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Numerical Simulation of Macromolecular Kinetics – Recent Developments

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Abstract

The mathematical modeling of macromolecular reactions leads to countable (possibly infinite) systems of ordinary differential equations (ODE's). This paper reviews two recent developments of the so-called discrete Galerkin method, which has been developed for the numerical treatment of countable systems, which arise e.g. in polymer chemistry. The first approach can be considered as a method of lines with moving basis functions and has been implemented recently in the program package MACRON. The second type of the Galerkin method is characterized by a so-called outer time discretization of the complete problem and an appropriate and efficient solution of the arising subproblems. This method is realized in the research code CODEX.

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1 Introduction

The mathematical modeling of macromolecular reactions leads to *countable* (possibly *infinite*) *systems of ordinary differential equations* (CODE's), describing e.g. the chain length distribution (CLD) of a polymer. The discrete Galerkin method for the numerical treatment of such problems has been suggested first by DEUFLHARD/WULKOW [5]. Since then this approach has been developed to a standard, which now allows the implementation in program packages. The discrete Galerkin method approximates the solution of a CODE by an error-controlled expansion into orthogonal polynomials of a discrete variable, which are generated by a weight function.

In the present summary two versions of the discrete Galerkin method are presented, which imply two different numerical concepts. In Section 2, the method is used in the context of a *method of lines* with *moving basis functions* as suggested in [5]. The problem is discretized first by an expansion into orthogonal polynomials, the resulting differential equations for the expansion coefficients are then numerically integrated in time. This approach has been successfully applied to practical examples [3], [7] and is implemented now in the package MACRON by ACKERMANN/WULKOW [1]. MACRON supplies the possibility of a fast numerical treatment of certain classes of realistic problems from polymer chemistry, soot formation and other fields.

A reversed order of approximation is applied in Section 3. The complete countable system is discretized in time first (*outer time discretization*), the arising stationary subproblems are solved by an extended Galerkin method using a two-parameter family of weight functions. The resulting research code CODEX by WULKOW [6] has, compared to MACRON, conceptual advantages concerning flexibility and reliability, but is not yet implemented for wide use.

Details of the presentation can be found in the literature referred to at the end of this paper.

2 Discrete Galerkin Method I – MACRON

Let $u_s(t)$ denote the concentration (or number) of macromolecules (e.g. polymer molecules) of chain length or size s at a time t . The sequence $u_1(t), u_2(t), \dots$, can be considered as a *chain length distribution*. The kinetics of a macromolecular reaction process (neglecting additional chemical reactions) can be expressed by a countable system of ordinary differential equations of the form (the prime denotes the derivative with respect to the time t):

$$u'_s(t) = f_s(u_1(t), u_2(t), \dots) \quad , \quad s = 1, 2, \dots, \quad (1)$$

in terms of right-hand side functions f_s . An initial distribution $u_s(0)$ is given. The index s may formally range up to infinity and is set to about $10^4 - 10^6$ in realistic examples.

Assume that the distribution $u_s(t)$ can be expanded in a series

$$u_s(t) = \Psi_\rho(s) \sum_{k=0}^{\infty} a_k(t) l_k(s; \rho) \quad , \quad s = 1, 2, \dots, \quad (2)$$

where $\Psi_\rho(s)$ is a positive weight function with a (possibly time-dependent) real parameter ρ and the $l_k(s; \rho)$, $k = 0, 1, \dots$, are polynomials of a *discrete* variable s . These polynomials are associated with $\Psi_\rho(s)$ by the *orthogonality relation*

$$\sum_{s=1}^{\infty} l_j(s; \rho) l_k(s; \rho) \Psi_\rho(s) = \begin{cases} \gamma_k^\rho, & \text{if } j = k \\ 0, & \text{if } j \neq k \end{cases} \quad , \quad \gamma_k^\rho > 0 \quad , \quad j, k = 0, 1, 2, \dots \quad (3)$$

Truncation of the expansion (2) after $n+1$ terms leads to a *Galerkin approximation*

$$u_s^n(t) := \Psi_\rho(s) \sum_{k=0}^n a_k(t) l_k(s; \rho) \quad , \quad s = 1, 2, \dots, \quad (4)$$

depending on the parameter ρ and the *truncation index* n . As pointed out in [5], the (projection) error of the approximation (4) can be efficiently estimated.

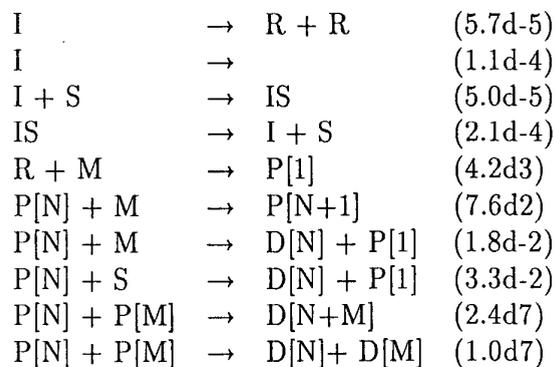
By inserting expansion (2) into the system (1) and by use of certain analytical properties of the orthogonal polynomials (see e.g. [6]), a (comparatively small) system of ordinary differential equations (ODE's) for the expansion coefficients $a_k(t)$ can be derived. This procedure is called *analytical preprocessing*.

In many applications the weight function $\Psi_\rho(s)$ can be chosen as the geometric (in polymer chemistry also called *Schulz-Flory*) distribution with parameter ρ . This distribution is associated with the *discrete Laguerre polynomials*. The selection of the parameter $\rho = \rho(t)$ is done adaptively on the basis of the so-called *moving weight function* concept [5], [6]. This leads to small truncation indices ($n \approx 10$) in many cases and to a fast and efficient treatment of reactions connected in some way

(e.g. characterized by the dispersion coefficient) with a Schulz-Flory distribution. For other types of processes at least the statistical moments and hints about the form of the distribution can be gained (see discussion and examples in [1]). In order to obtain more reliability, the modified weight function $\Psi_{\rho,\alpha}(s)$ from Section 3 below can be used for an additional a posteriori error control.

The *realization* of the above ideas requires an insight into analytical and numerical details of the method, which can not be expected from a user in a field of application. Thus the program package MACRON (MACROmolecular reaction kiNETics) [1] has been developed. The package is written in FORTRAN and available for workstations and personal computers. MACRON combines the discrete Galerkin techniques for the simulation of macromolecular reaction with standard software for the treatment of chemical reactions. In particular the chemical compiler from the simulation package LARKIN by DEUFLHARD/NOWAK [4], which has originally been written for LARge chemical KINetics, has been extended. The reaction equations, standard kinetics as well as polymerization steps, can be entered by the user in the chemical formalism. The analytical preprocessing required to perform the discrete Galerkin method is done automatically. The numerical standard of the routines build within the package (solution of ordinary differential equations by high sophisticated ODE solvers, pointwise evaluation of the Galerkin approximation by a stable summation algorithm, appropriate scaling and error norms) make the program very efficient. The application of MACRON is in particular recommended, if a repeated computation of a fixed process has to be done.

A part of an input file for MACRON is presented next.



Free radical polymerization system, part of a MACRON input

In this example, $\text{P}[N]$ denotes a radical polymer of degree N , $\text{D}[N]$ denotes a dead polymer. The actual notation is left to the user and not restricted. For reversible reactions the reverse rate coefficient can be computed via the equilibrium constant, whenever no kinetic parameters are explicitly given and thermodynamic data are available. By choosing an appropriate model parameter, thermodynamic

can be included. Up to now there are six different models possible, like constant (prescribed time-dependent) temperature, constant (prescribed time-dependent) density, constant (prescribed time-dependent) pressure.

A number of typical macromolecular reaction steps (chain addition, transfer reactions, termination processes) is implemented. Due to the modular character of the method, additional steps can easily be added (if analytically preprocessable). The size of a chemical system, determined by the number of polymer species, other chemical species and reaction steps, is only restricted by the available computer memory.

Note, that the complete reaction mechanism is checked in view of *stoichiometric* plausibility.

As illustrated in [1], realistic problems can be solved with MACRON, e.g. *free radical polymerization, soot formation in flames and plasma etching in semi conductor production.*

3 Discrete Galerkin Method II – CODEX

The concept of a method of lines realized in MACRON and the restricted choice of the weight function has some conceptual limitations :

- missing analytical properties (e.g. for reaction steps with chain length dependent rate coefficients) cannot be replaced by numerical approximations, because this induces perturbations on the right-hand side of the differential equations for the Galerkin coefficients a_k and destroys the order- and time-step control of a numerical integration code.
- expensive approximation (i.e. large truncation index n in (4)) arises for processes with a solution ‘far’ from the Schulz-Flory distribution, i.e. for very peaked or very broad distributions.

The new approach to be presented here is based on two concepts, which are related to the above two points. In order to overcome the first difficulty we apply a so-called outer time discretization of a linear countable system:

$$u'(t) = Au(t), \quad u(0) = u_0, \quad (5)$$

with $u(t) = (u_1(t), u_2(t), \dots)$ the distribution to be computed and A a very large, possibly infinite matrix, which is typically not sparse. The discretization of (5) at time t by means of the well-known *implicit Euler scheme* with step-size τ leads to a *countable system of algebraic equations* (CAE)

$$(I - \tau A) \tilde{u}(t + \tau) = u(t) \quad (6)$$

The solution $\tilde{u}(t + \tau)$ of this (generally infinite) system is the approximation of the exact solution u at time $t + \tau$. If one can compute $\tilde{u}(t + \tau)$ exactly, then a time-control of the complete system (5) – as known in algorithms for the solution of ordinary differential equations – will be possible. Fortunately it turns out, that (6) needs to be solved only up to an accuracy TOL, which is prescribed by the outer time discretization. If this accuracy TOL is achieved, the order- and time-step control, even with extrapolation in time, is not affected. This strategy has been developed by BORNEMANN [2] for parabolic partial differential equations (PDE’s) and applied to CODE’s in [6]. As a consequence, the solution $\tilde{u}(t + \tau)$ in each time-step may be represented by an appropriate Galerkin approximation \tilde{u}^n . Note that the type of this approximation is open at this point. In the following one possible choice will be discussed.

The modified weight function

$$\Psi_{\rho, \alpha}(s) = (1 - \rho)^{1+\alpha} \binom{s-1+\alpha}{s-1} \rho^{s-1}, \quad (7)$$

with parameters $0 < \rho < 1$ and $\alpha > -1$ has the following properties for special choices of ρ and α :

For $\alpha = 0$, $\Psi_{\rho,\alpha}(s)$ is the Schulz-Flory distribution.

For $\alpha = \lambda/\rho$ and $\rho \rightarrow 0$, $\Psi_{\rho,\alpha}(s)$ converges to a Poisson distribution with parameter λ .

For $\alpha < 0$ and $\rho \rightarrow 1$, $\Psi_{\rho,\alpha}(s)$ approximates a hyperbola of the form $1/s^\alpha$.

An examination of the dispersion coefficient d of $\Psi_{\rho,\alpha}(s)$ turns out, that it is possible to vary d continuously from $d = 1 + \varepsilon$, $\varepsilon > 0$, to $d \rightarrow \infty$ dependent on ρ and α . The truncation index n can be kept small by a choice of ρ and α based on an extended moving weight function concept. The weight function (7) generates the so-called *modified* discrete Laguerre polynomials $l_k(s; \rho, \alpha)$ by an expression similar to (3).

Insertion of the expansion

$$\tilde{u}_s^n := \Psi_{\rho,\alpha}(s) \sum_{k=0}^n a_k l_k(s; \rho, \alpha), \quad (8)$$

into (6) leads to an algebraic linear system (called *Galerkin equations*) for the coefficients a_k . In each time-step the index n and the parameters ρ and α are adapted due to an error control mechanism. The total error ε_n of the Galerkin approximation (8) and the error of the time integration can be controlled separately. Moreover, if one splits ε_n into two parts by writing:

$$\varepsilon_n^2 = \varepsilon_{n,P}^2 + \varepsilon_{n,C}^2$$

where $\varepsilon_{n,P}$ denotes the pure projection error and $\varepsilon_{n,C}$ an error introduced by possible perturbations of the coefficients a_k , it is obvious that $\varepsilon_{n,C} > 0$ does not affect the time-control and the extrapolation as far as the condition $\varepsilon_n < TOL$ is fulfilled. This implies the important fact, that analytical properties of the orthogonal polynomials can be replaced by numerical approximations and makes the discrete Galerkin method II applicable to general classes of problems. The required numerical evaluations of very large or infinite sums as in (3) are performed by an adaptive *multilevel summation algorithm* called SUMMATOR described in [6].

The program CODEX (*C*ountable systems of *O*rdinary *D*ifferential *E*quations by *eX*trapolation) is a research code written in the language C and has the following features:

- order- and step-size control in time
- global error control of the solution

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- adaptivity of the parameters ρ and α
 - adaptivity of the truncation index
 - numerical preprocessing possible
 - treatment of nonlinear problems using a *semi-implicit* Euler discretization

The algorithm is *fully adaptive*, i.e. the desired tolerance of the solution leads to automatic choices of order and time-steps, of truncation index and parameters in the Galerkin method and of the tolerance for the numerical preprocessing performed by the SUMMATOR. The time control uses extrapolation in time to obtain higher orders of discretization and an extended moving weight function concept for the choice of the parameters. In each Euler time-step the Galerkin equations are generated using analytical properties as in MACRON (as far as possible) or numerical preprocessing.

With the first version of CODEX interesting realistic models could be treated, in particular heterogeneous degradation processes and coagulation reactions from soot formation with very difficult reaction rate coefficients.

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