ELSEVIER

Computers and Chemical Engineering 24 (2000) 2571–2588

Computers & Chemical Engineering

www.elsevier.com/locate/compchemeng

Optimal selection of orthogonal polynomials applied to the integration of chemical reactor equations by collocation methods

L. Lefèvre [a], D. Dochain [b,*], S. Feyo de Azevedo [c], A. Magnus [d]

[a] *GSys Unit, ESISAR, 50 Rue Barthelemy de Laffemas, BP 54, 26902 Valence Cedex 09, France*
[b] *Cesame, Université Catholique de Louvain, Bât. Euler, av. G. Lemaître 4-6, 1348 Louvain-La-Neuve, Belgium*
[c] *Departmento de Engeneharia Quimica, Faculdade de Engenheria, Rua dos Bragas, 4099 Porto Codex, Portugal*
[d] *Numerical Analysis and Applied Mathematics Unit, Université Catholique de Louvain, Bât. de Hemptinne, chemin du Cyclotron 2, 1348 Louvain-La-Neuve, Belgium*

Received 5 November 1999; received in revised form 29 March 2000; accepted 22 May 2000

Abstract

In this paper, we analyse some properties of the orthogonal collocation in the context of its use for reducing PDE (partial differential equations) chemical reactor models for numerical simulation and/or control design. The approximation of the first order derivatives is first considered and analysed with respect to the transfer of the stability properties of the transport component from the PDE model to its approximated ODE (ordinary differential equations) model. Then the choice of the collocation points as zero of Jacobi polynomial is analysed and interpreted as an optimal choice with respect to a weighted norm. Finally, some guidelines for the use of orthogonal collocation are proposed and the results are illustrated on a simulation example. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Partial differential equations; Polynomial; Orthogonal collocation

1. Introduction

The dynamics of tubular reactors are described by partial differential equations (PDEs) derived from mass and energy balances (e.g. Feyo de Azevedo, Romero-Ogawa & Wardle, 1990). Either for numerical simulation or for control design, the PDEs model is commonly reduced to a set of ordinary differential equations (ODEs) by using approximation methods (e.g. finite differences, orthogonal collocation, …) (Georgakis, Aris & Amundson, 1977; Jorgensen, 1986) The approximation procedure may result in extensive computation studies before obtaining a satisfactory model approximation. For finite differences, the number of ODEs may easily become excessively high. The orthogonal collocation presents the advantage of substantially reducing the number of required ODEs. It has been the object of a very active research activity in order to draw guidelines for implementing it in the context of the reduction of tubular reactor models (see e.g. Finlayson & Scriven, 1965; Villadsen & Stewart, 1967; Stewart & Sorensen, 1972; Finlayson, 1971, 1972; Michelsen & Villadsen, 1972). However in spite of interesting attempts (e.g. Cho & Joseph, 1983), there exists no systematic procedure for choosing the reduction parameters (like the number of collocation points, or the value of the parameters α and β of the Jacobi polynomial, which influence the location of the discretization points). Beside this computation difficulty, generally speaking, it may be difficult to know the connection between the original distributed parameter (infinite dimensional) model and its (finite dimensional) discretised version, and as it is mentioned in Ray (1981), the dynamical properties of both models may be different. This is largely due to the lack of knowledge about the properties of such approximation method when applied for numerical simulation of chemical reactors.

The motivation for this study is basically two-fold. The first goal is to improve the current understanding

* Corresponding author. Tel.: +32-10-472378; fax: +32-10-472180.
E-mail address: dochain@csam.ucl.ac.be (D. Dochain).

PII: S0098-1354(00)00597-4

of the nature and performance of the orthogonal collocation method. For example, is there any rigorous mathematical basis behind the heuristic choices and recommendations usually mentioned by the practitioners (e.g. Cho & Joseph, 1983; Georgakis et al., 1977)? Is there any strong advantage in using the orthogonal collocation method over other integration methods and what are the main disadvantages with respect to them? Are there any criteria to guide the practitioner in the selection of this method for cases such as numerical simulation, dynamical analysis, or control applications? The second goal is focused on the formulation of mathematical guidelines that could be useful for a more systematic selection and implementation of the orthogonal collocation method.

The questions raised in the preceding paragraph are largely unanswered (e.g. Cho & Joseph, 1983; Georgakis et al., 1977). The results presented here are part of a research activity in distributed parameter system which has been dedicated to various connected topics (e.g. dynamical analysis of infinite dimensional model (Dochain & Winkin, 1995; Winkin, Dochain & Ligarius, 2000) and discretised finite dimensional model (Waldraff, Dochain, Bourrel & Magnus, 1998), numerical simulation and control design (Dochain, Tali Maamar & Babary, 1997), real-life control application (Bourrel, Dochain, Babary & Queinnec, 2000).

Within the framework described above, the objective of this paper is to analyse some properties of the orthogonal collocation approximation method and to suggest some guidelines which, we hope, could be useful when implementing the orthogonal collocation. The paper is organised as follows. In Section 2, we introduce the general dynamical PDE model for tubular reactors, and briefly present the orthogonal collocation as a method for reducing PDE models into ODE ones. Section 3 analyses the structural stability properties of the matrix characterising the reduction of the first order space derivative. Section 4 considers the choice of collocation points as an error minimisation problem and shows that the choice of zeros of Jacobi polynomials corresponds to an optimal choice for a weighted norm. Section 5 considers the numerical conditioning of the lumped model. Section 6 summarises the guidelines that can be drawn from the results of the numerical analysis performed in the preceding Section 3, Sections 4 and 5. And Section 7 illustrates the procedure on a simulation example.

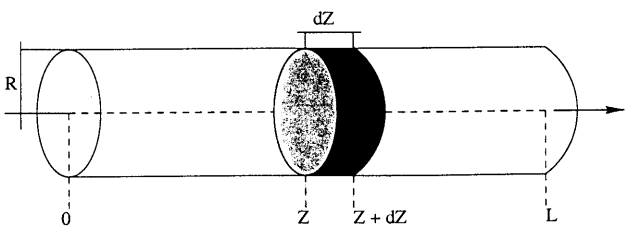

Fig. 1. Schematic view of a tubular reactor.

2. Dynamical models of chemical tubular reactors

Let us consider a tubular reactor as schematised in Fig. 1 and in which N_R non-isothermal reactions take place involving N_C components (reactants and products). Let us assume that the reactor is characterised by an axial dispersion. Then the dynamical model is readily derived by using mass and energy balances and can be written in the following matrix form,

$$\frac{\partial x}{\partial t} = -u\frac{\partial x}{\partial z} + D_m\frac{\partial^2 x}{\partial z^2} + \tilde{K}r(x) + U \tag{1}$$

with

$$x = \begin{pmatrix} C \\ T \end{pmatrix}, \quad \tilde{K} = \begin{pmatrix} K \\ -\Delta H^T/\rho C_p \end{pmatrix}, \quad U = \begin{pmatrix} 0 \\ -R_h/\rho C_p \end{pmatrix}$$

$$D_m = \begin{pmatrix} D_{am} I_{N_f} & 0 \\ 0 & \lambda_{ea}/\rho C_p \end{pmatrix} \tag{2}$$

and where T is the temperature (K), C is the component concentration vector (mol/l), t (s) and z (m) the time and space variables, λ_{ea} and D_{am} the axial energy and mass dispersion coefficients (kJ/ms K), u the superficial fluid velocity (m/s), L the reactor length (m), ΔH the reaction heat vector (kJ/mol), ρ the fluid density (kg/m^3), C_p the specific heat (kJ/kgK), $r(x)$ the reaction rate vector (mol/l s) and K the yield coefficient matrix. In a tubular reactor, the heat removal rate R_h is often given by the following expression,

$$R_h = \frac{4h}{d}(T - T_w) \tag{3}$$

where h, d and T_w are, respectively, the wall heat transfer coefficient (kJ/m^{2}Ks), the reactor diameter (m) and coolant temperature (K). An important particular situation is the plug flow reactor, i.e. when $D_m = 0$, the model is then hyperbolic (it is parabolic otherwise).

To complete the model, we have to add two boundary conditions (in order to be able to solve the equations (Eq. (1))). The most frequently used ones are the Danckwerts's boundary conditions (Danckwerts, 1953),

$$D_m\frac{\partial x}{\partial z}\Big|_{z=0} = -u(x_{in}(t) - x(z=0,\ t)) \tag{4}$$

$$\frac{\partial x}{\partial z}\Big|_{z=L} = 0 \tag{5}$$

where x_{in} denotes the influent value of x (for more details on the model derivation, see e.g. Feyo de Azevedo et al. (1990) and Dochain (1994) which con-

tain a number of older references including seminal papers like Langmuir (1908), Danckwerts (1953). It is also worth noting that the above dynamical model equations Eq. (1) have been presented following the traditional way but that there is a more rigorous methodology to derive it by following an averaging approach of the fundamental conservation equations, as it is explained e.g. in Deen (1987).

2.1. Reduction of the partial differential equations

Either for numerical simulation or for control design, the PDEs model is commonly reduced to a set of ordinary differential equations (ODEs) by using approximation methods (e.g. finite differences, orthogonal collocation, …) (Georgakis et al., 1977). The principle of the orthogonal collocation method is to search an approximation in the form of a finite series,

$$x^*(z,\ t) := \sum_{i=0}^{N} c_i(t) l_i^{(N)}(z) \tag{6}$$

where x^* denotes the approximation; N, the order of the reduction; $c_i(t)$, time-varying coefficients and $l_i^{(N)}(z)$, Nth order Lagrange interpolation polynomials, that is,

$$l_i^{(N)}(z) := \prod_{\substack{j=0 \\ \neq i}}^{N} \frac{z - z_j}{z_j - z_i} \tag{7}$$

where $z_0, \ldots, z_N \in (0, L)$, the interpolation (or 'collocation') points are parameters of the method, as well as N, the order of the reduction. The unknown time-varying coefficients $c_i(t)$ are chosen such that the approximated solution is the exact one at the collocation points. Since we have $l_i(z_j) = \delta_{ij}$, this means,

$$c_i(t) = x^*(z_i, t) = x(z, t)\big|_{z=z_i} \quad \forall i \in \{0,\ \ldots,\ N\} \tag{8}$$

For the system Eq. (1), we obtain the following set of ordinary differential equations,

$$\frac{\mathrm{d}x_d}{\mathrm{d}t} = (-uL_1 + D_m L_2)x_d + \tilde{K}_f r(x_d) + U_d + (-ul_1 + D_m l_2)x^*(z_0, t) \tag{9}$$

where x_d denotes the concentration vector of all components and temperature at the collocation points, that is,

$$x_d^T := (x_1^*(z_1),\ \ldots,\ x_1^*(z_r);\quad \ldots;\quad x_{N_C}^*(z_1),\ \ldots,\ x_{N_C}^*(z_r);\ T^*(z_1),\ \ldots,\ T^*(z_r)) \tag{10}$$

U_d and $r(x_d)$ are simply external heat exchange rate and reaction rate vectors computed at the collocation points, and listed in the same order than x_d. L_1 and L_2 are $(N_\mathrm{R}+1)\times(N_\mathrm{R}+1)$ block diagonal matrices where every block of the diagonal is identical, and are the discretised matrices operator obtained from the reduction of, respectively, the convection operator $(\partial/\partial z)$, and the dispersion operator $(\partial^2/\partial z^2)$, that is,

$$L_k := \begin{pmatrix} \tilde{L}_k & 0 & \ldots & 0 \\ 0 & \tilde{L}_k & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \ldots & 0 & \tilde{L}_k \end{pmatrix};\quad l_k := \begin{pmatrix} \tilde{l}_k \\ \tilde{l}_k \\ \vdots \\ \tilde{l}_k \end{pmatrix};\quad k = 1,\ 2 \tag{11}$$

with

$$\tilde{L}_1 := \left[\frac{\mathrm{d}l_i^{(N)}(z_j)}{\mathrm{d}z}\right]\{i, j = 1,\ \ldots,\ r\};$$

$$\tilde{l}_1 := \left[\frac{\mathrm{d}l_0^{(N)}(z_j)}{\mathrm{d}z}\right]\{j = 1,\ \ldots,\ r\} \tag{12}$$

$$\tilde{L}_2 := \left[\frac{\mathrm{d}^2 l_i^{(N)}(z_j)}{\mathrm{d}z^2}\right]\{i, j = 1,\ \ldots,\ r\};$$

$$\tilde{l}_2 := \left[\frac{\mathrm{d}l_0^{(N)}(z_j)}{\mathrm{d}z}\right]\{j = 1,\ \ldots,\ r\} \tag{13}$$

The dimension r of the state vector for each process component and the temperature is equal to N for plug flow reactors (i.e. when $D_m = 0$) (or in presence of a lack of confidence in the output boundary condition), otherwise it is equal to $N-1$. The value of variables x at the boundaries can be computed from the boundary conditions Eqs. (4) and (5) by introducing the expansion Eq. (6), i.e.

$$D_m \sum_{i=0}^{N} l_{1i0} x_{ki}(t) = -u[x_\mathrm{in} - x_{k0}(t)] \tag{14}$$

$$\sum_{i=0}^{N} l_{1i,N} x_{ki}(t) = 0 \tag{15}$$

3. Properties of the matrix L_1

Let us note that the above matrices $\tilde{L}_1$ and $\tilde{L}_2$ are full while the corresponding ones in the finite difference approximation are bi- and tri-diagonal. If we recall that the finite difference approximation is indeed equivalent of approximating the reactor by a cascade of reactors, we note that now the orthogonal collocation approximation indeed consists of a sequence of interconnected cascade reactors. This probably explains why the collocation method may reduce the order of the approximated lumped parameter model, and also why the calibration of the method may be quite long and difficult. The term $(-uL_1 + D_\mathrm{m}L_2)x_d$ approximates the transport component term of the PDE model, $-u(\partial x/\partial z) + D_m(\partial^2 x/\partial z^2)$. It is obvious that due to flow direction in the reactor, the convective-diffusive equation

$$\frac{\partial x}{\partial t} = -u\frac{\partial x}{\partial z} + D_m \frac{\partial^2 x}{\partial z^2}$$

is asymptotically stable, or in other words, the transport dynamics are stable. This property is easy to check by using standard PDE methods. Note that for the

approximated models because of the structure of L_1 and L_2, it is enough to look at the matrices $\tilde{L}_1$ and $\tilde{L}_2$. If we consider finite differences, the eigenvalues of the (bi- and tri-diagonal) matrices $\tilde{L}_1$ and $\tilde{L}_2$ are easy to compute, it is then routine to check that the term $(-uL_1 + D_mL_2)x_d$ in finite difference is exponentially stable (see e.g. Dochain, 1994). This means that the finite difference approximation correctly transfers the stability property of the transport component from the original PDE model to the approximated ODE model.

But what about the orthogonal collocation? The matrices $\tilde{L}_1$ and $\tilde{L}_2$ are full, and this renders the verification more intricate. For simplicity, we shall concentrate only on the matrix L_1 (which corresponds to the plug flow reactor approximation), i.e. on the term $-uL_1x_d$. The analysis is rather involved and is based on the properties of the Lagrange polynomials used as the base functions. The rth derivative of the expansion of the variable x can be expressed by the following equation, see Calogero (1985),

$$\frac{\partial^r}{\partial z^r}\begin{pmatrix} x^*(z=z_0) \\ x^*(z=z_1) \\ \vdots \\ x^*(z=z_N) \end{pmatrix} = BZ^rB^{-1}\begin{pmatrix} x^*(z=z_0) \\ x^*(z=z_1) \\ \vdots \\ x^*(z=z_N) \end{pmatrix} \tag{16}$$

with

$$Z = (z_{jk}) \tag{17}$$

$$z_{jk} = \sum_{i=0,\neq j}^{N} \frac{1}{z_j - z_i} \quad \text{if } j = k \tag{18}$$

$$= \frac{1}{z_j - z_k} \quad \text{if } j \neq k \tag{19}$$

$$B = \text{diag}(b_j), \quad b_j = \prod_{k=0,\neq j}^{N} (z_j - z_k) \tag{20}$$

Let us denote,

$$X^r = BZ^rB^{-1} \tag{21}$$

Note that $\tilde{L}_1$ and $\tilde{L}_2$ are one block of X and X^2, respectively,

$$X^r = \begin{pmatrix} x_{11} & X_{12} \\ \tilde{l}_r & \tilde{L}_r \end{pmatrix} \tag{22}$$

where x_{11} and X_{12} are the first entry and the first row of X^r, respectively. If we rewrite the matrices Z^r and B in the corresponding block formulation,

$$B = \begin{pmatrix} b_0 & 0 \\ 0 & B_{22} \end{pmatrix}, \quad Z^r = \begin{pmatrix} z^r_{11} & Z^r_{12} \\ Z^r_{21} & Z^r_{22} \end{pmatrix} \tag{23}$$

By straightforward matrix manipulations, we have,

$$\tilde{L}_r = B_{22}Z^r_{22}B^T_{22} \tag{24}$$

B_{22} can be viewed as a similarity transformation, therefore, the eigenvalues for L_r and Z^r_{22} are similar, and we can concentrate on the study of the matrix Z^r_{22}.

In the following, the plug flow reactor case will only be considered, and we shall concentrate on the analysis of Z_{22}. It may be worth nothing that the matrix Z_{22} presents a number of particular features,

- Z_{22} is the sum of diagonal matrix D and a skew-symmetric one S, $Z_{22} = D + S$;
- the trace of Z_{22} is strictly positive, $\text{tr}(Z_{22}) = \Sigma^N_{i=1}(1/z_i) > 0$.

Moreover, the elements z_i are as follows,

$$0 < z_1 < z_2 < \cdots < z_{q-1} < z_N = L \tag{25}$$

Let us first calculate the eigenvalues for the 2×2 matrix Z_{22}, which is then equal to,

$$Z_{22} = \begin{pmatrix} \dfrac{1}{z_1} + \dfrac{1}{z_1 - z_2} & \dfrac{1}{z_1 - z_2} \\ \dfrac{-1}{z_1 - z_2} & \dfrac{1}{z_2} - \dfrac{1}{z_1 - z_2} \end{pmatrix} \tag{26}$$

The determinant and trace of Z_{22} are equal to,

$$\text{Det}(Z_{22}) = \frac{2}{z_1 z_2}, \quad \text{tr}(Z_{22}) = \frac{1}{z_1} + \frac{1}{z_2} \tag{27}$$

Therefore, if we recall that for 2×2 matrices, the trace is the sum of the eigenvalues and the determinant, its product, we can conclude that the matrix Z_{22} has eigenvalues with positive real parts.

Different linear algebra tools have been used (Routh–Hurwitz (applied to $-Z_{22}$), Lyapunov equation, …) have been considered for generalisation, but up to now unsuccessfully. Mathematica has been used to compute the Routh–Hurwitz criterion coefficients, up to $N = 4$ (for larger values of q, Mathematica was not able to give a solution!). For instance, for $N = 3$, the characteristic polynomial of $-Z_{22}$,

$$\text{Det}(\lambda I + Z_{22}) = \frac{z_1z_2z_3\lambda^3 + (z_1z_2 + z_1z_3 + z_2z_3)\lambda^2 + 2(z_1 + z_2 + z_3)\lambda + 6}{z_1z_2z_3} \tag{28}$$

It is routine to check that the above polynomial is stable and, therefore, that the real parts of the eigenvalues of Z_{22} are all positive. The results are the same for $N = 4$.

However for larger values of $N (N > 4)$, the conjecture that the real parts of the eigenvalues of Z_{22} are positive is wrong. The argument is based on the following counter-example.

Let us first violate the condition Eq. (25) and consider that all the z_i are equal ($z_1 = z_2 = \ldots = z_N$). For $N = 5$, it is routine to check that the characteristic polynomial $\text{Det}(\lambda I + Z_{22})$ has the following complex conjugate roots with positive real part,

$$\lambda = \frac{z_1}{0.24 \pm 3.13i} \tag{29}$$

and therefore, Z_{22} has then an eigenvalue with a negative real part. The result can be extended to the situation when the z_i are distinct by considering the continuity theorem for the zeroes of a polynomial with respect to its coefficients. More precisely, the characteristic polynomial is built by considering,

$$z_k = z_1[1 + (k-1)\varepsilon], \quad k = 1 \text{ to } 5, \quad 0 < \varepsilon < \varepsilon_0 \tag{30}$$

And then the conjecture is wrong, and we cannot conclude that in general the orthogonal collocation approximation of the first order space derivative with Lagrange polynomial is characterised by a matrix whose eigenvalues have all positive real parts, if $N > 4$. This implies that for more than four internal collocation points, the approximation procedure may well result in a reduced model with an unstable transport component.

An important guideline at this point consists of checking the eigenvalues of $(-u\tilde{L}_1 + D_m\tilde{L}_2)$ before implementing the orthogonal collocation approximation.

4. Theoretical analysis of the accuracy of the collocation method

4.1. Orthonormal polynomials

The application of orthogonal collocation to the approximation of distributed parameter models has been the object of many works (e.g. Georgakis et al., 1977Jorgensen, 1986; Cho & Joseph, 1983; Khanna & Seinfeld, 1987; Jutan, Tremblay, MacGregor & Wright, 1977; Segall, MacGregor & Wright, 1984). Its implementation requires to choose (Michelsen & Villadsen, 1972):

1. the number of collocation points;
2. the location of the collocation points.

A classical choice of collocation points in chemical engineering is to take them as zeros of orthogonal polynomials, usually of Nth order monic Jacobi polynomials $p_N^{(\alpha,\beta)}$, that is polynomials defined by the three terms recurrence relation,

$$p_N^{(\alpha,\beta)} = (z - g_N(\alpha,\beta))p_{N-1}^{(\alpha,\beta)} - h_N(\alpha,\beta)p_{N-2}^{(\alpha,\beta)} \tag{31}$$

with $p_0^{(\alpha,\beta)} = 1$ and where coefficients $h_{N(\alpha,\beta)}$ are defined as follows:

$$h_N(\alpha,\beta) := \begin{cases} \dfrac{(N-1)(N+\alpha-1)(N+\beta-1)(N+\alpha+\beta-1)}{(2N+\alpha+\beta-1)(2N+\alpha+\beta-2)^2(2N+\alpha+\beta-3)} \\ \text{if } N > 2 \\ \dfrac{(\alpha+1)(\beta+1)}{(\alpha+\beta+2)^2(\alpha+\beta+3)} \quad \text{if } N = 2 \end{cases}$$

$$g_N(\alpha,\beta) := \begin{cases} 0 \quad \text{otherwise} \\ \dfrac{1}{2}\left(1 - \dfrac{\alpha^2-\beta^2}{(2N+\alpha+\beta-1)^2-1}\right) \text{ if } N > 1 \\ \dfrac{\beta+1}{\alpha+\beta+2} \text{ if } N = 1 \end{cases}$$

Choosing zeros of classical orthogonal polynomials as collocation points makes orthogonal collocation approximations able to integrate exactly polynomials up to order $2N-1$ by means of quadrature formulae (Gay, 1989), which actually is the maximum order of accuracy reachable with such Nth order approximations. In this sense, this choice can be considered as optimal, and, in practice, it provides results comparable with those obtained from Galerkin's method Fornberg (1996)[1]. This last method is often considered as a reference when regarding the accuracy of the numerical approximation of the solution, but it requires a huge computational effort.

Once this generic choice of collocation points agreed, we may wonder more specifically why to choose zeros of Jacobi polynomials. One possible reason to do so is that this choice leads to a numerical method which can be 'tuned' with two parameters, α and β. For instance (see Georgakis et al., 1977), α small (resp. > 1) and $\beta > 1$ (resp. small) tend to concentrate the collocation points close to the reactor output (resp. input).

This property provides an intuitive tuning for the method and has been used extensively by process engineers to define qualitative and experimental-based rules governing the appropriate use of the method in each specific application.

However, we will not, in this paper, restrict our a priori choice to Jacobi polynomials, but will consider general classical orthogonal polynomials.

4.2. Cauchy's formula for the interpolation error

In searching the approximated solution in the form Eq. (6), we actually look, at each fixed time t, for the Nth order polynomial which interpolates the unknown exact solution at the $N+1$ collocation points $(z_0, \ldots, z_N)$. The following Cauchy's result (see Davis, 1975), gives an upper error bound for such approximations.

if we define the interpolation error by: $e_N(z, t) := x(z, t) - \Sigma_{i=0}^{N} x_i(t)\, p_i(z)$ and assume that unknown solution $x(z, t)$ is sufficiently continuously differentiable, we have,

[1] The recent book by Bengt Fornberg (1996) addresses interesting issues on the approximation by series of special functions (the so-called pseudospectral methods). Hence, it applies to series of Lagrange polynomials, thus to orthogonal collocation. Noticeably for our problem, its chapter 3 discusses the convergence of the interpolating functions and the influence of the position of the collocation points on this convergence.

$$e_N(z,t) := w(z)\frac{x_z^{(N+1)}(\eta(z),t)}{(N+1)!} \tag{32}$$

where $w(z) := \Pi_{j=0}^{N}(z-z_j)$ and $\eta(z) \in [-1, +1]$.

Hence, we try to choose the interior collocation points $z_1, \ldots, z_{N-1}$ that minimise the interpolation error Eq. (32). Without any a priori knowledge on the behaviour of the exact solution, this problem reduces to finding the $z_1, \ldots, z_{N-1}$ such that $\|w(z)\|_\infty$ is minimal. The roots of the $(N-1)$th order Chebyshev polynomials

$$z_k^* := \cos\left(\pi\frac{2k+1}{2(N-1)}\right) \text{ for } k=0, \ldots, N-2 \tag{33}$$

are solution of this problem and the corresponding minimal norm is (see Ralston & Rabinowitz, 1978)

$$\|w(z)\|_\infty = \left\|\prod_{k=1}^{N-1}(z-z_k^*)\right\|_\infty = 2^{-(N-2)} \tag{34}$$

Hence,

$$\|e_N\|_\infty \le \frac{\|x_z^{(N+1)}(\cdot,t)\|_\infty}{(N+1)!2^{N-2}} \tag{35}$$

Note that Chebyshev polynomials belong to the family of Jacobi polynomials, and correspond to the values of the parameters $\alpha = \beta = -1/2$.

4.3. Theoretical analysis of the error minimisation

Eq. (32) suggests that we can handle the effect of large variations (typically, due to the presence of 'hot spots' i.e. large and concentrated variations in the spatial profiles of the temperature and/or concentrations) on the interpolation error by choosing suitable collocation points. Therefore, we suggest to choose the $N-1$ interior collocation points solutions of the following problem,

$$\min_{z_i \in [-1,+1] \forall i \in 1,\ldots,N}\left(\left\|\prod_{j=0}^{N}|(z-z_j)w_\infty(z)|\right\|_\infty\right) \tag{36}$$

where the weight $w_\infty(z)$ is supposed to be large around the hot spots, and small everywhere else. Doing this, we keep the interpolation error small where it would have been large if we had considered an 'uniform' choice of collocation points (zeros of a Chebyshev polynomial). Actually this choice follows the classical intuitive choices of collocation points, since, as we will show later on, it increases collocation points around hot spots. However, a compromise has to be found since the number of collocation points is limited (it is also the size of the differential system to solve) and since a too high concentration of collocation points around hot spots leads to poor approximation anywhere else. This compromise is automatically handled if collocation points are chosen according to Eq. (36).

In order to solve the minimisation problem Eq. (36), we will proceed in two steps. First we will slightly generalise the Chebyshev equi-oscillations theorem (which characterises the best polynomial approximation of a continuous function, see Cheney, 1966 and remarks in Appendix A). Then we will use this result, as well as results on the asymptotic behavior of orthogonal polynomials, to find an asymptotic solution to the problem.

Let us remark that the problem of finding the collocation points $z_1, \ldots, z_{N-1}$ which minimises the product $\Pi_{j=0}^{N}(z-z_j)w_\infty(z)$ is equivalent to the problem of finding the monic polynomial $\Pi_{j=0}^{N}(z-z_j)$ of minimal weighted uniform norm, defined in the following way,

$$\forall f \in C([a,b]), \|f\|_{w_\infty} := \sup_{x\in[a,b]}|f(z)w_\infty(z)| \tag{37}$$

Then note that this last problem is equivalent to the problem of finding the best Nth order (not monic) approximation polynomial for the function $-z^{N+1}$, in the sense of the weighted norm $\|\cdot\|_{w_\infty}$, that is finding the polynomial $\tilde{p}_{N-1}$ such that

$$\|(-z^{N+1})-\tilde{p}_{N-1}\|_{w_\infty} = \left\|-\prod_{j=0}^{N}(z-z_j)\right\|_{w_\infty} \tag{38}$$

is minimal. The solution of this last approximation problem may be characterised by using a generalisation of the Chebyshev equi-oscillation theorem presented hereafter.

Theorem 1. (*Alternation theorem*) *If* $f \in C([a,b])$; $\hat{p} \in \mathcal{P}_n$ $(N>0)$ *where* $\mathcal{P}_N$ *denotes the space of Nth order polynomial with real coefficients defined on* $[-1, +1]$. *Then* $\hat{p}$ *is the best approximation of f, in* $\mathcal{P}_N$, *in the sense of the norm* $\|\cdot\|_{w_\infty}$ *iff. There is a set of at least* $(N+2)$ *points such that the function* $\hat{e} := (f-\hat{p})w_\infty$ *equi-oscillates and reaches its extrema values at each of these points, that is,*

iff. $\exists (z_i)_{i\in 0,\ldots,N+1}$ *such that* $a \le z_0 < z_1 < \ldots < z_{N+1} \le b$

and $\hat{e}(z_i) = \sigma(-1)^i\|\hat{e}\|_\infty$

with $\sigma = 1$ or $\sigma = -1$ (39)

The proof is given in Appendix A.

In the case of general weights, only asymptotic results (that is, results when the polynomial order N tends to infinity) are available on equi-oscillation properties. From this theory [33], we point out the following result:

Assume $w(z)$ is the weight used to define a family of orthonormal polynomial with respect to the inner product $(u|v)L_w^2 := \int_{-1}^{+1} u(z)v(z)w(z)\mathrm{d}z$

Then the quantity $\sqrt{\sqrt{1-z^2}\,w(z)}p_N(z)$ (where p_N is the Nth order polynomial orthonormal polynomial associated to the weight w) tends[2] to asymptocially equi-oscillate on the interval $[-1, +1]$, when $N \to \infty$.

[2] See Erdelyi, Magnus and Nevai (1994) for recent results on error and speed estimation of this convergence.

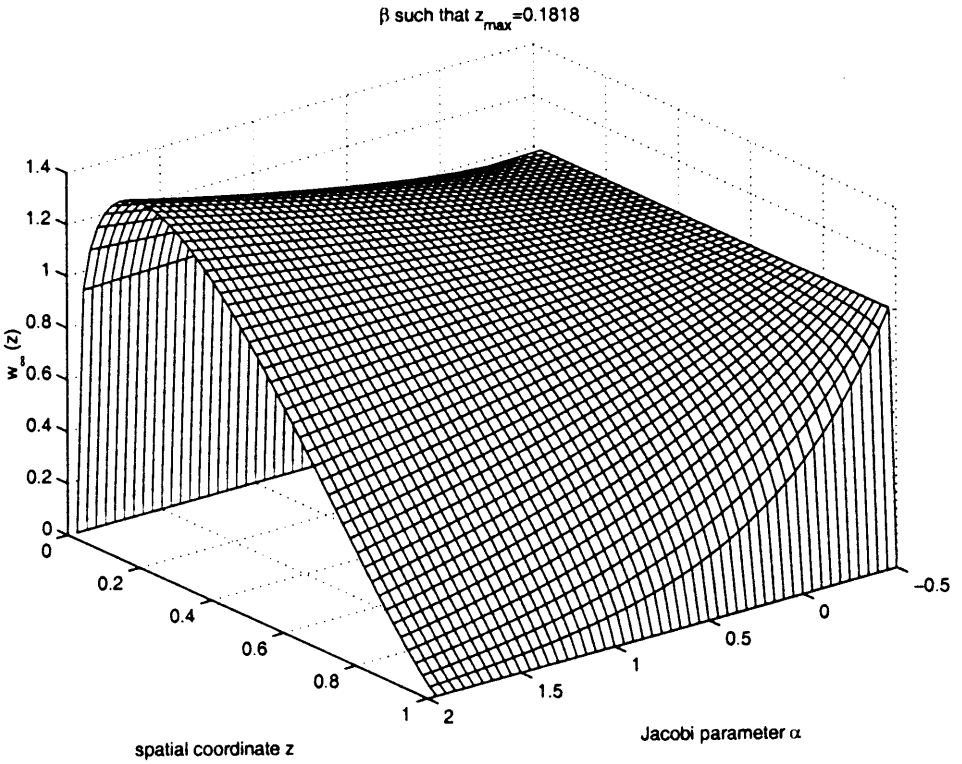

Fig. 2. Weights $w_\infty(z)$ with a maximum value in $z_{\max} = 0.1818$ when α and β range from $-1/2$ (uniform weighting) to 2.

If we assume that N is large enough, we can then conclude that $\sqrt{\sqrt{1-z^2}\,w(z)}p_N(z)$ nearly equi-oscillates.

A classical continuity argument, borrowed from the theory of the exchange algorithm (see Ralston & Rabinowitz, 1978; Powell, 1981) lead to a satisfactory approximation result. Indeed, since the operator of the best polynomial approximation is continuous, we may conclude that this $p_N(z)$ (which nearly equi-oscillates) is a good approximation of the optimal polynomial $\hat{p}_N(z)$, which minimises the norm $\|p\|_{w_\infty}$ with,

$$w_\infty(z) := \sqrt{\sqrt{1-z^2}\,w(z)} \tag{40}$$

At this point, it may be interesting to investigate the meaning of classical choices of collocation points in order to point out what implicit norm minimisation is made while using it. For instance, in the case where the collocation points are zeros of Jacobi polynomials, we know that ,

$$w(z) := (1-z)^\alpha(1+z)^\beta \tag{41}$$

Hence we know that using these collocation points, we will get an approximated solution which minimises an interpolation error weighted by the function,

$$w_\infty(z) := \sqrt{\sqrt{1-z^2}\,(1-z)^\alpha(1+z)^\beta} \text{ with } \alpha, \beta \geq \frac{-1}{2}$$

$$= (1-z)^{(2\alpha+1)/4}(1+z)^{(2\beta+1)/4} \tag{42}$$

Many shapes may be reached with weight of the form Eq. (42). They allow to emphasise the interpolation error from one side to the other of the reactor, according to the values of the tuning parameters α and β. In Section 7, weights defined on [0, 1] (reactor length $L = 1$) and centred around $z = 0.1818$ (the temperature profile 'hot spot') will be used. A simple scaling of the weights $w_\infty(z)$ on [0, 1] and short calculations show that these weighting functions reach their maximum in,

$$z_{\max} = \frac{1+2\beta}{2(\alpha+\beta+1)} \tag{43}$$

Weighting functions such that Eq. (43) is satisfied for $z_{\max} = 0.1818$ are illustrated in Fig. 2 for values of α ranging from $-1/2$ ('Chebyshev' or uniform weighting) to 2. The corresponding weighting functions slide from a uniform weight on the error to a weight more and more localised around $z_{\max} = 0.1818$.

5. Well-posedness of the reduced model

Efforts made to minimise theoretically the (weighted) interpolation error may become worthless if the choice of collocation points lead to a badly conditioned sys-

tem. In this section, a slightly modified classical result on the conditioning of systems of ordinary differential equations is presented, and then applied to the tubular reactor reduced model Eq. (9). The aim of these computations is to determine how well-posed this model could be according to a given choice of collocation points, that is how perturbations in the data are propagated. For this purpose, the following Cauchy problem will be considered,

$$(\mathscr{P}) \equiv \begin{cases} \dfrac{\mathrm{d}u}{\mathrm{d}t} = Mu + F(u) \\ u(0) = u_0 \end{cases} \tag{44}$$

where x is a vector of real valued functions, F a non-linear vector field, and M a matrix of appropriate dimension. In the reactor models generally considered in process engineering, it may be supposed that the reaction rates vector is differentiable, hence totally Lipschitzian. The following assumption will, therefore, holds in the following,

$$\|F(u_1) - F(u_2)\|_2 \leq L_F \|u_1 - u_2\|_2 \tag{45}$$

for every u_1 and u_2 in the space of admissible states. The norm in Eq. (45) is the classical Euclidean norm in $\Re^p$, where p is the state space dimension. Assumption Eq. (45) guarantees the global existence and uniqueness of a solution for equations Eq. (44). The next result establishes what is often called 'the continuous dependence of the solution', relatively to the data of $(\mathscr{P})$ (see e.g. Gottlieb & Orszag, 1977). It is here generalised slightly in order to take into account the specific features of tubular reactor models.

Theorem 2. (*Continuous dependence*) *Let a perturbed problem be defined according to*,

$$(\mathscr{P}_\delta) \equiv \begin{cases} \dfrac{\mathrm{d}v}{\mathrm{d}t} = Mv + F(v) + \delta(t) \\ v(0) = u_0 + \delta_0 \end{cases} \tag{46}$$

where the perturbation $\delta(t)$ *is assumed to be continuous. Let the distance between the solution of the initial problem* Eq. (44) *and the perturbed problem* Eq. (46) *be defined as* $d(t)$,

$$d(t) := v(t) - u(t) \tag{47}$$

Then, the Euclidean norm of this distance is upper bounded as follows,

$$\|d(t)\|_2 \leq \delta_0 e^{\kappa t} + \delta_\infty \frac{e^{\kappa t} - 1}{\kappa} \tag{48}$$

where $\delta_\infty := \max_{t \in \Re^+}(\delta(t))$, $\kappa := L_F + \bar{\sigma}(M)$ *and* $\bar{\sigma}(M)$ *the larger singular value of* M.

The proof is given in Appendix B.

Inequality Eq. (48) shows the continuous dependence of the (exact) solution of the problem Eq. (44) to its data. Moreover, it bounds the fastest propagation of floating points errors we may expect, as well as the propagation of errors due to modelling, inaccurate parameters estimation, or approximate initial conditions. All these errors should be evaluated carefully, when dealing with tubular reactor models.

Let us rewrite the reduced reactor model Eq. (9) as follows,

$$\frac{\mathrm{d}x_d}{\mathrm{d}t} = (-uL_1 + D_m L_2)x_d + F(x_d) \tag{49}$$

where $F(x)$ models the reactions rates, and, possibly, non-linear heat exchange phenomena. Its components essentially depend on the chosen reactor kinetic models. Hence a general theory on its behaviour cannot be made available. No general information on its structure, nor on its fastest variation rate (L_F), may be used to specify $F(x)$, due to the very large variety of reaction kinetics used in process engineering. However, the linear part of equations Eq. (49), representing the discretised transport component of the reactor, has always the same structure, and informations on it may be summarised in the matrix

$$M := -uL_1 + D_m L_2 \tag{50}$$

To improve the conditioning of the differential problem Eq. (44), that is to minimise κ, tuning the position of collocation points may be an efficient strategy. There is no simple analytic expression for the largest singular value of M, since it strongly depends on the superficial velocity u, and on the dispersion coefficients D_m, that is on operating conditions of the reactor. However, there are efficient numerical methods to compute it in a range of collocation points. Taking into account this conditioning problem, the position of collocation points has to be determined with two simultaneous criteria,

1. it should minimise the theoretical interpolation error, relatively to a suitable choice of a weighting factor, related to the dynamics of the reactor model (see Section 4.3);
2. it should give a reasonable conditioning number, which allows the computed solution (numerical integration) to be representative of the theoretical accuracy of the reduction method.

6. Guidelines for the implementation of the orthogonal collocation

The above mathematical analysis suggests several guidelines for the implementation of orthogonal collocation when applied to the numerical integration of tubula reactor models. It can be summarised into the following four-step procedure,

1. a first simulation run with an uniform choice of collocation points (zeros of Chebyshev polynomials, see Section 4.2), to grasp the basic features of the reactor dynamics (hot spots, slow variation areas), and to estimate the minimal number of collocation points needed in order to get satisfactorily results;
2. the design of a family of weights for the interpolation error, taking into account the characteristics of the model dynamics, and the computations of the corresponding collocation points positions;
3. the computations of the conditioning number of the reduced model (larger singular value of Eq. (50)), for the family of pre-selected collocation points, and of the eigenvalues of the transport and dispersion discretised operators (to force the stability of these two operators, see Section 3);
4. a final selection of the collocation points, and a final simulation run.

All these four steps will be detailed in the next section, when applied to the example of an exothermic plug-flow reactor. In this application, we have chosen, for the parametric family of collocation points, zeros of Jacobi polynomials, since it is, classically, the mostly used in chemical reactor modelling and simulation. This choice will allow us to point out what are the 'implicit' choices made when using these polynomials concerning the stability of convection and dispersion operators, the actual minimisation of the interpolation error and the range of used conditioning numbers. The numerical methods specific to our approach (computations of zeros of orthogonal polynomials, evaluation of matrices C_1 and C_2, and of their eigenvalues) are given in Lefèvre (1998).

7. Example of a simple reaction model

7.1. Model deivation

In this section, the example of a simple first order irreversible exothermic reaction

$$A \rightarrow B \tag{51}$$

Table 1
Parameters used for numerical simulations

Parameter	Value	Definition
Pe_h	5	Thermal Peclet number
Pe_m	5	Mass Peclet number
Le	1	Lewis number
Da	0.875	Damköhler number
γ	15	Activation energy
η	0.8375	Heat of reaction
μ	13	Heat transfer coefficient
$\tilde{T}_w$	1	wall temperature ratio

in a tubular reactor will be considered. Model derivation and numerical data are from Gay (1989). In this work, the author considers the model developed in Section 2 in its dimensionless form. The mass and head balance of reaction (Eq. (51)) may then be written as

$$\frac{\partial \tilde{C}}{\partial \tilde{t}} = \frac{1}{Pe_m}\frac{\partial^2 \tilde{C}}{\partial \tilde{z}^2} - \frac{\partial \tilde{C}}{\partial \tilde{z}} - \mathrm{Da}\, r(\tilde{C}, \tilde{T})$$

$$\frac{\partial \tilde{T}}{\partial \tilde{t}} = \frac{1}{Pe_h}\frac{\partial^2 \tilde{T}}{\partial \tilde{z}^2} - \frac{1}{Le}\frac{\partial \tilde{T}}{\partial \tilde{z}} - \eta r(\tilde{C}, \tilde{T}) + \mu(\tilde{T}_w - \tilde{T}) \tag{52}$$

with the dimensionless variables

$$\tilde{z} = \frac{z}{L}; \quad \tilde{t} = \frac{tu}{L}; \quad \tilde{C} = \frac{C}{C_r}; \quad \tilde{T} = \frac{T}{T_r} \tag{53}$$

where L denotes the reactor length, u the fluid velocity and $Tr = 500$ (K) and $Cr = 1$ (mol/l) are the temperature and concentration references which will be used in this section. In this dimensionless form, the Danckwerts boundary conditions become,

$$-\left.\frac{\partial \tilde{T}}{\partial \tilde{z}}\right|_{\tilde{z}=0} = Pe_h(\tilde{T}_{\mathrm{in}}(\tilde{t}) - \tilde{T}(\tilde{z}=0, \tilde{t}))$$

$$-\left.\frac{\partial \tilde{C}}{\partial \tilde{z}}\right|_{\tilde{z}=0} = Pe_m(\tilde{C}_{\mathrm{in}}(\tilde{t}) - \tilde{C}(\tilde{z}=0, \tilde{t}))$$

$$-\left.\frac{\partial \tilde{T}}{\partial \tilde{z}}\right|_{\tilde{z}=1} = -\left.\frac{\partial \tilde{T}}{\partial \tilde{z}}\right|_{\tilde{z}=1} = 0 \tag{54}$$

Where $\tilde{T}_{\mathrm{in}}(\tilde{t})$ and $\tilde{C}_{\mathrm{in}}(\tilde{t})$ are, respectively, the inlet temperature and concentration ratios. The first order reaction rate expression is here defined as,

$$\tilde{r}(\tilde{C}, \tilde{T}) = \frac{r(C, T)}{r(C_r, T_r)} = \tilde{C}(\tilde{z}, \tilde{t})\exp\left[\gamma\left(1 - \frac{1}{\tilde{T}(\tilde{z}, \tilde{t})}\right)\right] \tag{55}$$

The meaning of the parameters used in Eqs. (52), (54) and (55) is derived by application of the substitutions Eq. (53) in Eqs. (1)–(5). They are classical parameters and their values used in following sections for simulations are listed in Table 1 hereafter.

The influence of the position of collocation points on the error, stability, and well-posedness of the reduced model, will now be investigated on this example by following the guidelines developed in the previous section.

7.2. Model reduction

According to the procedure presented in Section 2.1, let $\tilde{C}_1, \ldots, \tilde{C}_N$ and $\tilde{T}_1, \ldots, \tilde{T}_N$ denote, respectively, the concentration of component A, and the temperature at the collocation points $\tilde{z}_1, \ldots, \tilde{z}_N \in [0, 1]$. Let $(\tilde{C}_0, \tilde{T}_0)$ and $(\tilde{C}_{N+1}, \tilde{T}_{N+1})$ denote, respectively, the couples of concentration and temperature at the reactor inlet and outlet. Then the reduction of partial differential equations Eq. (52) leads to the following set of ordinary differential equations

$$\frac{\mathrm{d}}{\mathrm{d}\tilde{t}}\begin{bmatrix}\tilde{C}_0\\ \vdots\\ \tilde{C}_{N+1}\\ \tilde{T}_0\\ \vdots\\ \tilde{T}_{N+1}\end{bmatrix} = \begin{pmatrix}\frac{1}{Pe_m}L_2 - L_1 & 0\\ 0 & \frac{1}{Pe_h}L_2 - \frac{1}{Le}L_1 + \mu I_{N+1}\end{pmatrix}\begin{bmatrix}\tilde{C}_0\\ \vdots\\ \tilde{C}_{N+1}\\ \tilde{T}_0\\ \vdots\\ \tilde{T}_{N+1}\end{bmatrix} + \mu\tilde{T}_w\begin{bmatrix}0\\ \vdots\\ 0\\ 1\\ \vdots\\ 1\end{bmatrix} + \begin{pmatrix}-\mathrm{Da}I_{N+1}\\ \eta I_{N+1}\end{pmatrix}\begin{bmatrix}\tilde{C}_0 e^{\gamma(1-(1/\tilde{T}_0))}\\ \vdots\\ C_{N+1}e^{\gamma(1-(1/\tilde{T}_{N+1}))}\end{bmatrix} \tag{56}$$

where I_{N+1} denotes the identity matrix of order $N+1$ and L_1, L_2 denote the matrices of, respectively, first and second order derivatives of Lagrange polynomials defined by,

$$(L_1)_{i,j} := \frac{\mathrm{d}l_i^{(N+1)}(\tilde{z}_j)}{\mathrm{d}\tilde{z}} \tag{57}$$

$$(L_2)_{i,j} := \frac{\mathrm{d}^2 l_i^{(N+1)}(\tilde{z}_j)}{\mathrm{d}\tilde{z}^2} \tag{58}$$

for $i, j \in 0, \ldots, N+1$. The boundary conditions Eq. (54) reduce to a set of four algebraic equations. These ones may be solved to obtain explicit values for the concentration and temperature at $\tilde{z}_0 = 0$ and $\tilde{z}_{N+1} = 1$.

$$\begin{bmatrix}\tilde{T}_0\\ \tilde{T}_{N+1}\end{bmatrix} = \alpha_T\begin{bmatrix}1\\ -\frac{(L_1)_{N+1,0}}{(L_1)_{N+1,N+1}}\end{bmatrix}\left(Pe_h\tilde{T}_{in} + \begin{bmatrix}\Phi_1\\ \Phi_2\end{bmatrix}\begin{bmatrix}\tilde{T}_1\\ \vdots\\ \tilde{T}_N\end{bmatrix}\right)$$

$$\begin{bmatrix}\tilde{C}_0\\ \tilde{C}_{N+1}\end{bmatrix} = \alpha_C\begin{bmatrix}1\\ -\frac{(L_1)_{N+1,0}}{(L_1)_{N+1,N+1}}\end{bmatrix}\left(Pe_m\tilde{C}_{\mathrm{in}} + \begin{bmatrix}\Phi_1\\ \Phi_2\end{bmatrix}\begin{bmatrix}\tilde{C}_1\\ \vdots\\ \tilde{C}_N\end{bmatrix}\right) \tag{59}$$

where

$$\alpha_T = \frac{1}{Pe_h - (L_1)_{0,0} + (L_1)_{0,N+1}(L_1)_{N+1,0}/(L_1)_{N+1,N+1}}$$

$$\alpha_C = \frac{1}{Pe_m - (L_1)_{0,0} + (L_1)_{0,N+1}(L_1)_{N+1,0}/(L_1)_{N+1,N+1}}$$

$$\begin{bmatrix}\Phi_1\\ \Phi_2\end{bmatrix} = \begin{pmatrix}I_N & 0\\ 0 & I_N\end{pmatrix}\left((L_1)_{0,.} - \frac{(L_1)_{0,N+1}}{(L_1)_{N+1,N+1}}(L_1)_{N+1,.}\right) + \begin{pmatrix}0 & 0\\ 0 & I_N\end{pmatrix}\frac{1}{\alpha_T(L_1)_{0,N+1}}(L_1)_{N+1,.} \tag{60}$$

When the solutions (Eq. (59)) are replaced in the reduced model (Eq. (56)), a set of $2N$ non-linear ordinary differential equations is obtained. The unknown functions are concentrations and temperatures at each interior collocation points.

Now, the steady state solution of this reduced model will be computed and compared with steady state solution of the distributed parameters model. It exhibits a hot spot in the stationary temperature profile and allows us to apply a selection of collocation points which emphasises the behaviour of the reactor around this hot spot.

The collocation points are chosen as zeros of the Jacobi polynomials $p_N^{(\alpha,\beta)}$ defined on [0, 1]. The influence of the parameters α and β will be discussed using the results concerning the stability and the well-posedness of the reduced differential model.

Finally, the dynamical behaviour of the reduced model after a variation in the feeding conditions will be computed. This will allow us to note that the benefits of the collocation points choice is preserved for dynamical simulations, in the studied case.

7.3. Stationary profiles and weights on the error

Stationary profiles are solutions of Eq. (52) with $\partial\bar{C}/\partial\bar{t} = \partial\bar{T}/\partial\bar{t} = 0$. They may be computed as the solution of the resulting ordinary differential initial value problem, integrated along the axial distance $\tilde{z}$ with the influent temperature and concentration as initial values.

Stationary profiles may also be computed as the equilibrium of the reduced model. Both solutions are compared in Fig. 3 in the case $\tilde{T}_{\mathrm{in}} = 1$ and $\tilde{C}_{\mathrm{in}} = 1$. A reduction with only three interior collocation points has been chosen. From a first computation of the initial temperature and concentration profiles[3], it has been observed that the temperature exhibits a hot spot around $\tilde{z} = 0.1818$. Then the family of weights on the error

[3] This first computation may be performed either by numerical integration of the stationary initial value problem (see the continuous lines on Fig. 3) or by solving the reduced stationary non-linear algebraic equations obtained with a uniform weight on the error, i.e. $\alpha = -1/2$ (see the dash-dot lines on Fig. 3).

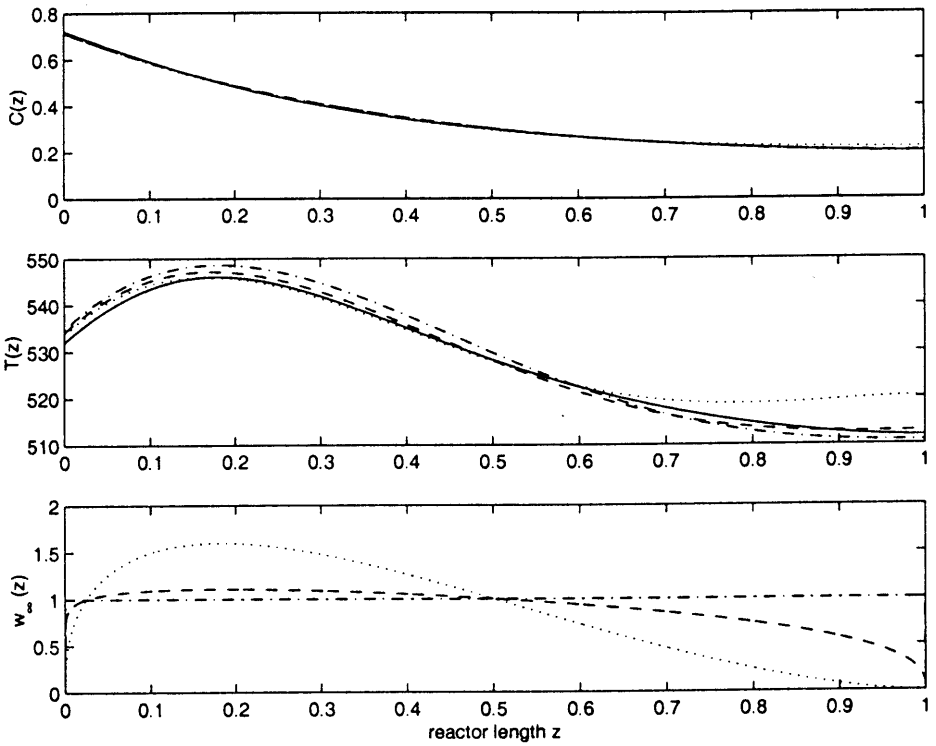

Fig. 3. Concentration (top part) and temperature (middle part) stationary profiles computed both by numerical integration of ODEs (continuous line) and by the three interior points collocation method for several values of the Jacobi parameters, $\alpha = \beta = -1/2$ (dash-dot lines), $\alpha = 1/4$, $\beta = -1/3$ (dashed lines) and $\alpha = 3$, $\beta = 0.2777$ (dot-dot lines). The corresponding weights on the error are represented in the bottom part.

defined by Eq. (42) which reach their maximal value in $\tilde{z}_{\max} = 0.1818$ according to Eq. (43) has been selected. Eq. (43) is, in this case, an equation with two unknowns, the Jacobi parameters α and β. Another equation between these two parameters may be obtained by choosing for instance any measure of the dispersion of the weight on the error around its maximal value. In Fig. 3 hereafter, three cases have been compared, a uniform weight on the error ($\alpha = \beta = -1/2$, see the dash-dot lines in Fig. 3-bottom), a weight centred in $\tilde{z}_{\max}$ but with a high dispersion $\alpha = 1/4$ and $\beta = -1/3$, see the dashed lines in Fig. 3-bottom) and a weight centred in $\tilde{z}_{\max}$ and highly localised around $\tilde{z}_{\max}$ ($\alpha = 3$ and $\beta = 0.2777$, see the dot-dot line in Fig. 3-bottom).

The results confirm what the theory predicts. Indeed a weight highly localised around $\tilde{z}_{\max}$ gives excellent results around this point but causes the solution to diverge significantly away from this point. Note that in the chose example, there are only three interior collocation points and consequently the asymptotic ($N \to \infty$) equi-oscillation behaviour of the error is not reached yet.

It remains now to check if the designed weight which is suitable for error minimisation on the stationary profiles ($\alpha = 1/4$, $\beta = -1/3$) leads also to a reasonable conditioning number and achieves stability of reduced transport component model.

7.4. Stability conditioning of the reduced reactor transport component model

The transport component of the reactor is represented by a matrix in the reduced model. Hence, the discretised transport component operator will be stable if all the eigenvalues of this matrix have negative real

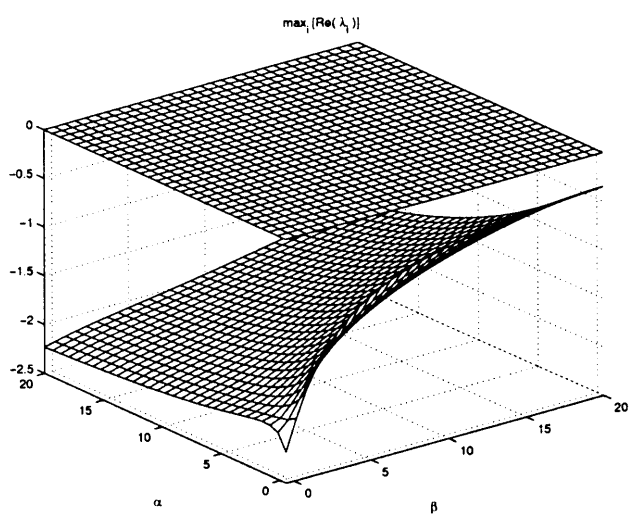

Fig. 4. Real part of the eigenvalue of the reduced transport, component matrix with the largest real part, max[Re$\{\lambda_i\}$]. This real part is computed for three interior collocation points and with α, β ranging from one and half to 20.

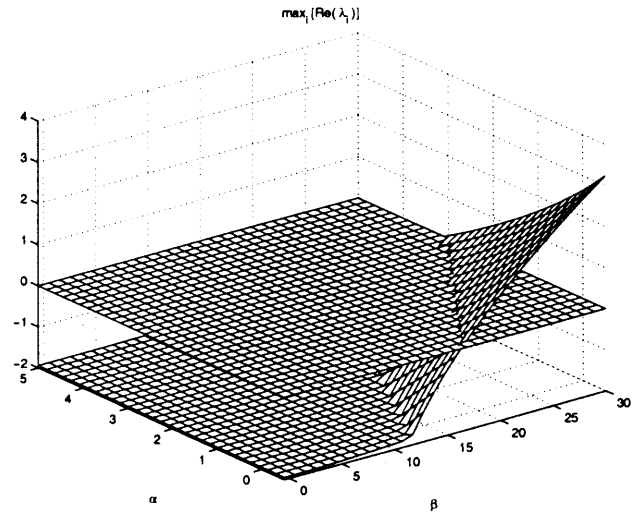

Fig. 5. Real part of the eigenvalue of the reduced transport component matrix with the largest real part, max[Re$\{\lambda_i\}$] . This real part is computed for 5 interior collocation points and when α ranges from $-1/2$ to 5 and β from $-1/2$ to 30.

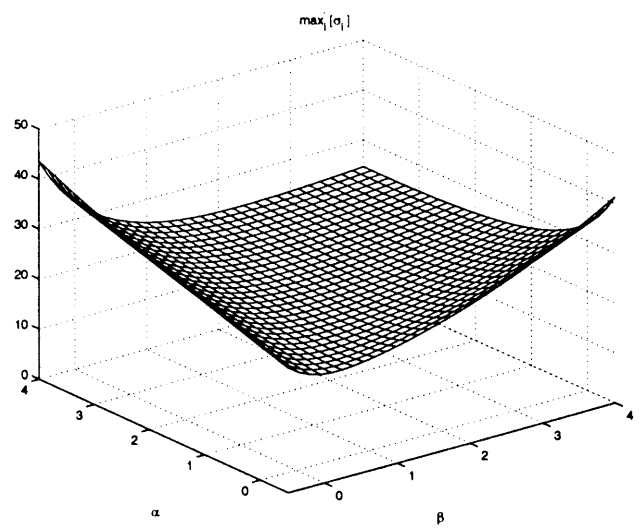

Fig. 6. Largest singular value $\sigma_{\max}$ of the reduced transport component matrix for three interior collocation points, when α and β range from $-1/2$ to 4.

parts. In Fig. 4 hereafter, the real part of the eigenvalue with the largest real part has been plotted, and compared with zero, for different values of the Jacobi parameters α and β and for $N=3$. As it may be seen on this figure when there are only three interior collocation points, instability of the reduced transport component never occurs. This fact has already been noted in Section 3 for the case of a plug-flow reactor. Following comments of this section, one should eventually expect instability problems for more than four interior collocation points. This is indeed the case as it is illustrated in Fig. 5 hereafter where the largest real part of the reduced transport component model with five interior collocation points becomes positive for very large values of β (around 15). However, for a large number of collocation points, this instability problem may occur for reasonably small values of α and β.

Another important point to check before proceeding to the numerical integration of the reduced differential model is to check the conditioning of this system. As it has been explained in Section 5, this conditioning is measured both by the Lipschitz constant of the reaction rate and by the largest singular value of the reduced transport component matrix.

In the chosen reactor example, the Lipschitz constant of the dimensionless reaction rate is about 120 for temperatures between 500 and 600 K and concentrations between 0 and 1 mol/l. For three interior collocation points, the maximum singular value of the reduced transport component matrix is of the same magnitude for reasonable values of the Jacobi Parameters α and β as it is illustrated in Fig. 6 hereafter.

However this maximum singular value increases rapidly with the number of collocation points. The case of ten interior collocation points is represented in Fig. 7 for Jacobi parameters α and β ranging from -0.5 and 4. For large values of either α or β, a very large maximum singular value for the reduced transport component is obtained. Such a choice should be ruled out, since this largest singular value largely exceeds the value of the Lipschitz constant and speeds up the error propagation during the numerical integration of the reduced differential model.

7.5. Simulation run of the reactor dynamic

The issues of the two previous sections suggest a choice of Jacobi parameters around $\alpha = 1/4$ and $\beta = -$

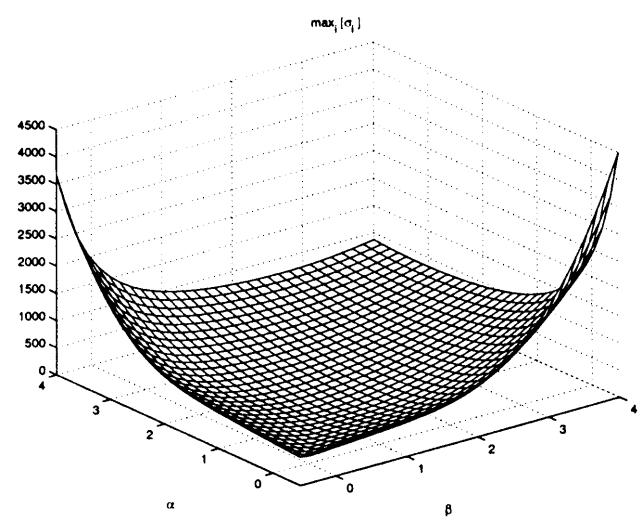

Fig. 7. Largest singular value $\sigma_{\max}$ of the reduced transport component matrix for ten interior collocation points, when α and β range from $-1/2$ to 4.

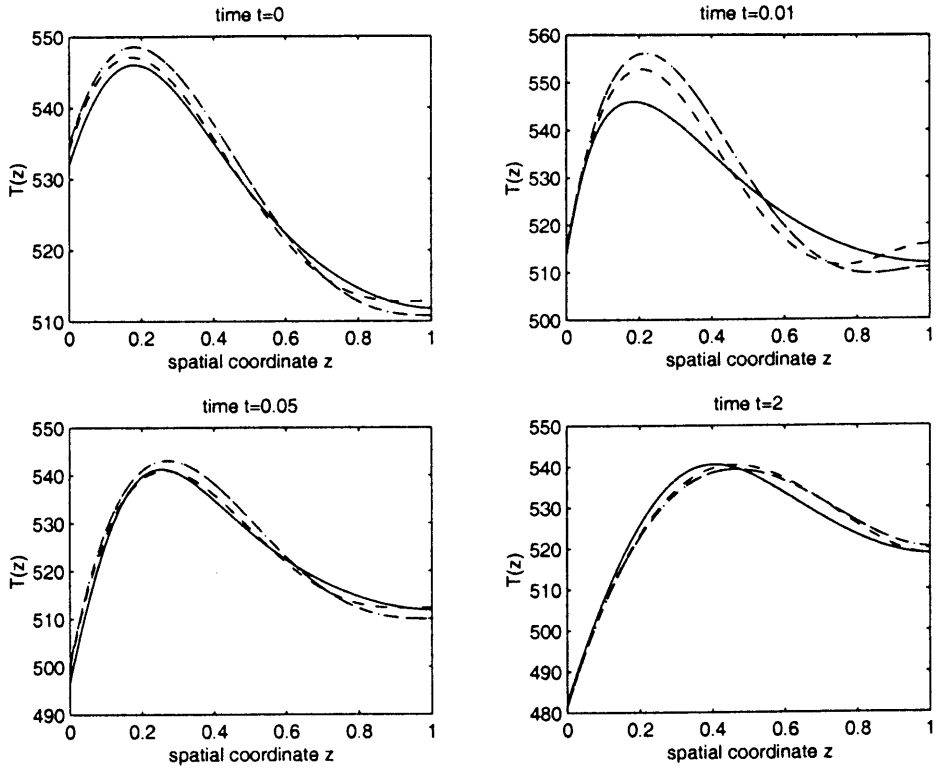

Fig. 8. Dynamical behaviour of the temperature (K) profile at times after a step change in the inlet boundary conditions (continuous lines, reference solution; dashed lines, three interior points collocation with $\alpha = 1/4$ and $\beta = -1/3$; dash-dot lines, three interior points uniformly weighted collocation).

1/3 which achieves satisfying stationary profiles, stability and good conditioning of the reduced dynamical model. It remains now to check if the dynamical behaviour of the reduced model is also satisfying for this choice of Jacobi parameters. We propose a dynamical simulation run with a step change at time $\tilde{t} = 0$ in the inlet boundary conditions, the inlet temperature ratio $\tilde{T}_{in}$ decreases from 1 to 0.85 and the inlet concentration ration $\tilde{C}_{in}$ increases from 1 to 1.15. The temperature and concentration initial conditions are given by the stationary profiles computed previously. The numerical results are given in Fig. 8 hereafter. The reference solution is here computed with a uniformly weighted 28 interior points collocation methods. The resulting reduced differential system (the reference solution and third order ones) are integrated using a simple Runge–Kutta (2, 3) method. The corresponding distances between the reference solution and the three interior points solutions are represented in Fig. 9.

Note the a third order differential model is not able to follow the high-speed variations of the temperature profile after the step change in the inlet boundary conditions (see result at time $\tilde{t} = 0.01$ in Fig. 8), whatever the chosen collocation points are. The delay resulting from this low order approximation is absorbed yet at time $\tilde{t} = 0.05$ (see Fig. 8) where the weighted collocation method is still more accurate than the uniformly wighted one. This improvement lasts till the stabilisation of the temperature profile which is achieved around time $\tilde{t} = 2$ (see Fig. 8).

Note that about the same conclusions apply for the case of eight interior collocation points represented in Fig. 10 hereafter. In this case, the error magnitude is about 30 times lesser than in the case of the three interior points collocation method, but improvement due to the design of a specific error weight and predicted by the theory still remains.

Hence, in this case, and due to the low displacement of the 'hot spot' in the temperature profile, it is not necessary to proceed to a continuous adaptation of the error weight (and consequently of the collocation points) during the numerical integration of the reduced dynamical model.

However, for more important displacements of the hot spot, or for significant changes in the profile shape, this continuous change in the designed weight may be a suitable strategy. We leave this question for further works.

8. Concluding remarks

In the example of Section 7, collocation points have been chosen to be zeros of third order Jacobi polynomi-

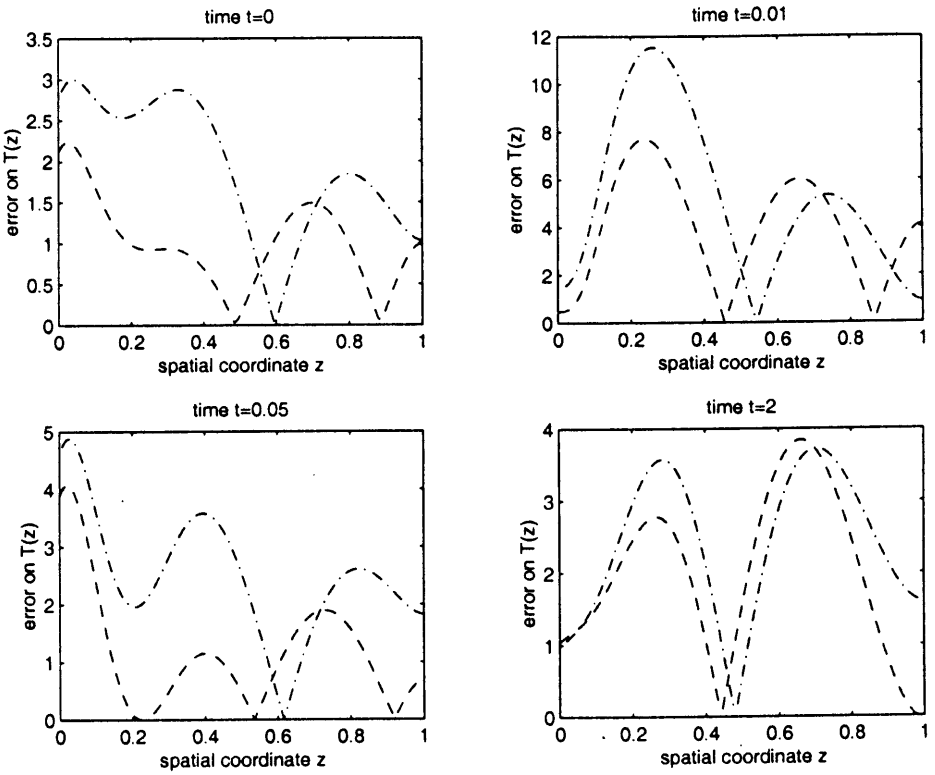

Fig. 9. Distance between the temperature reference solution and the temperature computed by a three interior points collocation with $\alpha = 1/4$ and $\beta = -1/3$ (dashed lines), or by a three interior points uniformly weighted collocation (dash-dot lines).

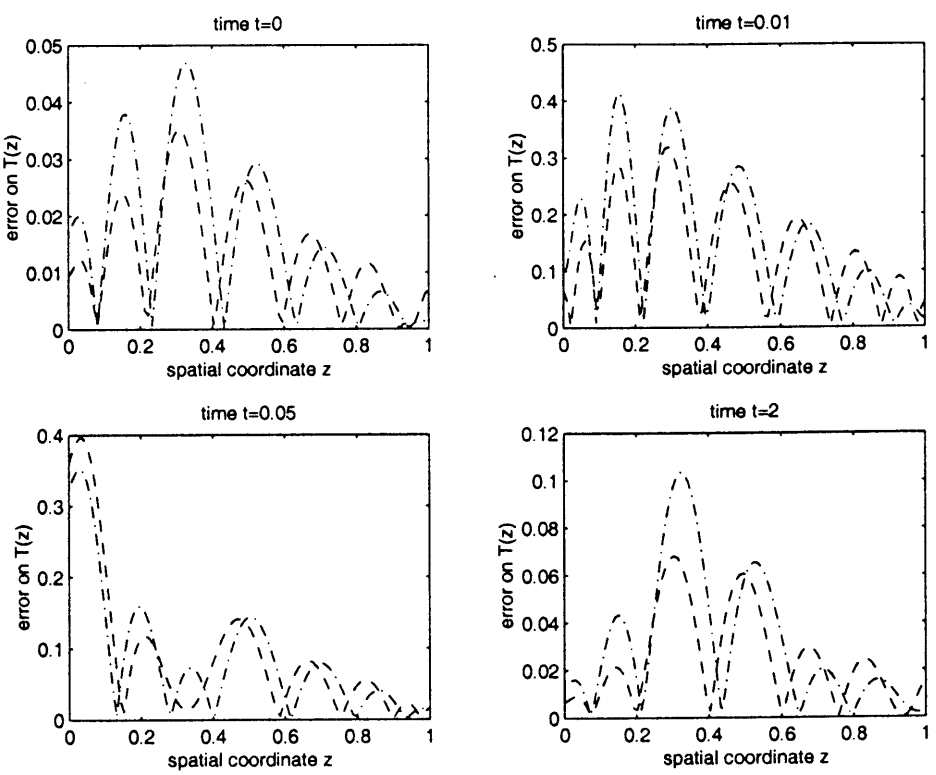

Fig. 10. Distance between the temperature reference solution and the temperature computed by an eight interior collocation with $\alpha = 1/4$ $\beta = -1/3$ (dashed lines), or by an eight interior points uniformly weighted collocation (dash-dot lines).

als (three interior collocation points). As it has been recalled in this paper, this choice leaves two tuning parameters (α and β) which determines the position of these collocation points. Taking into account considerations on conditioning, stability and accuracy developed in this paper, a more systematic approach (than the classical trials and errors methodology) has been adopted to make directly a nearly optimal choice of these parameters. The analysis performed in this paper about the relationship between the choice of collocation points and a weighted minimisation problem (see Section 4.3) has been confirmed by the numerical treatment of this example. Moreover, it has been shown that conditioning and stability of the reduced transport component operator may be translated into constraints on the selection of collocation points.

The method developed in this paper applies not only to seek for optimal Jacobi parameters, but also to design general weight on the interpolation error, and to compute the corresponding collocation points. Yet, as illustrated in Fig. 3, the design of a weight on the error is a complex problem. The numerical results obtained may change consequently for slight variation of the weight function. Consequently, for a general weight $w_\infty(z)$, two dispersion parameters (in the Jacobi case, we used the maximal temperature value and the dispersion of the temperature profile around this value) may not suffice. Theoretically, a wide variety of weight functions may be used. They lead to corresponding families of orthogonal polynomials. The zeros of these orthogonal polynomials may be computed easily and are the collocation points that correspond to the desired minimisation of the interpolation error. Hence, all the computations necesssary to obtain these collocation points may be achieved by using only standard orthogonal polynomial algorithms (see e.g. Powell, 1981). But the use that may be done of this rich variety of choices (weight designs) remains, to the best of our knowledge, an open and interesting problem. The same final remark applies to the use which could be done of a continuous sliding of the collocation points during the numerical integration of the reduced model. We hope that our contribution may help further works on the way to design such a suitable 'continuous sliding'.

Acknowledgements

One of the authors (L.L.) is gratefully acknowledging the support of the European Community (Training and Mobility of Researchers Grant, contract number ERBFMBICT-950582), as well as the support of the 'Fonds National de la Recherche Scientifique' (Belgium), and of the Belgian Programme on Interuniversity Poles of Attraction, initiated by the Belgian State, Prime Minister's Office for Science, Technology and Culture. He would also like to acknowledge Professor Jean Meinguet, from 'Université Catholiqe de Louvain' (Belgium) for his tremendous teachings in numerical analysis, in which he passed on enthusiasm, rigor and sense of mathematical beauty to his students. Finally, we would like to thank the anonymous reviewers for their fruitful comments and their input in several important matters handled in the present paper.

Appendix A. Proof of the generalised alternation theorem

The generalised alternation theorem presented in this paper is a modified version of the famous Chebyshev alternation theorem. This last one was sketched by a few Russian scientists and reported more completely by Chebyshev in 1859. Its final demonstration needed the compactness concept and therefore was achieved only in the 20th century. It is completely reported in Cheney (1966). This last demonstration has been adapted here to fit for the case of a non-uniform weight on the approximation error.

A.1. Sufficient condition

Assume that there is a sequence $\{z_i\}_{i\in 0,\ \ldots,\ N+1}$ with $a \le z_0 < z_1 < \ldots < z_{N+1} \le b$, and Nth order polynomial $\hat{p}$ such that the function $\hat{\mathrm{e}} := (\mathrm{f} - \hat{p})w_\infty$ equi-oscillates and reaches its extrema values for $z = z_i$; that is $\hat{\mathrm{e}}(z_i) = \sigma(-1)^i \|\hat{\mathrm{e}}\|_\infty$ with $\sigma = 1$ or $\sigma = -1$.

Assume (reductio ab absurdum) that there is an Nth order polynomial p which approximates f, strictly better than $\hat{p}$ in the sense of the weighted norm $\|\cdot\|w_\infty$; that is such that $\|f-p\|w_\infty < \|f-\hat{p}\|w_\infty$. In this case, from the decomposition.

$$((\hat{p}-p)w_\infty)(z_k) = ([(f-p)-(f-\hat{p})]w_\infty)(z_k)$$

$$k = 0,\ \ldots,\ N+1$$

$$= \left[\underset{> \|f-p\|w_\infty}{\sigma(-1)^k \|f-\hat{p}\|_{w_\infty}} - \underset{\le \|f-p\|w_\infty}{((f-p)_w)(z_k)} \right]$$

$$k = 0,\ \ldots,\ N+1$$

we may conclude that the function $(\hat{p}-p)w_\infty$ has at least $N+1$ zeros in $[a, b]$. This is also the case of the polynomial $(\hat{p}-p)$, since the weight $w_\infty(z)$ is assumed to take strictly positive values for $z \in [a, b]$. Hence, since $(\hat{p}-p)$ is a polynomial of order N, it is identically zero and $\hat{p} = p$, which contradicts the reductio ab absurdum assumption.

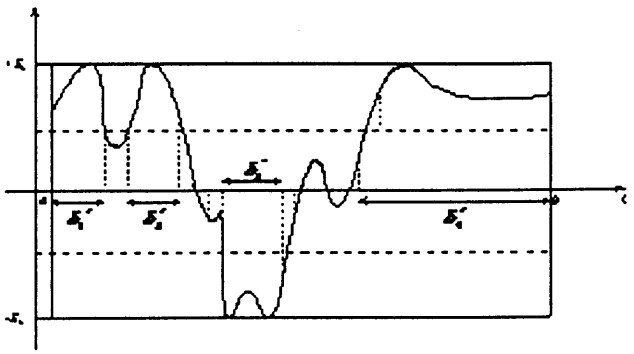

Fig. 11. Subdivision of the interval $[a, b]$, $\Delta_1 := \delta_1^+ \cup \delta_2^+$; $\Delta_2 := \delta_3^-$ and $\Delta_3 := \delta_4^+$.

A.2. Necessary condition

Assume that $\hat{p}$ is the Nth order polynomial of best approximation of a continuous function $f \in C([a, b])$, in the sense of the norm $\|\cdot\|_{w_\infty}$. Let us define the weighted error function $\hat{e} := (f - \hat{p})w_\infty$, and its absolute maximal value $E_N := \|\hat{e}\|_{w_\infty}$.

Then the function reaches the values $+E_N$ and $-E_N$ in $[a, b]$. Indeed, otherwise (reductio ab absurdum), there is a $h > 0$ such that $-E_N + h \le (f - \hat{p})w_\infty + h \le E_N - h$, that is

$$-E_N + h \le \left(f(z) - \left[\hat{p}(z) + \frac{h}{\|w_\infty\|_\infty} \right] \right) w_\infty + h \le +E_N - h \quad \forall z \in [a, b]$$

Hence, the polynomial $\hat{p}(z) + h/\|w_\infty\|_\infty$ is a polynomial of better approximation than $\hat{p}(z)$, which contradicts the assumptions.

This last observation makes sense to the following subdivision of the real interval $[a, b]$. Let $[\alpha_i, \alpha_{i+1}]$ be a subdivision of $[a, b]$ such that $\forall \xi, \eta \in [\alpha_i, \alpha_{i+1}]$, the inequality $|\hat{e}(\xi) - \hat{e}(\eta)| < E_N/2$ holds (uniform continuity of $\hat{e}(z)$). Among these intervals, denote δ_i^+ and δ_i^- those in the closure of which $\hat{e}(z)$ reach, respectively, the values $+E_N$ and $-E_N$. Finally, define the interval Δ_k iteratively, in the following way

$\Delta_1 := \cup \{$first δ_i^+ (or δ_i^-)$|\hat{e}(z)$
$\times$ keeps a constant positive (negative) sign$\}$

$\Delta_2 := \cup \{$next δ_i^- (or δ_i^+)$|\hat{e}(z)$
$\times$ keeps a constant negative (positive)
$\times$ sign, after the first zero of $\hat{e}(z)$.$\}$

$\Delta_{m+1} := \cup \{$next δ_i^- (or δ_i^+)$|\hat{e}(z)$
$\times$ keeps a constant negative or positive)
$\times$ sign, after the first zero of $\hat{e}(z)$.$\}$

Fig. 11 illustrates the subdivision of $[a, b]$, and the consequent definitions of intervals δ_i^+ and δ_i^- and Δ_k. It also illustrates the way the 'candidate' alternating set will be selected, in each $\overline{\Delta_k}$ the points z_k for which $|\hat{e}(z)_k| = E_N$ will be included to this set. Hence, to complete the proof of the theorem it has only to be proved that there is at least $N+2$ points $z_{K,}$ that is $m + 1 \ge N + 2$. This last assertion will be proved, reductio ab absurdum. For this purpose, assume that $m \le N$. In this case, it will be constructively proved that there is a polynomial approximation strictly more accurate than $\hat{p}$, which may be written in the form

$$p(z) = \hat{p}(z) + \lambda q(z) \tag{A.1}$$

where $q(z)$ is an Nth order polynomial in z, which has the same sign than $\hat{e}$ in each $\overline{\Delta_k}$ and λ is a real number.

Let ξ_i, for $i = 1, \ldots, m$, be the zeros of $\hat{e}$. They are, by construction, located in $[a, b] \setminus \left\{ \bigcup_k \overline{\Delta_k} \right\}$ Hence the polynomial

$$q(z) := \sigma \prod_{i=1}^{m} (\xi_i - z) \tag{A.2}$$

(with $\sigma = -1$ or $\sigma = +1$) has the same sign than $\hat{e}$ for any $z \in \left\{ \bigcup_k \overline{\Delta_k} \right\}$. Since our 'absurd' assumption is that $m \le N$, $q(z)$ and $p(z)$ are well defined as Nth order polynomials. In order to point out a suitable λ, let D and $\bar{D}$ be the real domains defined according to $D := (\cup_{k=1}^{m} \Delta_k)$, $\bar{D} := [a, b] \setminus D$ and the constant E'_N according to $E'_N := \sup_{z \in \bar{D}} |\hat{e}(z)| < E_N$. The construction of the subdivision of $[a, b]$ insures that $E_N/2 \le E'_N$, hence $E_N/2 \le E'_N < E_N$. We may, thus, define a constant λ such that

$$0 < \lambda \|q\|_{w_\infty} < E'_N - E_N \tag{A.3}$$

It is now sufficient, to conclude the proof, to show that the polynomial $p(z)$ defined in Eq. (A.1), using the definitions Eqs. (A.2) and (A.3) is a polynomial of better approximation than $\hat{p}(z)$.

It is the case, since

1. If $z \notin D$, then

$$\begin{aligned} |[f(z) - (\hat{p}(z) + \lambda q(z))]w_\infty(z)| &\le E'_N + |\lambda q(z) w_\infty(z)| \\ &\le E'_N + \lambda \|q\|_{w_\infty} \\ &\le E'_N + (E_N - E'_N) \\ &< E_N \end{aligned}$$

2. If $z \in D$, then $\hat{e}(z)$ has the same sign than $q(z)$ hence,

$$\begin{aligned} &|[f(z) - (\hat{p}(z) + \lambda q(z))]w_\infty(z)| \\ &\le |(f(z) - (\hat{p}(z) - \lambda q(z)|w_\infty(z) \\ &\le \|\hat{e}(z)| - |\lambda q(z)|w_\infty(z)| \end{aligned}$$

and, by construction, $|\hat{e}(z)| \in [E_N/2, E_N]$ and $|\lambda q(z)|w_\infty(z) \in [0, E_N/2]$. Hence

$$|[f(z) - (\hat{p}(z) + \lambda q(z))]w_\infty(z)| < E_N$$

Appendix B. Proof of the continuous dependence theorem

This proof is only an adaptation of a classical result on the continuous dependence of the solution of non-linear problems relatively to data of this problem. The demonstration has been adapted from standard arguments which are developed in Gottlieb and Orszag (1977), in order to make use of the specific structure of the reduced differential problem (a linear part for the transport component and a non-linear one for the reaction rate). Its main idea is to develop a differential inequality which characterises the evolution of the distance $\mathrm{d}(t) := v(t) - u(t)$ between the solution of the problem Eq. (44) and the solution of the perturbed problem Eq. (46). This distance is continuously differentiable, since so are the two functions $u(t)$and $v(t)$. Hence, it is the solution of a new differential problem.

$$\begin{cases} \dfrac{\mathrm{d}(d)}{\mathrm{d}t} = Md + F(v) - F(u) + \delta(t) \\ d(0) = v(0) - u(0) = \delta_0 \end{cases} \tag{B.1}$$

Choosing an euclidean vector norm $\| \cdot \|_2$ and defining, classically, its associated matrix norm by

$$\|M\|_2 := \sup_{\|x\|=1} \|Mx\|_2 \tag{B.2}$$

a new differential inequality (scalar), giving an upper bound for the error, may be derived from the system Eq. (B.1),

$$\begin{cases} \left\| \dfrac{\mathrm{d}(d)}{\mathrm{d}t} \right\|_2 \le (\|M\|_2 + L_F)\|d(t)\|_2 + \|\delta(t)\|_2 \\ \|d(0)\|_2 = \|\delta_0\|_2 \end{cases} \tag{B.3}$$

Now observe that

$$\begin{aligned} \|d(t) - d(0)\|_2 &= \left(\left\| \int_0^t d'(\tau)\mathrm{d}\tau \right\|_2^2 \right)^{1/2} \\ &\le \left(\sum_i \int_0^t (d_i'(\tau))^2 \mathrm{d}\tau \right)^{1/2} \\ &= \left(\int_0^t \|d'(\tau)\|_2^2 \mathrm{d}\tau \right)^{1/2} \\ &\le \int_0^t \|d'(\tau)\|_2 \mathrm{d}\tau \end{aligned} \tag{B.4}$$

and that $\|d(t)\|_2 \le \|d(t) - d(0)\|_2 + \|d(0)\|_2$. Defining the auxiliary function $w(t) := \int_0^t \|d'(\tau)\|_2 \, \mathrm{d}\tau$, the differential inequality Eq. (B.3) may be written (with the help of inequality Eq. (B.4), in the form

$$\begin{cases} \dfrac{\mathrm{d}w}{\mathrm{d}t} \le (\|M\|_2 + L_F)(w(t) - \|\delta_0\|_2) + \|\delta(t)\|_2 \\ w(0) = 0 \end{cases} \tag{B.5}$$

In order to simplify the writing of further derivations, let us define the following notations

$$\delta_0 := \|\delta_0\|_2; \quad \delta_\infty := \max_{t \in \Re^+} \|\delta(t)\|_2; \quad \kappa := \|M\|_2 + L_F \tag{B.6}$$

With these notations, the differential inequality Eq. (B.5) may be written

$$\begin{cases} \dfrac{\kappa(\mathrm{d}w/\mathrm{d}t)}{\kappa w + \kappa\delta_0 + \delta_\infty} \le \kappa \\ w(0) = 0 \end{cases} \tag{B.7}$$

And after integration of this last differential inequality on [0, t],

$$w(t) \le \left(\frac{e^{\kappa t} - 1}{\kappa} \right)(\kappa\delta_0 + \delta_\infty) \tag{B.8}$$

Finally, observe from Eq. (B.4) that

$$w(t) \ge \|d(t) - d(0)\|_2 \ge \|d(t)\|_2 - \|d(0)\|_2$$

Hence,

$$\begin{aligned} \|d(t)\|_2 &\le w(t) + \|d(0)\|_2 = w(t) + \delta_0 \\ &\le \delta_0 e^{\kappa t} + \delta_\infty \left(\frac{e^{\kappa t} - 1}{\kappa} \right) \end{aligned} \tag{B.9}$$

To conclude the proof, we use the well known Courant–Fischer representation of $\|M\|_2$ (see, e.g. Stewart and Sun, 1990),

$$\|M\|_2^2 := \sup_{\|x\|_2=1} \|Mx\|_2^2 = \max_{\|x\|_2=1} x^T M^T M x = \tilde{\sigma}^2(M) \tag{B.10}$$

References

Bourrel, S., Dochain, D., Babary, J. P., & Queinnec, I. (2000). Modeling, identification and control of a denitrifying biofilter. *Journal of Process Control*, *10*, 73–91.

Calogero, S. (1985). Some applications of a convenient finite-dimensional matrix representation of the differential operator. *Rendiconti del seminario matematico*, 23–61.

Cheney, E. W. (1966). *Introduction to Approximation Theory*. New York: McGraw-Hill.

Cho, Y. S., & Joseph, B. (1983). Reduced-order steady state and dynamic models, Parts I & II. *American Institute of Chemical Engineering Journal*, *29*(2), 261–276.

Danckwerts, P. V. (1953). Continuous flow systems. Distribution of residence times. *Chemical Engineering Science*, *2*(1), 1–13.

Davis, P. J. (1975). *Interpolation and Approximation*. Blaisdell.

Deen, W. M. (1987). Hindered transport of large molecules in liquid-filled pores. *American Institute of Chemical Engineering Journal*, *33*(9), 1409–1425.

Dochain, D. (1994). Contribution to the analysis and control of distributed parameter systems with application to (bio)chemical processes and robotics. In *Thèse d'Aggrégation de l'Enseignement Supérieur*. Belgium: Université Catholique de Louvain.

Dochain, D. & Winkin, J. (1995). Dynamical analysis of a class of distributed parameter fixed bed reactors. *Proceedings of CDC 95*, 3225–3230.

Dochain, D., Tali Maamar, & Babary, J. P. (1997). On modeling, monitoring and control of fixed bed reactors. *Comparative Chemical Engineering*, *21/11*, 1255–1266.

Erdelyi, T., Magnus, A. P. Nevai, P. (1994). Generalised Jacobi weights, Christoffel functions and Jacobi polynomials. *SIAM Journal of Mathematical Analysis*, *25 (2)*, 602–614, 1461.

Feyo de Azevedo, S., Romero-Ogawa, M. A., & Wardle, A. P. (1990). Modelling of tubular fixed-bed catalytic reactors: a brief review. *Transactions on I. Chemical Engineering*, *68*(A), 2–8.

Finlayson, B. A. (1971). Packed bed reactor analysis by orthogonal collocation. *Chemical Engineering Science*, *26*, 1081–1091.

Finlayson, B. A. (1972). *The method of weighted residuals and variational principles*. New York: Academic Press.

Finlayson, B. A., & Scriven, L. E. (1965). The method of weighted residuals and its relation to certain variational principles for the analysis of transport processes. *Chemical Engineering Science*, *20*, 395–404.

Fornberg, B. (1996). *A practical guide to pseudospectral methods*. Cambridge: Cambridge University Press.

Gay, D. H. (1989). Identification and control of distributed parameters systems by means of the singular value decomposition. Ph.D. thesis, University of Wisconsin.

Georgakis, C., Aris, R., & Amundson, R. (1977). Studies in the control of tubular reactors-I. General considerations. *Chemical Engineering Science*, *32*, 1359–1369.

Gottlieb, D., & Orszag, S. A. (1977). Numerical analysis of spectral methods. *SIAM Conference Ser. Applied Mathematics*, *26*.

Khanna, R., & Seinfeld, J. H. (1987). Mathematical modelling of packed bed reactors: numerical solutions and control model development. *Advances in Chemical Engineering*, *13*, 113–191.

Jorgensen, S. B. (1986). Fixed bed reactor dynamincs and control — a review. In *Proc. IFAC Control of Distillation Columns and Chemical Reactors* (pp. 11–24). Oxford: Pergamon.

Jutan, A., Tremblay, J. P., MacGregor, J. F., & Wright, J. D. (1977). Multivariable computer control of a butane hydrogenolysis reactor. *AIChE J.*, *23*(5), 732–742.

Langmuir, I. (1908). The velocity of reactions in gases moving through heated vessels and the effect of convection and diffusion. *J. Am. Chem. Soc.*, *30*, 1742–1754.

Lefèvre, L. (1998). *Specific numerical algorithms used in the PDE's reduction method*. Internal report CESAME.

Michelsen, M. L., & Villadsen, J. (1972). A convenient computational procedure for collocation constants. *Chem. Eng. J.*, *4*, 64–68.

Powell, M. J. D. (1981). *Approximation theory and methods*. Cambridge: Cambridge University Press.

Ralston, A., & Rabinowitz, P. (1978). *A first course in numerical analysis*. New York: McGraw-Hill.

Ray, W. H. (1981). *Advanced process control*. Boston, MA: Butterworths.

Segall, N. L., MacGregor, J. F., & Wright, J. D. (1984). Collocation methods for solving packed bed reactor models with radial gradients. *Can. J. Chem. Eng.*, *62*, 808–817.

Stewart, W. E. & Sorensen, J.P. (1972). Transient reactor analysis by orthogonal collocation, *Proc. 5th European Symposium on Chemical Reaction Engineering*, Amsterdam, B8, pp. 75–87.

Stewart, G. W., & Sun, J. (1990). *Matrix perturbation theory*. New York: Academic Press.

Villadsen, J. V., & Stewart, W. E. (1967). Solution of boundary-value problems by orthogonal collocation. *Chem. Eng. Sci.*, *22*, 1483–1501.

Waldraff, W., Dochain, D., Bourrel, S., & Magnus, A. (1998). On the use of observability measures for sensor location in tubular reactors. *J. Process Control*, 497–505

Winkin, J., Dochain, D., & Ligarius, Ph. (2000). Dynamical analysis of a class of distributed parameter tubular reactors. *Automatica*, *36*(3), 349–361.