. In other words, the supersaturation of B will decrease quickly around the growing precipitate. Therefore, nucleation within the neighborhood of the growing precipitate is less likely. This idea is not new in solidification. One can find the idea of an “exclusion zone” or a “nucleus-free zone” associated with the region near the interface between a solid particle and the liquid [11–13]. Shu et al. [12] developed an analytical model to explain why nucleation can be suppressed around growing grains. In a recent paper, Prasad et al. [13] used phase-field to model the formation of a nucleation free zone surrounding a growing grain. In solidification, one prefers the term “nucleus-free zone.” We will continue to use the denomination: “exclusion zone” as in our previous work [8,9].

Ventura et al. [8] employed several point processes that had an exclusion radius around each nucleus. Ventura et al. [8] used Matérn I, Matérn II, Strauss hard core, and Sequential point processes [8,14]. In the work of Ventura et al. [8], the Sequential point process was particularly convenient and comparatively more straightforward to simulate. A “Sequential point process” is a synonym of a “simple Sequential inhibition process.” Rios et al. [9] employed a Sequential point process to generate a range of nuclei arrangement in 2D and obtained excellent results. Nonetheless, most solid-state transformations take place in the 3D case. Therefore, a 3D treatment of the problem is much more critical.

The objective of this work is to model the effect of an “exclusion zone” on the nucleation and subsequent growth of a new transformed region. The Sequential point process models the exclusion zone around each nucleus. Analytical modeling of a nucleation and growth transformation nucleated according to a Sequential point process is not available. Therefore, a computer simulation was necessary. Notice that this work does not model a specific transformation in a given material. Instead, the present results can be used to analyze any nucleation and growth transformation. The microstructures generated as well as measurements of the pair correlation function, cumulative nearest neighbor distance distribution function, contiguity, and correction function may be compared with those obtained by experiment in a specific transformation. This comparison may, as we discuss below, provide the experimentalist with valuable information permitting him/her to detect whether nucleation took place according to a Poisson point process.

In summary, we compare 3D computer simulations with nuclei generated by the Sequential point process with nuclei generated by a Poisson point process.

2. Mathematical background

2.1. Simple sequential inhibition point process

A realization of a Sequential point process [8,9,14] inside a computational matrix is generated as follows. The first point arises randomly within the domain. An exclusion zone is delimited by a ball of radius r around it – inside this exclusion zone, no other nucleus may appear. The next point is also randomly generated with its exclusion zone, but its localization is restricted to regions outside an exclusion zone. This process is repeated sequentially for n points or until there is no more available space (saturated state). Notice that the exclusion zones may overlap. Nucleation within an exclusion zone of a particular nucleus is forbidden.

2.2. Functions to describe the nucleation process

a) The pair correlation function of point processes

The pair correlation function, g(r), may be defined as the ratio of the number of points (nuclei) per unit of volume, \( N_v(r) \),
contained within two spherical shells of radius \( r \) and \( r + dr \) and the total number of nuclei per unit of volume, \( N_v \):

\[
g(r) = \frac{N_v(r)}{N_v} \tag{1}
\]

Eq. (1) can be applied when the points are isotropic in space. For a homogeneous Poisson point process \( g(t) \equiv 1 \).

b) Cumulative nearest neighbor distance distribution function

The cumulative nearest neighbor distance distribution function of a point process is the cumulative distribution function \( G(d) \) of the distance, \( d \), from a typical random point of \( x \) to the nearest point of \( x \). For the Poisson point process, \( G(d) \) has an analytic form

\[
G(d) = 1 - \exp \left( - \frac{4}{3} \pi N_v d^3 \right) \tag{2}
\]

2.3. Transformation kinetics

The transformation kinetics of site-saturated nucleation on nuclei located in space according to a homogeneous Poisson point process is the well-known expression \([1-3,15] \):

\[
V_t(t) = 1 - \exp \left( - \frac{4}{3} \pi N_v G^3 t^3 \right) \tag{3}
\]

\( V_t(t) \) is the volume fraction transformed at time \( t \), \( G \) is the growth velocity and \( N_v \) is the number of nuclei per unit of volume.

Furthermore, one can define a normalized time \( t \) as \( t = \sqrt[3]{N_v G t} \). This definition is necessary because, as shall be seen below, \( N_v \) is different for the different cases examined. Using the normalized time permits the observation of the effect of nuclei distribution in space without the influence of \( N_v \).

2.4. Correction function

In this work, we calculated the two-point correlation function, \( C_2 \) \([16] \), and the correction function, \( \gamma_3 \), proposed by Rickman and Barmak \([17] \) to analyze the simulation results in addition to the usual parameters used in quantitative metallography. For convenience, only the correction function’s plots are shown.

The two-point correlation function is the probability that two random points within the matrix be transformed (or untransformed) at the same time. In this work, the two-point correlation function was measured on a planar section. The examination of planar sections is common in practice. Notice that, for isotropic materials, the two-point correlation function is the same regardless it is measured on two normal directions, that is, on a planar section or in three normal directions, that is, in 3D. For nuclei distributed in space according to a homogeneous Poisson point process in 3D, Eq. (4) provides an exact expression for \( C_2 \) \([17] \).

\[
C_2(r, t) = \left[ 1 - V_t(t) \right] \exp \left( \frac{4}{3} \pi N_v G^3 t^3 \gamma_3(s) \right) \tag{4}
\]

\( s = r/2Gt \) and \( \gamma_3(s) \) is the correction function. \( \gamma_3 \) also can be obtained from Eq. (5) \([17] \):

\[
C_2(r, t) = \left[ 1 - V_t(t) \right]^{2 - \gamma_3(s)} \tag{5}
\]

For a more detailed explanation of \( C_2 \) and \( \gamma_3(s) \), see \([16,17] \).

3. Computer simulation methodology

The nuclei locations within a 3D cubic matrix 300 x 300 x 300 cells were determined by a Sequential point process described above. A computer simulation was carried out using the causal-cone method \([18,19] \). The causal cone method has been used in many computer simulation papers by the authors \([7,19–22] \).

Fig. 1 illustrates the causal cone method for a site-saturated transformation. Fig. 1a shows a point “x” inside a ball of radius \( R = G_t \) centered in x (solid line). The ball in Fig. 1a is the causal cone of point x at time t. The expression “causal cone” is used because when one considers time, one has a 4-D “cone” that has the ball of Fig. 1a as the “base” and the time as the “height.” Whenever a nucleus is “captured” by this cone, the point x transforms. The ball in Fig. 1a contains no nuclei. Therefore, no growing region can overtake x within time t. As a result, x remains untransformed. By contrast, Fig. 1b shows an identical ball but containing one nucleus. At a specific time, t, the new region originated at the nucleus (dashed line) contained within the ball may grow and reach a radius \( R = G_t \). This ball of transformed region overtakes and transforms the point x. In summary, to transform the point x at least one nucleus must be present within the ball centered in x. Of course, this ball may contain more than one nucleus.

Each matrix dimension was considered to have a length equal to 1 mm. As a result, the simulated domain has a volume equal to 1 mm$^3$. Therefore, \( N_v \) is expressed as a number per mm$^3$. We simulate 3 cases increasing the nuclei density to evaluate their effect on the transformation. That is, we simulate transformations with \( N_v = 100 \) per mm$^3$, \( N_v = 1500 \) per mm$^3$ and \( N_v = 5346 \) per mm$^3$ (saturated). The inhibition radius, \( R_i \), was 0.05 mm (5% of the matrix side length). For convenience, the units will be omitted in the text.

Each quantity reported here is the mean value of 50 simulations. Several of our previous work used this number of repetitions with reliable results \([8,9] \).

4. Results

4.1. Nuclei distribution in space

Fig. 2a–c show 2D sections of the exclusion zones generated for nuclei located in 3D. In a 2D section, the exclusion zones are overlapping disks with different sizes. The uniformity of the exclusion zone regions increases with a higher nuclei density. Fig. 2c is of particular interest as it shows the situation in which one has a saturated Sequential point process. A Sequential point process is saturated when there is no space left for the introduction of new nuclei.
Fig. 1 – (a) Fig. 1a shows a point $x$ inside a ball of radius $R = Gt$ centered in $x$ (solid line). This ball is called the causal cone of $x$. No nuclei are inside this ball. As a consequence, no transformed region can overtake $x$ that remains untransformed. (b) Fig. 1b shows a ball centered in $x$ with one nucleus inside it. At time $t$ the transformed region originated at the nucleus has grown to a ball of radius $R = Gt$ (dashed line) encompassing the point $x$ so that $x$ is inside the transformed region.

Fig. 2 – 2D section of exclusion zone aspect for (a) $N_v = 100$, (b) $N_v = 1500$ and (c) $N_v = 5346$.

Fig. 3 exhibits the pair correlation function for the nuclei displayed in Figs. 2a–c. As the point process reaches saturation, a well-defined peak develops.

Fig. 4 depicts the cumulative nearest neighbor distance distribution function for the nuclei displayed in Fig. 2a–c. The behavior of $G(d)$ in Fig. 4 shows that the distance between nuclei becomes more uniform as the number of nuclei increases.

Here, we defined a normalized distance $d = \sqrt{\frac{d}{N_v}}$ to compare the results. For the saturated case, $G(d) = 0$ up to $d = 0.85$, meaning that there are no nuclei closer to $d = 0.05$, as expected. At $d = 0.85$, $G(d)$ rises steeply, reaching a constant
Fig. 3 – Pair correlation function plotted against distance.

Fig. 4 – Cumulative nearest neighbor distance distribution plotted against normalized distance.

Fig. 5 – 3D representation of the fully transformed microstructure for (a) $N_v = 100$, (b) $N_v = 1500$ and (c) $N_v = 5346$. 
value: \( G(d) = 1 \). In the saturated case, the function rises almost vertically; this means that the distance between nuclei is more uniform than for the simulations with a smaller number of nuclei.

### 4.2. Microstructure

Fig. 5a–c show the fully transformed microstructure of each case in 3D. The grain size decreases from Fig. 5a to c with the increase in the number of nuclei. It is difficult to see the difference between the grains in Fig. 5a–c.

Fig. 6a–c display the fully transformed microstructure of each case in 2D. Fig. 6a–c have different magnifications. This difference in magnification ensures that the apparent number of grains per unit of area is approximately constant for all of them. The figure caption indicates the relative magnification of each case. In Fig. 6a–c, it is easier to compare the three figures by visual inspection only. The difference is not very significant. Still, one can notice a more uniform grain size for the saturated Sequential point process.

### 4.3. Volume fraction against normalized time

Fig. 7 depicts the analytical solutions for transformation curves obtained for nuclei located within the matrix according to a Poisson point process and for nuclei located on a periodic cubic lattice. Fig. 7 also shows the computer simulation results for nuclei located according to the Sequential point process. Fig. 7 demonstrates that the Sequential point process transformation approaches the behavior of the Poisson point process transformation for the smallest number of nuclei employed. For the saturated Sequential point process, the transformation kinetics is faster than for a Poisson point process nucleated transformation. Moreover, for the saturated Sequential point process transformation, its kinetics is near the kinetics of a

Fig. 6 – 2D section of the fully transformed microstructure for (a) \( N_v = 100 \), (b) \( N_v = 1500 \) and (c) \( N_v = 5346 \).

Fig. 7 – Volume fraction transformed against normalized time. Dashed lines represent the Sequential process results.
transformation in which nuclei are located in the vertices of a cubic lattice. The kinetics is faster for the saturated Sequential process because the impingement takes place later for the saturated process than for the other processes. This is consistent with the behavior of the cumulative nearest neighbor distance distribution function shown in Fig. 4. The point is that the closer one is to a Poisson point process, the slower is the kinetics when each nucleus has an exclusion zone. This slower kinetics is a consequence of the fact that, when there is an exclusion zone, impingement takes place earlier in the transformation than when no exclusion zone is present.

Fig. 8 shows the classical double logarithm plot corresponding to Fig. 7. The curves of Fig. 7 are straight lines in Fig. 8. The zero of the y-axis corresponds to a volume fraction of 0.63. Therefore, as in Fig. 7, Fig. 8 shows the effect of the increase in the volume fraction of the exclusion zone. Consistently with Fig. 7, as the volume fraction of the inclusion zone increases, one obtains faster kinetics. Therefore the straight line corresponding to the highest number of nuclei is the line on the left. The slope of the lines also changes. The slope is equal to 3.0 for the homogeneous Poisson point process, Eq. (1), but increases to about 3.1 for the line in the middle and to 3.3 for the line on the left. Therefore, an increase in the exponent may reflect the effect of the exclusion zone. It is worthy of note that all three lines are straight. The coefficient of determination, $R^2$, is higher than 0.99 for all lines Figs. 7 and 8 give some information about the effect of the increase in the volume fraction of the inclusion zone. Nonetheless, solely from Figs. 7 and 8, it is difficult to infer that nuclei are associated with an exclusion zone. One needs additional measurements.

4.4 Contiguity

Contiguity, defined by Eq. (6), is an excellent parameter to detect deviations from nucleation randomness [23]. For example, contiguity is strongly affected if nuclei form clusters or are arranged periodically. Fig. 9 displays the contiguity as a function of volume fraction transformed.

$$C^{\beta} = \frac{2S^{\beta}_{\psi}}{2S^{\beta}_{\psi} + S^{\beta}_{\psi}}$$

In Eq. (6), $\psi$ is the parent phase, and $\beta$ is a new phase. $S^{\beta}_{\psi}$ is the interface area per unit of volume between the new phase and the parent phase. $S^{\beta}_{\psi}$ is the interface area per unit of volume between the grains of the new phase.

The contiguity of the transformation nucleated from a Poisson point process lies above all contiguity curves. According to Vandermeer [23], this means that nuclei obtained from the Sequential point process approach an ordered state. For example, the situation in which the vertices of a simple cubic lattice are the nucleation sites. By contrast, Vandermeer [23] states that the contiguity being above the contiguity from a Poisson point process nucleation signifies that clusters of nuclei take place. This is not the case here.

4.5 Correction function

Fig. 10 shows the correction function for the simulations. The correction function gives a clear picture of how the transformation behaves in each case. For the smallest number of nuclei, the transformation behaves in a way not far from a Poisson point process nucleated transformation. For the highest number of nuclei, the saturated Sequential point process, one can even detect a point of maximum. That is, the underlying nucleation sites have a consistent influence throughout the transformation. It is interesting that in this case, the information provided by the correction function is similar to that provided by the contiguity and the kinetics. Papers that use quantitative metallography do not often report the two-point correlation function from which the correction function derives. In Physics, the two-point correlation function has widespread use. It is not only applied to Materials Science but other branches of Science as well. Our simulation shows that the correction function is an excellent addition to the met-
Fig. 10 – Correction function. To compare the results, following Rickman and Barmak [17], we calculated \( \gamma_2 (s) \) for the same volume fraction transformed in all cases: \( V_T = 0.2 \).

allographic quantities. The correction function is particularly viable to measure when computer simulated microstructures are involved, like in the present work.

Moreover, for isotropic materials, the correction function is the same when measured in 3D or on a planar section. Measurements conducted here confirmed this.

5. Discussion

As mentioned above, it is not difficult to check whether the nucleation deviated from a Poisson point process when nucleation takes place on the grain boundaries [4] or in clusters [6]. To check whether the nucleation deviated from a Poisson point process when nuclei location remains uniform is more complicated.

The pair correlation function and the cumulative nearest neighbor distance distribution function are directly related to the nuclei location in space. Unfortunately, the experimental determination of the nuclei location in space is a daunting task. Therefore, the experimental determination of the pair correlation function and the cumulative nearest neighbor distance distribution function is not feasible in practice. Another possibility is the one used by Sudbrack et al. [10]. Sudbrack et al. [10] determined the pair correlation function of the points located at the center of transformed regions on planar sections. Of course, the centers of the transformed regions on planar sections of a 3D transformation are not directly related to the 3D location of the nuclei in space. Besides, the centers of the transformed regions on a planar section do not coincide with the nuclei of 2D transformed regions. Therefore, the centers of the transformed regions cannot be considered nuclei of a 2D or a 3D transformation. Despite this fundamental objection, the experimentally measured pair correlation function gave a good indication that an exclusion zone was indeed present. One may qualitatively compare the 3D and the 2D [9] pair correlation functions of the Sequential point process with Sudbrack et al.’s [10] experimental pair correlation function. Fig. 11a and b show such a comparison. The x-axis coordinate was multiplied by a scale factor so that the peaks of the pair correlation function of the saturated Sequential point process and the experimental pair correlation function approximately coincided. Fig. 11a and b show that there is a qualitative similarity between the simulated and Sudbrack et al.’s [10] experimental pair correlation functions.

Section 4.2 showed that the grains were more uniform when nucleation took place according to a Sequential point process than when nucleation took place according to a Poisson point process. The problem here is that in Section 4.2, the microstructure arising from a Poisson point process was available for comparison. This is not always the case in practice. Nevertheless, once could at least have some indication the nucleation was not Poissonian using the methods of Section 4.2. We believe that this on its own would not be enough to conclude non-Poissonian nucleation.

Section 4.3 showed it is problematic to ascertain nuclei distribution from the examination of curve volume fraction against time only. An exclusion zone around each nucleus results in a faster transformation owing to a delay in the impingement. This is clear from the transformation curves. Nonetheless, if one only has the transformation curve of a single transformation, it is difficult to say that the nuclei of this transformation possess an exclusion zone.

The contiguity, Section 4.4, is probably the most natural measurement that gives a direct indication that nucleation was not resultant from a Poisson point process. The contiguity can be easily obtained from a planar section. Moreover, an analytical expression for the contiguity of a transformation nucleated according to a Poisson point process is available [24]. The theoretical line is a reliable reference. The contiguity

Fig. 11 – Comparison of Sudbrack et al. [10] experimental pair correlation function with a simulated pair correlation function. For a detailed explanation, see the text.
above this line indicates that nucleation clustering took place [23]. Section 4.4 demonstrated that for the Sequential point process, the contiguity lies below this line. Consequently, to measure the contiguity would provide a strong indication that nucleation did not take place conforming to a Poisson point process.

Section 4.5 examines yet another quantity that gives a sure indication of the nucleation point process: measuring the correction function. It would be easier and equally reliable to measure the correction function on a planar section, as mentioned in Section 4.5. The disadvantage here is that one would have to determine the two-point correlation function experimentally [25].

In summary, it would be easier to start measuring the contiguity. After measuring the contiguity, if necessary, one can measure the correction function and, finally, the pair correlation function of the centers of the transformed regions on a planar section.

6. Conclusions

In this work, we carried out computer simulations of transformations in which there is an exclusion zone around the nucleus in 3D using the Sequential point process. The Sequential point process is comparatively more straightforward to simulate than other point processes [8]. The results obtained in the 3D simulation were qualitatively like the 2D simulations that we carried out in previous work [9]. In 3D simulations, likewise, in 2D simulations, the Sequential point process showed to be expedient. The Sequential point process can simulate transformations ranging from a Poisson point process to a periodic arrangement of nuclei. For the Sequential point process, when the number of nuclei is small, the microstructure and transformation kinetics approach that of a Poisson point process nucleated transformation. By contrast, for the saturated Sequential point process, the microstructure and transformation kinetics approach that in which nuclei are located on the vertices of a simple cubic lattice. Moreover, we can say that the effect of an exclusion zone around each nucleus on the microstructure and the transformation is the opposite effect of nuclei clustering. Finally, the findings of the computer simulation carried out here may be helpful for the experimentalist to find out the likelihood of an exclusion zone in a real transformation.

Declaration of interests

The authors declare that they have no conflict of interest.

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