

Stochastic and deterministic models for nucleation and growth in non-isothermal and/or non-isobaric powder transformations

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Abstract

The calculation of fractional conversion can be very difficult in certain cases of nucleation and growth transformations (Mampel assumptions): it has only been developed for a few shapes of grains (spheres, cylinders) and only in isobaric and isothermal conditions. Here, a stochastic model which is intrinsically independent on geometry and which stands for non-isobaric and/or non-isothermal reactions is presented. The numerical evaluation of this model can be carried out in two different ways. First a slow Monte Carlo approach which is valid for all kinds of shapes and external conditions is presented, then, a faster, more classical approach is given which allows changing external conditions but only for well-known shapes.

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1. Introduction

In industry, for solid rate reactions, the modelling of the reactor requires the calculations of kinetic rates all along the reacting bed, at any time. This is particularly difficult in cases of nucleation–growth transformations, where a competition between the formation of nuclei and their growth can occur and needs to be taken into account. In isothermal and isobaric conditions, models have been established for various grain shapes, nucleation and growth situations (Delmon, 1969; Johnson and Mehl, 1939; Mampel, 1940). In non-isothermal or isobaric conditions, Micheletti and Burger (2000) have solved the case of polymer crystallization processes for which the nucleation occurs in the grain bulk (according to Avrami, 1939). However, this model is not easily transposed to inorganic solids, because, with these solids, the nucleation process is generally localized at the grain surface. The Mampel model (Mampel, 1940) describes a random nucleation process at the surface of grains and their isotropic growth. However, it does not allow the

calculation of the rate when temperature or pressure change with time. To our knowledge, this problem has not been treated yet.

In this paper, we present a new model, based on Mampel assumptions, but treated with a stochastic approach, similar to the one introduced by Kolmogorov (1937). This allows us to model non-isothermal and non-isobaric situations, and moreover, is valid for all kinds of grains shapes. Mathematical details can be found in Helbert (in preparation).

2. Stochastic approach

In this section a new and more general representation of Mampel model is given. This new representation has two main advantages: the first one is its independence on geometry and the second is the fact that non-isothermal and non-isobaric reactions may be considered. This section is divided into four parts:

- (i) assumptions;
- (ii) mathematical expression for the fractional conversion of a powder at any time;

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- (iii) comparison between this new representation and the classical one;
- (iv) numerical computation by Monte Carlo.

2.1. Assumptions

The following assumptions are made:

(1) The reaction proceeds by nucleation and growth: nuclei are assumed to form on the surface of grains and to grow inward. Other kinds of growth may be integrated in the model. The limiting reaction takes place at the internal interface between grain and nuclei, and the expansion coefficient is equal to 1. Furthermore, pressure and temperature are functions of time only.

(2) The nucleation is the process wherein spots (called nuclei or germs) appear in space and time. It is assumed to be a stochastic process, or rather a space–time Poisson process (Stoyan et al., 1987), with a mean areic frequency of nucleation γ which is expressed as a number of nuclei per unit of time and per unit of surface. In the case of non-isothermal and/or non-isobaric reactions, γ is a function of time.

(3) The growth process is deterministic and spatially homogeneous. The areic rate of radial growth ϕ , is a function of time in the case of non-isothermal and/or non-isobaric reactions. The rate ϕ is number of moles per unit of time and per unit of surface.

(4) A powder G is considered to be composed of infinite amount of grains which transform independently. All the grains g of the powder G are subject to the same stochastic process of transformation and are homothetic with a random size factor R_g . Moreover, we suppose that the random variables R_g , $g \in G$ are independent and identically distributed. Their distribution is noted μ_R . For a grain of size R , S_R will be the boundary of the grain, interface between the grain and the gas, V_R will be the part of \mathbb{R}^3 constituting the grain, $\text{surf}(S_R)$ the measure of S_R and $\text{vol}(V_R)$ the measure of V_R .

2.1.1. Discussion about our assumptions

A1. The first hypothesis defines the reaction and its external conditions. Particularly, temperature and pressure are assumed to be homogeneous in space, therefore gradients of temperature and pressure inside the powder are neglected.

A2. The second assumption concerns the nucleation process. It means that for all $F \subset S_R \times \mathbb{R}^+$, the number of nuclei formed on F , $N(F)$, is a random variable which has a Poisson distribution with an intensity of $\gamma(F) = \int_F \gamma(t) dt d\sigma$. The expression $\gamma(t) dt d\sigma$ represents the mean number of nuclei formed on $[\sigma, \sigma + d\sigma]$ (infinitesimal element of space) during $[t, t + dt]$ (infinitesimal element of time). Therefore, the second assumption is equivalent to:

- (i) For two non-overlapping parts of space–time, F_1 and F_2 , the number of nuclei formed on F_1 , denoted by $N(F_1)$, and the number of nuclei formed on F_2 , denoted by $N(F_2)$, are independent.



Fig. 1. Example of a nucleus which grows inside another nucleus. Nucleus number 2 exists virtually but does not have any effect on the fractional conversion.

- (ii) Nuclei arrive one at a space–time, i.e. two nuclei cannot form at the same place and at the same moment.

Actually, these classical hypotheses are the same as Mampel's (Mampel, 1940). For instance, let $F_1 = S \times [0, t_1[$ and $F_2 = S \times [0, t_2[$ be two parts of $S_R \times \mathbb{R}^+$. $N(F_1)$ represents the number of nuclei formed on S before the moment t_1 and $N(F_2)$ the number of nuclei formed on S between the moment t_1 and the moment t_2 . “ $N(F_1)$ and $N(F_2)$ are independent” means that the number of nuclei formed previous to t_1 does not influence the number of nuclei that will be formed in the future. Every nucleus is counted. This implies that new nuclei can appear on some sites which are already transformed. From a chemical point of view, these nuclei will not have any influence on the fractional conversion (cf. Fig. 1). From now on, N_t will represent the nucleation process up to time t , on the whole surface of the grain, that is to say, the number of nuclei appeared until time t and their position, i.e. $N_t = (N(F))_{F \subset S_R \times [0, t]}$.

A3. The growth process is considered homogeneous in space because of the thinness of the sample. At a given time t , the radius r of a nucleus formed at the moment τ is expressed by

$$r(\tau, t) = \int_{\tau}^t \phi(u) V_{mA} du = V_{mA} (\Phi(t) - \Phi(\tau))$$

if $\tau \leq t$, (1)

where $\Phi(t)$ is equal to $\int_0^t \phi(u) du$ and V_{mA} is the molar volume of the initial phase. As ϕ is strictly positive, Φ is a strictly growing function and thus the inverse of Φ exists. It should be noted that the model can be modified in order to include a growth process spatially non-homogeneous.

A4. Grains can be easily observed through electronic microscopy. Their shapes can be very different from one powder to another: spheres, cubes, parallelepipeds, cylinders, etc. can be observed. Furthermore, grain sizes are heterogeneous in a powder. The size distribution μ_R can be obtained thanks to a granulometer.

2.2. Expression of the fractional conversion

Now that the assumptions for the model have been defined, expressions for the fractional conversion of a single grain, the fractional conversion of a sample of identical grains, as well as, the fractional conversion of a sample where there is a grain-size distribution can be given.

2.2.1. Fractional conversion of a single grain

If we consider a grain of size R , let $\beta(t)$ be the fractional conversion of a grain at time t . As $\beta(t)$ depends on the accomplishment of the nucleation process on this grain, $\beta(t)$ is a random variable representing the exact fraction of the volume occupied by the nuclei. In other words β is the proportion of the points which are occupied by a nucleus.

$$\beta(t) = \frac{1}{\text{vol}(V_R)} \int_{V_R} 1_{\Omega(N_t)}(x) dx, \tag{2}$$

where $\Omega(N_t)$ is the occupied part of the grain, it is a random region and $\beta(t)$ is a random variable which only depends on the nucleation process before t , N_t . In the integral, only points inside the occupied part are summed up.

Let x be a point of V_R and σ a point on the boundary S_R . Let us consider $\tau(x, \sigma, t)$ the time of birth of a nuclei which is formed at σ and which reaches the point x at the moment t . Hence, any germ formed at σ before time $\tau(x, \sigma, t)$ will reach x before t (cf. Fig. 2), where

$$\tau(x, \sigma, t) = \begin{cases} 0 & \text{if } |x - \sigma| > V_{mA}\Phi(t), \\ \Phi^{-1}\left(\Phi(t) - \frac{|x - \sigma|}{V_{mA}}\right) & \text{otherwise.} \end{cases} \tag{3}$$

So that, if $S_{t,x} = \{(\sigma, u) \in S_R \times [0, t], u \leq \tau(x, \sigma, t)\}$, the following equivalence holds:

x not reached by any germ at the moment

$$t \Leftrightarrow N(S_{t,x}) = 0.$$

Hence,

$$\beta(t) = 1 - \frac{1}{\text{vol}(V_R)} \int_{V_R} 1_{N(S_{t,x})=0} dx, \tag{4}$$

where $1_{N(S_{t,x})=0}$ is equal to 1 when there is no germ in $S_{t,x}$ and equal to 0 otherwise.

The last expression shows that the fractional conversion of a single grain depends straightforwardly on the nucleation process N . Besides, this expression stands for all kinds of grain shapes whatever its size R is.

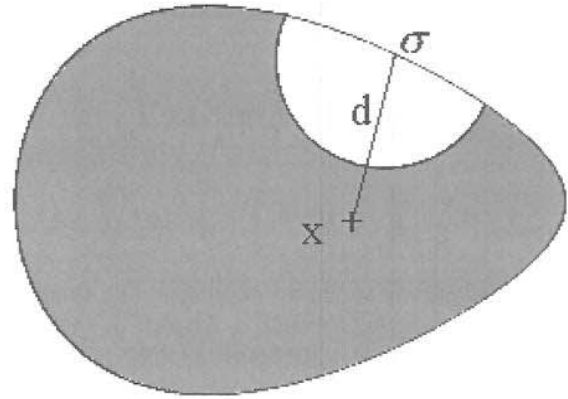


Fig. 2. Example of a nucleus born at σ , d is the distance that separates x from σ .

2.2.2. Fractional conversion of a powder of identical grains

Let us consider a powder of an infinite number of identical grains, so that R is in fact a constant r_0 . The powder fractional conversion will be denoted by $\alpha(t)$. According to A4, the law of large numbers can be applied, so that

$$\alpha(t) = E(\beta(t)) \quad \text{a.s.} \tag{5}$$

It can be interpreted like the fractional conversion of a “mean grain”. According to Eq. (4), $\alpha(t)$ becomes

$$\alpha(t) = 1 - \frac{1}{\text{vol}(V_{r_0})} \int_{V_{r_0}} P(N(S_{t,x}) = 0) dx \quad \text{a.s.,} \tag{6}$$

where $P(N(S_{t,x}) = 0) = \exp\left(-\int_{S_{t,x}} \gamma(t) dt d\sigma\right)$ because of the Poisson distribution. Thus,

$$\alpha(t) = 1 - \frac{1}{\text{vol}(V_{r_0})} \int_{V_{r_0}} \exp\left(-\int_{S_{t,x}} \gamma(t) dt d\sigma\right) dx \quad \text{a.s.} \tag{7}$$

$$\text{with } \int_{S_{t,x}} \gamma(t) dt d\sigma = \int_{S_{r_0}} \int_0^{\tau(x,\sigma,t)} \gamma(u) du d\sigma.$$

One can notice that the grain shape is a priori not defined. In fact, it is contained in the general term $S_{t,x}$.

2.3. Adaptability to different sizes

Let us consider now that the size R of each grain is a random variable of probability distribution denoted by μ_R . Thanks to the law of large numbers, the fraction of powder which is transformed is

$$\alpha(t) = \frac{1}{E(\text{vol}(V_R))} E(\text{vol}(V_R)\beta_R(t)) \quad \text{a.s.,} \tag{8}$$

where $\beta_R(t)$ is the fractional conversion of a grain of size R , i.e.

$$\alpha(t) = \frac{1}{\int \text{vol}(V_r) d\mu_R(r)} \left(\int \left(\text{vol}(V_r) - \int_{V_r} \exp\left(-\int_{S_{r,x}} \gamma(t) dt d\sigma\right) dx \right) d\mu_R(r) \right) \quad \text{a.s.} \quad (9)$$

This last formula is similar to expression (5), except that each grain fractional conversion is weighed by the proportion of volume it holds in the entire volume.

2.4. Link between this approach and the classical one

This approach is in agreement with Mampel results for spherical grains. To demonstrate this, let us consider a powder composed only of spherical grains, of the same radius r_0 . Let us also consider that the reaction takes place in isothermal and isobaric conditions. Thus, the parameters ϕ and γ are constants. Expression (7) will be developed in order to show that the formula is the same as in conventional literature (Delmon, 1969).

It can be noted that for every point x of the grain, the expression $\exp\left(-\gamma \int_{S_{r_0}} \int_0^{\tau(x,\sigma,t)} du d\sigma\right)$ only depends on the depth of x . Therefore, the integral in the whole volume can be replaced by an integral in one direction, i.e.

$$\alpha(t) = 1 - \frac{4\pi}{\text{vol}(V_{r_0})} \int_0^{r_0} \exp\left(-\gamma \int_{S_{r_0}} \int_0^{\tau(\dot{\rho},\sigma,t)} du d\sigma\right) \times \rho^2 d\rho \quad \text{a.s.,} \quad (10)$$

where $\dot{\rho}$, in the expression $\tau(\dot{\rho},\sigma,t)$, represents the point $(\rho, 0, 0)$ in spherical co-ordinates. According to Tonelli's theorem, it is then possible to permute the order of integration, to obtain

$$\alpha(t) = 1 - \frac{4\pi}{\text{vol}(V_{r_0})} \int_0^{r_0} \exp\left(-\gamma \int_0^t \int_{S_{\rho,u}} d\sigma du\right) \times \rho^2 d\rho \quad \text{a.s.,} \quad (11)$$

where $S_{\rho,u}$ is a set of points on the grain boundary so that a nucleus formed on these points at the moment u reaches ρ before t .

This last expression is the same as the one usually developed in Mampel model kinetics, therefore both approaches are identical.

Another expression of $\alpha(t)$ had also been found for platelets by Delmon (1969). However, for every new shape the whole reasoning of the classical approach had to change. With our method, it is not the case. Because expressions (7) and (8) are true for all shapes, only numerical computation will change.

2.5. Mampel by Monte Carlo

In this section we want to estimate (numerically) the fractional conversion of a powder at any time t , for every functions ϕ and γ , for every shape and every size distribution.

The well-known Monte Carlo methods (Fishman, 1996), largely employed to estimate mathematical expectations, will be used in the following, since $\alpha(t)$ is itself almost surely an expectation given in Eq. (8).

Furthermore, conditional to the realizations of the Poisson process and of the size of the grain, the fractional conversion of one grain is deterministic, so that

$$\beta(t) \Big|_{\substack{R=r_0 \\ N_t=N_t(\omega)}} = \int_{V_{r_0}} 1_{\Omega(N_t(\omega))}(x) \frac{dx}{\text{vol}(V_{r_0})}. \quad (12)$$

But $\beta(t) \Big|_{\substack{R=r_0 \\ N_t=N_t(\omega)}}$ may also be interpreted as the expectation of the random variable, $1_{\Omega(N_t(\omega))}(X)$ where X is uniformly distributed in the volume of the grain. Thus, the fractional conversion of the powder is

$$\alpha(t) = \frac{1}{E(\text{vol}(V_R))} E(\text{vol}(V_R) E(1_{\Omega(N_t)}(X) | N_t)) = \frac{1}{E(\text{vol}(V_{R_R}))} E(\text{vol}(V_R) 1_{\Omega(N_t)}(X)) \quad \text{a.s.} \quad (13)$$

Let us now consider the following estimator of the expression above:

$$T_t = \frac{1}{\bar{V}} \frac{1}{n} \sum_{i=1}^n \text{vol}(V_{R_i}) 1_{\Omega(N_t^i)}(X_i), \quad (14)$$

where

- $R_1 \dots R_n$ are independent and identically distributed random variables with probability distribution μ_R .
- $X_1 \dots X_n$ are independent random variables with uniform probability distribution, for all $i \in [1; n]$ X_i is a point of V_{R_i} .
- $N_t^1 \dots N_t^n$ are independent nucleation processes with intensities so that for

$$\forall i \in [1, n], \quad \forall F_i \in S_{R_i} \times [0, t],$$

$$\gamma(F_i) = \int_{S_{R_i}} \int_0^t \gamma(t) dt d\sigma.$$

Expression (14) comes naturally from Eq. (13) and gives a consistent estimator of $\alpha(t)$ with a small bias, when n is large, due to the division by \bar{V} .

The implementation comes directly from expression (14). For each time step and for each grain, a size is simulated from a given distribution μ_R , as well as, a Poisson process and a uniformly distributed random variable inside the grain. The entire simulation experiment is redone for each considered value of t independently. Thus, the curve $(T_t)_{t_1 < t_2 < \dots < t_n}$ is a set of n independent variables, which simplifies the parameters estimation because of the whiteness of the noise.

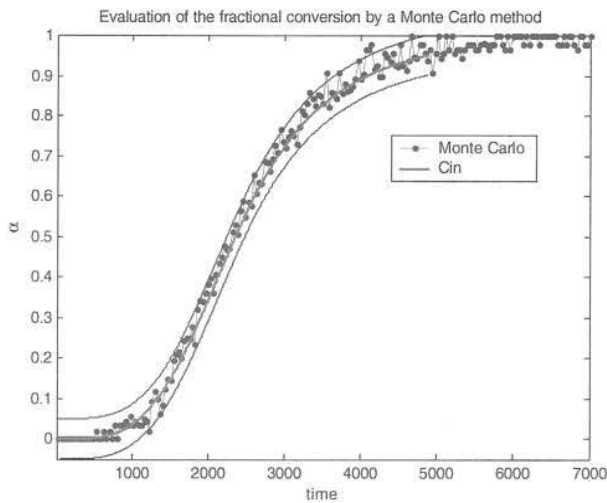


Fig. 3. Comparison between the analytical solution of $\alpha(t)$ denoted by "Cin" and the probabilistic one denoted by "Monte Carlo", in black represent the error conditions.

2.5.1. Examples of Monte Carlo applications

Four examples will be presented.

To begin with, a comparison between the estimation of $\alpha(t)$ obtained by the Monte Carlo method and the result obtained by numerical recipes is made. The comparison is only possible in the case of a powder composed of spherical grains of the same size. The fractional conversion $\alpha(t)$ is determined with an error less than 0.05 with a probability of 95%. The number of grains necessary to fill the error condition is time-dependent and it is continuously adjusted during the computation. This comparison is presented in Fig. 3. The parameters are fixed to realistic values:

$$\gamma = 3 \times 10^6,$$

$$\phi = 10^{-4},$$

$$V_{mA} = 3.7 \times 10^{-5},$$

$$r_0 = 5 \times 10^{-6}.$$

Temperature and pressure are kept to constant values. In order to simplify the interpretation of Fig. 3, instead of enclosing the curve $t \rightarrow \hat{\alpha}(t)$ by the curves $t \rightarrow \hat{\alpha}(t) - 0.05$ and the $t \rightarrow \hat{\alpha}(t) + 0.05$ and situating the numerical curve in the obtained interval, we decided to inverse the rolls.

The second example is similar to the one above except for the shape of the grains which are here considered cubic. Comparison between a powder of spherical grains and a powder of cubic grains is presented in Fig. 4. The radii of the grains are chosen so that the specific surface (grains surface per unit of bulk mass), denoted by S_{BET} , and the density, denoted by ρ , are identical. Actually, in the case of spherical gains, the specific surface is equal to $4\pi r_s^2 / \frac{4}{3}\pi r_s^3 \rho$ where r_s is the radius. In the case of cubic grains, it is equal to $24r_c^2 / 8r_c^3 \rho$, where r_c is the half side of the cube.

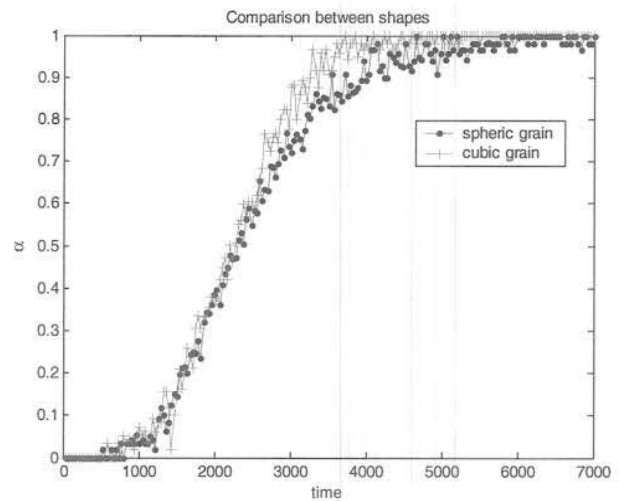


Fig. 4. Comparison between the simulations of fractional conversion of two powders: the first one is composed of spherical grains and the second one of cubic grains.

In this case, the parameters γ and ϕ are taken so that

$$\gamma = 3 \times 10^6,$$

$$\phi = 10^{-3},$$

$$V_{mA} = 3.7 \times 10^{-5},$$

$$r_0 = 5 \times 10^{-6}.$$

In Fig. 4 a real difference between the simulations can be observed. Mainly in the second part of the curve. The shape has a strong influence on the fractional conversion. Thus, it will be important to choose the right model to do estimations.

A third example is the case of a powder with a grain size distribution as seen in Fig. 5 for a CaCO_3 sample observed by scanning electron microscopy. Comparison between a powder of cubic grains of the same size and a powder of cubic grains whose sizes come from an experimental distribution is shown in Fig. 6. In this case, the parameters γ and ϕ are taken so that

$$\gamma = 3 \times 10^6,$$

$$\phi = 10^{-4},$$

$$V_{mA} = 3.7 \times 10^{-5}.$$

It can be seen in Fig. 6 that the curves of fractional conversion are not superimposed throughout the reaction. The difference between the two curves can be emphasized for other values of parameters.

A fourth, and last, example is presented to show the impact of the nucleation rate variation on the change of the fractional conversion with time. Here, the case of a jump (factor 10) of γ is considered, cf. Fig. 7. The other

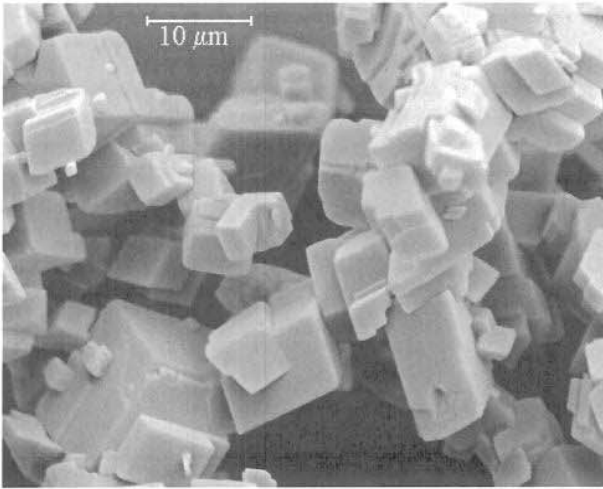


Fig. 5. Micrograph of a CaCO₃ powder by scanning electronic microscopy.

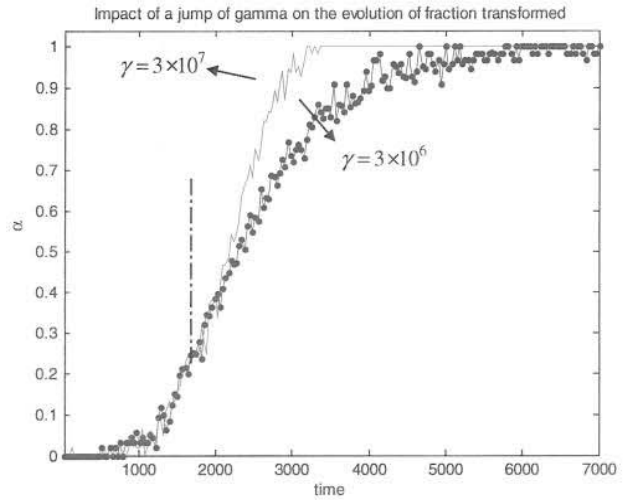


Fig. 7. Evolution of the fractional conversion for a jump of gamma at time 1500.

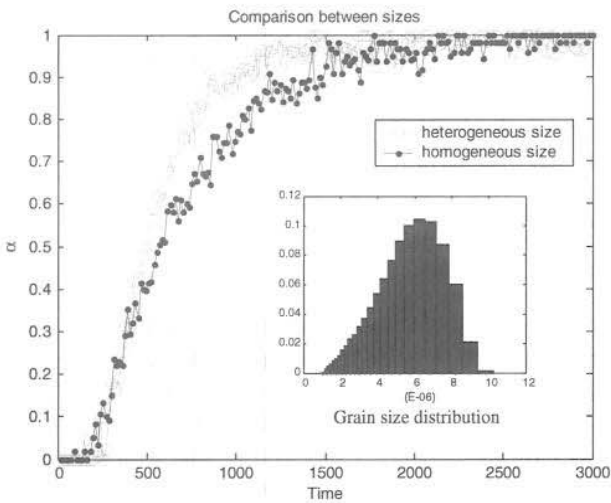


Fig. 6. Comparison between the simulations of fractional conversion of two powders: the first one is composed of cubic grains of the same size and the second one of cubic grains whose sizes come from an experimental distribution.

parameters are fixed to

$$\begin{aligned} \phi &= 10^{-4}, \\ V_{mA} &= 3.7 \times 10^{-5}, \\ r_0 &= 5 \times 10^{-6}. \end{aligned}$$

It can be seen in Fig. 7 that Monte Carlo allows simulations in non-isothermal and non-isobaric conditions, that is to say, when growth and nucleation parameters depend on time.

3. Analytical treatment of the nucleation process

The Monte Carlo approach presented above is very versatile. It is, nevertheless, rather long to run. This can be a drawback when one is interested in solving the inverse problem using optimization techniques, where the direct simulation has to be done a hundred times. This is the reason why, beside the Monte Carlo method, another approach is presented, that consists in solving analytically the random process of nucleation, and numerically the growth process. Contrary to what is commonly done in Mampel model computations, where the growth computations are partially analytical (Delmon, 1969), here they are completely numerical. This representation allows to handle variations of γ and ϕ with time, or with pressure and temperature. Compared to the Monte Carlo method presented earlier, this method is limited in terms of grain shape (spheres and cylinders). On the other hand, it involves a very short computation time, well suited to inverse solving.

The principle of the numerical computation for spherical grains is first exposed. Then, the model is validated against a fully analytical method (classical Mampel method) in the case of isothermal and isobaric process. Finally, an example in the case of non-isothermal reaction is given.

3.1. Analytical treatment of nucleation

The same assumptions as those mentioned above are made, except that the grains are spherical.

Let us consider a grain of radius r_0 . A nucleus born at time τ on the surface of the grain has, at time t , a radius $r(\tau, t)$; its expression is given in Eq. (1).

The fractional conversion of a single grain at time t is obtained by considering the transformation of all the concentric spherical layers into the grain. The nucleation

being a random process, the fractional conversion of the whole powder, made of an infinity of grains, is derived by a probability computation on a single grain, based on the mean of the Poisson law (Stoyan et al., 1987). If $L(\rho)$ is an internal spherical layer of radius $\rho < r_0$, all the nuclei born at a given time τ , cross $L(\rho)$ on a spherical cap of same radius r_{cap} and of area $A(r, \tau, t)$ at the time t (can be zero if t is too short). A particular point of $L(\rho)$ is not attained by any of the nuclei born at τ , if none of the centres of the spherical caps is included in a spherical cap of radius r_{cap} centred on this particular point.

The probability $H(\rho, t)$ for any point of $L(\rho)$ not being reached by a nucleus born between time 0 and t is given by the Poisson law:

$$H(\rho, t) = \exp\left(-\int_0^t \gamma(\tau) \times \left(\frac{r_0}{\rho}\right)^2 \times A(\rho, \tau, t) d\tau\right), \quad (15)$$

where $\gamma(\tau)$ is the average nucleation rate (number of nuclei per unit of time and surface) on the surface of the grain, function of time t , $A(\rho, \tau, t)$ is the area at time t of the intersection of a nucleus born at τ , with $L(\rho)$ (spherical cap). This area is given by

$$A(\rho, \tau, t) = \frac{\pi\rho}{r_0} (\rho^2(\tau, t) - (r_0 - \rho)^2) \quad (16)$$

and $\gamma(\tau)(r_0/\rho)^2 d\tau$ is the average density of centres of spherical intersection caps per unit of surface of $L(\rho)$, corresponding to nuclei born between τ and $\tau + d\tau$. In standard Mampel computations, the term γ is assumed to be constant with time, and the surface S has a simple expression since the growth rate ϕ is also assumed to be constant. This integral can thus be analytically computed. This is no longer the case when both γ and ϕ vary with time. We propose, thus, the following procedure to calculate $\alpha(t)$.

The area A is derived as the intersection of two spheres of radii ρ and r , $r(t)$ being derived from Eq. (1). If the nuclei are not large enough to intersect the layer $L(\rho)$, the term $A(\rho, \tau, t)$ is zero.

The average fractional conversion of the whole grain, which is the effective fractional conversion of the whole powder, is given through an integration along ρ :

$$\alpha(t) = 1 - \frac{1}{\text{vol}(V_{r_0})} \int_0^{r_0} 4\pi\rho^2 H(\rho, t) d\rho. \quad (17)$$

3.2. Changing variables

The spherical cap surface A depends, in fact, only on two parameters: the radius of the nucleus, r , and the radius of the internal layer, ρ . The time variable can be replaced by the radius r_t of a nucleus born at $t = 0$, $r(t)$ being an increasing function of t . The relationship between t and r is given by the growth rate. Considering the nucleus radius, instead of the time, allows the decoupling of the geometrical aspect of the process from the time-dependent aspect. The expression

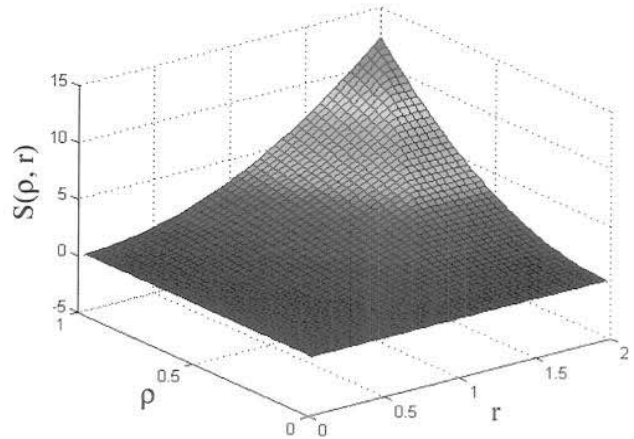


Fig. 8. Values of intersection surface between germ and grain internal layers, versus germ and internal layer radii.

of the transformation rate at a time t corresponding to the radius r_t is thus

$$\begin{aligned} \alpha(r_t) = & 1 - \frac{1}{\text{vol}(V_{r_0})} \int_{\rho=0}^{r_0} 4\pi\rho^2 \\ & \times \exp\left(-\int_{r=0}^{r_t} \gamma(r) \left(\frac{r_0}{\rho}\right)^2 \right. \\ & \left. \times A(\rho, r) \frac{1}{V_{mA}\Phi(r)} dr\right) d\rho. \end{aligned} \quad (18)$$

The geometrical part of the model, basically consisting of the surface intersection computations $A(\rho, r)$, does not depend on the rate of growth, nor on the nucleation rate; it can be computed separately (see Fig. 8).

3.3. Numerical method

The above computation involves integration that is treated using numerical quadrature. The principle of the computations is described in Fig. 9. The grain is divided into concentric layers, with a step $d\rho$. The nucleus progression is divided into radius steps, all equal to dr .

Significant computing time is saved since the area of the spherical caps are computed separately, and prior to the simulation. These geometrical computations remain the same whatever the functions $\phi(t)$ and $\gamma(t)$ are.

Moreover, the relationship between germ radii and time, governed by Φ , can be computed independently.

The general algorithm is the following:

- (1) The intersection areas $A(\rho, r)$ on a grid of values of (ρ, r) . This is the rectangle in Fig. 9. On some parts of the rectangle, the expression of A is particularly simple.
- (2) These values are used to integrate numerically Eq. (18) with simple trapezoid method. These integrations are

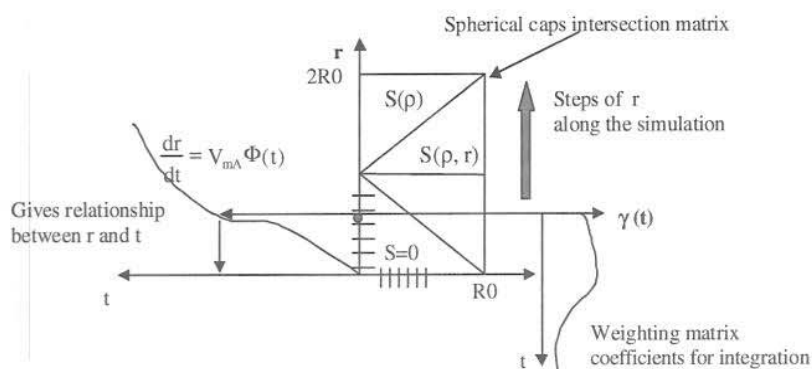


Fig. 9. Principle of numerical computations.

done on each layer (inner part of the integral), between time zero and current time, then across all the layers (ρ).

- (3) The current time is upgraded and step 2 is repeated into a loop.

3.4. Validation against fully analytical model

In the case of isothermal and isobaric reactions, the results have been compared to the fully analytical method classically used and mentioned above (Delmon, 1969), for validation. This fully analytical method does not allow non-isobaric or isothermal reactions, while the one presented here does. The normalized reaction rate ω was derived: $\omega = d\alpha/dt / (d\alpha/dt)_{x=0.5}$.

The results (see Fig. 10a, b, and c) were compared for different values of a non-dimensional number, A , proportional to the ratio of the nucleation frequency to the areic growth rate, according to: $A = (4\pi r_0^3 / V_{mA})(\gamma/\phi)$.

3.5. Results in case of non-isothermal reaction

The transformation of calcium carbonate was performed under linearly increasing temperature with the gas pressure remaining constant. The measurement of CaCO_3 decomposition was performed with thermogravimetry, under a pressure of CO_2 equal to 10 hPa. The sample mass was equal to 5 mg. The rate of temperature increase was fixed to 0.18°C/s (see Fig. 10).

The expressions of ϕ and γ versus pressure and temperature were taken on the form

$$\gamma(T, P) = a \exp\left(-\frac{b}{T}\right) \left(1 - \frac{P}{P_0 \exp\left(-\frac{E_0}{RT}\right)}\right), \quad (19)$$

$$\phi(T, P) = \frac{a \exp\left(-\frac{b}{T}\right)}{c \exp\left(-\frac{d}{T}\right) + P} \left(1 - \frac{P}{P_0 \exp\left(-\frac{E_0}{RT}\right)}\right), \quad (20)$$

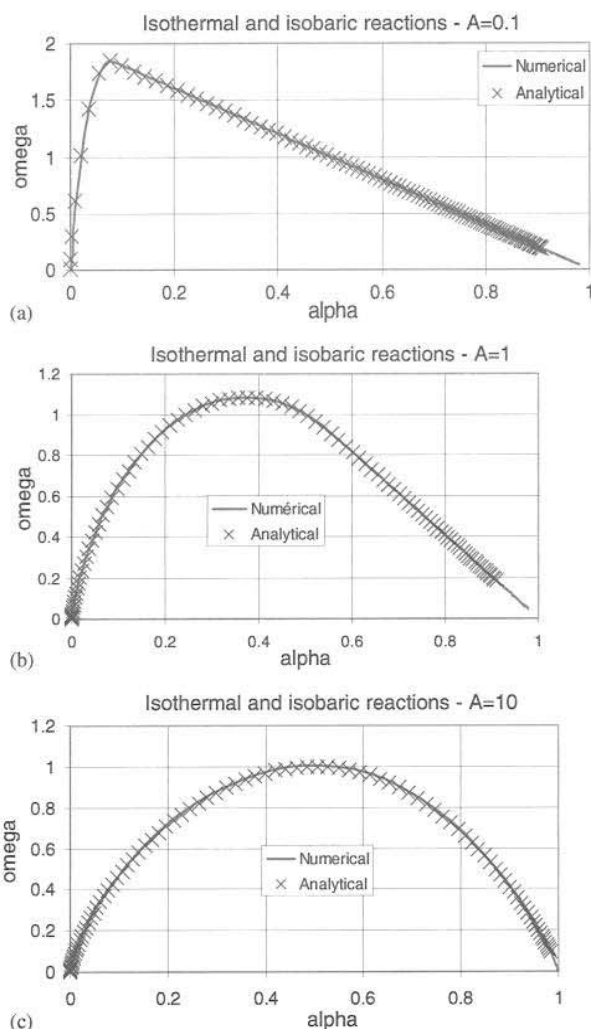


Fig. 10. Values of intersection surface between nucleus and grain internal layers, versus nucleus and internal layer radii. (a–c) Validations against fully analytical model in case of isothermal and isobaric reaction.

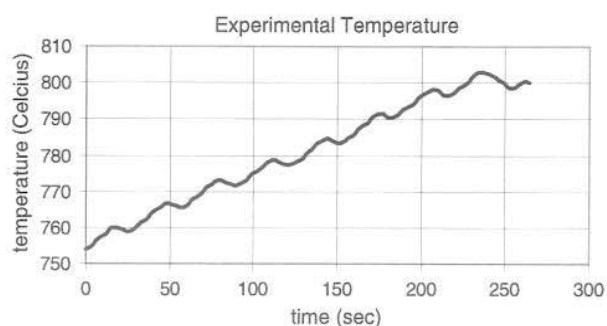


Fig. 11. Experimental temperature history.

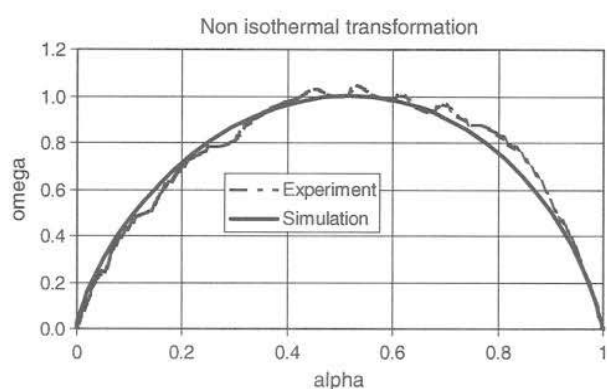


Fig. 12. Comparison with experimental results in case of linearly increasing temperature.

where E_0 and P_0 are known (170 kJ and 4.4 Pa), while a, b, c , and d have to be identified.

The comparison model and experiment are shown in Fig. 11. The possibility to model this reaction under varying pressure and temperature will lead to the identification of the parameters governing the variation of ϕ and γ (a and b), within a minimum number of experiments (Fig. 12).

4. Conclusion

Models for the calculation of the kinetic rate of the nucleation–isotropic growth reaction under various temperature and pressure have been developed. The first model presented, based on a stochastic computation, is interesting since all shapes of the grains can be considered, as illustrated for the CaCO_3 decomposition with cubic grains.

In order to use such a model in inverse calculation applications, it is necessary to lower the computing time; it can be done by means of a second approach in which the nucleation process is treated with an analytical solution. Future work will be devoted to inverse computation to evaluate the kinetic constants related to

the nucleation and growth processes with temperature and pressure.

Notation

$A(\rho, \tau, t)$	area at time t of the intersection of a nucleus born at τ , with $L(\rho)$
$B(r)$	ball of radius r
$E(\dots)$	expectation of a random variable
F	part of space–time
$H(\rho, t)$	average proportion of $L(\rho)$ not yet transformed at time t
$L(\rho)$	internal layer of radius ρ
N_t	Poisson's process
r_0	radius of a grain
R	size of the grain
S_R	surface of a grain of size R
t	time
V_{mA}	molar volume of the initial phase, that is to say the volume of 1 mol of the reactant solid A .
V_R	volume of a grain of size R
x, X	point of the grain volume

Greek letters

$\alpha(t), \alpha_n(t)$	fractional conversion of a powder
$\beta(t)$	fractional conversion of a grain
γ	areic frequency of nucleation
μ_R	probability distribution of random set G
ρ	radius of an internal layer
σ	point of the grain surface
τ	nucleation date
ϕ	areic rate of radial growth
ω	random event
$\Omega(N_t)$	grain part occupied by the nuclei

References

- Avrami, M., 1939. Kinetics of phase change. *Journal of Chemical Physics* 7, 1103–1112.
- Delmon, B., 1969. Introduction à la cinétique hétérogène. Technip.
- Fishman, G.S.T., 1996. Monte Carlo. Springer, Berlin.
- Helbert, C. Heterogeneous kinetics: stochastic modelisation and Monte Carlo simulations, in preparation.
- Johnson, A., Mehl, R., 1939. Reaction kinetics in processes of nucleation and growth.
- Kolmogorov, A.N., 1937. On the statistical theory of the crystallization of metals. *Bulletin of the Academy Sciences of the USSR, Mathematics Series*.
- Mampel, K.L., 1940. Zeitemsatzformeln für heterogene Reaktionen an Phasengrenzen fester Körper.
- Micheletti, A., Burger, M., 2000. Stochastic and deterministic simulation of non-isothermal crystallization of polymers.
- Stoyan, D., Kendall, W.S., Mecke, J., 1987. *Stochastic Geometry and its Applications*. Wiley, New York.