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Modelling of nucleation - isotropic surface growth for finite platelet-like particles

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Abstract

This article concerns the realistic modelling of gas-solid reactions ubiquitous in industrial reactors. A simplistic deterministic model describing the stochastic isotropic nucleation-growth process in a powder of platelets has been strongly improved. Comparisons with a rigorous Monte-Carlo (MC) method that was used as a benchmark show that for realistic platelets, the current deterministic approach can strongly overestimate the reaction rate and underestimate the reaction duration because it considers the platelet surface to be infinite. A new deterministic model considering the finite dimensions of the platelets was developed and leads to the same results as MC simulations. Virtual experimental data were generated with this new model. Kinetic parameters were then optimised using the old and new deterministic method. The optimal curves obtained under the infinite platelet hypothesis are far from the measurements. This paper underscores that chemical kinetic parameters are only reliable if the underlying theoretical model is sound.

Keywords:

Heterogeneous chemical kinetics, Powder, Modeling, Parameter optimization, metamodeling

1. Introduction

Gas-solid reactions correspond to $A = \nu_B B + \sum_j \nu_j G_j$ where A and B are the solid reactant and the solid product respectively, G_j are the gases involved in the reaction, ν_B is the stoichiometric coefficient related to solid B (the

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stoichiometric coefficient related to solid A is chosen equal to 1 by convention) and ν_j is the stoichiometric coefficient of gas j ($\nu_j < 0$ for a reactant and $\nu_j > 0$ for a product). These heterogeneous reactions play an important role in our modern industrial world. They are employed in various processes, such as clinker production for cement industry [1], plaster manufacture [2], CO₂ capture and storage [3, 4], nuclear fuel cycle [5], thermal energy storage [6, 7], the decomposition of potassium dinitramide [8] to name but a few. Gas-solid reactions are widely considered to involve a nucleation process and a growth process that usually take place successively on one particle but parallelly if we consider the whole powder [9, 10, 11]. They are most often studied through a thermal analysis technique such as thermogravimetry or calorimetry [12, 13, 14]. Heterogeneous chemical kinetics is crucial to making sense of the experimental data one has obtained in this way [15, 16]. Numerical modelling has proved to be an indispensable tool for the optimal design of reactors. It relies on the combined description of mass transfer, heat transfer and chemical kinetic [15, 17, 11, 18]. However, until now many chemical kinetic models used to describe solid-gas reactions can be untrustworthy because the physical meaning of the determined parameters is uncertain [19]. In most models, the reaction rate is expressed as a function of the reaction progress α according to Eq. 1.

$$\frac{d\alpha}{dt} = Ae^{-\frac{E_a}{RT}} f(\alpha). \quad (1)$$

A , E_a and $f(\alpha)$ are the apparent pre-exponential factor, the apparent activation energy and the reaction model, respectively. The combination of A , E_a and $f(\alpha)$ is generally called the kinetic triplet. Eq. 1 is based on the assumption of a single-step [20] and it can be applied to multi-step kinetics only when the overall rate of the reaction is either dominated or limited by the rate of one step [21]. Such a kinetic analysis requires a good justification and must be carried out with meticulous care [22]. In the case of gas-solid reactions, it means that either the nucleation or the growth must be very rapid in comparison to the other process. If the rates of both processes have the same order of magnitude, the whole reaction rate cannot be adequately described by Eq. 1. In situations where these conditions are not fulfilled, the estimated kinetic parameters have no physical meaning so that predictions based on them are usually only valid within a very narrow range of conditions. This is most problematic as the optimal design of industrial reactors demands the development of chemical kinetic models of increasing accuracy and reliability [15].

In numerous gas-solid reactions, such a behaviour has been experimentally observed particularly in the case of dehydration and decomposition reactions [23, 24, 25, 26, 27, 28, 29, 30, 31].

Two kinds of behaviour may be distinguished depending on the type of growth: i) the development of the nuclei across the surface is very fast in comparison to the bulk so that the growth is anisotropic; ii) the nuclei grow at the same rate in all directions and the growth is isotropic. As for the first type of behaviour, i.e. surface nucleation and anisotropic growth, kinetic models were originally proposed by Yoshioka and al. [32], Masuda et al. [33] and Bianchet and Rigotti [34]. These models were the precursors of the nucleation and anisotropic growth model of Favergeon et al. [35] which accounts for various particles shapes, directions of growth and localizations of the rate-limiting step. Simplified chemical kinetic differential equations including an induction period, surface reactions and phase-boundary reactions were derived by Ogasawara et al. [36].

The second case corresponds to the situation where the nucleation is followed by an isotropic inward growth in platelet-like particles. The physical model consists of nuclei appearing at random times on random spots of the particle surface. They then grow isotropically and can be considered as (incomplete) hemispheres of growing radius with a rate-limiting step taking place at the internal interface between solid A and solid B. A deterministic approach was initially introduced by Mampel [37] for spherical particles based on the overlapping theory proposed by Johnson and Mehl [38]. Delmon [39] then adapted this method to account for platelet-like particles. Currently, the deterministic model for platelets is based on the assumption that the surfaces of the platelets are infinite in the plane (x, y) , which means that all grown nuclei are hemispheres and that their intersections with a z -plane are complete circles. Platelets are defined in such a way that if L_z is the thickness and L_x and L_y are the two other dimensions, we have $L_z \leq 0.1 \min(L_x; L_y)$. The nuclei then grow isotropically and can be considered (incomplete) spheres of growing radius. There also exists a Monte-Carlo method allowing one to simulate such a nucleation-growth process taking place in particles having an arbitrary shape [40, 41]. Whilst this method has been successfully applied to the kinetic modelling of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration [29, 42], its use for the optimisation of chemical parameters and its coupling with complex CFD simulations of real industrial reactors would be computationally prohibitive. At this stage, it is worth mentioning that CFD simulations have already been successfully applied to gas-solid reactors. Currently, different

strategies are being pursued to simulate these types of reactors. For example, Wu et al. [43] simulated the reacting flow during a catalytic cracking process through a combination of Discrete Element Method (DEM) (which captures the motion of discrete particles and the cohesion of a powder) and of Computational Fluid Dynamics (CFD) (which accounts for the gas-phase flow) whilst describing the gas-solid reactions and the catalyst deactivation. They were able to predict interesting aspects of the catalyst particle activity across the reactor. Likewise, Zhuang et al. used a combination of CFD and DEM to study a methanol-to-olefins conversion process in a fluidised bed reactor (FBR) through a lumped chemical kinetic model [44]. The authors were capable of describing the bed pressure drop profile and the outlet product concentrations well enough. Wu et al. [45] conducted Eulerian-Eulerian simulations of coal combustion in a circulating fluidised bed where the particles are considered to belong to a second fluid phase that interacts with the gas phase via mass and heat transfer, momentum exchanges, and chemical reactions. They showed the importance of a suitable definition of the gas-solid drag model to obtain reliable predictions of important quantities such as the outlet solid flow, pressure, solid volume fraction, and chemical species concentrations. However, the combination of CFD simulations and chemical kinetic modelling is generally very demanding [46] so that only our deterministic model can realistically be utilised in such codes as of now.

The main goal of this paper is to develop a more realistic model for surface nucleation and isotropic growth based on the deterministic approach that takes into account the finite dimension of the platelets. The impact of the infinite platelet surface hypothesis is assessed by comparing the results with those stemming from Monte-Carlo simulations.

The remainder of this article is as follows. In Section 2, the method is first developed and validated in the case of two-dimensional platelets, i.e. rectangles. In Section 3, it is further developed and applied to real three-dimensional platelets. In Section 4, the chemical kinetic parameters are optimised with respect to virtual experimental data about a typical dehydration reaction. In this way, the effects of having a more precise model onto the chemical kinetic parameter estimation can be assessed. Section 5 concludes this article.

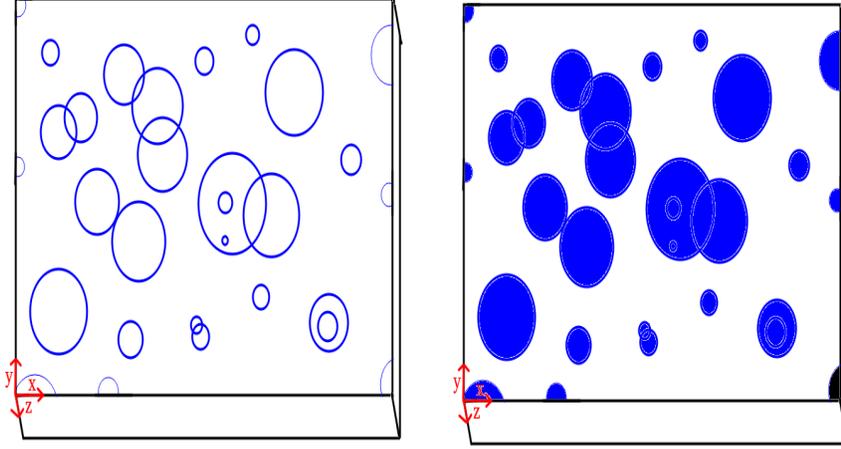


Figure 1: Grown nuclei on a particle surface. In 2D, we only consider the plane (x, y) .

2. Two-dimensional platelets

The details of the development and validation of the methods can be found in Appendix A: 2D Models. Here, only the main points are highlighted.

2.1. Deterministic approach (2D)

An heterogeneous reaction can be described through two parameters: the surface nucleation rate γ (nuclei/m²/s) representing the number of nuclei of the new phase born by unit of surface and unit of time and the areic rate of growth ϕ (mol /m²/s) representing the growth of the new phase in mol by unit of surface and unit of time. An example of a reacting platelet at a given time t can be seen in Figure 1. Nuclei are born randomly at the surface of the platelet and merge together as the growth progresses. Nuclei appearing within an already grown nucleus are virtual in that they play no role in the conversion of A into B. Nucleation is a space-time Poisson process with a rate equal to γ [40]. The reaction progress in the powder is defined as the ratio between the surface occupied by the new phase and the total surface of all grains. It is given by Eq. 2

$$\alpha(t) = \frac{1}{L_x L_y} \int_{x=0}^{L_x} \int_{y=0}^{L_y} p(M, t) dx dy \quad (2)$$

where $p(M, t) = 1 - e^{-\int_{\tau=0}^t \gamma S_r(M) d\tau}$ is the probability that the point M is covered by the new phase at time t . By virtue of the law of large numbers, $p(M, t)$ is also approximately equal to the percentage of platelets where M is covered by the new phase. $S_r(M)$ is the part of the platelet surface such that any nucleus born there in the interval $[\tau, \tau + d\tau]$ will reach M at time t because of its grown radius $r = r(t, \tau)$. If the platelet is infinite, all grown nuclei are complete circles so that $S_r(M) = \pi r(t, M)^2 = \pi \phi^2 V_{m,A}^2 (t - \tau)^2$ where $V_{m,A}$ is the molar volume of species A. As a consequence, $p(M, t)$ does not depend on M.

This allows us to derive an analytical formula for the conversion:

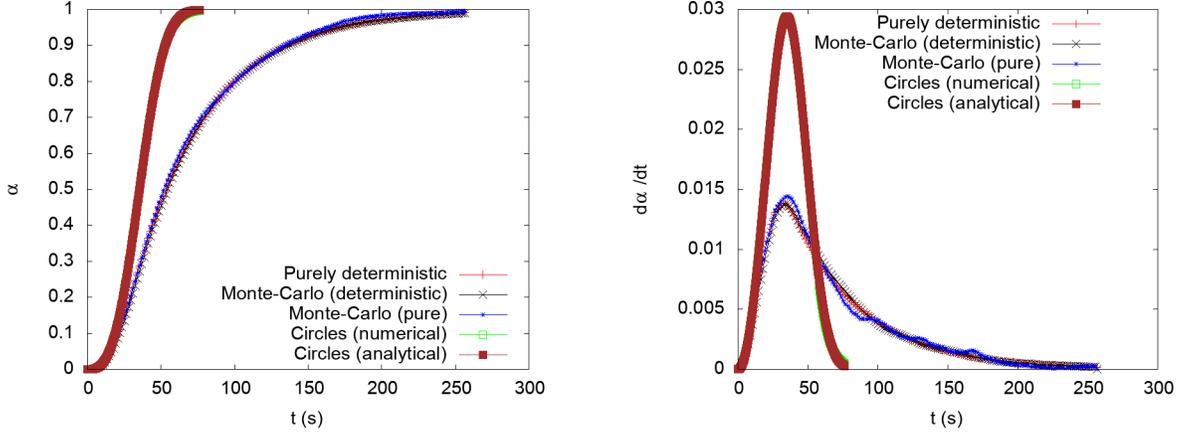
$$\alpha(t) = 1 - e^{-\frac{1}{3} \gamma \pi \phi^2 V_{m,A}^2 t^3}. \quad (3)$$

In the case of a finite platelet, $S_r(M)$ depends on the position of the point M. For points that are too close to the edges of the surface, $S_r(M)$ is an incomplete circle (see Figure 1). By assuming that the platelet surface area is infinite, the current model ignores this situation and considers that $S_r(M)$ always corresponds to a complete circle as if the platelet surface were laterally infinite. As presented in Appendix A: 2D Models, analytical formula have been developed to quickly compute $S_r(M)$ depending on the position of M. They have been thoroughly validated through comparison with the numerical integration of $S_r(M)$.

2.2. Monte-Carlo approach (2D)

We consider a powder composed of an extremely large number of two-dimensional platelets. We simulate the behaviour of n virtual particles. For each particle, we randomly choose the time of birth of the first nucleus τ_1 which follows an exponential distribution whose parameter is $\gamma S_0 = \gamma L_x L_y$. The time t_{end} at which the entire platelet is covered by the first nucleus is computed. Until t_{end} is reached, we generate the next times of birth given that $\tau_{k+1} - \tau_k$ always follows the same exponential distribution. At each time of birth, the location of birth is randomly selected on the platelet surface with a uniform probability. m control points are then uniformly generated on the platelet surface. The overall conversion of the powder is then approximately given by

$$\alpha(t) \approx \frac{1}{n} \sum_{i=1}^n \frac{1}{m} \sum_{j=1}^m 1_{\Omega(N_{t,i})}(x_{i,j}, y_{i,j}) \quad (4)$$



(a) $\gamma = 3\text{E}+08$ nuclei/m²/s,
 $\phi = 3\text{E}-06$ mol /m²/s

(b) $\gamma = 3\text{E}+08$ nuclei/m²/s,
 $\phi = 3\text{E}-06$ mol /m²/s

Figure 2: a): Simulation of $\alpha(t)$ (2D). b): $d\alpha(t)/dt$ (2D). See Appendix A: 2D Models for more details

$1_{\Omega(N_{t,i})}(x_{i,j}, y_{i,j}) = 1$ if at time t , the control point j on particle i has been reached by the new phase and $1_{\Omega(N_{t,i})}(x_{i,j}, y_{i,j}) = 0$ otherwise. The reader is referred to Appendix A: 2D Models for more details.

2.3. Results of the comparison (2D)

The new deterministic approach has been compared with that grounded on the complete circle hypothesis and with the results of Monte-Carlo simulations naturally taking into account the finite dimension of the platelets. Three situations can be distinguished. If the nucleation is (relatively speaking) much faster than the growth, the growth model does not matter much so that the results from the traditional (infinite surface) deterministic approach are in good agreement with those from the new deterministic approach and the Monte-Carlo simulations. If the nucleation and growth happen at a comparable rate, the infinite surface model can result in a considerable overestimation of the reaction rate and underestimation of the reaction duration, as shown in Figure 2 which was obtained with $\gamma = 3\text{E}+08$ nuclei/m²/s, $\phi = 3\text{E}-06$ mol /m²/s. "Purely deterministic" stands for the deterministic computations with the finite platelet model. "Monte-Carlo (deterministic)" is a Monte-Carlo method where n random particles are considered but where

the occupied area on each particle is computed numerically without any random number (See Appendix A: 2D Models). In "Monte-Carlo (pure)", random numbers are employed two times according to Eq. 4. "Circle (numerical)" corresponds to deterministic numerical computations under the infinite platelet hypothesis whereas "Circle (Analytical)" was obtained through Eq. 3 for infinite platelets. If the growth is much faster than the nucleation, the discrepancies are tremendous. All results can be seen in Appendix A: 2D Models alongside a detailed explanation of the reasoning.

3. Three-dimensional platelets

3.1. Deterministic approach (3D)

3.1.1. Imperfect circle assumption (3D)

We can easily generalise the approach described in 2.1 to the 3D-case. Let us consider a platelet characterised by the three dimensions L_x, L_y, L_z whereby the last one is the thickness that is assumed to be considerably smaller than L_x and L_y (see Figure 1). A point M is defined by its three coordinates ($x \in [0; L_x], y \in [0; L_y], z \in [-L_z/2; L_z/2]$). The overall conversion at time t is given by Eq. 5.

$$\alpha(t) = \frac{1}{L_x L_y L_z} \int_{z=-L_z/2}^{L_z/2} \int_{x=0}^{L_x} \int_{y=0}^{L_y} p(M, t) dx dy dz \quad (5)$$

$$= \frac{1}{\frac{L_x}{2} \frac{L_y}{2} \frac{L_z}{2}} \int_{z=0}^{\frac{L_z}{2}} \int_{x=0}^{\frac{L_x}{2}} \int_{y=0}^{\frac{L_y}{2}} p(M, t) dx dy dz \quad (6)$$

$$(7)$$

with $p(M, t) = 1 - e^{-\int_{\tau=0}^t \gamma S_r(M) d\tau}$ where $S_r(M)$ is the set of all points M_0 located at the particle's surface such that a nucleus born there at τ and having attained the radius $r(t, \tau) = r$ will reach M at t . We have made use of the symmetry of the platelet to simplify the integral with respect to x, y and z . This time, $S_r(M)$ also depends on $z \in [0; \frac{L_z}{2}]$. We suppose that nuclei are only born on the two largest faces of the platelet. It is then possible to distinguish three cases based on the value of the nucleus radius $r = r(t, \tau)$. They can be visualised in Figure 3 .

$$i) r < \frac{L_z}{2} - z.$$

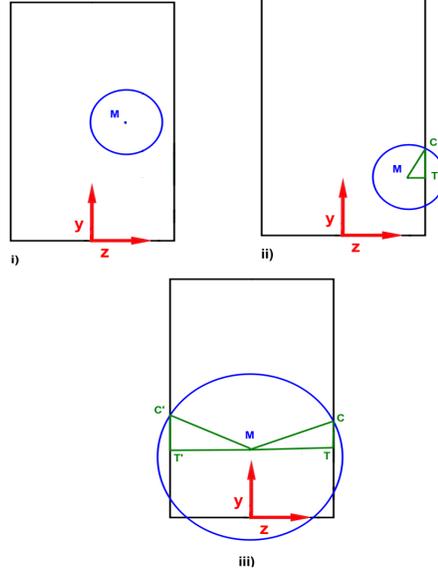


Figure 3: Three situations for the nucleation-growth

The nucleus is not large enough to reach M regardless of whether it was born on the right or on the left surface of the platelet. Consequently, $S_r(M) = 0$.

$$ii) \frac{L_z}{2} - z \leq r < z + \frac{L_z}{2}.$$

M can only be reached by a nucleus born on the right surface of the platelet. $S_r(M)$ is the intersection of the sphere of centre M (x, y, z) and of radius r with the right surface of the platelet. It is a circle (or an incomplete circle in the case of finite platelets) whose centre is T ($x, y, L_z/2$) and whose radius is given by

$$CT = \sqrt{CM^2 - MT^2} = \sqrt{r^2 - \left(\frac{L_z}{2} - z\right)^2}.$$

$$iii) r \geq \frac{L_z}{2} + z.$$

In that case, M can be reached by nuclei born on both largest surfaces of the platelet. $S_r(M)$ is the union of the intersection of the sphere of centre M (x, y, z) and of radius r with the right surface and the left surface of the platelet. This corresponds to two (potentially incomplete) circles of centres

$T(x, y, L_z/2)$ and $T'(x, y, -L_z/2)$ and of radii equal to $\sqrt{r^2 - (\frac{L_z}{2} - z)^2}$ and $\sqrt{r^2 - (\frac{L_z}{2} + z)^2}$, respectively.

Given that we know the centres of the (incomplete) circles and their radii, we can use the same analytical formula as those mentioned in 2.1 to compute the surfaces $S_r(M)$ of the incomplete circles.

3.1.2. Perfect circle approximation (3D)

If we make the assumption that the platelet is *laterally* infinite, we can further simplify the integral since $p(M, t)$ only depends on z .

$$\begin{aligned}\alpha(t) &= \frac{1}{\frac{L_x}{2} \frac{L_y}{2} \frac{L_z}{2}} \int_{z=0}^{\frac{L_z}{2}} \int_{x=0}^{\frac{L_x}{2}} \int_{y=0}^{\frac{L_y}{2}} p(M, t) dx dy dz \\ &= \frac{1}{\frac{L_z}{2}} \int_{z=0}^{\frac{L_z}{2}} p(z, t) dz\end{aligned}$$

with $p(z, t) = 1 - e^{-\int_{\tau=0}^t \gamma S_r(M) d\tau}$ where M is any point such that $z_M = z$. This is the method currently implemented in CIN4, a multiphysics software designed for the simulation of industrial reactors that seeks to consider the chemical kinetics governing the process in a realistic fashion [15].

3.2. Monte-Carlo approach (3D)

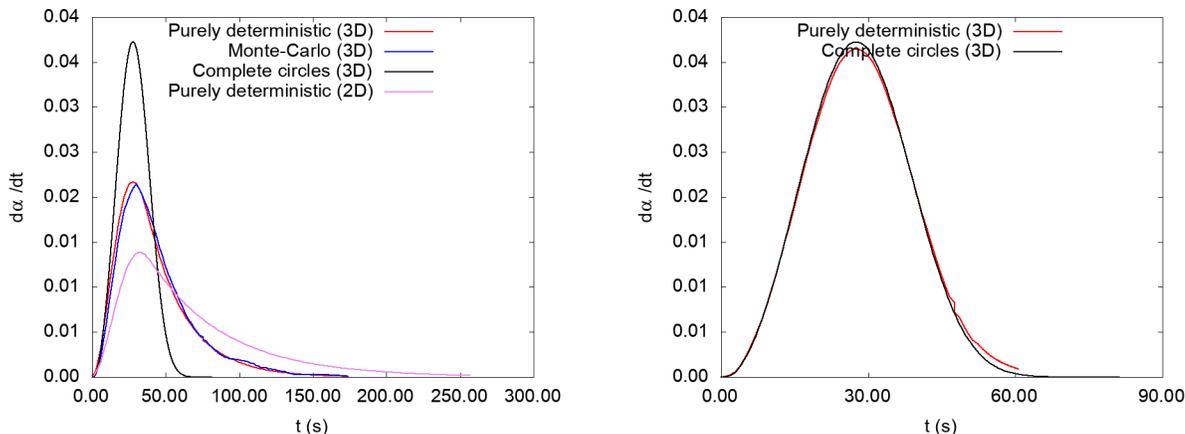
The reasoning is the same as in 2.2 but this time 3D control-points $M_{i,j} = (x_{i,j}, y_{i,j}, z_{i,j})$ are uniformly generated in space inside the particle and the reaction progress is given by Eq. 8.

$$\alpha(t) \approx \frac{1}{n} \sum_{i=1}^n \frac{1}{m} \sum_{j=1}^m 1_{\Omega(N_{t,i})}(x_{i,j}, y_{i,j}, z_{i,j}) \quad (8)$$

The nucleation process is simulated as before but with small modifications. In the 3D-case, the arrival time of a new nucleus $\Delta\tau$ follows the distribution

$$f(d\Delta\tau) = \gamma 2S_0 e^{-\gamma 2S_0 \Delta\tau}.$$

The location of birth of a nucleus is uniformly and randomly chosen on one of the two largest surfaces of the platelet. The probability that the right (or the left) surface is chosen is equal to 1/2.



(a) $L_x = 8.10\text{E-}06$ m, $L_y = 8.10\text{E-}06$ m, $L_z = 8.90\text{E-}07$ m

(b) $L_x = 8.10\text{E-}04$ m, $L_y = 8.10\text{E-}04$ m, $L_z = 8.90\text{E-}07$ m

Figure 4: Simulation of $d\alpha(t)/dt$ (3D) for $\gamma = 3\text{E+}08$ nuclei/m²/s, $\phi = 3\text{E-}06$ mol /m²/s

3.3. Computation of $\alpha(t)$ and $d\alpha(t)/dt$ (3D)

The 3D deterministic profiles $\alpha(t)$ and $d\alpha(t)/dt$ with and without the infinite platelet hypothesis were compared with the results obtained with a straightforward Monte-Carlo simulation (See Figure 4 where the notations are similar to those of Figure 2). The details can be read in Appendix B: Nucleation-Growth Situations and Impact of the Platelet Dimensions.

For platelets whose length and width are roughly only ten times larger than their thickness ($L_x = 8.10\text{E-}06$ m, $L_y = 8.10\text{E-}06$ m and $L_z = 8.90\text{E-}07$ m), the complete circle hypothesis leads to a very good agreement with the more realistic model if the nucleation is much faster than the growth. However, the agreement is extremely poor if the growth is much quicker than the nucleation. In general, the agreement is bad when the nucleation and the growth take place at similar rates.

For platelets whose length and width are much larger than their thickness ($L_x = 8.10\text{E-}04$ m, $L_y = 8.10\text{E-}04$ m and $L_z = 8.90\text{E-}07$ m), the agreement is not perfect if the growth is much faster than the nucleation, but it is still much better than for a platelet with a much smaller surface. In all other conditions (very fast nucleation, nucleation and growth at a comparable rate), the results stemming from the complete circle assumption are nearly indistinguishable from those of the more realistic model. No Monte-Carlo simulation could be carried out because the computational time would have

been unmanageable for such large platelets.

4. Optimisation of the kinetic parameters (3D)

To assess the impact of the erroneous simplistic model (infinite platelet hypothesis) upon the optimisation of the chemical kinetic parameters γ and ϕ , two virtual experimental rate profiles were generated under the finite platelet assumption based on the rate parameter values $\gamma_0 = 1.23\text{E}+07$ (nuclei/m²/s) - $\phi_0 = 1.31\text{E}-07$ (mol /m²/s) and $\gamma_0 = 2.80\text{E}+08$ (nuclei/m²/s) - $\phi_0 = 2.12\text{E}-07$ (mol /m²/s), respectively. The powder platelets have always the following physical features: $L_x = L_y = 8\text{E}-06$ m, $L_z = 8\text{E}-07$ m and $V_{mA} = 74.4e - 3\text{m}^3.\text{mol}^{-1}$. Random residuals were then added to the model predictions in order to imitate measurement uncertainties. All details of our approach can be seen in Appendix C: Optimisation of Chemical Kinetic Parameters.

Blanchard et al. [47] have developed the Uranie platform for model optimisation, metamodelling and uncertainty analysis whereas Juillet et al. [48] successfully applied it to a problem of heterogeneous chemical kinetics. Since the determination of the parameter uncertainties can require a very large number of expensive simulations, the authors approximated the results of the numerical simulations through three possible surrogate models: a polynomial chaos expansion, an artificial neural network and a kriging approximation. This approach is known as meta-modelling and can be applied to many other situations related to process engineering [49]. While we followed their general approach, we used bivariate spline interpolation methods instead which resulted in a very good agreement with the results of our model, unlike their methods which often lead to considerable discrepancies in our particular situation.

Random fluctuations were introduced to make the profiles resemble true measurements. Our goal was to compute the *feasible sets*, which are the ensembles of parameter values compatible with every experimental data point given its uncertainty [50, 51, 52]. The feasible sets under the finite platelet hypothesis are shown in Figure 5. Interestingly, these feasible sets somewhat resemble the crescent-shaped optimisation landscapes mentioned by Miller et al. during the determination of combustion chemical kinetic parameters [53]. The feasible sets obtained under the infinite platelet hypothesis are *empty*, which implies that all parameter values of γ and ϕ are incompatible with the rate measurements if we use this too simplistic model.

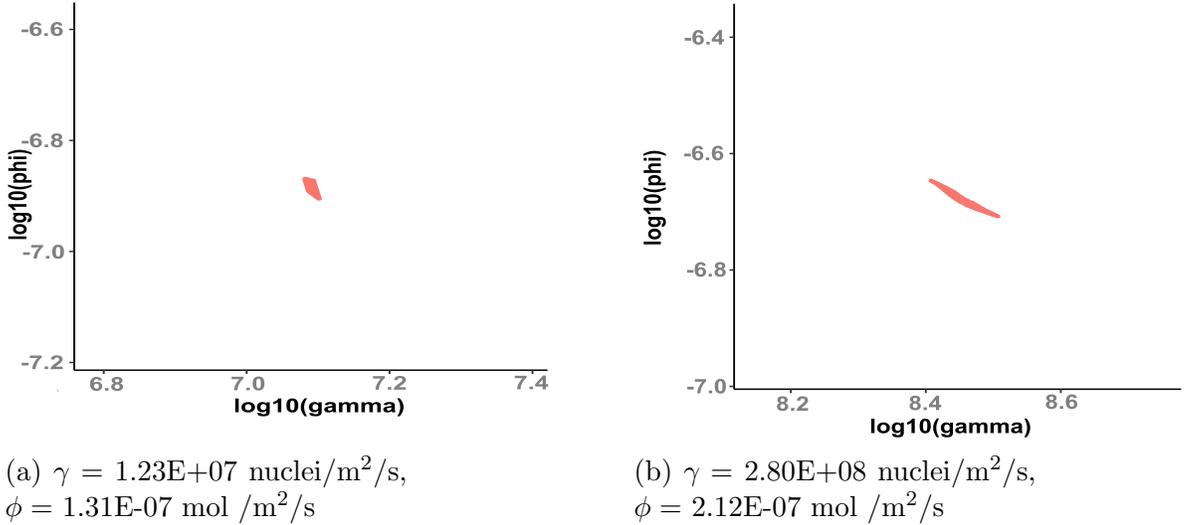


Figure 5: Feasible sets

The optimised rate profiles can be visualised in Figure 6. The optimal parameter values are shown in Table 1. To conclude, we see that the predictions obtained with the simplistic model are incompatible with the measurements and that the optimal parameter values obtained with the two methods are significantly different from one another. A researcher only knowing the infinite platelet model and accepting the optimised coefficients in spite of the unsatisfying fit to the measurements would produce completely unreliable predictions of the optimal functioning of an industrial reactor. The growth of the new solid species B within a particle of the powder generally consists of several elementary steps taking place at different reaction zones. When the approximation of the rate-determining step is valid, i.e. one of these elementary steps governs the reaction rate, one can establish an analytical expression of the areic reactivity of growth ϕ [54, 55]. The parameter ϕ depends then on the chemical kinetics of the elementary steps of the growth, so that false values of ϕ can lead to an erroneous understanding of the het-

Experiment	Finite platelet ($\gamma - \phi$)	Infinite platelet ($\gamma - \phi$)
1	1.23E+07 - 1.30E-07	2.89E+06 - 2.19E-07
2	2.76E+08 - 2.13E-07	6.46E+06 - 9.92E-07

Table 1: Optimal parameter values

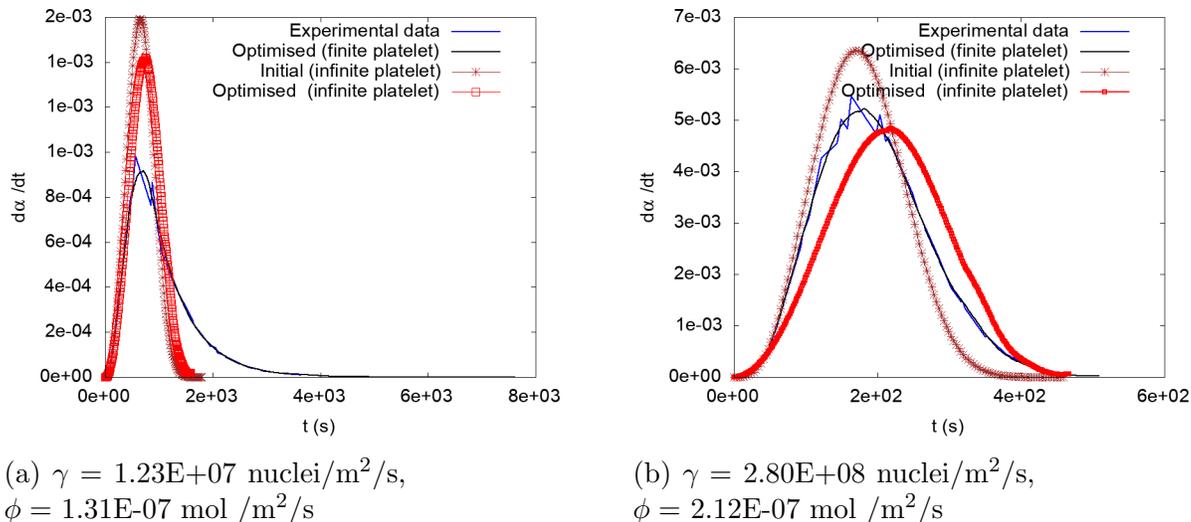


Figure 6: Optimal profiles

erogeneous reaction mechanism of the growth process.

The optimisation method developed here can be used to determine the optimal values of γ and ϕ alongside their uncertainties as a function of the temperature and the partial pressures of all species involved. Such a knowledge is vital to the optimisation of an industrial reactor and the determination of the optimal initial and boundary conditions leading to the highest possible yield.

5. Conclusion

Methods based on thermogravimetry and calorimetry play a very important role in the industrial world where they greatly contribute to the design of novel systems, problem solving and product optimisation [56, 57]. As in many other areas such as combustion and mechanical engineering, numerical modelling and simulations can substantially reduce the costs related to new experiments and help the applied researcher or R&D engineer reach important scientific and practical insights into the chemical behaviour of the reactions he or she is interested in. However, it is necessary that the theoretical chemical and physical models closely reflect reality so that the parameters of the models have a physical meaning. In the present work, we focused on a specific kind of reactions between solids and gases, namely si-

multaneous nucleation-growth processes where the inward growth is isotropic and we considered a powder made of platelets. Monte-Carlo based models allow one to simulate these reactions in particles having arbitrary shapes but the computational costs can be enormous, which makes it extremely hard to combine them with CFD simulations that are already very slow without taking the chemistry into account. A computationally much cheaper deterministic approach exists for platelets having an infinite lateral surface so that grown nuclei are always complete spheres. In this study, we wanted to verify if that model can also be applied to more realistic platelets found in powders where the thickness might be only ten times smaller than the square root of the lateral surface area.

We were able to develop a realistic deterministic model predicting the reaction progress that was validated through comparisons with Monte-Carlo simulations. The optimisation of the chemical kinetic parameters based on realistic virtual measurements shows that the initial naive model assuming an infinite lateral surface is at odds with the results of the MC-simulations it is supposed to correspond to. This illustrates the crucial fact that using a physically unsound model can easily lead to false conclusions and to a flawed optimisation of an industrial reactor.

The methodology and techniques we used throughout this article can be profitably applied to other theoretical studies related to thermogravimetry and calorimetry and to all types of chemical engineering challenges.

6. Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper in any way.

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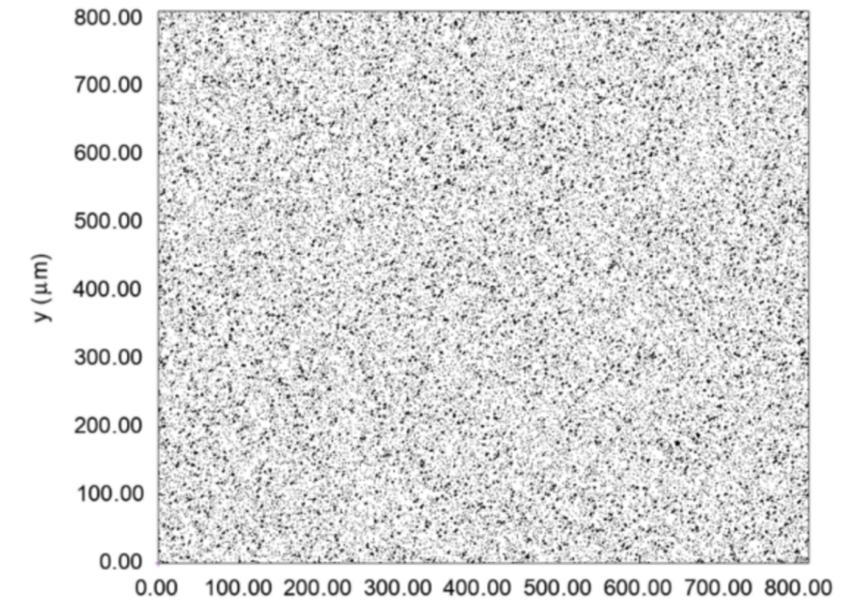
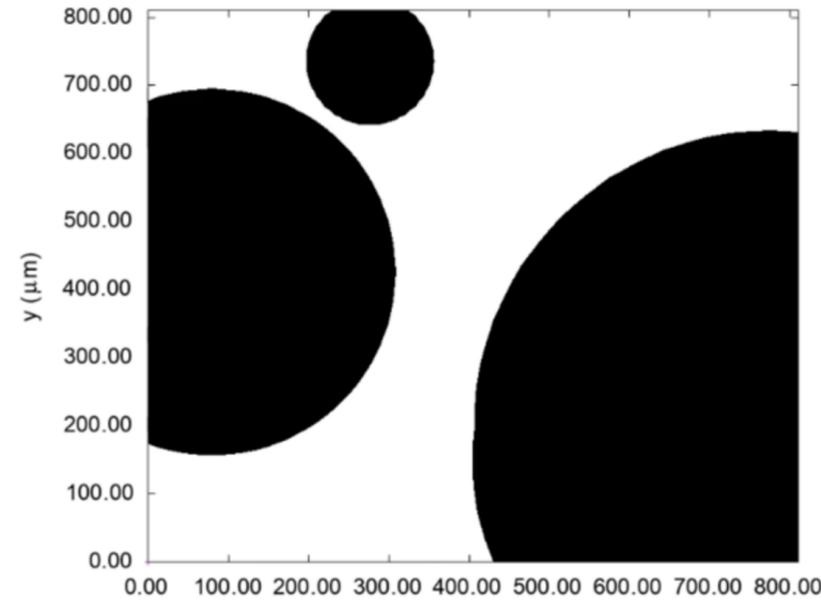
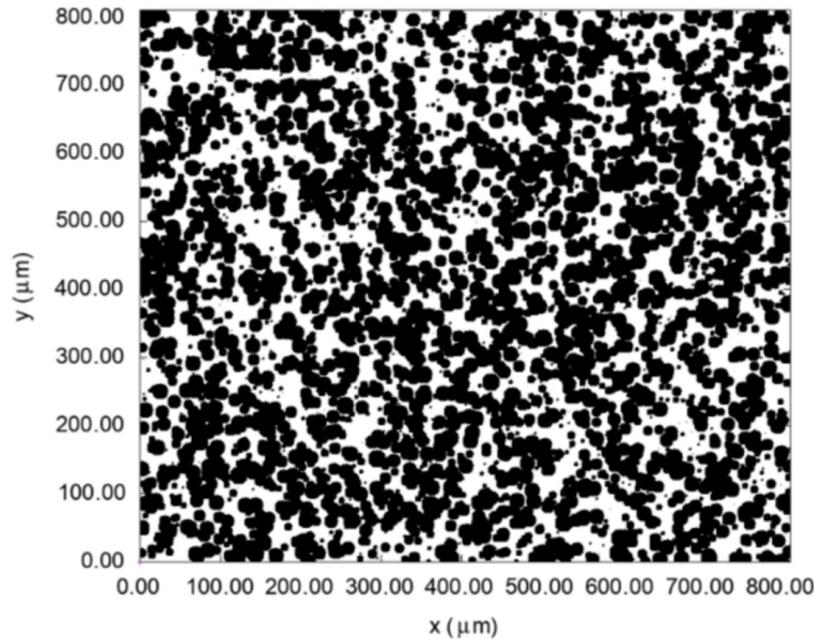
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Isotropic nucleation-growth (Monte-Carlo)

Deterministic infinite platelet model versus realistic finite platelet model

Parameter optimisation

