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Original Research Paper

TRANSFORMATION KINETICS FOR NUCLEATION ON RANDOM PLANES AND LINES

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ABSTRACT

Birth and growth processes are known in materials science as nucleation and growth processes. In crystalline materials nucleation almost always takes place in an internal crystalline defect. These defects are classified according to their dimensionality: point, line or planar defects. Therefore, investigating nucleation on sets of dimensionality lower than the set in which the transformation takes place is of paramount importance. Cahn (1956) in a classical work derived expressions for transformation kinetics when nucleation took place on random planes and on random straight lines. He used these expressions to describe nucleation in polycrystalline materials. He considered that nucleation on grain faces could be treated as nucleation on random planes and, likewise, nucleation on grain edges could be treated as nucleation on random lines. The present work revisits and generalizes Cahn's treatment of nucleation on planes and lines. First a general expression for the case of nucleation on lower dimensional sets is obtained. After that general expressions for nucleation on random planes and random lines are given. This paper provides the mathematical basis for the development of more specific expressions to be used in practical applications. Although this work has been done bearing applications to materials science in mind the results obtained here may be applied to birth and growth processes in any field of science.

Keywords: birth-and-growth process, formal kinetics, phase transformations, point process, Poisson process, random set, recrystallization.

INTRODUCTION

Formal kinetics is frequently employed to analyze a variety of heterogenous transformations in condensed phases. This methodology has its origin in the early work by Kolmogorov (1937), Johnson and Mehl (1939) and Avrami (1939; 1940; 1941) and is often called KJMA theory. Heterogeneous transformations may be defined as those transformations in which there is a moving boundary between the transformed and untransformed region. This formalism envisages that the heterogeneous transformations may be decomposed in two stages. The first stage, the nucleation, is that in which the transformed region originates. On the other hand, the second stage, the growth stage, is that in which the transformed region grows consuming the parent matrix. These processes are usually called *nucleation and growth* processes in materials science or also *birth and growth* processes in mathematics. The application of this formalism is by no means restricted to materials science. Tomellini and Fanfoni (2008) pointed out that it is applied to a variety of situations, such as, the phase separations in multicomponent alloys (Starink, 2004), the film growth on solid substrates (Fanfoni and Tomellini, 2005), the kinetics of Ising lattice-gas model (Ramos *et al.*, 1999), and the DNA replication (Jun and Bechhoefer, 2005). To these we may add a recent extensive work by Aquilano *et al.* (2009) on crystallization processes.

In materials science, the applicability of KJMA formalism may be extended to transformations in which nucleation and growth are treated as purely "operational" concepts. Therefore, examples of formal kinetics modeling can be found associated with a variety of transformations, such as, austenite to perlite transformation (Johnson and Mehl, 1939), recrystallization (Vandermeer and Jensen, 2001), abnormal grain growth in $BaTiO_3$ (Rios *et al.*, 1998; Kondo *et al.*, 1998), martensite "spread" (Rios and Guimaraes, 2007; 2008) and polymer crystallization (Burger *et al.*, 2002a;b).

Specifically, nucleation in crystalline materials almost always takes place in an internal crystalline "defect". These defects are classified in three kinds according to their dimensionality: point, line or planar defects. A good example is a polycrystalline material. In this case the grain boundaries are planar defects, the common edge belonging to three grains is a line defect and the vertex(or "corner") that is

common to four grains is a point defect. Classical nucleation theory demonstrates the importance of these internal defects as nucleation sites. According to the classical nucleation theory, the free energy barrier for nucleation strongly depends on which boundary site the nucleus is located. The free energy barrier is smallest for vertices and progressively larger for nucleation on edges and faces (Cahn, 1956). Even in transformations in which classical nucleation theory is thought not to be applicable, for example, recrystallization, grain boundary sites are often the places at which the transformation originates. Other examples of nucleation sites are lattice vacancies, dislocation lines and the particle/matrix interface in the case that the polycrystal contains a particle dispersion. In addition to internal defects in small specimens like powders, thin wires or thin films nucleation on the external surface give a significant contribution to the transformation (Villa and Rios, 2010). From these examples, it is clear that nucleation on sets of dimensionality lower than the set in which the transformation takes place is of paramount importance.

In its original form KJMA theory considered that nucleation sites were uniform randomly located in space. In other words, that the internal defects were point defects and that they were located in space according to a homogeneous Poisson point process. Expressions for two fundamental nucleation modes were obtained. The first fundamental nucleation process takes places when the nuclei are "potent" so that nucleation takes place very fast and all possible nucleation sites are exhausted very early in the reaction. This case is called "site-saturation". Mathematically speaking one may suppose that all transformed regions originate at the start of the reaction taken to be the time origin, $t = 0$. The second fundamental nucleation mode considered that the internal point defects were not equally "potent". As a consequence there was a different "incubation" time for each site to become a new transformed region. Therefore nucleation took place over time with what they called a "constant nucleation rate". In mathematical terms they supposed that nucleation was a point process in $\mathbb{R}_+ \times \mathbb{R}^d$. It is clear that KJMA considered only one possibility of nuclei distribution in space whereas in real materials, as discussed above, there are many possibilities.

Many metallic and ceramic engineering materials are polycrystalline. As mentioned above, nucleation of a transformed region in polycrystals does often take place at grain boundaries, edges and vertices. Grain boundaries are not exactly flat neither grain edges are exactly straight lines. Nonetheless the accurate analytical description of these boundaries and lines in a real polycrystal would be unfeasible. Clearly, it is necessary to represent grain boundaries and edges by simple curves or surfaces. Cahn (1956) in a classical work proposed that grain faces may be approximated by random planes and grain edges by random straight lines provided that there is an equivalence between the area per unit of volume of the real grain boundaries and the area per unit of volume of the random planes. Cahn's paper has been extensively cited not only in connection with metallic materials recrystallization and phase transformations, but also in connection with non-metallic materials as well, such as, glass, cement and even geological formations.

Cahn's method has two main characteristics. The first is that it captures the "randomness" in the location of boundary sites. This randomness is a consequence of the randomness in the distribution of grain sizes and of the spatial location of the grains. The second characteristic is that it also captures the dimensionality of the nucleation site. Thus distinct formal kinetics expressions are obtained for nucleation in each boundary site. Dimensionality of the operative nucleation site is clearly a key issue for transformations taking place in polycrystalline materials. These characteristics are probably what has prompted metallurgists to continually apply Cahn's model to many transformation problems.

One complication that may arise in practice is that metallic polycrystalline materials may be and indeed they are often deformed. The deformation may change the spatial arrangement of the grain boundaries. For example, after severe rolling the grains are "flattened" and are often called "pancake" grains. Clearly these grains have most of their grain boundaries nearly parallel to the rolling plane. In this case the grain boundaries might be approximated by parallel planes. Therefore depending on how the deformation is conducted the spatial arrangement of planes or lines may assume some specific characteristics. So it is of practical interest to study how different spatial arrangements of planes or lines may affect the transformation originating from nuclei on these planes or lines. This is the main goal of the present paper.

In previous work (Rios and Villa, 2009; Villa and Rios, 2009; 2010), the present authors resorted to the causal cone (Jackson, 1974; Cahn, 1996) concept and to recent developments in stochastic geometry (Capasso and Villa, 2007a;b) to obtain analytical expressions for transformations in which nuclei were located in space according to an inhomogeneous Poisson point processes, in spherical clusters and in the bulk and on the surface of small specimens (Villa and Rios, 2010). In this work we continue to examine situations of engineering and

scientific interest exerting the same mathematical tools adopted in our previous work. In the present work we revisit and generalize the problem of nucleation on planes and lines treated by Cahn (1956) in the aforementioned paper.

This paper is organized as follows. First a short mathematical background is given. Then a general expression for the case of nucleation on lower dimensional sets is obtained. After that the mathematical derivations of general expressions for nucleation on random planes are given. The next section is similar to the previous one excepting that it treats lines instead of planes. Additional mathematical background may be found in our previous papers and references therein (Rios and Villa, 2009; Villa and Rios, 2009; 2010).

MATHEMATICAL BACKGROUND AND BASIC NOTATION

Detailed mathematical background may be found in previous work by the authors (Rios and Villa, 2009; Capasso and Villa, 2007a;b). Here only some essential definitions and some useful relationships will be presented to make this paper more self contained and easier to read. For a brief description of homogeneous and inhomogeneous Poisson point process, the reader is referred to Rios and Villa (2009) or for a more detailed presentation to specific texts on stochastic geometry (Stoyan *et al.*, 1995).

BIRTH-AND-GROWTH PROCESSES AND MEAN RELATED DENSITIES

A *birth-and-growth (stochastic) process* is a dynamic germ-grain model (Stoyan *et al.*, 1995), used to model situations in which *nuclei* (germs) are born in time and are located in space randomly, and each nucleus generates a *grain* evolving in time according with a given growth law. Since, in general, the nucleation is random in time and space, then the transformed region at any time $t > 0$ will be a random set (Stoyan *et al.*, 1995) in $\mathbb{R}^d$, that is a measurable map from a probability space to the space of closed subsets in $\mathbb{R}^d$. Denote by T_j the $\mathbb{R}_+$-valued random variable representing the *time of birth* of the j-th nucleus, and by X_j the $\mathbb{R}^d$-valued random variable representing the *spatial location* of the nucleus born at time T_j. Let $\Theta^t_{T_j}(X_j)$ be the grain obtained as the evolution up to time $t \geq T_j$ of the nucleus born at time T_j in X_j; then, the transformed region Θ^t at time t is

$$\Theta^t = \bigcup_{T_j \leq t} \Theta^t_{T_j}(X_j) \,, \qquad t \in \mathbb{R}_+ \,.$$

The family $\{\Theta^t\}_t$ is called birth-and-growth process. Birth-and-growth and nucleation and growth will be used as synonyms in this paper.

Since Θ^t is a random set, it gives rise to a random measure $\nu^d(\Theta^t \cap \cdot\,)$ in $\mathbb{R}^d$ for all $t > 0$, having denoted by ν^d the d-dimensional Lebesgue measure in $\mathbb{R}^d$. In particular, it is of interest to consider the *expected volume measure* $\mathbb{E}[\nu^d(\Theta^t \cap \cdot\,)]$ and its density (i.e., its Radon-Nikodym derivative), called *mean volume density of* Θ^t and denoted by V_V, provided it exists:

$$\mathbb{E}[\nu^d(\Theta^t \cap A)] = \int_A V_V(t,x)\,\mathrm{d}x \qquad \forall A \in \mathscr{B}_{\mathbb{R}^d} \,, \quad (1)$$

where $\mathscr{B}_{\mathbb{R}^d}$ is the Borel σ-algebra of $\mathbb{R}^d$.

Whenever A is the region of the physical sample under observation, the ratio

$$\mathbf{V}_\mathbf{V}(t,A) := \frac{\int_A V_V(t,x)\,\mathrm{d}x}{\nu^d(A)}$$

is also called *volume fraction*. Let us notice that whenever V_V is independent of x (*e.g.*, under assumptions of homogeneous nucleation and growth), then $\mathbf{V}_\mathbf{V}$ is independent of A and $\mathbf{V}_\mathbf{V}(t) = V_V(t)$. (see also Rios and Villa, 2009, Stoyan *et al.*, 1995, p. 342). We also mention that other quantities of interest in real applications are the so-called *mean extended volume density* at time t, denoted by $V_E(t,\cdot)$, defined as the density of the *mean extended volume measure* at time t, $\mathbb{E}[\mu^{\mathrm{ex}}_{\Theta^t}](\cdot) := \mathbb{E}[\sum_{j:T_j \leq t} \nu^d(\Theta^t_{T_j}(X_j) \cap \cdot\,)]$ on $\mathbb{R}^d$, that is

$$\mathbb{E}[\mu^{\mathrm{ex}}_{\Theta^t}](A) = \int_A V_{\mathrm{ex}}(t,x)\,\mathrm{d}x \,, \qquad \forall A \in \mathscr{B}_{\mathbb{R}^d} \,,$$

and the *mean surface density* $S_V(t,\cdot)$ and the *mean extended surface density* $S_E(t,\cdot)$ at time t, defined as the density of the *mean surface measure* at time t, $\mathbb{E}[\mu_{\partial\Theta^t}](\cdot) := \mathbb{E}[\mathscr{H}^{d-1}(\partial\Theta \cap \cdot\,)]$ and of the *mean extended surface measure* at time t, $\mathbb{E}[\mu^{ex}_{\partial\Theta^t}](\cdot) := \mathbb{E}[\sum_{j:T_j \leq t} \mathscr{H}^{d-1}(\partial\Theta^t_{T_j}(X_j) \cap \cdot\,)]$, respectively, where $\mathscr{H}^{d-1}$ is the $(d-1)$-dimensional Hausdorff measure. In other words, the mean extended volume and surface measures represent the mean of the sum of the volume measures and of the surface measures of the grains which are born and grown until time t, supposed *free to grow*, ignoring overlapping (see also Rios and Villa, 2009; Villa, 2008).

It is clear that to find out formulas for the mean volume density V_V (and so for $\mathbf{V}_\mathbf{V}$ and the other quantities we mentioned above, as a consequence) is of particular interest in real applications.

Of course, different kinds of nucleation and growth models gives rise to different kinds of processes $\{\Theta^t\}_t$.

Aim of this paper is the study of the mean volume density of birth-and-growth processes with different types of nucleations on planes and lines, and so, for sake of simplicity, we shall assume throughout the paper that the velocity of growth of each grain is constant and homogeneous in space, so that any grain $\Theta^t_{T_j}(X_j)$ born in X_j at time T_j and grown up to time t is given by the ball $B_{G(t-T_j)}(X_j)$ centered in X_j with radius $G(t-T_j)$. Such a simplification does not limit the applications of our results to real situation; moreover the interested reader in the more general case of non-constant velocity could generalize our results by applying the same approach presented here. We also refer to Burger *et al.* (2002a); Capasso and Villa (2007a); Villa (2008) for models of birth-and-growth processes whose grains have space and time dependent growth rate.

MODELLING THE NUCLEATION PROCESS

As mentioned in the Introduction, we shall consider the case in which all the nucleation takes place at $t = 0$ (namely, site-saturated case), and the case in which the nucleation takes place in time (namely, time-dependent case).

Site-saturated nucleation processes and space-time dependent nucleation processes can be modeled by *point processes* and *marked point processes*, respectively. We give here some basic concepts and definitions useful for the sequel (see also, for instance, Rios and Villa, 2009, Sec. 2.3) We remind that a *point process in* $\mathbb{R}^d$ is an almost surely locally finite sequence of points $\{X_i\}_i$ randomly located in $\mathbb{R}^d$, according with a given probability law. It can be described by the *counting process*, say N, associated to the sequence $\{X_i\}$ defined as

$$N(A) := \text{number of the } X_i\text{'s, which belong to } A,$$

for any $A \in \mathscr{B}_{\mathbb{R}^d}$.

A *marked point process in* $\mathbb{R}_+ \times \mathbb{R}^d$, is a sequence $N := \{(T_i, X_i)\}_i$ of points in $\mathbb{R}_+ \times \mathbb{R}^d$ such that the sequence $\{T_i\}_i$ is a point process in $\mathbb{R}_+$, while each $X_i \in \mathbb{R}^d$ is said to be the *mark* associated to the point T_i. A space-time nucleation process can be modeled by a marked point process, identifying T_i as the time of birth of the i-th nucleus, and X_i as its spatial location in $\mathbb{R}^d$. Analogously to the site-saturation case, a counting process N on $\mathbb{R}_+ \times \mathbb{R}^d$ can be defined as

$$N([s,t] \times A') := \text{number of nuclei, which are born in } A' \text{ during the time interval } [s,t].$$

The measure Λ on $\mathbb{R}^d$ and on $\mathbb{R}_+ \times \mathbb{R}^d$, respectively, defined as $\Lambda(A) := \mathbb{E}[N(A)]$ for all $A \in \mathscr{B}_{\mathbb{R}^d}$ and $A \in \mathscr{B}_{\mathbb{R}_+} \times \mathscr{B}_{\mathbb{R}^d}$, respectively, is called intensity measure of N; in other words, $\Lambda(A)$ represents the mean number of nuclei born in $A \subset \mathbb{R}^d$ of a site-saturated process, and the mean number of nuclei born in A' during a time interval $[s,t]$, where $A = [s,t] \times A' \subset \mathbb{R}_+ \times \mathbb{R}^d$, of a time-dependent nucleation. We intentionally use the same notation N for the site-saturated nucleation process and for the time-dependent one because the site saturated process may be seen as a particular case of the time-dependent one by assuming $T_j \equiv 0$ for any j. In the sequel it will be clear from the context which process we are referring to (note also that Λ is a measure on $\mathbb{R}^d$ in the site saturated case, and on $\mathbb{R}_+ \times \mathbb{R}^d$ in the time-dependent case).

In this paper we shall assume Poissonian nucleation, that is N will be a Poisson process (in $\mathbb{R}^d$ in the site-saturated case, and in $\mathbb{R}_+ \times \mathbb{R}^d$ in the time-dependent case). We point out that the resulting birth-and-growth process is then a particular case of the well-known general Boolean model (Matheron, 1975); namely, due to the assumption of constant velocity, a time dependent Boolean model of spheres.

CAUSAL CONE AND MEAN VOLUME DENSITIES: BASIC DEFINITION AND RESULTS

It is well known and easy to prove that

$$V_V(t,x) = \mathbb{P}(x \in \Theta^t) \qquad \text{for } \nu^d\text{-a.e. } x \in \mathbb{R}^d .$$

The so-called "causal cone" of a point x at time t, denoted here by $\mathscr{C}(t,x)$, plays a fundamental role in evaluating $V_V(t,x)$. It is defined as the space-time region in which at least one nucleation event has to take place in order to cover the point x at time t; namely, it is the subset of $\mathbb{R}_+ \times \mathbb{R}^d$

$$\mathscr{C}(t,x) := \{(s,y) \in [0,t] \times \mathbb{R}^d : x \in \Theta^t_s(y)\}.$$

(see, *e.g.*, also Rios and Villa, 2009, Sec 2.4.)

Let us observe that under our assumption above on G, it follows that

$$\mathscr{C}(t,x) = \begin{cases} B_{Gt}(x) \\ \{(s,y) \in [0,t] \times \mathbb{R}^d : y \in B_{G(t-s)}(x)\} \end{cases}$$

in the site-saturated and in the time-dependent case, respectively. (For the general case of space-time dependent growth rate, see, *e.g.*, Villa (2008); Rios and Villa (2009) and references therein.) Quite general results on $V_V(t,x)$ in terms of the causal cone are proved in Villa (2008). In particular we recall here that

$$V_E(t,x) = \Lambda(\mathscr{C}(t,x)) ,$$

and that

$$G = \frac{1}{S_V(t,x)}\frac{\partial V_V(t,x)}{\partial t} = \frac{1}{S_E(t,x)}\frac{\partial V_E(t,x)}{\partial t}\,, \qquad (2)$$

moreover, under Poissonian assumption on the nucleation process it holds

$$V_V(t,x) = 1 - \mathrm{e}^{-V_E(t,x)} \qquad (3)$$

and

$$S_V(t,x) = (1 - V_V(t,x))S_E(t,x)\,.$$

It is clear the importance of the relationships above in real applications. For instance, if the velocity G is known, Eq. 2 can be used to find out the mean interfacial area density or the interfacial area per unit of volume from the corresponding mean volume density or volume fraction.

GENERAL EXPRESSION IN THE CASE OF NUCLEATION ON LOWER DIMENSIONAL SETS

In order to model the situation in which the nucleation takes place spatially in lower dimensional subsets and subspaces of $\mathbb{R}^d$, we shall make use of the so called "delta-formalism", as follows. Let S_n be a $\mathscr{H}^n$-measurable subset of $\mathbb{R}^d$ with Hausdorff dimension $n \in \{1,2,\ldots,d-1\}$, having denoted by $\mathscr{H}^n$ the n-dimensional Hausdorff measure; then $\delta_{S_n}(y)$ is the so-called *delta function* associated to S_n (which can be seen as a generalization to the well-known delta-function δ_{x_0} associated to a point $x_0 \in \mathbb{R}^d$). It is the *generalized function* defined formally by

$$\int_A \delta_{S_n}(y)\,\mathrm{d}y := \mathscr{H}^n(S_n \cap A) \qquad \forall A \in \mathscr{B}_{\mathbb{R}^d}\,.$$

Thus, we may consider Poisson nucleation processes on S_n with intensity measure Λ given by

$$\Lambda(\mathrm{d}y) = \lambda(y)\delta_{S_n}(y)\,\mathrm{d}y\,,$$

and

$$\Lambda(\mathrm{d}(s,y)) = \lambda(s,y)\delta_{S_n}(y)\,\mathrm{d}s\,\mathrm{d}y\,,$$

in the site-saturated and in the time-dependent case, respectively.

Therefore $V_V(t,x)$ is given by Eq. 3 with

$$V_E(t,x) = \begin{cases} \displaystyle\int_{B_{Gt}(x)} \lambda(y)\delta_{S_n}(y)\,\mathrm{d}y \\ \displaystyle\int_0^t \Big(\int_{B_{G(t-s)}(x)} \lambda(s,y)\delta_{S_n}(y)\,\mathrm{d}y\Big)\,\mathrm{d}s \end{cases}$$

in the site-saturated and in the time-dependent case, respectively.

Of course in real situations nucleation cannot take place on unbounded subsets; nevertheless there are situations in which it could be more convenient (because more tractable mathematically in order to obtain explicit formulas) to consider nucleation on unbounded domains, such as planes or lines, as we shall see in the sequel. Anyway, in order to model the real general case in which nucleation takes place in a bounded region C (the sample where the reaction takes place) it is sufficient to consider the nucleation process having intensity measure Λ of the type

$$\Lambda(\mathrm{d}y) = \lambda(y)\delta_{S_n\cap C}(y)\,\mathrm{d}y\,,$$

and

$$\Lambda(\mathrm{d}(s,y)) = \lambda(s,y)\delta_{S_n\cap C}(y)\,\mathrm{d}s\,\mathrm{d}y\,,$$

in the site-saturated and in the time-dependent case, respectively.

In what follows, we consider the case $d = 3$ and $n = 2$ or $n = 1$ to model situations in which nucleation takes place on planes or lines, respectively, which are of particular interest in real applications. In particular, we shall consider the case in which the nucleation is homogenous in space in the site-saturated case, and homogeneous in space and time in the time-dependent case, which corresponds to take $\lambda(y) \equiv \lambda > 0$ and $\lambda(s,y) \equiv c > 0$, respectively, in the above equations. This assumption allows us to provide explicit formulas for V_V (and so for their related quantities), useful in various real applications. Indeed, under such homogeneity assumption the above expressions for V_E simplify as follows:

$$V_E(t,x) = \begin{cases} \lambda\,\mathscr{H}^n(S_n \cap C \cap B_{Gt}(x))\,, \\ c\displaystyle\int_0^t \mathscr{H}^n(S_n \cap C \cap B_{G(t-s)}(x))\,\mathrm{d}s\,, \end{cases} \qquad (4)$$

in the site-saturated and in the time-dependent case, respectively; so the problem reduces to evaluate the $\mathscr{H}^n$ measure of the intersection of a ball with the spatial region $(S_n \cap C)$ where the nucleation takes place. Note also that for point x and time t such that $B_{Gt}(x) \subset C$ (for instance at the very beginning of a reaction or for points x sufficiently far from the boundary of the sample), then $\mathscr{H}^n(S_n \cap C \cap B_{G(t-s)}(x)) = \mathscr{H}^n(S_n \cap B_{G(t-s)}(x))$ for any $s \in [0,t]$, so that the computation of V_E might be simpler.

In the subsequent sections the constants λ and c in Eq. 4 will be denoted by λ_S and I_S, respectively, in the case of nucleation on planes, and by λ_L and I_L, respectively, in the case of nucleation on lines. Thus, λ_S will represent the mean number of nuclei per unit of

area of a plane, whereas λ_L the mean number of nuclei per unit of length of a line, and I_S and I_L will represent the nucleation rate in the time-dependent nucleation (i.e., the mean number of nuclei per unit of time) in the plane case and the line case, respectively.

NUCLEATION ON RANDOM PLANES

In Villa and Rios (2010, supplementary material) explicit expressions for V_V and V_E in the case of nucleation on one fixed plane B in $\mathbb{R}^3$ are provided, both in the case of time dependent nucleation and in the case of site-saturation. By denoting $r(x)$ the distance of a point $x \in \mathbb{R}^3$ to B, we recall that

$$V_E(t,x) = \begin{cases} \lambda_S \pi (G^2 t^2 - r(x)^2) \mathbf{1}_{[0,Gt]}(r(x)) \\ I_S \pi \left(\frac{2r(x)^3}{3G} - r(x)^2 t + \frac{G^2 t^3}{3} \right) \mathbf{1}_{[0,Gt]}(r(x)) \end{cases}$$

in the site-saturated and in the time-dependent case, respectively, where $\mathbf{1}_A(a)$ is the indicator function of any set A.

Let us notice from the formulas above that the value of V_E depends on the distance $r(x)$ from x to the plane; thus, in order to find out explicit formulas for unions of random planes it is convenient to represent any plane B by giving its orientation and distance from the origin. Indeed, we recall that a plane B in $\mathbb{R}^3$ is uniquely determined by its distance from the origin, say u, and by its normal outer vector, say $w \in \mathbf{S}^2$ ($\mathbf{S}^2$ is the unit sphere in $\mathbb{R}^3$). The equation of $B = B(w,u)$ is then given by

$$B(w,u) := \{x \in \mathbb{R}^3 : \langle w,x \rangle = u\}$$

and it is well known that $\mathrm{dist}(x,B) = |\langle w,x \rangle - u|$ for any $x \in \mathbb{R}^3$ ($\langle w,x \rangle$ is the scalar product of w and x). As a consequence, by denoting $V_V^{u,w}(t,x)$ and $V_E^{u,w}(t,x)$ the corresponding mean volume density and the mean extended volume density, respectively, associated to the transformed region $\Theta^t = \Theta^t(w,u)$ at time t due to the nucleation on the plane $B(w,u)$, it follows that

$$V_V^{u,w}(t,x) \overset{\text{Eq. 3}}{=} 1 - \mathbb{P}(x \notin \Theta^t(w,u)) = 1 - \mathrm{e}^{-V_E^{u,w}(t,x)}, \tag{5}$$

with

$$V_E^{u,w}(t,x) = \begin{cases} \lambda_S \pi (G^2 t^2 - |\langle w,x \rangle - u|^2) \mathbf{1}_{[0,Gt]}(|\langle w,x \rangle - u|) \\ I_S \pi \left(\frac{2|\langle w,x \rangle - u|^3}{3G} - |\langle w,x \rangle - u|^2 t + \frac{G^2 t^3}{3} \right) \\ \qquad \cdot \mathbf{1}_{[0,Gt]}(|\langle w,x \rangle - u|) \end{cases} \tag{6}$$

in the site-saturated and in the time-dependent case, respectively.

Remark 1 *In Cahn (1956, p. 451) a formula for the mean total volume at time t (denoted by V_0 in that paper) occupied by the grains with nucleus on a unit area of B is given in the site-saturated case. We may notice that such a formula coincide with the mean volume of Θ^t in the spatial region $A := [0,1] \times [0,1] \times [-\infty, +\infty]$, due to the time-dependent nucleation on the plane $B := \{x_3 = 0\}$. Indeed, by Eqs. 1 and 6 we get*

$$\begin{aligned} &\mathbb{E}[V^3(\Theta^t \cap A)] \\ &= \int_0^1 \int_0^1 \left(\int_{-\infty}^{+\infty} \left(1 - \mathrm{e}^{-I_S \pi \left(\frac{2|x_3|^3}{3G} - |x_3|^2 t + \frac{G^2 t^3}{3} \right)} \right) \right. \\ &\qquad \left. \cdot \mathbf{1}_{|x_3| < Gt} \, \mathrm{d}x_3 \right) \mathrm{d}x_1 \, \mathrm{d}x_2 \\ &= 2 \int_0^{Gt} \left(1 - \mathrm{e}^{-I_S \pi \left(\frac{2x_3^3}{3G} - x_3^2 t + \frac{G^2 t^3}{3} \right)} \right) \mathrm{d}x_3 \, , \end{aligned}$$

which coincides with the above mentioned result in Cahn's paper, after the change of variable $z = x_3/Gt$.

NUCLEATION ON ONE RANDOM PLANE

Let us now consider the case in which B is random, i.e let $B = B(W,D) := \{x \in \mathbb{R}^3 : \langle W,x \rangle = D\}$ be a random plane in $\mathbb{R}^3$, where W is a random unit vector in $\mathbf{S}^2$ with probability law P_W, and D is the random distance from the origin, with probability law P_D. We denote by $P_{D,W}$ their joint probability on $\mathbb{R}_+ \times \mathbf{S}^2$. It follows that the transformed region Θ^t at time t is due to double stochasticity: the random location of the plane, and the random nucleation on the plane. Thus, observing that $P_{D,W}(\mathbb{R}_+ \times \mathbf{S}^2) = 1$, the following chain of equalities holds:

$$\begin{aligned} V_V(t,x) &= 1 - \mathbb{P}(x \notin \Theta^t) \\ &= 1 - \int_{\mathbb{R}_+} \int_{\mathbf{S}^2} \mathbb{P}(x \notin \Theta^t(w,u)) P_{D,W}(\mathrm{d}(u,w)) \\ &= 1 - \int_{\mathbb{R}_+} \int_{\mathbf{S}^2} \exp\{-V_E^{u,w}(t,x)\} P_{D,W}(\mathrm{d}(u,w)) \\ &= \int_{\mathbb{R}_+} \int_{\mathbf{S}^2} (1 - \exp\{-V_E^{u,w}(t,x)\}) P_{D,W}(\mathrm{d}(u,w)) \\ &= \int_{\mathbb{R}_+} \int_{\mathbf{S}^2} V_V^{u,w}(t,x) P_{D,W}(\mathrm{d}(u,w)) \end{aligned} \tag{7}$$

Analogously, we get that

$$V_E(t,x) = \int_{\mathbb{R}_+} \int_{\mathbf{S}^2} V_E^{u,w}(t,x) P_{D,W}(\mathrm{d}(u,w)) \, .$$

By noticing that

$$1 - \mathrm{e}^{g(s)\mathbf{1}_A(s)} = (1 - \mathrm{e}^{g(s)}) \mathbf{1}_A(s) \, ,$$

then from Eqs. 5, 6 and 7 we obtain the following general expressions for V_V, for the site-saturated case:

$$V_V(t,x) = \int_{\mathbb{R}_+}\int_{\mathbf{S}^2}\Big(1-\exp\{-\lambda_S\pi(G^2t^2-|\langle w,x\rangle-u|^2)\}\Big) \cdot \mathbf{1}_{[0,Gt]}(|\langle w,x\rangle-u|)P_{D,W}(\,\mathrm{d}(u,w))\,, \quad (8)$$

and for the time-dependent case:

$$V_V(t,x) = \int_{\mathbb{R}_+}\int_{\mathbf{S}^2}\Big(1-\exp\{-I_S\pi(\frac{2|\langle w,x\rangle-u|^3}{3G}-|\langle w,x\rangle-u|^2t + \frac{G^2t^3}{3})\}\Big)\mathbf{1}_{[0,Gt]}(|\langle w,x\rangle-u|)P_{D,W}(\,\mathrm{d}(u,w))\,.$$

Example: uniform orientation and uniform distance from the origin

As a simple example of applicability of the above formulas, let us consider the case in which W is uniform in $\mathbf{S}^2$ and the distance D from the origin is uniform in $[0,M]$, and they are independent. In such a case Eq. 8 becomes

$$V_V(t,x) = \frac{1}{4\pi M}\int_0^M\int_{\mathbf{S}^2}\big(1-\exp\{-\lambda_S\pi(G^2t^2-|\langle w,x\rangle-u|^2)\}\big) \mathbf{1}_{[0,Gt]}(|\langle w,x\rangle-u|)\mathscr{H}^2(\,\mathrm{d}w)\,\mathrm{d}u\,,$$

by changing to spherical coordinates ($w_1=\sin\theta\cos\phi$; $w_2=\sin\theta\sin\phi$; $w_3=\cos\theta$, $\theta\in[0,\pi]$, $\phi\in[0,2\pi]$), it can be written in an even more explicit form, useful for practical purposes:

$$V_V(t,x) = \frac{1}{4\pi M}\int_0^{2\pi}\int_0^{\pi}\Big(\int_0^M(1-\exp\{-\lambda_S\pi(G^2t^2-(f(\theta,\phi,x)-u)^2\}) \mathbf{1}_{[f(\theta,\phi,x)-Gt,f(\theta,\phi,x)+Gt]}(u)\,\mathrm{d}u\Big)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi,$$

where

$$f(\theta,\phi,x) := x_1\sin\theta\cos\phi + x_2\sin\theta\sin\phi + x_3\cos\theta. \quad (9)$$

Obviously, one might proceed similarly for the time-dependent case.

NUCLEATION ON UNION OF RANDOM PLANES

In this section we model nucleation on union of random planes.

Assumptions: Let $B_1 = B_1(W_1,D_1),\ldots,B_M = B_M(W_M,D_M))$ independent random planes, distributed as $B = B(W,D)$, where M is a positive integer-valued random variable with mean $\mathbb{E}[M] = m$; that is m is the mean number of planes where nucleation takes place. We assume that $D_1,D_2,\ldots$ and $W_1,W_2,\ldots$ are independent and identically distributed as D and W, respectively, and independent of M, and that D is a continuous random variable (this implies that the probability that two or more planes B_i coincide is zero).

Then, by denoting $\Theta^t_{B_i}$ the union of the grains with nuclei on B_i, the transformed region Θ^t at time t is the random set given by

$$\Theta^t = \bigcup_{i=1}^{M}\Theta^t_{B_i}.$$

Theorem 2 *Under the above Assumptions, we have that*

$$V_E(t,x) = m\int_{\mathbb{R}_+}\int_{\mathbf{S}^2}V_E^{u,w}(t,x)P_{D,W}(\,\mathrm{d}(u,w))\,,$$

and

$$V_V(t,x) = 1-\mathscr{G}_M\Big(\int_{\mathbb{R}_+}\int_{\mathbf{S}^2}\mathrm{e}^{-V_E^{u,w}(t,x)}P_{D,W}(\,\mathrm{d}(u,w))\Big) \quad (10)$$

where $\mathscr{G}_M$ is the probability generating function of M, and $V_E^{u,w}(t,x)$ is given by Eq. 6.

Remark 3 *Note that, if $t=0$, then $V_V(0,x) = 1-\mathscr{G}(1) = 0$, as expected.*

Proof. Given $M=n$, we know that $B_1,\ldots,B_n$ are independent with random distances $D_i\sim D$ and random orientation $W_i\sim W$. Given then the distances $D_1=u_1,\ldots,D_n=u_n$ of $B_1,\ldots,B_n$, respectively, to the origin, and given the orientations $W_1=w_1,\ldots,W_n=w_n$, the *mean volume extended density conditioned to* $(n,u_1,\ldots,u_n,w_1,\ldots,w_n)$, say $V_E^{n,u_1,\ldots,u_n,w_1,\ldots,w_n}(t,x)$, is given by

$$V_E^{n,u_1,\ldots,u_n,w_1,\ldots,w_n}(t,x) = \sum_{i=1}^{n}V_E^{u_i,w_i}(t,x) \quad (11)$$

It follows that

$$\begin{aligned}V_E(t,x) &= \sum_n n\int_{\mathbb{R}_+}\int_{\mathbf{S}^2}V_E^{u,w}(t,x)P_{D,W}(\,\mathrm{d}(u,w))\mathbb{P}(M=n)\\ &= \int_{\mathbb{R}_+}\int_{\mathbf{S}^2}V_E^{u,w}(t,x)P_{D,W}(\,\mathrm{d}(u,w))\sum_n n\mathbb{P}(M=n)\\ &= m\int_{\mathbb{R}_+}\int_{\mathbf{S}^2}V_E^{u,w}(t,x)P_{D,W}(\,\mathrm{d}(u,w))\,.\end{aligned}$$

By noticing that

$$\underbrace{\int_A \dots \int_A}_{n\text{-times}} f(a_1)f(a_2)\cdots f(a_n)\,\mathrm{d}a_1\cdots\mathrm{d}a_n = \Big[\int_A f(a)\,\mathrm{d}a\Big]^n,$$

we obtain

$$\begin{aligned}
V_V(t,x) &= 1-\mathbb{P}(x\notin\Theta^t)\\
&= 1-\sum_n \underbrace{\int_{\mathbb{R}_+}\int_{\mathbf{S}^2}\cdots\int_{\mathbb{R}_+}\int_{\mathbf{S}^2}}_{n\text{-times}} \mathrm{e}^{-V_E^{n,u_1,\dots,u_n,w_1,\dots,w_n}(t,x)}\\
&\quad\cdot P_{D,W}(\mathrm{d}(u_1,w_1))\cdots P_{D,W}(\mathrm{d}(u_n,w_n))\,\mathbb{P}(M=n)\\
&\overset{\text{Eq. 11}}{=} 1-\sum_n \underbrace{\int_{\mathbb{R}_+}\int_{\mathbf{S}^2}\cdots\int_{\mathbb{R}_+}\int_{\mathbf{S}^2}}_{n\text{-times}} \prod_{i=0}^{n}\mathrm{e}^{-V_E^{u_i,w_i}(t,x)}\\
&\quad\cdot P_{D,W}(\mathrm{d}(u_1,w_1))\cdots P_{D,W}(\mathrm{d}(u_n,w_n))\,\mathbb{P}(M=n)\\
&= 1-\\
&\quad\sum_n\Big(\int_{\mathbb{R}_+}\int_{\mathbf{S}^2}\mathrm{e}^{-V_E^{u,w}(t,x)}P_{D,W}(\mathrm{d}(u,w))\Big)^n\mathbb{P}(M=n)\\
&= 1-\mathscr{G}(z)\,,
\end{aligned}$$

where $\mathscr{G}$ is the probability generating function of M, and

$$z := \int_{\mathbb{R}_+}\int_{\mathbf{S}^2}\mathrm{e}^{-V_E^{u,w}(t,x)}P_{D,W}(\mathrm{d}(u,w))$$

□

Remark 4 *Let us notice that if M is a Poisson random variable with mean m, then $\mathscr{G}_M(z)=\mathrm{e}^{-m(1-z)}$, and so, by Eq. 10 and $P_{D,W}(\mathbb{R}_+\times\mathbf{S}^2)=1$,*

$$V_V(t,x) = 1-\exp\Big\{-m\int_{\mathbb{R}_+}\int_{\mathbf{S}^2}\Big(1-\mathrm{e}^{-V_E^{u,w}(t,x)}\Big)P_{D,W}(\mathrm{d}(u,w))\Big\} \tag{12}$$

More numerically tractable expressions for the above equations can be obtained by passing into spherical coordinates as the example given in the previous section.

PARTICULAR PROBABILITY DISTRIBUTIONS OF THE RANDOM ORIENTATION *W* USEFUL IN APPLICATIONS

Throughout this section, without any other specification, the number M of planes is assumed to be a Poisson random variable, so that Eq. 12 holds. As a consequence, such a model can be seen as a network of Poisson hyperplanes in 3D (Matheron, 1975). We consider here a few particular cases of interest in applications.

Parallel and orthogonal planes

Let us consider the general case in which the distribution of the orientation W is discrete, and assume that D and W are independent. Therefore W is a discrete random vector in $\mathbf{S}^2$, that is there exist $w_1,w_2,\dots$ in $\mathbf{S}^2$ and $p_1,p_2,\dots$ in $[0,1]$ such that $\sum_i p_i = 1$ and $\mathbb{P}(W=w_i)=p_i$ for all i. Then Eq. 12 simplifies as follows:

$$V_V(t,x) = 1-\exp\Big\{-m\int_{\mathbb{R}_+}\sum_i\Big(\Big(1-\mathrm{e}^{-V_E^{u,w_i}(t,x)}\Big)p_i\Big)P_D(\mathrm{d}u)\Big\} \tag{13}$$

with $V_E^{u,w_i}(t,x)$ given by Eq. 6.

A particular case of the above model is obtained by assuming that the planes are parallel. In such a case, the outer normal vector of each plane is fixed, say $\bar{w}=(0,0,1)$ (that is, the planes are parallel to the xy plane); as a consequence we obtain

$$V_V(t,x) = 1-\exp\Big\{-m\int_{\mathbb{R}_+}\Big(1-\mathrm{e}^{-V_E^{u,\bar{w}}(t,x)}\Big)P_D(\mathrm{d}u)\Big\}.$$

An explicit expression in the case D is uniformly distributed in [0,K] is then given by

$$V_V(t,x) = \begin{cases} 1-\exp\Big\{-\dfrac{m}{K}\displaystyle\int_0^K\Big(1-\mathrm{e}^{-\lambda_S\pi(G^2t^2-(x_3-u)^2)}\Big)\\ \qquad\cdot\mathbf{1}_{[x_3-Gt,x_3+Gt]}(u)\,\mathrm{d}u\Big\} \\ 1-\exp\Big\{-\dfrac{m}{K}\displaystyle\int_0^K\Big(1-\mathrm{e}^{-I_S\pi(\frac{2|x_3-u|^3}{3G}-|x_3-u|^2t+\frac{G^2t^3}{3})}\Big)\\ \qquad\cdot\mathbf{1}_{[x_3-Gt,x_3+Gt]}(u)\,\mathrm{d}u\Big\} \end{cases}$$

in the site-saturated and in the time-dependent case, respectively.

Note that m/K is the mean area fraction of the planes in $[0,K]\times[0,1]^2$.

Remark 5 *Let us consider for instance the site-saturated case. Since we assumed that each random plane B_i is of the type $x_3=D$ with $D\sim U[0,K]$, and λ_S nuclei per unit of area in mean for each plane, then nucleation takes place in the spatial region between the plane $x_3=0$ and the plane $x_3=K$ with $\lambda_s m$ nuclei in mean in $[0,1]^2\times[0,K]$. Thus, we expect that for*

m sufficiently large, such a birth-and-growth process approximates one with nucleation process given by a homogeneous Poisson point process between the two parallel planes $x_3 = 0$ and $x_3 = K$, with intensity $\lambda = \lambda_s m/K$. Indeed, e.g., in the case $t > K/G$, for any $x = (x_1, x_2, x_3)$ with $x_3 \in [0, K]$,

$$V_V(t,x) = 1 - \exp\left(-\frac{m}{K}\int_0^K (1 - \mathrm{e}^{-\lambda_S \pi (G^2 t^2 - (x_3 - u)^2)})\,\mathrm{d}u\right)$$
$$\sim 1 - \exp\left\{1 - \lambda\pi\left(G^2 t^2 K - \frac{K^3}{3} + K^2 x_3 - M x_3^2\right)\right\},$$

that coincides with Eq.(101) in Villa and Rios (2010), where the case of nucleation between two parallel planes is studied.

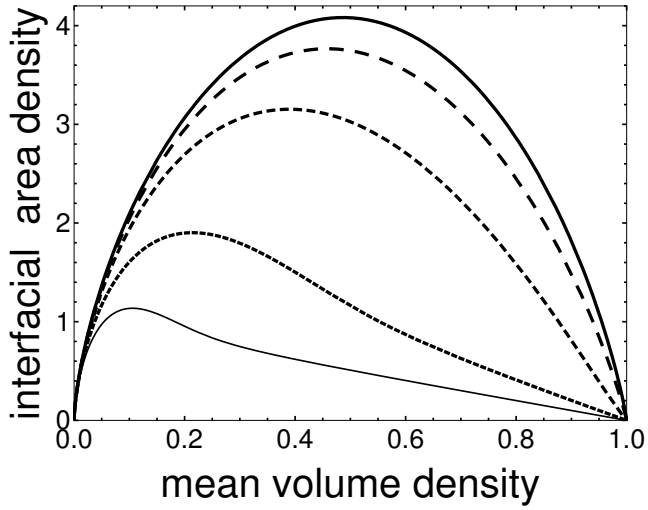

Fig. 1. *Microstructural path for transformations nucleated on random points and planes. The solid black line: homogeneous Poisson point process with intensity $\lambda = 10$. The other lines represent a transformation nucleated on m planes $x_3 = [-K, K]$ with λ_S number of nuclei per unit of area, so that $\lambda_S m/2K = 10$: a)thin solid line $\lambda_S = 20$; b)short-dashed line: $\lambda_S = 10$; c)medium-dashed line: $\lambda_S = \sqrt{10}$; d)dashed line: $\lambda_S = 1$. The clustering effect is accentuated for low $m/2K$ and high λ_S, thin solid line. In contrast for high $m/2K$ and low λ_S, dashed line, the microstructural path approaches that of a reaction nucleated according with a homogeneous Poisson point process, solid curve.*

Fig. 1 illustrates the above Remark. The thick solid line is the microstructural path, evaluated in $x = 0$, of a transformation for which nuclei are located in space according to a homogeneous Poisson point process with intensity $\lambda = 10$. The other lines represent transformations nucleated on m planes $x_3 \in [-K, K]$, with λ_S number of nuclei per unit of area, so that $\lambda_S m/2K = 10$ The thin solid line represents the case in which $m/2K = 0.5$ and $\lambda_S = 20$. A pronounced left-hand skew is apparent. As the number of nuclei per unit of area decreases and the area per unit of volume increases (thus keeping the total number of nuclei per unit of volume constant) the curves progressively approach the thick solid line as expected. Preferential nucleation on planes and lines may be understood as a clustering effect according to Vandermeer (2005). It is the severity of this clustering that shows as an asymmetry in the microstructural path plot. Such a clustering effect is more intense for low $m/2K$ and high λ_S.

It might be of interest also to model nucleations on orthogonal planes. Since in many real applications it is of interest the behavior of the process in the centre of the specimen, for sake of simplicity we shall assume here that the distance D from the origin is uniformly distributed in $[0, K]$, so that it is easy to get an explicit expression for $V_V(t,x)$, which might be used to represent the mean volume density at points x sufficiently far from to the boundary of the specimen. Therefore, denoted by $w_1 = (1,0,0)$, $w_2 = (0,1,0)$, and $w_3 = (0,0,1)$, with $\mathbb{P}(W = w_i) = p_i$, we obtain

$$V_V(t,x) \overset{\text{Eqs. 13,5}}{=} \begin{cases} 1 - \exp\left\{-\frac{m}{K}\int_0^K \sum_{i=1}^3 p_i (1 - \mathrm{e}^{-\lambda_S \pi (G^2 t^2 - (x_i - u)^2)}) \right. \\ \qquad \left. \mathbf{1}_{[x_i - Gt, x_i + Gt]}(u)\,\mathrm{d}u\right\} \\ 1 - \exp\left\{-\frac{m}{M}\int_0^M \sum_{i=1}^3 p_i (1 - \mathrm{e}^{\frac{2|x_i - u|^3}{3G} - (x_i - u)^2 t + \frac{G^2 t^3}{3}}) \right. \\ \qquad \left. \mathbf{1}_{[x_i - Gt, x_i + Gt]}(u)\,\mathrm{d}u\right\} \end{cases}$$

in the site-saturated and in the time-dependent case, respectively.

An example of continuous not-uniform distribution of *W*

Let us consider the following simple model where nucleation takes place on planes having continuous but not uniform orientation. It may be used as model for recrystallization processes in which nucleation takes places on ellipsoidal grains, for instance.

For sake of simplicity we consider here the site-saturated case, and we assume, as above, that the distance D from the origin in uniformly distributed, but now dependent on the orientation of the plane. Thus, denoted by $P_{D|W}(\mathrm{d}u|w)$ the conditioned probability law of D given W, let us assume

$$P_{D|W}(\mathrm{d}u|w) := \frac{1}{M(\alpha w_1^2+\beta w_2^2+\gamma w_3^2)}\mathbf{1}_{[0,M(\alpha w_1^2+\beta w_2^2+\gamma w_3^2)]}(u)\,\mathrm{d}u\,,$$

and

$$P_W(\mathrm{d}w) := \frac{3}{4\pi}\frac{a^2w_1^2+b^2w_2^2+c^2w_3^2}{a^2+b^2+c^2}\mathbf{1}_{\mathbf{S}^2}(w)\mathscr{H}^2(\mathrm{d}w)\,,$$

where $a := 1/\sqrt{\alpha}$, $b := 1/\sqrt{\beta}$, and $c := 1/\sqrt{\gamma}$.

Then it follows

$$V_V(t,x) = 1-\exp\left\{-\frac{3m}{4\pi(a^2+b^2+c^2)}\int_0^{2\pi}\int_0^{\pi}\eta(u;\theta,\phi)\Big(a^2\sin^2\theta\cos^2\phi + b^2\sin^2\theta\sin^2\phi + c^2\cos^2\theta\Big)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\right\}$$

with

$$\eta(u;\theta,\phi) := \int_0^{M(\alpha\sin^2\theta\cos^2\phi+\beta\sin^2\theta\sin^2\phi+\gamma\cos^2\theta)} \frac{(1-\exp\{-\lambda_S\pi(G^2t^2-(f(\theta,\phi,x)-u)^2)\})}{M(\alpha\sin^2\theta\cos^2\phi+\beta\sin^2\theta\sin^2\phi+\gamma\cos^2\theta)} \cdot\mathbf{1}_{[f(\theta,\phi,x)-Gt,f(\theta,\phi,x)+Gt]}(u)\,\mathrm{d}u$$

and $f(\theta,\phi,x)$ given by Eq. 9.

Remark 6 *Note that the case of uniform distribution of W in $\mathbf{S}^2$, with W and D independent, follows as a particular case with $a=b=c=1$.*

NUCLEATION ON RANDOM LINES

As mentioned before, nucleation on lines might be used as model for nucleation on the edges of grains in recrystallization processes. Thus, let L be a fixed line in $\mathbb{R}^3$, and λ_L and I_L be as in Sec "General expression in the case of nucleation on lower dimensional sets". Then it is not difficult to see that Eq. 4 becomes in this case

$$V_E(t,x) = \begin{cases} \lambda_L 2\sqrt{G^2t^2-r(x)^2}\,\mathbf{1}_{[0,Gt]}(r(x)) \\ I_L G\Big[t\sqrt{t^2-(r(x)/G)^2}-(r(x)/G)^2 \\ \qquad\cdot\log\left(\frac{t+\sqrt{t^2-(r(x)/G)^2}}{r(x)/G}\right)\Big]\mathbf{1}_{[0,Gt]}(r(x)) \end{cases} \tag{14}$$

in the site-saturated and in the time-dependent case, respectively, where $r(x)$ is the distance of $x\in\mathbb{R}^3$ from L.

By following the representation given in Stoyan *et al.* (1995, Sec. 8.5)) (see also Matheron (1975)), we may uniquely determine a line L in $\mathbb{R}^3$ with positive distance u from the origin by u and by a pair $(v,w)\in T(\mathbf{S}^2)$, being $T(\mathbf{S}^2)$ the *tangent bundle* to $\mathbf{S}^2$, that is the collection of pairs (v,w) with $v\in\mathbf{S}^2$ and w unit vector tangent to $\mathbf{S}^2$ at v. In other words, v is the outer normal vector to the plane on which the line lies, while w is the direction of the line. If $u=0$, only the direction w is needed to identify the line, so $T(\mathbf{S}^2)$ has to be replaced by $\mathbf{S}^2$ and L is the line $L(0,w)$ through the origin with direction $w\in\mathbf{S}^2$. We are going to consider nucleation on random lines of interest for real applications, whose distance from the origin is random with continuous distribution, so that $\mathbb{P}(u=0)=0$. Then, let us denote by $L^{u,(v,w)}$ the line having distance u from the origin uniquely determined by the pair $(v,w)\in T(\mathbf{S^2})$; it follows that $L^{u,(v,w)}$ is the line through the point uv and direction w, and so

$$\mathrm{dist}(x,L^{u,(v,w)}) = \sqrt{(x_1-uv_1)^2+(x_2-uv_2)^2+(x_3-uv_3)^2-\langle x-uv,w\rangle^2} := j(x;u,(v,w))$$

As a consequence, denoted by $V_V^{u,(v,w)}(t,x)$ and $V_E^{u,(v,w)}(t,x)$ the corresponding mean volume density and the mean extended volume density, respectively, associated to the transformed region $\Theta^t=\Theta^t(u,(v,w))$ at time t due to the Poissonian nucleation on the line $L^{u,(v,w)}$, it follows that

$$V_V^{u,(v,w)}(t,x) = 1-\mathbb{P}\left(x\notin\Theta^t(u,(v,w))\right) = 1-\exp\left(-V_E^{u,(v,w)}(t,x)\right)\,,$$

with

$$V_E^{u,(v,w)}(t,x) = \begin{cases} 2\lambda_L\sqrt{G^2t^2-j^2(x;u,(v,w))}\,\mathbf{1}_{[0,Gt]}(j(x;u,(v,w))) \\ I_L G\Big[t\sqrt{t^2-(j(x;u,(v,w))/G)^2}-(j(x;u,(v,w))/G)^2 \\ \qquad\cdot\log\left(\frac{t+\sqrt{t^2-(j(x;u,(v,w))/G)^2}}{j(x;u,(v,w))/G}\right)\Big]\mathbf{1}_{[0,Gt]}(j(x;u,(v,w))) \end{cases}$$

in the site-saturated and in the time-dependent case, respectively.

By proceeding along the same lines of the previous sections in the case of nucleation on a random line $L^{D,(V,W)}$ with D and (V,W) random quantities

with probability law P_D on $\mathbb{R}_+$, and P_T on $T(\mathbf{S}^2)$, respectively, we have that

$$V_V(t,x) = \int_{\mathbb{R}_+}\int_{T(\mathbf{S}^2)} \Big(1-\exp\Big\{-V_E^{u,(v,w)}(t,x)\Big\}\Big) \cdot P_{D,T}(\,\mathrm{d}(u,(v,w))\,,$$

and

$$V_E(t,x) = \int_{\mathbb{R}_+}\int_{T(\mathbf{S}^2)} V_E^{u,(v,w)}(t,x)\,P_{D,T}(\,\mathrm{d}(u,(v,w))\,,$$

having denoted by $P_{D,T}$ the joint probability of D and (V,W) on $\mathbb{R}_+ \times T(\mathbf{S}^2)$. Whereas, by considering now the nucleation on unions of M independent random lines $L_1,\ldots,L_M$ as $L^{D,(V,W)}$, with $\mathbb{E}[M]=m$, and denoted by $\Theta^t_{L_i}$ the union of the grains with nuclei on L_i, the transformed region Θ^t at time t is the random set given by $\Theta^t = \bigcup_{i=1}^M \Theta^t_{L_i}$. Then, by proceeding similarly to the case of random planes, we obtain

$$V_V(t,x) = 1-\mathscr{G}_M\Big(\int_{\mathbb{R}_+}\int_{T(\mathbf{S}^2)} \mathrm{e}^{-V_E^{u(v,w)}(t,x)}P_{D,T}(\,\mathrm{d}(u,(v,w))\Big),$$

and if M has Poisson distribution

$$V_V(t,x) = 1-\exp\Big\{-m\int_{\mathbb{R}_+}\int_{T(\mathbf{S}^2)} \big(1-\mathrm{e}^{-V_E^{u,(v,w)}(t,x)}\big)P_{D,T}(\,\mathrm{d}(u,(v,w))\Big\}.$$

The model proposed above might be particularly useful in real applications when the behavior at the origin would be investigated; indeed, by noticing that $j(0;u,(v,w))=u$, it follows that $V_V(t,0)$ does not depend on the orientation of the lines, but only on their distance D from the origin.

Nevertheless, in dependence of different purposes it might be useful to consider different line models; for instance, by defining the random lines by a point process of their intersection with planes containing the origin and with different orientations, or, more simply, if the mean number of lines is finite (as occurs in applications), by giving a finite (in mean) collection $\{A_i,W_i\}$ of random points A_i in $\mathbb{R}^3$ and random directions W_i in $\mathbf{S}^2$, so that $L(A_i,W_i) := \{A_i+tW_i : t\in\mathbb{R}\}$ is the random line through A_i with direction W_i. By observing that for any $x,a\in\mathbb{R}^3$ and $w\in\mathbf{S}^2$

$$\mathrm{dist}(x,L(a,w)) = \sqrt{(x_1-a_1)^2+(x_2-a_2)^2+(x_3-a_3)^2-\langle x-a,w\rangle^2} := h(x;a,w)\,, \quad (15)$$

and denoted by $V_V^{a,w}(t,x)$ and $V_E^{a,w}(t,x)$ the mean volume density and the mean extended volume density, respectively, associated to the transformed region at time t due to the nucleation on the line $L(a,w)$, it follows that

$$V_V^{a,w}(t,x) = 1-\mathrm{e}^{-V_E^{a,w}(t,x)},$$

with

$$V_E^{a,w}(t,x) \overset{\text{Eq. 14}}{=} \begin{cases} \lambda_L 2\sqrt{G^2t^2-h^2(x;a,w)}\;\mathbf{1}_{[0,Gt]}(h(x;a,w)) \\ I_L G\Big[t\sqrt{t^2-(h(x;a,w)/G)^2}-(h(x;a,w)/G)^2 \\ \qquad \log\Big(\frac{t+\sqrt{t^2-(h(x;a,w)/G)^2}}{h(x;a,w)/G}\Big)\Big]\mathbf{1}_{[0,Gt]}(h(x;a,w)) \end{cases} \quad (16)$$

in the site-saturated and in the time-dependent case, respectively. Therefore, similarly as above, we may consider now the nucleation on the union of random lines $L(A_1,W_1),\ldots,L(A_M,W_M)$, with $\mathbb{E}[M]=m\in\mathbb{R}$ and $\{(A_i,W_i)\}$ independent and identically distributed as (A,W) with joint probability distribution $P_{A,W}$ on $\mathbb{R}^3\times\mathbf{S}^2$ and independent of M. Under the assumption that A is a continuous random point (so, the probability that two or more lines L_i coincide is zero), we get

$$V_E(t,x) = m\int_{\mathbb{R}^3}\int_{\mathbf{S}^2} V_E^{a,w}(t,x)P_{A,W}(\,\mathrm{d}(a,w))\,,$$

and

$$V_V(t,x) = 1-\mathscr{G}_M\Big(\int_{\mathbb{R}^3}\int_{\mathbf{S}^2}\mathrm{e}^{-V_E^{a,w}(t,x)}P_{A,W}(\,\mathrm{d}(a,w))\Big)\,. \quad (17)$$

Such a model makes the particular case of nucleation on parallel lines easier to study, with respect to the previous one, as shown in the next section.

PARALLEL LINES

A particular case of the above model is obtained assuming that the lines are parallel. In such a case, the direction of each line is fixed, say $\bar{w}=(0,0,1)$ (that is the lines are parallel to the z-axis); as a consequence, by assuming $M\sim Po(m)$, Eq. 17 simplifies as follows

$$V_V(t,x) = 1-\exp\Big\{-m\int_{\mathbb{R}^3}\Big(1-\mathrm{e}^{-V_E^{a,\bar{w}}(t,x)}\Big)P_A(\,\mathrm{d}a)\Big\}$$

with $V_E^{a,\bar{w}}(t,x)$ as in Eq. 16 and noticing that $h(x;a,\bar{w}) = \sqrt{(x_1-a_1)^2+(x_2-a_2)^2}$.

Remark 7 *Let us consider for instance the site-saturated case. If in particular A is uniformly*

distributed in $[0,K]^3$*, then*

$$V_V(t,x) = 1 - \exp\left\{ -\frac{m}{K^2} \int_{[0,K]^2} \left(1 - \mathrm{e}^{-\lambda_L 2\sqrt{G^2t^2-((x_1-a_1)^2+(x_2-a_2)^2))}}\right) \mathbf{1}_{[0,Gt]}\left(\sqrt{(x_1-a_1)^2+(x_2-a_2)^2}\right) \mathrm{d}a_1\,\mathrm{d}a_2 \right\} \quad (18)$$

Note that $\frac{m}{K^2}$ *is the length volume fraction of the lines in* $[0,K]^3$*, and that the mean number of nuclei on the lines in* $[0,K]^3$ *is* $\lambda_L mK$*.*

Similarly to the case of nucleation on random parallel planes discussed in Remark 5, if the mean number m of lines is sufficiently large, we expect that for any point x not too close to the boundary of $[0,K]^2 \times (-\infty,+\infty)$ *(in particular for any x such that* $Gt \le x_1 \le K - Gt$ *and* $Gt \le x_2 \le K - Gt$*), the value of* $V_V(t,x)$ *have to approximate that one associated to a Poisson homogeneous nucleation with intensity* $\lambda = \lambda_L \frac{m}{K^2}$*.*

Indeed, for any x such that $Gt \le x_i \le K - Gt$ *for* $i = 1,2$*,*

$$\begin{aligned} V_V(t,x) &\overset{\text{Eq. 18}}{=} 1 - \exp\left\{ -\frac{m}{K^2} \int_0^{Gt} \int_0^{2\pi} \left[1 - \mathrm{e}^{-2\frac{\lambda}{\frac{m}{K^2}}\sqrt{G^2t^2-\rho^2}}\right] \cdot \rho\,\mathrm{d}\theta\,\mathrm{d}\rho \right\} \\ &\sim 1 - \exp\left\{ -4\pi\lambda \int_0^{Gt} \sqrt{G^2t^2-\rho^2}\,\rho\,\mathrm{d}\rho \right\} \\ &= 1 - \mathrm{e}^{-\frac{4}{3}\pi\lambda G^3 t^3}, \end{aligned}$$

which is just the mean volume density associated to a homogeneous Poisson nucleation with intensity λ*.*

SUMMARY AND CONCLUSIONS

- General expressions were derived for the mean volume density of the transformed phase when nucleation takes place on random planes and lines in $\mathbb{R}^3$. The general expression makes no assumption on the distribution of planes and of lines in space.
- Using superposition of processes (see, *e.g.*, Stoyan *et al.*, 1995), one may derive an expression for the situation in which nucleation takes place simultaneously on planes (grain boundaries) and lines (grain edges) and points (grain corners). Namely, we recall that if $\Phi_1,\ldots,\Phi_n$ are independent nucleation processes, then

$$V_V(t,x) = 1 - \prod_{i=1}^{n} \left(1 - V_V^i(t,x)\right) , \quad (19)$$

having denoted by V_V^i the mean volume density associated with the nucleation process Φ_i. Note that nucleation on grain corners may be easily modelled by point processes. Thus, by assuming simultaneous independent nucleation on planes, lines and points, and by denoting V_V^S, V_V^L and V_V^P the corresponding mean volume densities, we have

$$V_V(t,x) \overset{\text{Eq. 19}}{=} 1 - \left(1 - V_V^S(t,x)\right) \cdot \left(1 - V_V^L(t,x)\right)\left(1 - V_V^P(t,x)\right) .$$

We point out that, even if the independence assumption may seem to be too restrictive for practical purposes, actually it is often implicitly assumed in modelling various situations. For instance, analysis of experimental results with the assumption of independence are discussed in Rios and Padilha (2003); Vandermeer and Rath (1989a;b).

- This paper provides the mathematical basis for the development of more specific expressions to be used in practical applications. By studying particular cases of practical relevance new expressions, such as the expression for parallel planes, may be obtained. These expressions significantly increase the scope of exactly solvable cases available to formal kinetics.

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