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Geometric limitations of nucleation and growth models: Revisiting the impingement assumption

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ABSTRACT

The nucleation and growth process is known to control the kinetics of many important phase transformation processes. However, models of this process are often applied to systems, such as cements, which are different from the ones for which the models were originally developed. The applicability of the assumptions used in the development of these models to such systems has been questioned. One of the most common assumptions in nucleation and growth models is that the impingement between growing nuclei is proportional to the fraction of the untransformed volume. Through numerical simulations, this study investigates the validity of this assumption for various systems, including multiphase systems, different dimensionalities of growth and nucleation on boundaries of spherical particles. It is shown that although in some cases the models can be easily adapted for use in more complex systems, other systems are too complicated to be accurately represented by this simple rule.

1. Introduction

The nucleation and growth process is known to control the kinetics of several phase transformation processes from the decomposition of austenite to the hydration of cements [1,2]. Various models of nucleation and growth have been developed to predict the growth of systems where this process is known to control the kinetics. The Johnson–Mehl–Avrami–Kolmogorov equation [3–7], more commonly known as the JMAK or simply the Avrami equation is one of the most commonly used models for such systems. It models the growth of randomly distributed nuclei that grow at a constant rate, eventually impinging with each other and filling the entire system. A simplified form of the Avrami equation is shown in Eq. (1).

$$-\ln(1-V) = kt^n \tag{1}$$

In this equation, V is the fraction of the volume transformed, k is a constant that depends on the rate of nucleation and growth, and t is time. For processes where growth is the rate-controlling step, the parameter n can be calculated as the sum of two other parameters: P, the dimensionality of the growth, and Q, which is 1 for processes that have a constant rate of nucleation and 0 for processes that have a single nucleation event.

Cahn developed an equation (Eq. (2)) based on similar principles, for systems where nucleation takes place on a surface rather than at random locations in the available space [8].

$$V = 1-\exp\left[-S\int_0^{Gt}\left[1-\exp\left(\frac{-\pi N}{3}G^2t^3\left(1-\frac{3y^2}{G^2t^2}+\frac{2y^3}{G^3t^3}\right)\right)\right]dy\right] \tag{2}$$

In this equation, S is the surface area of the substrate per unit volume, N is the rate of production of nuclei, G is the rate of growth and y is a dummy variable. Various corrections and modifications for these models (e.g. [9]) are available in the literature.

Nucleation and growth models were initially applied to cementitious materials because of the similarity of the reaction kinetics with the hydration kinetics observed in Portland cements [10]. Results from fits of nucleation and growth equations are often used to understand the hydration of cement and to compare various systems [11–13]. However, since these equations were developed for systems that differ significantly from cementitious systems, the applicability of the simplifications and assumptions made in the derivation of these equations to cementitious systems can be questioned.

These simplifications may range from assumptions regarding the shape and location of the nuclei to the interaction between different nuclei as they grow together and compete for the same space. This article focuses on the assumption that the incremental impingements between the particles depend linearly on the fraction of space available for growth. This assumption is used in most nucleation and growth equations and although it is seen to work well in relatively simple systems, its applicability to more complex systems is not known. The basis

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Table 1
Parameters used in simulations of needles and spheres nucleating randomly in space.

	Needles (alone)	Spheres (alone)	Needles (with spheres)	Spheres (with needles)
Length of computational volume (arbitrary unit length)	100	100	100	
Resolution (arbitrary unit length)	0.05	–	0.05	
Rate of nucleation (number per unit time per unit volume)	1×10^{-5}	1×10^{-2}	9×10^{-5}	1×10^{-5}
Rate of growth (unit length per unit time)	2	0.02	1	0.1
Initial radius (unit length)	1	0	1	0

of this assumption and its implications on the equations are discussed in Section 2 of this article. In Section 3, the applicability of this assumption to various complex systems is examined using numerical simulations.

2. Rule of impingement in nucleation and growth models

Most nucleation and growth equations including the Avrami [5] and Cahn [8] equations are based on the assumption that either the number or the rate of production of growing nuclei per unit free volume is constant with time. As in these processes, growth is considered to be the rate controlling process and therefore the slowest process, the rate of growth of individual nuclei is assumed to be proportional to the surface available for growth on that nucleus throughout the transformation process.

As growth occurs, the size and therefore the surface area of the nuclei increase, leading to an increase in the rate of phase transformation. However, as the process progresses, impingements between the growing nuclei continue to increase, leading to a reduction in the rate of growth. This leads to bell-shaped rate curves and sigmoidal phase transformation curves characteristic of nucleation and growth processes. In order to satisfactorily model this process, any equation must model both the processes of growth and impingement correctly. While growth is relatively easy to model and can be written on the basis of its shape and rate, the impingements are harder to calculate. Based on the assumption that the probability of impingement increases with the fraction of the volume that has already been transformed, it is generally considered that the incremental impingements are linearly related to the fraction of transformed volume.

In order to use this assumption, the total volume of all nuclei in the system, ignoring all impingements is first calculated. This volume, V^*, is generally known as the extended volume. For a set of N spheres in a unit volume, with radii growing at the rate of G unit lengths per unit time, at time t from the moment all the spheres were produced, this can be written as:

$$V^* = \frac{4}{3}N\pi G^3 t^3. \tag{3}$$

If V is the real total volume of all nuclei after correcting for impingements, it is assumed that the fraction of the incremental extended volume that is lost to impingements is equal to the fraction of the total volume that has already transformed. This assumption is explained in Eq. (4).

$$\frac{dV}{dV^*} = (1-V) \tag{4}$$

Eq. (4) can be integrated to obtain Eq. (5) below.

$$\int_0^V \frac{dV}{1-V} = \int_0^{V^*} dV^* \Rightarrow V = 1-\exp(-V^*) \tag{5}$$

It can be seen that the assumption discussed above is the source of the exponential that is seen in both Avrami and Cahn equations. The Cahn equation (Eq. (2)) uses this exponential twice, first to account for the impingements between the nuclei growing on the same boundary and then for impingements with nuclei growing on different boundaries.

In the following sections, the applicability of the assumption in Eq. (4) is tested by comparing predictions from equations using this assumption to results from numerical simulations.

3. Numerical simulations of growths

Simulations of spherical and acicular growths were carried out using a mixture of what are known as the vector and discrete approaches. In the vector approach, the elements in the simulation are stored as geometrical shapes with known centroids and dimensions and overlaps between elements are calculated using simple rules of geometry. Due to the time consuming nature of these calculations for other shapes, the vector approach is generally limited to spheres. In the discrete approach, the computational volume is divided into smaller elements,

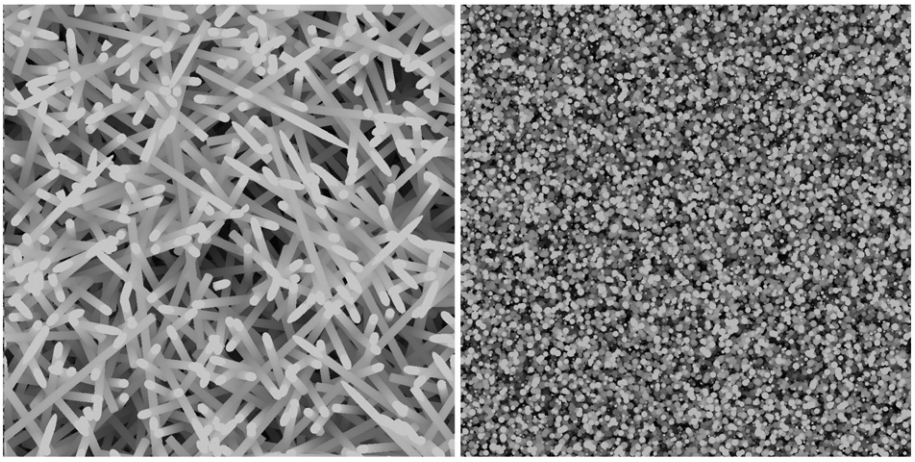

Fig. 1. Three-dimensional images of the simulated microstructures at approximately 20% transformation for acicular and spherical particles.