

# Simultaneous and Sequential Transformations

Paulo R. Rios<sup>1,2,\*</sup> and Elena Villa<sup>3</sup>

<sup>1</sup>Universidade Federal Fluminense

Escola de Engenharia Industrial Metalúrgica de Volta Redonda  
Av. dos Trabalhadores 420, 27255-125, Volta Redonda, RJ, Brasil

<sup>2</sup>RWTH Aachen University

Institut für Metallkunde und Metallphysik

D-52056 Aachen, Germany

prrios@metal.eeimvr.uff.br

<sup>3</sup>University of Milan

Department of Mathematics

via Saldini 50, 20133 Milano, Italy

elena.villa@unimi.it

## Abstract

A new formal kinetics methodology suitable for the situation in which transformations take place simultaneously or sequentially is presented. Based on the distinction between theoretical and experimental quantities and with the help of the superposition principle general relationships were obtained to deal with simultaneous and sequential reactions. The equations presented here are able to deal with position dependent quantities and there is no need to rely on extended volume. They are suitable both for model building, *i. e.* obtaining expressions for simultaneous or sequential reactions from models of the kinetics of each reaction in isolation as well as for extracting theoretical information from the experimentally measured quantities.

Key words: *microstructure; analytical methods; phase transformations; kinetics; recrystallization*

## 1 Introduction

Formal kinetics methodology is frequently employed to analyze a variety of heterogenous transformations in condensed phases [1–5]. This methodology has its origin in the early work of Kolmogorov [6], Johnson-Mehl [7] and Avrami [8–10].

Usually theoretical developments are concerned with the formation of a single phase at a certain nucleation site that grows with a given interface velocity. Nonetheless, sometimes more than one transformation (“transformation” and “reaction” are used interchangeably in this paper) takes place simultaneously. A methodology to model simultaneous reactions was proposed by Vandermeer and Juul-Jensen [11, 12] in connection with recrystallization in a textured matrix. Recrystallization in a textured matrix can be quite complex because the recrystallized regions may belong to specific texture components. Moreover, each texture component may nucleate on a distinct nucleation site and may grow with different velocities. Subsequently, a similar methodology was used by Jones and Bhadeshia [13, 14] to model simultaneous precipitation of more than one phase. In the context of glass crystallization [15–17] corresponding ideas were also proposed to deal with transformations proceeding simultaneously nucleated both on the surface and in the bulk of small specimens. More

recently, also the potential overlap of recrystallization and austenite formation during heating of cold worked steels has gained significant attention [18,19]. In fact, we may have a more general situation than that described above, namely, when the reactions do not start simultaneously but consecutively. For example, reaction 1 starts at  $t = 0$  whereas reaction 2 starts at  $t = \tau > 0$ . One might say that reactions 1 and 2 are *sequential* reactions. If reaction 1 starts and finishes before reaction 2 starts then these sequential reactions are *non-overlapping*. In contrast if reaction 2 starts before reaction 1 stops then we have *overlapping* reactions. One may regard simultaneous transformations as a particular case of sequential transformations when all reactions start at  $t = 0$ . One example from steels would be the decomposition of austenite. Austenite decomposition starts by transforming into ferrite and as the carbon content of austenite increases pearlite starts to form. Therefore there is a sequence of transformations: first ferrite and next pearlite. If austenite decomposition takes place during cooling one may further increase the number of sequential reactions because bainite and the martensite can form. Sequential transformations, overlapping or non-overlapping, are often observed in practice, perhaps even more often than simultaneous transformations. Nonetheless such a situation has not received much theoretical attention [20].

We may identify transformations according to their specific characteristics with regard to nucleation and growth:

1. Spatial location: nucleation sites may have different dimensionality: points, lines and internal interfaces [21] and we may also include clusters [22, 23]. In small specimens, nucleation may occur on the surface and/or in the bulk of the small specimen [24]. In addition nuclei distribution may be position dependent as in an inhomogeneous Poisson point process [25].
2. Time dependence: nucleation may be site-saturated, constant nucleation rate or have a more general time dependence [26].
3. Growth: constant growth rate or time dependent growth [26].
4. Shape: the growing regions may be spherical or ellipsoidal [25,26].

Transformations may take place with each reaction belonging to one or more of the groups above. The above classification essentially deals with the *geometrical interdependency* among the simultaneous reactions. But there may be another interdependency a *kinetic interdependency*. Such kinetic interdependency may happen, for example, when two growing phases compete for the same solute in order to grow. Thus the velocity of the two phases are related to the common amount of solute in the parent matrix and are therefore interdependent. In this work we will restrict our treatment to the geometric interdependency, *i.e.* the growing regions only compete for space.

Modeling simultaneous reactions normally involves two distinct but closely related objectives:

1. Predict the overall kinetics quantities of the combined reactions such as the mean volume density( to be more rigorously defined in Section 2),  $V_V(t, x)$ , from theoretical expressions developed for each individual reaction. For example, one may wish to predict the overall behavior of a combination of two reactions, one nucleated on the external surface another in the bulk of a finite specimens as described by Villa and Rios [24].
2. Extract the kinetics, *i.e* mean volume density as a function of time, for an individual reaction from experimental measurements. One might or might not have an analytical model for the nucleation and growth of this specific reaction beforehand but the experimental data may be useful precisely to establish which model would be suitable to describe it. Therefore one needs to know how to use the measured data to obtain quantities suitable for comparison with available theoretical models.

Of course one may also have a combination of both: the experimental kinetics is known for some reactions whereas the theoretical behavior is known for other reactions.

In previous work, the present authors resorted to recent developments in stochastic geometry [27–30] and obtained exact analytical expressions for the situation in which nuclei were located in space according to an inhomogeneous Poisson point processes [25], for nuclei located in spherical clusters according to a Matérn cluster process [22] and for nuclei located in the bulk and on the surface of small specimens [24]. This paper follows up the idea of these previous papers that is to obtain exact mathematical expressions, thus, increasing the number of the exactly solvable cases available to formal kinetics applications.

In this work we use stochastic geometry methods to develop a general formal kinetic methodology for treating the situation in which several heterogeneous transformations take place simultaneously or sequentially.

sectionMathematical background

## 1.1 Nucleation and growth and birth and growth processes

Consider a specimen that initially contains a single phase, say  $\alpha$ . Let  $\alpha$  partially transform to another phase,  $\beta$ . In the solid state this transformation frequently involves two steps: the first is the initiation of  $\beta$  from the  $\alpha$  matrix, which is called nucleation of  $\beta$  and the second is the subsequent growth of the  $\beta$  phase as it consumes the  $\alpha$  phase. This process is called “nucleation and growth” by the materials scientist whereas the mathematicians prefer to call it “birth and growth”. This transformation is a physical phenomenon and its progress may be followed, for example, by direct observation of the microstructure of transformed samples by means of a microscope. In order to model such a transformation it is necessary to describe it in the language of abstract mathematics, *i. e.* using set theory. Thus, the transformed region is regarded as a set designated  $\Theta^t$ . The superscript  $t$  indicates that the transformed region depends on time, it is a *dynamic* process. Suppose that we observe the transformed region (the set  $\Theta^t$ ) with the help of an optical microscope. We fix the observation window under the lens but move the stage of the microscope so that several different transformed regions can be seen within the observation window. Mathematics has a powerful tool to deal with such a situation that is to consider that  $\Theta^t$  is a *random set*. These ideas may be expressed in a more formal way as follows.

A *birth and growth (stochastic) process* is a dynamic germ-grain model [28], 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 [28] 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  $\Theta_{T_j}^t(X_j)$  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  $\Theta^t$  at time  $t$  is

$$\Theta^t = \bigcup_{T_j \leq t} \Theta_{T_j}^t(X_j), \quad t \in \mathbb{R}_+. \quad (1)$$

The family  $\{\Theta^t\}_t$  of all transformed regions  $\Theta^t$  over time is called birth and growth process. Birth and growth and nucleation and growth will be used as synonyms in this paper.

## 1.2 Meaning of $V_V, S_V$

A point of paramount practical importance is to be able to quantify the volume of the transformed region and the area between the transformed region and the parent matrix. This quantification is carried out on the set representing the transformed region with the help of measure theory. Measure theory is the mathematical counterpart of everyday experimental measure carried out by the materials scientist. For technical mathematical reasons measure theory prefers to deal with a special class of sets: the Borel sets [31]. Unions and intersections of closed and/or open sets are Borel sets. In practice, any set of engineering interest is going to be a Borel set. The objective of the following mathematical formalism is to define quantities that will be useful to quantify the transformed region. The general  $d$ -dimensional euclidian space  $\mathbb{R}^d$  is used but naturally  $d = 2, 3$  are the cases of physical interest in this paper.

A measure  $\mu$  on  $\mathbb{R}^d$  admits density if there exists a locally integrable function  $f : \mathbb{R}^d \rightarrow \mathbb{R}$  such that

$$\mu(A) = \int_A f(x)dx \quad \forall A \in \mathcal{B}_{\mathbb{R}^d}, \quad (2)$$

where  $\mathcal{B}_{\mathbb{R}^d}$  is the Borel  $\sigma$ -algebra of  $\mathbb{R}^d$  [31];  $x = (x_1, x_2, x_3, \dots, x_d)$  is the spatial coordinate and  $A$  is a subset of  $\mathbb{R}^d$ , corresponding to the region of the physical sample under observation. We denote by  $\nu^d$  the usual  $d$ -dimensional Lebesgue measure in  $\mathbb{R}^d$ , that is, the usual  $d$ -dimensional volume measure.

Since  $\Theta^t$  is a random set, its volume  $\nu^d(\Theta^t)$  will be a random quantity, so that we may deal with its *expected volume*  $\mathbb{E}[\nu^d(\Theta^t)]$  at time  $t$ . In particular, it is of interest to consider the *expected volume measure*  $\mathbb{E}[\nu^d(\Theta^t \cap \cdot)]$  and its density, said *mean volume density of  $\Theta^t$*  and denoted by  $V_V$ , provided it exists,

$$\mathbb{E}[\nu^d(\Theta^t \cap A)] = \int_A V_V(t, x)dx \quad \forall A \in \mathcal{B}_{\mathbb{R}^d}. \quad (3)$$

Eq.(3) shows that in general  $V_V$  depends on space and time. If  $\Theta^t$  is so-to-say *homogeneous* (*i.e.* its probability law is invariant under translations, in other words, the microstructure remains “invariant” if the observation window is moved only by translations.) in space, then  $V_V$  is independent of  $x$

$$\mathbb{E}[\nu^d(\Theta^t \cap A)] = V_V(t)\nu^d(A) \quad \forall A \in \mathcal{B}_{\mathbb{R}^d}. \quad (4)$$

Therefore, for the homogeneous case,  $V_V(t)$  is a positive constant, representing the mean volume density per unit of volume also called the *volume fraction*

$$V_V(t) = \frac{\mathbb{E}[\nu^d(\Theta^t \cap A)]}{\nu^d(A)} \quad \forall A \in \mathcal{B}_{\mathbb{R}^d}. \quad (5)$$

For the inhomogeneous case, Eq.(3) implies that the value of the volume fraction depends on  $A$

$$\mathbf{V}_V(t, A) := \frac{\int_A V_V(t, x)dx}{\nu^d(A)} \quad \forall A \in \mathcal{B}_{\mathbb{R}^d} \quad (6)$$

In the homogeneous case one normally uses the volume fraction, which is independent of  $x$ . Therefore, for the homogeneous case there is no distinction between  $V_V$  and  $\mathbf{V}_V$ .

Similarly, the mean volume density of interfaces or mean interfacial area density [29] can be defined as

$$\mathbb{E}[\nu^{d-1}(\partial\Theta^t \cap A)] = \int_A S_V(t, x)dx \quad \forall A \in \mathcal{B}_{\mathbb{R}^d}. \quad (7)$$

where  $\partial\Theta^t$  is the topological boundary of  $\Theta^t$ , and  $\nu^{d-1}$  is the Lebesgue surface measure. When the meaning is clear “interfacial area density” will be used for brevity.

### 1.3 Probabilities and $V_V(t, x)$

The advantage of the mathematical formalism employed here is that one may readily identify  $V_V(t, x)$  with the probability of  $x$  belonging to the transformed region,  $\Theta^t$

$$V_V(t, x) = \mathbb{P}(x \in \Theta^t) \quad (8)$$

The probability that  $x$  *does not* belong to  $\Theta^t$  is simply

$$1 - V_V(t, x) = \mathbb{P}(x \notin \Theta^t) \quad (9)$$

Suppose that there are two transformations  $\Theta_1^t$  and  $\Theta_2^t$  with boundaries  $\partial\Theta_1^t$  and  $\partial\Theta_2^t$ , respectively. Suppose also that the reactions take place independently of one another. If the reactions are superposed one has the situation depicted in Fig. 1. We can use set operations and the equivalence between probability and mean volume density to describe the combination of these two transformations.

The overall transformed area  $\Theta^t$  is simply the union  $\Theta_1^t \cup \Theta_2^t$ . The region in which the transformations overlap is described by  $\Theta_1^t \cap \Theta_2^t$ . If the transformations are *independent* the probability that a point belongs to this intersection is the product of the probabilities of the point belonging to  $\Theta_1^t$  and  $\Theta_2^t$

$$\mathbb{P}(x \in \Theta_1^t \cap \Theta_2^t) = \mathbb{P}(x \in \Theta_1^t)\mathbb{P}(x \in \Theta_2^t) \quad (10)$$

identifying  $V_{V_1}(t, x) = \mathbb{P}(x \in \Theta_1^t)$  and  $V_{V_2}(t, x) = \mathbb{P}(x \in \Theta_2^t)$  one obtains the mean volume density of the overlapping regions

$$V_{V_{\Theta_1^t \cap \Theta_2^t}}(x, t) = \mathbb{P}(x \in \Theta_1^t \cap \Theta_2^t) = V_{V_1}(x, t)V_{V_2}(x, t) \quad (11)$$

Similar reasoning could be applied, for example, to  $\Theta_1^t \cup \Theta_2^t$  or to  $\Theta_1^t \setminus \Theta_2^t$ . In the sequel this kind of operation will be frequently used in the definitions and in the demonstrations.

### 1.4 Useful relationships and definitions

Under quite general assumptions, normally satisfied in practical applications, it can be proved that [29]

$$G(t) = \frac{1}{S_V(t, x)} \frac{\partial V_V(t, x)}{\partial t} \quad (12)$$

where  $G$  is the overall velocity of the moving boundaries, also called the growth rate. This equation was introduced to materials science by Cahn and Hagel [32]. It is worth mentioning that in the general case [33] Eq.(12) has to be taken in weak form, which means that the following equation holds:

$$\int_A V_V(t, x)dx = \int_A V_V(t_0, x)dx + \int_{t_0}^t \int_A G(x, s)S_V(s, x)dxds$$

for any Borel subset  $A$  of  $\mathbb{R}^d$  such that  $\mathbb{E}[\nu^{d-1}(\partial\Theta^t \cap \partial A)] = 0$ . Therefore Eq.(12) hides a possible exchange between derivative and integral, which is valid whenever  $G$  and  $S_V$  are sufficiently regular. In all our applications we may suppose  $G$  and  $S_V$  regular enough so that Eq.(12) holds.

Finally, it is worth mentioning two definitions that will be used below.

The indicator function  $\mathbf{1}_A(x)$  is defined as equal to 1 if  $x \in A$  and 0 if  $x \notin A$ .  $A$  may be any set, for example, the interval  $[0, t]$ .

$A \oplus B$  is the so-called *Minkowski addition* of  $A$  and  $B$  defined as

$$A \oplus B := \{a + b : a \in A, b \in B\} = \bigcup_{a \in A} B + a. \quad (13)$$

Note that if  $B = B_r(0)$ , then  $A \oplus B$  is the set of points of  $\mathbb{R}^d$  which have a distance from  $A$  less than or equal to  $r$ . This latter definition is only used in the proofs given in the Appendix.

## 2 Model building: total quantities from theoretical quantities

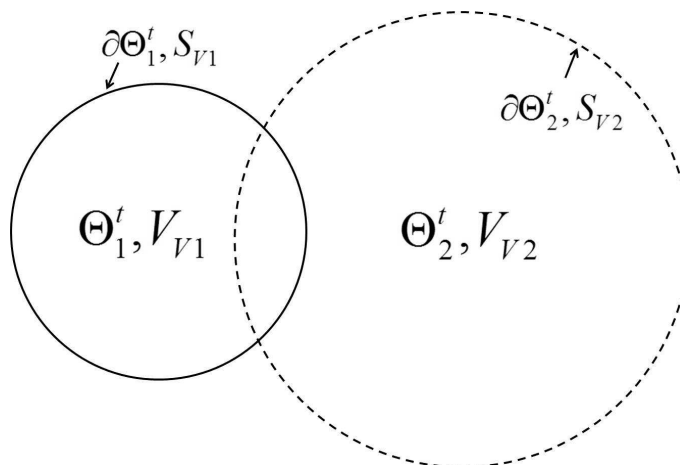


Figure 1: A schematic example of superposition of two transformations, 1 and 2. The transformed area of each is indicated by  $\Theta_1^t$  and  $\Theta_2^t$ . Their boundaries,  $\partial\Theta_1^t$  (solid line) and  $\partial\Theta_2^t$  (dashed line), are indicated by arrows. The mean volume densities of  $\Theta_1^t$  and  $\Theta_2^t$  are  $V_{V1}$  and  $V_{V2}$ , respectively. The mean interfacial densities of  $\partial\Theta_1^t$  and  $\partial\Theta_2^t$  are  $S_{V1}$  and  $S_{V2}$ , respectively.  $V_{V1}$ ,  $V_{V2}$ ,  $S_{V1}$  and  $S_{V2}$  are called “theoretical quantities”.

In this section we show how to use models developed for a single reaction to obtain a model for the combined reaction with the help of the superposition principle. The total mean volume density and the total interfacial area density are denoted here  $V_V(t, x)$  and  $S_V(t, x)$ , respectively. We define here the theoretical mean volume density of reaction  $i$  as the mean volume density if reaction  $i$  were the only reaction to take place. What is called here theoretical mean volume density is therefore the expression that is normally obtained from modeling a single reaction. The theoretical mean volume density and mean interfacial area density of reaction  $i$  will be denoted as  $V_{Vi}(t, x)$  and  $S_{Vi}(t, x)$ , respectively. See Fig.1 for a schematic view. The reason for this definition will become clear in the next section.

Whenever the nucleation process  $\Phi$  is given by the union of two or more nucleation processes, say  $\Phi := \bigcup_{i=1}^n \Phi_i$ , then  $\Phi$  is said to be the superposition of  $\Phi_1, \dots, \Phi_n$ . For more details about the superposition operation of point processes, see, *e.g.*, [28]. Recalling that  $V_V(t, x)$  represents the probability that the point  $x$  belongs to the transformed region at time  $t$ , say  $\Theta^t$ , then  $1 - V_V(t, x) = \mathbb{P}(x \notin \Theta^t) = \mathbb{P}(\{x \notin \Theta_1^t\} \cap \dots \cap \{x \notin \Theta_n^t\})$ , where  $\Theta_i^t$  denotes the transformed region at time  $t$  due to the nucleation process  $\Phi_i$ . If the nucleation processes  $\Phi_1, \dots, \Phi_n$  are independent then the events  $\{x \notin \Theta_i^t\}$  are independent as well; as a consequence  $\mathbb{P}(\{x \notin \Theta_1^t\} \cap \dots \cap \{x \notin \Theta_n^t\}) = \prod_{i=1}^n \mathbb{P}(x \notin \Theta_i^t)$  and so

$$V_V(t, x) = 1 - \prod_{i=1}^n (1 - V_{Vi}(t, x)) \quad (14)$$

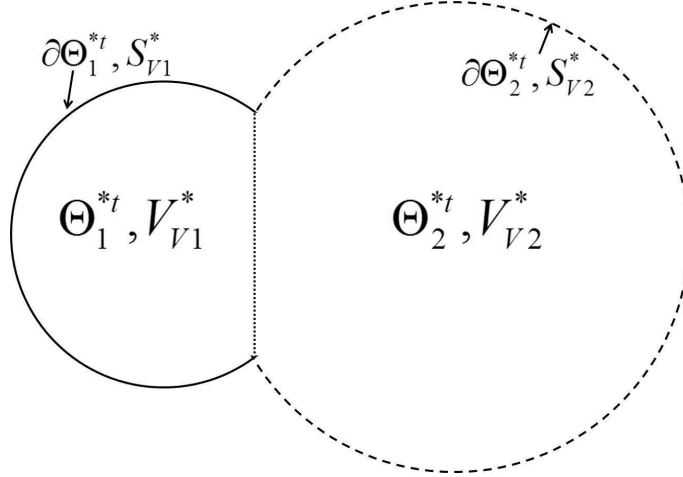


Figure 2: A schematic example of two simultaneous transformations, 1 and 2. The “visible” or “experimental” transformed area of each is indicated by  $\Theta_1^{*t}$  and  $\Theta_2^{*t}$ . Their boundaries,  $\partial\Theta_1^{*t}$  (solid line) and  $\partial\Theta_2^{*t}$  (dashed line), are indicated by arrows. The mean volume densities of  $\Theta_1^{*t}$  and  $\Theta_2^{*t}$  are  $V_{V1}^*$  and  $V_{V2}^*$ , respectively. The mean interfacial densities of  $\partial\Theta_1^{*t}$  and  $\partial\Theta_2^{*t}$  are  $S_{V1}^*$  and  $S_{V2}^*$ , respectively.  $V_{V1}^*$ ,  $V_{V2}^*$ ,  $S_{V1}^*$  and  $S_{V2}^*$  are called “experimental quantities”. The dotted line is the boundary between reactions 1 and 2 and is *not* counted as part of  $\partial\Theta_1^{*t}$  and  $\partial\Theta_2^{*t}$ .

having denoted by  $V_{Vi}$  the mean volume density associated with the nucleation process  $\Phi_i$ . Fig. 1 depicts the superposition of two independent reactions: 1 and 2.

The corresponding equation for  $S_V(t, x)$  is

$$S_V(t, x) = \sum_{i=1}^n \frac{1 - V_V(t, x)}{1 - V_{Vi}(t, x)} S_{Vi}(t, x) \quad (15)$$

The proof of Eq.(15) requires results that are obtained in Section 4 and will be postponed until then.

The overall velocity of the simultaneous reactions,  $G$ , is given by

$$G(t, x) = \frac{1}{S_V(t, x)} \frac{\partial V_V(t, x)}{\partial t} \quad (16)$$

The overall velocity  $G$  may be position dependent even if the boundary velocities of the individual reactions,  $i$ , are not position dependent. This point will become clear examining Eq. (24), which is introduced in Section 4. Notice that this may happen because the overall velocity has no actual physical existence, that is, no interface actually moves with the overall velocity.

These expressions are the mathematically exact method to handle superposition when one has expressions derived for single reactions and wishes to use these expressions to build a model for the simultaneous reactions. Eqs.(14) and (15) permit obtaining a wide range of analytical models from theoretical models for each nucleation and growth process.

### 3 Experimental and theoretical quantities

First, it is necessary to make a distinction between an experimental and a theoretical quantity. As its own name implies an experimental quantity is a quantity that is directly measured from the

transformed microstructure. For example, suppose that a transformation occurs by means of  $n$  simultaneous reactions. Then the experimental mean volume density of a certain reaction  $i$  will be denoted  $V_{V_i}^*(t, x)$ , and analogous notation applies to the experimental mean interface area density, namely,  $S_{V_i}^*(t, x)$ . In contrast, we recall that in Section 2 the theoretical mean volume density and the mean interfacial area density of a reaction  $i$  were denoted as  $V_{V_i}(t, x)$  and  $S_{V_i}(t, x)$ , respectively. Obviously, for a single reaction the experimental and theoretical quantities will be the same. Figs. 1 and 2 schematically show these definitions. In what follows we sometimes refer to “reaction  $\Theta_i^t$ ” meaning reaction  $i$ .

We now give more precise definitions of the experimental quantities.  $V_{V_i}^*$  and  $S_{V_i}^*$ , the mean experimental volume density and mean interfacial area density, respectively, of reaction  $i$ , say,  $\Theta_i^t$ , may be defined as

$$\mathbb{E}[\nu^d(\Theta_i^{*t} \cap A)] = \int_A V_{V_i}^*(t, x) dx \quad \forall A \in \mathcal{B}_{\mathbb{R}^d} \quad (17)$$

where  $\Theta_i^{*t}$  denotes the visible part of the transformed region due to the reaction  $\Theta_i^t$ , and

$$\mathbb{E}[\nu^{d-1}((\partial\Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^t) \cap A)] = \int_A S_{V_i}^*(t, x) dx \quad \forall A \in \mathcal{B}_{\mathbb{R}^d} \quad (18)$$

$V_{V_i}(t, x)$  is the mean volume density of the transformed region,  $\Theta_i^t$ , due to the reaction  $i$  when only such a reaction takes place. In contrast,  $V_{V_i}^*(t, x)$  is the mean volume density of the visible part of the transformed region due to the reaction  $\Theta_i^t$  when all the other reactions also take place, and so it is the mean volume density of  $\Theta_i^{*t}$ . Note that, because of impingement, transformed regions of different reactions cannot overlap, so that  $\Theta^t$  is given by the union of all  $\Theta_i^{*t}$ . In particular, any interior point  $x \in \Theta^t$  belongs to only one transformed region  $\Theta_i^{*t}$ , and so the following relationship between total and experimental quantities holds

$$V_V(t, x) = \sum_{i=1}^n V_{V_i}^*(t, x) \quad (19)$$

Analogously, definition (18) means that  $S_{V_i}^*(t, x)$  is the mean surface density of the visible part of the boundary of the transformed region due to the reaction  $\Theta_i^t$ , (*i.e.* the free or moving boundary of  $\Theta_i^{*t}$ , given by  $\partial\Theta_i^t \setminus (\bigcup_{j \neq i} \Theta_j^t)$ ). In particular, any boundary point  $x \in \partial\Theta^t$  belongs to the free boundary of only one transformed region  $\Theta_i^{*t}$ , and so the following relationship between total and experimental quantities holds

$$S_V(t, x) = \sum_{i=1}^n S_{V_i}^*(t, x) \quad (20)$$

It is worthy emphasizing that  $\partial\Theta_i^{*t}$  and consequently  $S_{V_i}^*$  comprise solely the interfacial area between the transformed region  $i$  and the parent matrix. In other words,  $\partial\Theta_i^{*t}$  and  $S_{V_i}^*$  refer to the moving boundary between transformed region  $\Theta_i^{*t}$  and the parent matrix. For example, the immobile boundaries between regions 1 and 2 that result from impingement, see dotted line in Fig. 2, are *not* counted as part of  $\partial\Theta_1^{*t}$  and  $\partial\Theta_2^{*t}$ . Likewise, immobile boundaries resulting from impingement between regions of the same reaction  $i$  also *do not* count as part  $\partial\Theta_i^{*t}$ .

### 3.1 Derivation of an expression for the interface velocity

A grain associated with reaction  $i$  may have a boundary velocity  $G_i$  that is different from the boundary velocity of grains associated with another reaction  $j \neq i$ . This may happen, for example,



when there are different texture components [11] or different constituents [13]. In this paper, the boundary velocities of the individual reactions,  $G_i$ , are assumed to be only time dependent and to have the same value at every point of the moving boundary of a certain reaction. This assumption is not overly restrictive and considerably simplifies the mathematics. Position dependent velocities would make the problem much more difficult if exactly solvable at all. As an example of the complications involved, consider that if the boundary velocity is position dependent one cannot assume that the shape of the individual region remains constant.

$G_i$  may be obtained from the theoretical quantities by

$$G_i(t) = \frac{1}{S_{V_i}(t, x)} \frac{\partial V_{V_i}(t, x)}{\partial t} \quad (21)$$

but a boundary velocity  $G_i^*$  may also be obtained from the experimental quantities by

$$G_i^*(t) = \frac{1}{S_{V_i}^*(t, x)} \frac{\partial V_{V_i}^*(t, x)}{\partial t} \quad (22)$$

It is “intuitive” that  $G_i = G_i^*$  so that

$$G_i(t) = \frac{1}{S_{V_i}^*(t, x)} \frac{\partial V_{V_i}^*(t, x)}{\partial t} \quad (23)$$

Even though Eq.(23) looks reasonable its proof is not trivial. For this reason the proof is given in the Appendix.

### 3.2 Derivation of relationships between experimental, $V_{V_i}^*$ and $S_{V_i}^*$ , and theoretical quantities, $V_{V_i}$ and $S_{V_i}$ ,

Taking the derivative with respect to  $t$  of  $V_V(t, x)$  in Eq. (19) and using Eqs.(16) and (23)

$$G(t, x)S_V(t, x) = \sum_{i=1}^n G_i(t)S_{V_i}^*(t, x) \quad (24)$$

Eq. (24), as anticipated in Section 3, shows that the overall velocity,  $G(t, x)$ , may be position dependent even if all  $G_i(t)$  are only time dependent. Eq. (24) shows that this may happen when at least one reaction has the interfacial area density position dependent. Furthermore, it can be proved (see Appendix) that

$$\frac{\partial V_{V_i}^*(t, x)}{\partial t} = \frac{1 - V_V(t, x)}{1 - V_{V_i}(t, x)} G_i(t) S_{V_i}(t, x) \quad (25)$$

Combining Eqs. (23) and (25) gives

$$S_{V_i}^*(t, x) = \frac{1 - V_V(t, x)}{1 - V_{V_i}(t, x)} S_{V_i}(t, x) \quad (26)$$

Eq. (15) may be obtained by inserting Eq. (26) into Eq. (20). It is now possible to relate theoretical and experimental quantities. From Eqs. (21) and (26)

$$\frac{\partial V_{V_i}^*(t, x)}{\partial t} = -(1 - V_V(t, x)) \frac{\partial \ln(1 - V_{V_i}(t, x))}{\partial t} \quad (27)$$

and therefore

$$V_{V_i}(t, x) = 1 - \exp\left(-\int_0^t \frac{1}{1 - V_V(s, x)} \frac{\partial V_{V_i}^*(s, x)}{\partial s} ds\right) \quad (28)$$

$$V_{V_i}^*(t, x) = \int_0^t \frac{1 - V_V(s, x)}{1 - V_{V_i}(s, x)} \frac{\partial V_{V_i}(s, x)}{\partial s} ds \quad (29)$$

In Eq. (28) the theoretical quantity is on the left hand side and the experimentally measurable quantities are on the right hand side. This permits obtaining theoretical quantities from experimental quantities. By contrast in Eq. (29) the experimental quantity is on the left hand side whereas the theoretical quantities are on the right hand side. This permits obtaining experimental quantities from theoretical quantities. Notice that  $V_V(t, x)$  may be either obtained experimentally or from the theoretical quantities by means of Eq. (14).

## 4 Sequential transformations

In many cases transformations might not start at the same time but at different times. We call these sequential reactions. In the general case one might imagine a situation in which a second reaction starts while the first reaction is still in progress, so that the reactions overlap, *i. e.* they proceed simultaneously only during a certain time. As mentioned above, simultaneous reactions may be seen as a particular case when all starting times are the same. Moreover, there is no need to treat the case in which the first reaction starts and finishes before the second reaction starts, the non-overlapping case. Indeed, the non-overlapping case may also be considered a particular case of the overlapping case.

We present here a general model for these situations based on the equations derived in the previous section. In order to modify previous equations to encompass these cases we need to define the time,  $t_{is}$ , at which reaction  $i$  starts. As usual let us denote by  $\Theta_i^t$  the transformed region due to reaction  $i$  at time  $t$ ; clearly  $\Theta_i^t = \emptyset$  for any  $t < t_{is}$ . It follows that

$$V_{V_i}(t, x) = \mathbb{P}(x \in \Theta_i^t) = \mathbb{P}(x \in \Theta_i^t \mid t \geq t_{is}) \mathbf{1}_{[t_{is}, \infty)}(t)$$

where  $\mathbf{1}_{[t_{is}, \infty)}(t)$  is the indicator function; it is equal to 1 if  $t_{is} \leq t < \infty$  and 0 otherwise.

Defining  $\tilde{V}_{V_i}$  and  $\tilde{S}_{V_i}$  to be the mean volume density and the mean surface density, respectively, associated to the same reaction  $i$  starting at time  $t = 0$ , we get that  $\mathbb{P}(x \in \Theta_i^t \mid t \geq t_{is}) = \tilde{V}_{V_i}(t - t_{is}, x)$  and so,

$$V_{V_i}(t, x) = \tilde{V}_{V_i}(t - t_{is}, x) \mathbf{1}_{[t_{is}, \infty)}(t) \quad (30)$$

$$S_{V_i}(t, x) = \tilde{S}_{V_i}(t - t_{is}, x) \mathbf{1}_{[t_{is}, \infty)}(t) \quad (31)$$

Then, using Eq.(14), one finally obtains

$$V_V(t, x) = 1 - \prod_{i=1}^n \left(1 - \tilde{V}_{V_i}(t - t_{is}, x) \mathbf{1}_{[t_{is}, \infty)}(t)\right) \quad (32)$$

For any  $t > t_{is}$ , from Eqs. (21) and (23) we know that

$$\begin{aligned} G_i(t) &= \frac{1}{\tilde{S}_{V_i}(t - t_{is}, x)} \frac{\partial \tilde{V}_{V_i}(t - t_{is}, x)}{\partial t} \\ &= \frac{1}{S_{V_i}^*(t, x)} \frac{\partial V_{V_i}^*(t, x)}{\partial t} \end{aligned} \quad (33)$$

From Eq (26)

$$S_{V_i}^*(t, x) = \frac{1 - V_V(t, x)}{1 - \tilde{V}_{V_i}(t, x)} \tilde{S}_{V_i}(t, x) \quad (34)$$

and from Eq. (27)

$$\frac{\partial V_{V_i}^*(t, x)}{\partial t} = -(1 - V_V(t, x)) \frac{\partial \ln(1 - \tilde{V}_{V_i}(t - t_{is}, x))}{\partial t} \quad (35)$$

therefore, also for any  $t > t_{is}$ ,

$$\tilde{V}_{V_i}(t - t_{is}, x) = 1 - \exp\left(-\int_{t_{is}}^t \frac{1}{1 - V_V(s, x)} \frac{\partial V_{V_i}^*(s, x)}{\partial s} ds\right) \quad (36)$$

$$V_{V_i}^*(t, x) = \int_{t_{is}}^t (1 - V_V(s, x)) \frac{\partial \ln(1 - \tilde{V}_{V_i}(t - t_{is}, x))}{\partial t} ds \quad (37)$$

These equations may be used when one has sequential, non-overlapping or overlapping, transformations.

## 5 Examples and Discussion

### 5.1 Two simultaneous reactions

Suppose that there are two simultaneous reactions denoted reaction 1 and 2. Each reaction has its own velocity,  $G_1$  and  $G_2$ , supposed constant. Nucleation is site saturated in both of them. In reaction 1 and 2 nuclei are located uniform randomly in space and the number of nuclei per unit of volume is  $N_{V1}$  and  $N_{V2}$ , respectively. For a more precise treatment of nucleation employing homogeneous and inhomogeneous Poisson point process see Rios and Villa [25]. The theoretical mean volume density or volume fraction and interfacial area density for reaction 1 are

$$V_{V1}(t) = 1 - \exp\left(-\frac{4\pi N_{V1}}{3} G_1^3 t^3\right) \quad (38)$$

$$S_{V1}(t) = 4\pi N_{V1} G_1^2 t^2 \exp\left(-\frac{4\pi N_{V1}}{3} G_1^3 t^3\right) \quad (39)$$

Analogous expressions may be written for reaction 2 just by exchanging the subscript 1 by 2. The total mean volume density may be found using Eq.(14)

$$V_V(t) = 1 - (1 - V_{V1}(t))(1 - V_{V2}(t)) = 1 - \exp\left(-\frac{4\pi}{3} (N_{V1} G_1^3 + N_{V2} G_2^3) t^3\right) \quad (40)$$

$V_{V1}^*$  can be obtained from Eqs. (29) and (38)

$$V_{V1}^*(t) = \int_0^t (1 - V_{V2}(s)) \frac{dV_{V1}(s)}{ds} ds = \int_0^t 4\pi N_{V1} G_1^3 s^2 \exp\left(-\frac{4\pi}{3} (N_{V1} G_1^3 + N_{V2} G_2^3) s^3\right) ds \quad (41)$$

This equation may be integrated analytically and simplified

$$V_{V1}^*(t) = \frac{N_{V1} G_1^3}{N_{V1} G_1^3 + N_{V2} G_2^3} V_V(t) \quad (42)$$

Analogous expression may be derived for  $V_{V2}^*(t)$ , recalling that  $V_{V2}^*(t) = V_V(t) - V_{V1}^*(t)$ . These equations may be used to investigate the effect of the growth rate on the transformation when all

other parameters are kept constant. For a numerical example reasonable values are  $N_{V1} = N_{V2} = 10^5 \text{mm}^{-3}$ ,  $G_1 = 10^{-5} \text{mm/s}$  and  $G_2 = 1.5G_1$ . The value of 1.5 was chosen here because Vandermeer and Jensen [12] found that, during recrystallization of copper, cube + cube twin grains grew about 1.5 times faster than the random grains. Fig. 3 shows the mean volume density or volume fraction transformed as a function of time for these parameters. In Fig. 3  $V_{V1}^*$  and  $V_{V2}^*$  are represented by the dotted line and by the dashed line, respectively. It is clear that reaction 2, which has the higher velocity, develops much faster than reaction 1. In order not to be overwhelmed it would be necessary for reaction 1 to have some other advantage, such as a higher number of nuclei per unit of volume [12]. A better overview of the effect of the growth rate may be achieved by plotting the final volume fraction of reaction 2,  $V_{V2}^*(t \rightarrow \infty)$ , as a function of the velocity ratio,  $G_2/G_1$ . Such an expression may be found from Eq. (42) and from  $N_{V1} = N_{V2}$

$$V_{V2}^*(t \rightarrow \infty) = \frac{(G_2/G_1)^3}{1 + (G_2/G_1)^3} \quad (43)$$

Eq. (43) is plotted in Fig. 4. If  $G_1 = G_2$  then  $V_{V2}^*(t \rightarrow \infty) = V_{V1}^*(t \rightarrow \infty) = 0.5$ . It can be seen that for  $G_2/G_1 = 2$ , reaction 2 overwhelms reaction 1,  $V_{V2}^*(t \rightarrow \infty) = 0.89$ . Therefore, even this highly simplified example shows an interesting result: for equal number of nuclei per unit of volume growth rates differences over a factor of about 2 would lead to the reaction with the higher growth rate overwhelming the other.

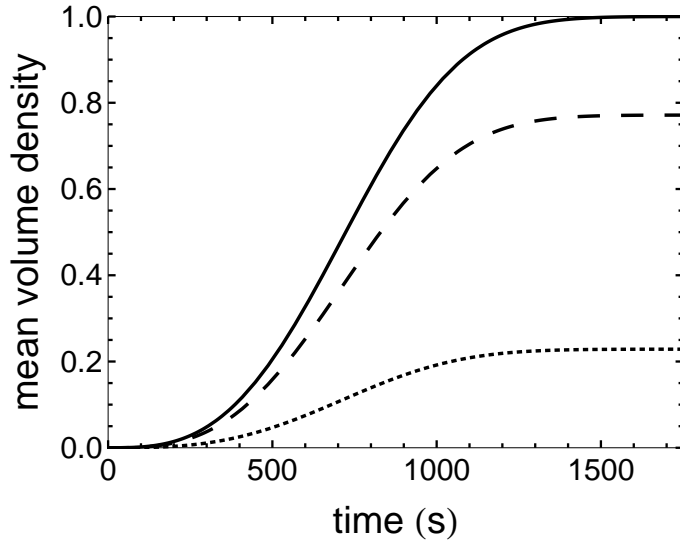


Figure 3: Mean volume density plotted as a function of time. The overall reaction,  $V_V$ , is represented by the solid line.  $V_{V1}^*$  and  $V_{V2}^*$  are represented by the dotted line and by the dashed line, respectively. For both reactions nucleation is site saturated and they have the same number of nuclei per unit of volume. The boundary velocity of reaction 2, is 1.5 times the boundary velocity of reaction 1. As a consequence reaction 2 takes place much faster and constitutes the major part of the total fraction transformed.

Similar expressions may be obtained for the interfacial area densities. From Eq. (26)

$$S_{V1}^*(t) = (1 - V_{V2}(t))S_{V1}(t) = 4\pi N_{V1} G_1^2 t^2 \exp\left(-\frac{4\pi}{3}(N_{V1} G_1^3 + N_{V2} G_2^3)t^3\right) \quad (44)$$

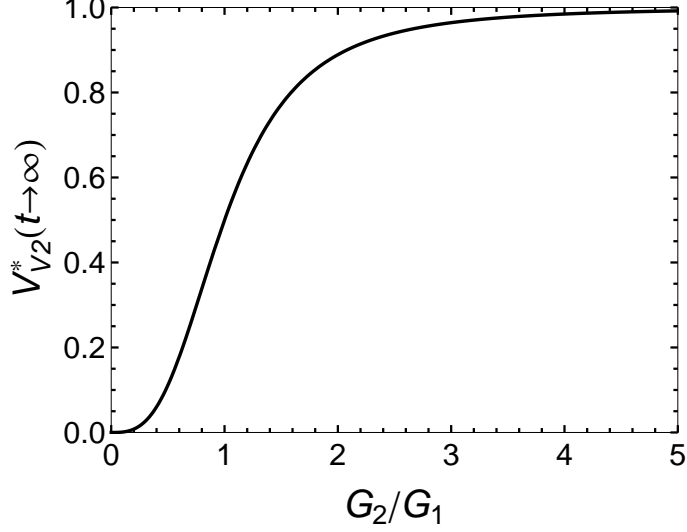


Figure 4: Experimental mean volume density of reaction 2,  $V_{V_2}^*(t \rightarrow \infty)$ , at the end of the transformation as a function of the ratio of the velocities of reaction 2,  $G_2$ , and 1,  $G_1$ . For both reactions nucleation is site saturated and they have the same number of nuclei per unit of volume. For  $G_2/G_1 = 1$  each reaction transforms 0.5 of the total transformation. It can be seen that for  $G_2/G_1 = 2$ , reaction 2 overwhelms reaction 1,  $V_{V_2}^*(t \rightarrow \infty) = 0.89$ .

$S_V$  can be obtained from Eq. (20)

$$S_V(t) = 4\pi(N_{V_1}G_1^2 + N_{V_2}G_2^2)t^2 \exp\left(-\frac{4\pi}{3}(N_{V_1}G_1^3 + N_{V_2}G_2^3)t^3\right) \quad (45)$$

and

$$S_{V_1}^*(t) = \frac{N_{V_1}G_1^2}{N_{V_1}G_1^2 + N_{V_2}G_2^2} S_V(t) \quad (46)$$

$G$  can be obtained from Eq. (16)

$$G = \frac{N_{V_1}G_1^3 + N_{V_2}G_2^3}{N_{V_1}G_1^2 + N_{V_2}G_2^2} \quad (47)$$

For  $N_{V_1} = N_{V_2}$  and  $G_2 = 1.5G_1$  the overall velocity,  $G \approx 1.35G_1$ , as expected closer to  $G_2$  than to  $G_1$  because reaction 2 dominates the overall kinetics.

The microstructural path gives an interesting result

$$S_V(t) = (36\pi)^{1/3} \frac{N_{V_1}G_1^2 + N_{V_2}G_2^2}{(N_{V_1}G_1^3 + N_{V_2}G_2^3)^{2/3}} (1 - V_V(t)) \left(\ln \frac{1}{(1 - V_V(t))}\right)^{2/3} \quad (48)$$

The microstructural path corresponding to reactions 1 and 2 (see Fig. 3) are plotted in Fig. 5. In Fig. 5 the microstructural path for the overall reaction ( $V_V, S_V$ ) is represented by the solid line, for reaction 1 ( $V_{V_1}^*, S_{V_1}^*$ ) by the dotted line and for reaction 2 ( $V_{V_2}^*, S_{V_2}^*$ ) by the dashed line. The ( $V_{V_1}^*, S_{V_1}^*$ ) curve (and similarly the ( $V_{V_2}^*, S_{V_2}^*$ ) curve) is a parametric plot of Eqs. (42) and (44). It is interesting that the peaks in  $S_{V_1}^*, S_{V_2}^*$  and  $S_V$  take place at different mean volume densities of the overall reaction.

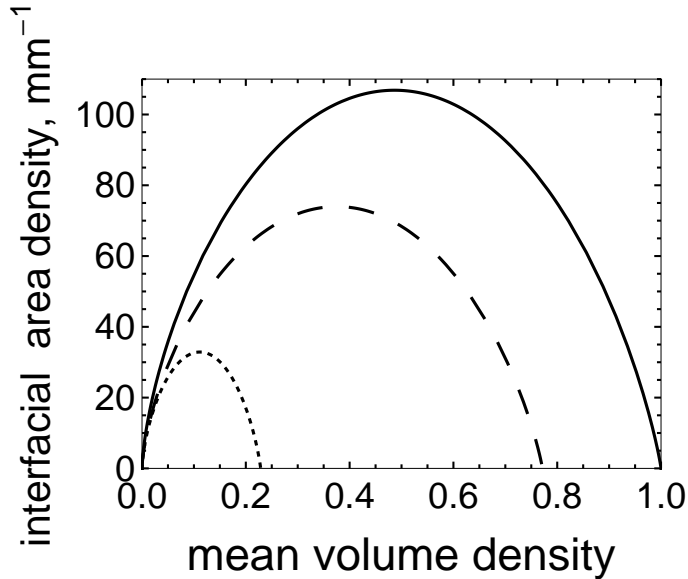


Figure 5: Mean interfacial area density as a function of mean volume density time for the overall reaction ( $V_V, S_V$ ) (solid line), for reaction 1 ( $V_{V1}^*, S_{V1}^*$ ) (dotted line) and for reaction 2 ( $V_{V2}^*, S_{V2}^*$ ) (dashed line). For both reactions nucleation is site saturated and they have the same number of nuclei per unit of volume. The boundary velocity of reaction 2, is 1.5 times the boundary velocity of reaction 1. As a consequence reaction 2 takes place much faster and constitutes the major part of the total fraction transformed. For this reason, the microstructural path of reaction 2 extends up to  $V_{V2}^* = 0.77$ .

It is worthy of note that the microstructural path, Eq. (48) depends on  $G_1$  and  $G_2$ . This behavior is a consequence of the simultaneous reactions. It is well known that for a single site-saturated reaction the microstructural path is *independent* of the velocity [26]. Indeed for a single reaction, the microstructural path is often used to estimate the number of nuclei per unit of volume [34]. Therefore, one must be careful when using the microstructural path for this purpose if there is the possibility of simultaneous reactions. One particular transformation in which this could be a problem is recrystallization. If there are more than one texture component with distinct velocities and if the transformation is analysed as if it were a single reaction, then estimating number of nuclei per unit of volume from the microstructural path is going to yield erroneous values.

This example shows that, given the theoretical expressions for the two reactions, one may obtain expressions for *all* experimental quantities. Conversely, from the experimental quantities it is possible to determine the theoretical quantities.

## 5.2 Two sequential reactions

Yet another possibility would be that reactions 1 and 2 take place sequentially. So, reaction 1 initiates at  $t = t_{1s}$  and reaction 2 starts at  $t = t_{2s} > t_{1s}$ .

A numerical example is given here concerning the effect of the incubation time. The incubation time for reaction 1 is supposed to be equal to zero,  $t_{1s} = 0$ , but reaction 2 has  $t_{2s} > 0$ . All other quantities are supposed to be the same for both reactions. So,  $N_{V1} = N_{V2} = 10^5 \text{ nuclei/mm}^3$  and

$G_1 = G_2 = 10^{-5}$ mm/s. From Eq. (30) the mean volume density is

$$V_{V_1}(t) = \tilde{V}_{V_1}(t) = 1 - \exp\left(-\frac{4\pi}{3}10^{-10}t^3\right) \quad (49)$$

$$V_{V_2}(t) = \tilde{V}_{V_2}(t - t_{2s}) = 1 - \exp\left(-\frac{4\pi}{3}10^{-10}(t - t_{2s})^3\right), \quad \text{for } t > t_{2s} \quad (50)$$

and by superposition, Eq. (32),

$$V_V(t) = 1 - \exp\left(-\frac{4\pi}{3}10^{-10}\left(t^3 + (t - t_{2s})^3 \mathbf{1}_{[t_{2s}, \infty)}(t)\right)\right) \quad (51)$$

Using Eq. (37)

$$V_{V_1}^*(t) = \int_0^t 4\pi 10^{-10} t^2 \exp\left(-\frac{4\pi}{3}10^{-10}\left(u^3 + (u - t_{2s})^3 \mathbf{1}_{[t_{2s}, \infty)}(u)\right)\right) du \quad (52)$$

where for  $t < t_{2s}$ ,  $V_{V_1}^*(t) = V_{V_1}(t)$ . This integral can be evaluated numerically.

Fig. 6 shows the plot of mean volume density against time for the situation in which reaction 2 starts at  $t_2 = 496.6$ s. This incubation time means that reaction 2 started when  $V_{V_1}^*(t_2 = 496.6) = 0.05$ . The overall reaction,  $V_V$ , is represented by the solid line.  $V_{V_1}^*$  and  $V_{V_2}^*$  are represented by the dotted line and by dashed the line, respectively. It can be seen that the volume fraction transformed of reaction 1 was still relatively small, 0.05, when reaction 2 started. Notwithstanding, reaction 1 constitutes the major part of the overall transformation. A better overview of the effect of the incubation time may be achieved by plotting the final volume fraction of reaction 2,  $V_{V_2}^*(t \rightarrow \infty)$ , as a function of the incubation time for reaction 2,  $t_{2s}$ . This plot is shown in Fig. 7. The corresponding mean volume density of reaction 1 at which reaction 2 starts,  $V_{V_1}^*(t_2)$  is shown on the top horizontal axis. Relatively small mean volume densities of reaction 1 present at the start of reaction 2, *i. e.*  $V_{V_1}^*(t_2)$  about 0.05 – 0.1, are enough to give reaction 1 an overwhelming advantage over reaction 2. In a way the effect is similar to the velocity effect discussed in the previous example. Unless reaction 2 has some compensating feature, such as, higher number of nuclei per unit of volume or higher boundary velocity than reaction 1, reaction 1 will constitute the major part of the fully transformed product.

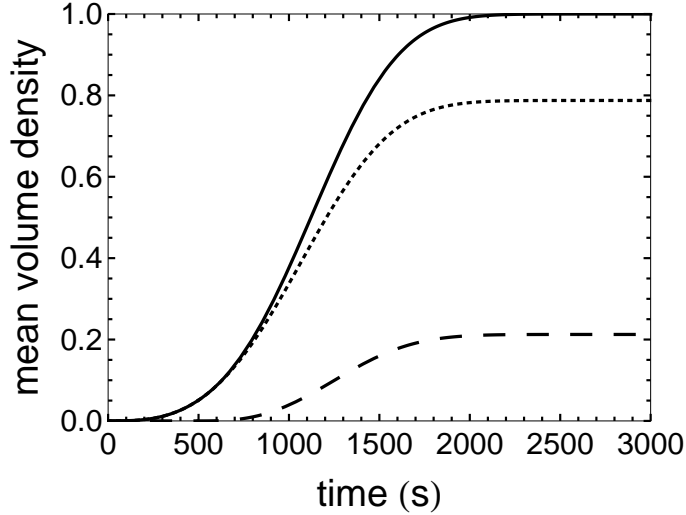


Figure 6: Mean volume density plotted as a function of time. The overall reaction,  $V_V$ , is represented by the solid line.  $V_{V_1}^*$  and  $V_{V_2}^*$  are represented by the dotted line and by dashed the line, respectively. For both reactions nucleation is site saturated and they have the same number of nuclei per unit of volume. The boundary velocities are the same for each reaction. Reaction 2 starts at  $t_2 = 496.6\text{s}$ . This incubation time means that reaction 2 started when  $V_{V_1}^* = 0.05$ . Reaction 1 dominates the overall transformation.

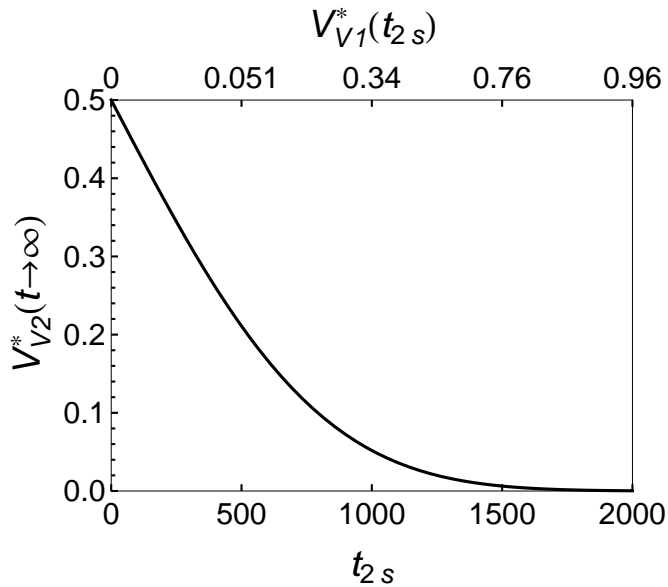


Figure 7: Experimental mean volume density of reaction 2,  $V_{V_2}^*(t \rightarrow \infty)$ , at the end of the transformation as a function of incubation time,  $t_{2s}$ . The corresponding mean volume volume density of reaction 1 at which reaction two starts,  $V_{V_1}^*(t_2)$  is shown on the top horizontal axis. For both reactions nucleation is site saturated and they have the same number of nuclei per unit of volume. The boundary velocities are the same for each reaction. Therefore if both reactions start at the same time each will have a final fraction transformed equal to 0.5. It can be seen that for  $V_{V_1}^*(t_2 = 496.6) = 0.05$  the final fraction transformed by reaction 2 is significantly reduced,  $V_{V_2}^*(t \rightarrow \infty) = 0.21$ .



### 5.3 Two reactions described by the Avrami equation

The present methodology places no restriction on the function that describes the theoretical quantities,  $V_{V_i}(t, x)$ . The term “theoretical” is used rather to emphasize its difference from the “experimental” or “visible” quantities. It does not mean that the function  $V_{V_i}(t, x)$  must be derived theoretically from some arbitrary assumptions. On the contrary,  $V_{V_i}(t, x)$  may be obtained empirically from the study of the kinetics of the reaction in isolation. It is worthy of note to mention that no requirement was placed on the reaction path. The transformations need not to proceed isothermally but may take place during heating or cooling or along some more complex time-temperature path.

Quite often  $V_{V_i}(t, x)$  is represented by an equation that is known to describe reasonably well a large number of transformations, that is, the so called Avrami equation(See ref. [35] for an explanation of the reason why this equation takes this name.)

$$V_{V_i}(t) = 1 - \exp(-k_i t^{n_i}) \quad (53)$$

where  $k_i$  and  $n_i$  are adjustable parameters. The procedure here would be exactly the same that was carried out in the previous examples. So for two simultaneous reactions

$$V_V(t) = 1 - (1 - V_{V_1}(t))(1 - V_{V_2}(t)) = 1 - \exp(-(k_1 t^{n_1} + k_2 t^{n_2})) \quad (54)$$

$$V_{V_1}^*(t) = \int_0^t (1 - V_{V_2}(s)) \frac{dV_{V_1}(s)}{ds} ds = \int_0^t k_1 n_1 s^{n_1-1} \exp(-(k_1 s^{n_1} + k_2 s^{n_2})) ds \quad (55)$$

Eq. (55) cannot in general be integrated by analytical methods. Mean interfacial area densities may be also determined if equations for  $S_{V_i}(t)$  corresponding to Eq. (53) are available. The procedure is analogous for sequential reactions.

### 5.4 Final remarks

Finally, it is worthy to discuss how the present methodology relates to previous work [11,12]. In the case that  $V_{V_i}(t) = 1 - \exp(-V_{E_i}(t))$  is valid(see Rios and Villa [25] for more details), then Eq. (27) reduces to

$$dV_{V_i}^*(t) = (1 - V_V(t))dV_{E_i}(t) \quad (56)$$

where  $V_{E_i}(t)$  is the so-called mean extended volume density of reaction  $i$  or more informally the “extended volume” of reaction  $i$ .

Eq. (56) was used in previous work [11,12] and is a particular case of Eq. (27).

There are basically two advantages of Eq. (27) compared to Eq. (56). The first is that Eq. (27) can handle position dependent nucleation. The second advantage is that Eq. (27) relates  $V_{V_i}^*(t, x)$  *directly* to  $V_{V_i}(t, x)$ . As a consequence, there is no need to resort to extended volumes. In fact it is not desirable to use extended volumes because  $V_{V_i}(t) = 1 - \exp(-V_{E_i}(t))$  is *not* generally valid. For example, consider nucleation on random lines, on random planes [21] and in clusters [22]. In all these three cases one obtains expressions of the form  $V_V(t) = 1 - \exp(-f(t))$  but in all these cases  $f(t) \neq V_E(t)$ . Moreover, when  $V_{V_i}(t, x)$  is represented by the Avrami equation, Eq. (53),  $k_i t^{n_i}$  cannot in general be identified with the extended volume.

The reason why it was possible to obtain more general expressions than in previous work lies not only in the distinction between theoretical and experimental quantities but also in the application of the superposition principle, Eq.(14), together with Eq. (23).

## 6 Summary and Conclusions

- A new methodology to treat simultaneous and sequential transformations has been proposed based on the distinction between theoretical and experimental quantities. The theoretical mean volume density,  $V_{V_i}(t, x)$ , is the mean volume density of a reaction if this reaction were the only reaction to take place. In contrast the experimental mean volume density,  $V_{V_i}^*(t, x)$ , is the mean volume density of a certain reaction  $i$  that can actually be measured when more than one reaction takes place simultaneously, see Figs. 1 and 2 for a schematic view and Eqs.(17) and (18) for precise mathematical definitions.
- Based on the distinction between theoretical and experimental quantities general relationships were obtained. The equations presented here are able to deal with position dependent quantities and there is no need to rely on extended volumes.
- These relationships are suitable for model building, *i. e.* obtaining expressions for simultaneous and sequential transformations involving several reactions from models of the kinetics of each reaction in isolation.
- Moreover, we have developed a methodology for relating theoretical quantities to experimentally measured quantities. Quantities suitable for theoretical analysis may be obtained from quantities measured experimentally. Conversely, experimentally measurable quantities may be predicted from theoretical ones.
- For model building, *i. e.* to predict the overall kinetics quantities of simultaneous reactions from the theoretical expressions for individual kinetics one may use Eqs. (14) and (15).
- The relationships between the theoretical and experimental quantities are given by Eqs.(23),(24) and (26) to (29). These equations *directly* relate theoretical and experimental quantities.
- For sequential reactions, either overlapping or non-overlapping, the corresponding equations are given in Section 4: Eqs. (32) to (37).
- Furthermore, it has been shown here that the equation previously used, Eq. (56), may be derived as a particular case of the general equation obtained here, Eq. (27).

## Acknowledgements

P.R.R. is grateful to the Conselho Nacional de Desenvolvimento Científico e Tecnológico, CNPq, and to the Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro, FAPERJ, for financial support. P. R. R. would like to thank the Alexander von Humboldt Foundation for the Humboldt Research Award and Professor Günter Gottstein for his hospitality at the Institut für Metallkunde und Metallphysik, RWTH-Aachen, where this work was carried out. E.V. would like to thank Professor Günter Gottstein for the financial support during her stay in Aachen. The authors would also like to thank the anonymous reviewer for useful suggestions that improved the paper.

## 7 Appendix

### 7.1 Proof of Eq. (23)

(23) repeated here for convenience:

$$G_i(t) = \frac{1}{S_{V_i}^*(t, x)} \frac{\partial V_{V_i}^*(t, x)}{\partial t}$$

The proof presented here needs to assume technical conditions [29] that are generally satisfied in practical applications.

Let us notice that  $\Theta_i^{*t} = \Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t}$  and that  $\partial \Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^t = \partial \Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t}$ ; as a consequence, by similar arguments of Section 3.1 in [33], Eq. (23) holds if

$$\begin{aligned} \lim_{\Delta t \downarrow 0} \frac{\mathbb{E}[\nu^d((\Theta_i^{t+\Delta t} \setminus \bigcup_{j \neq i} \Theta_j^{*t+\Delta t}) \cap A) - \nu^d((\Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t}) \cap A)]}{\Delta t} \\ = G_i(t) \mathbb{E}[\nu^{d-1}(\partial \Theta_i^t \setminus (\bigcup_{j \neq i} \Theta_j^{*t}) \cap A)] \end{aligned}$$

for any  $A \in \mathcal{B}_{\mathbb{R}^d}$  such that  $\mathbb{E}[\nu^{d-1}(\partial \Theta_i^t \setminus (\bigcup_{j \neq i} \Theta_j^{*t}) \cap \partial A)] = 0$ .

The above equation holds if we prove that

$$\lim_{\Delta t \downarrow 0} \frac{\nu^d(\Theta_i^{t+\Delta t} \setminus \bigcup_{j \neq i} \Theta_j^{*t+\Delta t}) - \nu^d(\Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t})}{\Delta t} = G_i(t) \nu^{d-1}(\partial \Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t}) \quad \mathbb{P}\text{-a.s.} \quad (57)$$

So, let us prove the above equation. Without any other specification, the following equations are meant to hold  $\mathbb{P}$ -a.s. Since  $\Theta_i^t$  is a finite union of balls for each  $i = 1, \dots, n$ , for all  $t \in \mathbb{R}_+$ , it is well known that

$$\lim_{r \downarrow 0} \frac{\nu^d((\Theta_{i \oplus r}^t \setminus \Theta_i^t) \cap A)}{r} = \nu^{d-1}(\partial \Theta_i^t \cap A) \quad (58)$$

for any Borel set  $A \subset \mathbb{R}^d$  such that  $\nu^{d-1}(\partial \Theta_i^t \cap \partial A) = 0$ , having denoted by  $\Theta_{i \oplus r}^t$  the parallel set of  $\Theta_i^t$  at distance  $r$ , i.e.  $\Theta_{i \oplus r}^t := \{x \in \mathbb{R}^d : \text{dist}(x, \Theta_i^t) \leq r\}$ . By noticing that  $\nu^{d-1}(\partial \Theta_i^t \cap \partial(\bigcup_{j \neq i} \Theta_j^{*t})) = 0$ , we have that

$$\begin{aligned} & \lim_{\Delta t \downarrow 0} \frac{\nu^d(\Theta_i^{t+\Delta t} \setminus \bigcup_{j \neq i} \Theta_j^{*t+\Delta t}) - \nu^d(\Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t})}{\Delta t} \\ & \leq \lim_{\Delta t \downarrow 0} \frac{\nu^d(\Theta_i^{t+\Delta t} \setminus \bigcup_{j \neq i} \Theta_j^{*t}) - \nu^d(\Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t})}{\Delta t} \\ & = \lim_{\Delta t \downarrow 0} \frac{\nu^d((\Theta_i^{t+\Delta t} \setminus \Theta_i^t) \cap (\bigcup_{j \neq i} \Theta_j^{*t})^c)}{\Delta t} \\ & = \lim_{\Delta t \downarrow 0} \frac{\nu^d((\Theta_{i \oplus G_i(t)\Delta t}^t \setminus \Theta_i^t) \cap (\bigcup_{j \neq i} \Theta_j^{*t})^c)}{\Delta t} \\ & = G_i(t) \lim_{r \downarrow 0} \frac{\nu^d((\Theta_{i \oplus r}^t \setminus \Theta_i^t) \cap (\bigcup_{j \neq i} \Theta_j^{*t})^c)}{r} \\ & \stackrel{(58)}{=} G_i(t) \nu^{d-1}(\partial \Theta_i^t \cap (\bigcup_{j \neq i} \Theta_j^{*t})^c), \end{aligned}$$

and so

$$\lim_{\Delta t \downarrow 0} \frac{\nu^d(\Theta_i^{t+\Delta t} \setminus \bigcup_{j \neq i} \Theta_j^{*t+\Delta t}) - \nu^d(\Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t})}{\Delta t} \leq G_i(t) \nu^{d-1}(\partial \Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t}). \quad (59)$$

Now, let  $\tilde{G}(t) := \max_{j \neq i} G_j(t)$ ; then

$$\begin{aligned} & \lim_{\Delta t \downarrow 0} \frac{\nu^d(\Theta_i^{t+\Delta t} \setminus \bigcup_{j \neq i} \Theta_j^{*t+\Delta t}) - \nu^d(\Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t})}{\Delta t} \\ & \geq \lim_{\Delta t \downarrow 0} \frac{\nu^d(\Theta_{i \oplus G_i(t)\Delta t}^t \setminus (\bigcup_{j \neq i} \Theta_j^{*t})_{\oplus \tilde{G}(t)\Delta t}) - \nu^d(\Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t})}{\Delta t} \\ & \geq \lim_{\Delta t \downarrow 0} \frac{\nu^d((\Theta_{i \oplus G_i(t)\Delta t}^t \setminus \Theta_i^t) \cap ((\bigcup_{j \neq i} \Theta_j^{*t})_{\oplus \tilde{G}(t)\Delta t})^c)}{\Delta t} \\ & = G_i(t) \lim_{r \downarrow 0} \frac{\nu^d((\Theta_{i \oplus r}^t \setminus \Theta_i^t) \cap ((\bigcup_{j \neq i} \Theta_j^{*t})_{\oplus \frac{\tilde{G}(t)}{G_i(t)}r})^c)}{r}. \end{aligned}$$

By observing that for any  $R > 0$  fixed,

$$\nu^d((\Theta_{i \oplus r}^t \setminus \Theta_i^t) \cap ((\bigcup_{j \neq i} \Theta_j^{*t})_{\oplus \frac{\tilde{G}(t)}{G_i(t)}r})^c) \geq \nu^d((\Theta_{i \oplus r}^t \setminus \Theta_i^t) \cap ((\bigcup_{j \neq i} \Theta_j^{*t})_{\oplus R})^c) \quad \forall r \leq \frac{G_i(t)}{\tilde{G}(t)}R,$$

it follows that

$$\begin{aligned} & \lim_{\Delta t \downarrow 0} \frac{\nu^d(\Theta_i^{t+\Delta t} \setminus \bigcup_{j \neq i} \Theta_j^{*t+\Delta t}) - \nu^d(\Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t})}{\Delta t} \\ & \geq G_i(t) \lim_{r \downarrow 0} \frac{\nu^d((\Theta_{i \oplus r}^t \setminus \Theta_i^t) \cap ((\bigcup_{j \neq i} \Theta_j^{*t})_{\oplus R}))}{r} = G_i(t) \nu^{d-1}(\partial \Theta_i^t \setminus (\bigcup_{j \neq i} \Theta_j^{*t})_{\oplus R}) \quad \forall R > 0. \quad (60) \end{aligned}$$

By taking now the limit for  $R \downarrow 0$  in (60), we obtain

$$\lim_{\Delta t \downarrow 0} \frac{\nu^d(\Theta_i^{t+\Delta t} \setminus \bigcup_{j \neq i} \Theta_j^{*t+\Delta t}) - \nu^d(\Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t})}{\Delta t} \geq G_i(t) \nu^{d-1}(\partial \Theta_i^t \setminus (\bigcup_{j \neq i} \Theta_j^{*t})). \quad (61)$$

Thus, (59) and (61) imply (57), and so the assertion follows.

## 7.2 Proof of Eq. (25)

From the definition of  $V_{V_i}^*$  in Eq. (17), and by  $\Theta_i^{*t} = \Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t}$ , it follows that

$$V_{V_i}^*(t, x) = \mathbb{P}(x \in \Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t}),$$

and so

$$\begin{aligned} \frac{\partial V_{V_i}^*(t, x)}{\partial t} &= \lim_{\Delta t \downarrow 0} \frac{V_{V_i}^*(t + \Delta t, x) - V_{V_i}^*(t, x)}{\Delta t} \\ &= \lim_{\Delta t \downarrow 0} \frac{\mathbb{P}(x \in \Theta_i^{t+\Delta t} \setminus \bigcup_{j \neq i} \Theta_j^{*t+\Delta t}) - \mathbb{P}(x \in \Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t})}{\Delta t} \end{aligned}$$

By proceeding similarly as above, we have that

$$\begin{aligned}
& \lim_{\Delta t \downarrow 0} \frac{\mathbb{P}(x \in \Theta_i^{t+\Delta t} \setminus \bigcup_{j \neq i} \Theta_j^{*t+\Delta t}) - \mathbb{P}(x \in \Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t})}{\Delta t} \\
& \leq \lim_{\Delta t \downarrow 0} \frac{\mathbb{P}(\{x \in \Theta_i^{t+\Delta t} \setminus \Theta_i^t\} \cap \{x \notin \bigcup_{j \neq i} \Theta_j^{*t}\})}{\Delta t} \\
& = \lim_{\Delta t \downarrow 0} \frac{\mathbb{P}(\{x \in \Theta_i^{t+\Delta t} \setminus \Theta_i^t\} \cap \{x \notin \bigcup_{j \neq i} \Theta_j^t\})}{\Delta t} \\
& = \mathbb{P}(x \notin \bigcup_{j \neq i} \Theta_j^t) \lim_{\Delta t \downarrow 0} \frac{\mathbb{P}(x \in \Theta_i^{t+\Delta t} \setminus \Theta_i^t)}{\Delta t} \tag{62}
\end{aligned}$$

and that

$$\begin{aligned}
& \lim_{\Delta t \downarrow 0} \frac{\mathbb{P}(x \in \Theta_i^{t+\Delta t} \setminus \bigcup_{j \neq i} \Theta_j^{*t+\Delta t}) - \mathbb{P}(x \in \Theta_i^t \setminus \bigcup_{j \neq i} \Theta_j^{*t})}{\Delta t} \\
& \geq \lim_{\Delta t \downarrow 0} \frac{\mathbb{P}(\{x \in \Theta_i^{t+\Delta t} \setminus \Theta_i^t\} \cap \{x \notin \bigcup_{j \neq i} \Theta_{j \oplus \bar{G}(t)\Delta t}^{*t}\})}{\Delta t} \\
& = \lim_{\Delta t \downarrow 0} \frac{\mathbb{P}(\{x \in \Theta_i^{t+\Delta t} \setminus \Theta_i^t\} \cap \{x \notin \bigcup_{j \neq i} \Theta_{j \oplus \bar{G}(t)\Delta t}^t\})}{\Delta t} \\
& = \lim_{\Delta t \downarrow 0} \mathbb{P}(x \notin \bigcup_{j \neq i} \Theta_{j \oplus \bar{G}(t)\Delta t}^t) \lim_{\Delta t \downarrow 0} \frac{\mathbb{P}(x \in \Theta_i^{t+\Delta t} \setminus \Theta_i^t)}{\Delta t} \tag{63} \\
& = \mathbb{P}(x \notin \bigcup_{j \neq i} \Theta_j^t) \lim_{\Delta t \downarrow 0} \frac{\mathbb{P}(x \in \Theta_i^{t+\Delta t} \setminus \Theta_i^t)}{\Delta t}
\end{aligned}$$

where Eq.(62) and Eq.(63) follow by the independence of the reactions.

Therefore

$$\begin{aligned}
\frac{\partial V_{V_i}^*(t, x)}{\partial t} & = \mathbb{P}(x \notin \bigcup_{j \neq i} \Theta_j^t) \lim_{\Delta t \downarrow 0} \frac{\mathbb{P}(x \in \Theta_i^{t+\Delta t} \setminus \Theta_i^t)}{\Delta t} \tag{64} \\
& = \prod_{j \neq i} (1 - V_{V_j}(t, x)) \frac{\partial V_{V_i}(t, x)}{\partial t} \\
& \stackrel{(14)}{=} \frac{1 - V_V(t, x)}{1 - V_{V_i}(t, x)} G_i(t) S_{V_i}(t, x)
\end{aligned}$$

## References

- [1] Vandermeer RA, Jensen DJ. Acta Mater 2001;49:2083.
- [2] Yamamoto T, Sakuma T and Rios PR. Scr Mater 1998;39:1713.
- [3] Rios PR, Guimaraes JRC. Scr Mater 2007;57:1105.
- [4] Capasso V, Burger M, Micheletti A, Salani C. in: Capasso V ( Ed.). Mathematical modelling for polymer industry. Capasso V (Ed.), Math in Industry Series, vol. 2. Berlin: Springer Verlag; 2002, p. 167.

- [5] Burger M, Capasso V, Salani C. *Nonlinear Analysis, Series B* 2002;3:139.
- [6] Kolmogorov AN. *Izv Akad Nauk USSR-Ser Matemat* 1937;1:355.
- [7] Johnson WA, Mehl RF. *Trans AIME* 1939;135:416.
- [8] Avrami MJ. *J Chem Phys* 1939;7:1103.
- [9] Avrami MJ. *J Chem Phys* 1940;8:212.
- [10] Avrami MJ. *J Chem Phys* 1941;9:177.
- [11] Vandermeer RA, Jensen DJ. *Acta Metal Mater* 1994;42:2427.
- [12] Vandermeer RA, Jensen DJ. *Metall Trans* 1995;26A:2227.
- [13] Jones SJ, Bhadeshia HKDH. *Acta Mater* 1997;45:2911.
- [14] Jones SJ, Bhadeshia HKDH. *Metall Mater Trans A* 1997;28A:2005.
- [15] Kelton KF, Spaepen F. *Acta Metall* 1985;33:455.
- [16] Weinberg MC. *J Non-Cryst Solids* 1992;142:126.
- [17] Kelton KF, Narayan KL, Levine LE, Cull TC, Ray CS. *J Non-Cryst Solids* 1996;204:13
- [18] Huang J, Poole WJ, and Militzer M. *Metall Mater Trans A* 2004;35A:3363.
- [19] Militzer M. *ISIJ International* 2007;47:1.
- [20] Valencia Morales E, Galeano Alvarez NJ, Vega Leiva J, Castellanos LM, Villar CE, Hernandez RJ. *Acta Mater* 2004;52:1083.
- [21] Cahn JW. *Acta Metall* 1956;4:449.
- [22] Villa E, Rios PR. *Acta Mater* 2009;57:3714.
- [23] Rios PR, Jardim D, Assis WLS, Salazar TC, Villa E. *Mater Res* 2009;12:219.
- [24] Villa E, Rios PR. *Acta Mater* 2010;58:2752
- [25] Rios PR, Villa E. *Acta Mater* 2009;57:1199.
- [26] Vandermeer RA, Masumura RA, Rath B. *Acta Metall Mater* 1991;39:383.
- [27] Capasso V, Villa E. On the evolution equations of mean geometric densities for a class of space and time inhomogeneous stochastic birth-and-growth processes. in: Weil W(Ed.). *Stochastic Geometry, Lecture Notes in Mathematics* 1892, CIME-subseries. Heidelberg:Springer; 2007.
- [28] Stoyan D, Kendall WS and Mecke J. *Stochastic Geometry and its Application*. Chichester:Wiley; 1995.
- [29] Villa E. *Int J Contemp Math Sci* 2008;3:1141.
- [30] Villa E. *Methods of Geometric Measure Theory in Stochastic Geometry*, Ph. D. Thesis, Università degli Studi di Milano, Milano, 2007.

- [31] Billingsley P. Probability and Measure, Wiley & Sons, New York, 1995
- [32] Cahn JW, Hagel W. Theory of the Pearlite Reaction. In: Zackay ZD, Aaronson HI, editors. Decomposition of austenite by Diffusional Processes. New York: Interscience; 1960, p. 131-196.
- [33] Capasso V, Villa E. Stoch Anal Appl 2008;26:784.
- [34] Vandermeer RA, Rath BB. Metall Trans 1989;20A:391.
- [35] Barmak K. Metall Mater Trans A, in press, DOI: 10.1007/s11661-010-0421-1.