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**Towards an Efficient Computational Treatment
of
Heterogeneous Polymer Reactions**

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Abstract

The discrete Galerkin method developed by the authors has turned out to be an efficient tool for the computational treatment of very large scale ODE systems arising in polyreaction kinetics. Up to now, this approach has been worked out in detail for homogeneous polymer reactions. The present paper deals with one line of possible extensions of the method to the case of so-called heterogeneous processes, which may appear e. g. in smog reactions. The associated mathematical models involve reaction coefficients depending on the chain length of the reacting polymer. The herein suggested extension is worked out in some detail on the basis of the earlier paper. In addition, a numerical example describing polymer degradation is included.

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0. Introduction

The mathematical modeling of polymer reaction kinetics naturally leads to countable infinite systems of ordinary differential equations. Approximations of finite dimensions will have to represent at least the maximum relevant polymer chain length, which may range from 10^4 to 10^6 in cases of practical interest. One of the most efficient computational techniques for such systems has recently been suggested by the authors in [7]. The approach advocated therein is a Galerkin method based on orthogonal polynomials of a discrete variable. In this context that discrete variable represents the polymer chain length or polymer degree. The efficiency of the method has been exemplified in terms of typical model problems in [7] and for a real life reaction system (MMA polymerization) in [4].

However, the above articles do not cover the situation when the reaction rate coefficients depend on *fractional* powers of the polymer degree – a typical feature of so-called *heterogeneous* reactions such as soot formation [8], gel-effect modeling for free radical polymerization systems [13] or polymer degradation [2]. The aim of the present paper is to work out a possible extension of the discrete Galerkin method to this important class of problems. For this purpose a special modification of the so-called discrete Laguerre polynomials is introduced first in Section 1. In Section 2 the analytical properties of these polynomials are applied to an analytic preprocessing of a heterogeneous degradation process. Finally, in Section 3, numerical results are presented.

1. Modified Discrete Laguerre Polynomials

Let $s \in \mathbf{N}$ denote a discrete variable and $\Psi(s)$ a (positive) weight function. Then, by virtue of the discrete inner product

$$\begin{aligned} (f, g) &:= \sum_{s=1}^{\infty} f(s)g(s)\Psi(s), \\ f, g &: \mathbf{N} \rightarrow \mathbb{R}, \end{aligned} \tag{1.1}$$

a separable Hilbert space H_{Ψ} can be constructed under some mild theoretical assumptions on the weight function Ψ . This weighted sequence space may be spanned by a set of orthogonal polynomials $\{l_k\}_{k \geq 0}$ as basis functions. In connection with the discrete Galerkin method suggested in [7], the weight function Ψ may be normalized to be a probability distribution. In this way, the *geometrical* distribution generates the discrete Laguerre polynomials, whereas the *Poisson* distribution leads to the Charlier polynomials – for details see [7].

As will be shown in Section 2 below, some applications require the evaluation of scalar products of the form

$$(s^{-\alpha} l_k, l_j) = \sum_{s=1}^{\infty} s^{-\alpha} l_k(s) l_j(s) \Psi(s), \tag{1.2}$$

where the polynomials $l_k(s)$ are orthogonal with respect to the scalar product (1.1). The fractional power $s^{-\alpha}$, $0 \leq \alpha < 1$ arises from the modeling of certain chemical processes mentioned in the introduction. The task is then the analytical computation of the expressions in (1.2). In order to do that one may proceed as follows : For a given set of orthogonal polynomials $\{l_k\}$ connected with a weight function Ψ one tries to construct modified polynomials $\{l_k^{\alpha}\}$ which are orthogonal with respect to a scalar product with weight function

$$\hat{\Psi}(s) := \frac{\Psi(s)}{s^{\alpha}}, \quad 0 \leq \alpha < 1. \tag{1.3}$$

Then analytical relations between both polynomial systems can be derived, which permit an easy and convenient computation of (1.2).

From the classical case of a *real* variable s it is well known, that such a modification can be done successfully. As an example let $\Psi(s) = e^{-s}$, the associated polynomials being the Laguerre polynomials $L_k(s)$ (after substituting the sum in definition (1.1) by an integral, of course). Then $\hat{\Psi}$ generates the modified Laguerre polynomials $L_k^{\alpha}(s)$. The construction of the $L_k^{\alpha}(s)$ is a straightforward extension

of the polynomials $L_k(s)$, if one uses standard techniques for orthogonal polynomials (such as the Rodrigues formula).

Things turn out to be more complicated for a *discrete* variable s . In principle, $\hat{\Psi}$ would generate a set of orthogonal polynomials as well (defined by means of a Gram-Schmidt orthogonalization) – however, without convenient analytical properties. Basically the reason for this undesirable occurrence is that the factor $s^{-\alpha}$ nicely goes with the differential operator D in the Rodrigues formula for classical orthogonal polynomials. The construction of orthogonal polynomials of a discrete variable requires the validity of a discrete Rodrigues formula in terms of the difference operator $(\Delta f)(s) := f(s+1) - f(s)$ instead of D . The difference operator, in turn, naturally goes with the so-called *factorial powers*

$$\frac{1}{(s-1)^{(\alpha)}} := \frac{\Gamma(s-\alpha)}{\Gamma(s)} = \binom{s-1-\alpha}{s-1} \Gamma(1-\alpha), \quad (1.4)$$

with Γ the classical Gamma-function. These factorial powers can be regarded as asymptotic approximations of real powers.

Lemma 1 *Let $1/(s-1)^{(\alpha)}$ be defined as above. Then for $\alpha < 1$ and $s \gg 1$ the following estimation holds:*

$$\ln \frac{s^\alpha}{(s-1)^{(\alpha)}} = \frac{\alpha(1+\alpha)}{2s} + \mathcal{O}(1/s^2) \quad (1.5)$$

Proof. Straightforward application of Stirling's formula [3]:

$$\ln \Gamma(s) \doteq (s-1/2) \ln(s-1) - s + 1 + \ln \sqrt{2\pi} \quad (1.6)$$

and Taylor expansion of \ln around argument 1. ■

As an illustration of the lemma the approximation $1/(s-1)^{(\alpha)}$ is compared with $s^{-\alpha}$ in Fig. 1 for several α -values of practical interest. The straight lines indicating the factorial powers intersect roughly at $s = 2$. Already for $s = 5$ the approximation is correct up to 5% for the case $\alpha = 1/3$ regarded in Section 2.

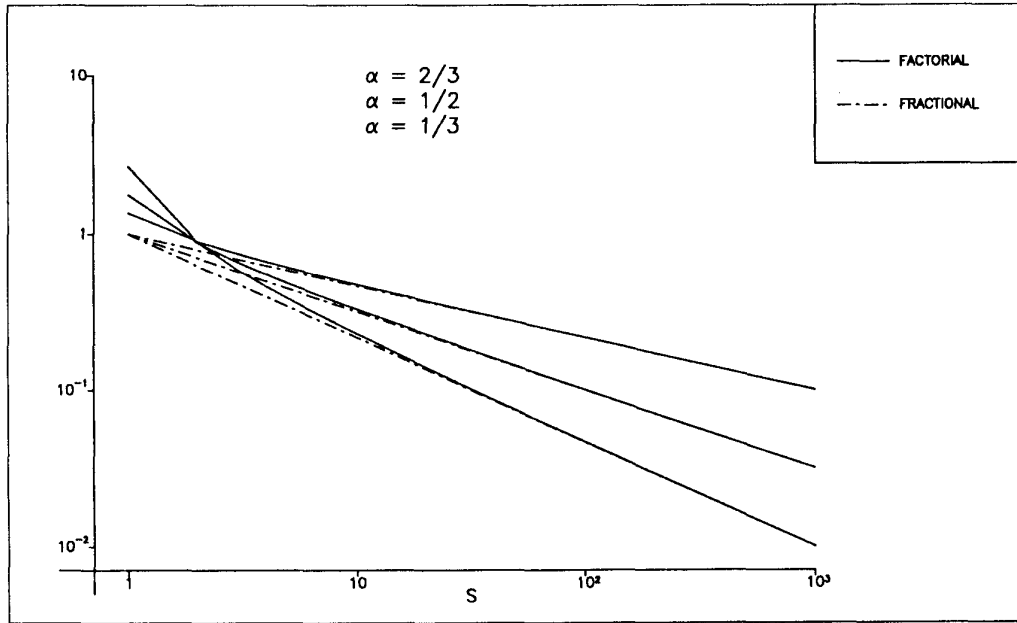


Figure 1: Fractional versus factorial powers for $\alpha = \frac{1}{3}, \frac{1}{2}, \frac{2}{3}$.

As the polymer models under consideration are also only asymptotically correct in the factor $s^{-\alpha}$, one may take the freedom to replace $\hat{\Psi}$ from (1.3) by weight functions of the type

$$\hat{\Psi}(s) := \frac{\Psi(s)}{(s-1)^{(\alpha)}} = \Psi(s) \frac{\Gamma(s-\alpha)}{\Gamma(s)}, \quad s = 1, 2, \dots \quad (1.7)$$

This modification opens the door to exploit associated special functions with nice analytical properties, which are essentially known in modern literature [12].

The most promising candidates in the present context are the *modified discrete Laguerre* polynomials $l_k^\alpha(s; \rho)$, $s \in \mathbb{N}$, which have been studied by LESKY ([10],[11]) as a discrete analog of the classical polynomials $L_k^\alpha(s)$, $s \in \mathbb{R}$. They can be interpreted as special *Meixner* polynomials – see e.g. the recent textbook of NIKIFOROV, UVAROV [12]. The associated *normalized weight function* is

$$\Psi(s; \rho, \alpha) := \frac{C(\rho, \alpha)}{(s-1)^{(\alpha)}} \cdot (1-\rho)\rho^{s-1}, \quad 0 < \rho < 1, \quad 0 \leq \alpha < 1, \quad (1.8)$$

with the normalizing constant

$$C(\rho, \alpha) := (\Gamma(1-\alpha)(1-\rho)^\alpha)^{-1}. \quad (1.9)$$

Observe that $\Psi(s; \rho, 0)$ is the geometric distribution (Schulz-Flory distribution). In what follows, several properties of the polynomials $l_k^\alpha(s; \rho)$ are listed – even though only part of these properties will be used in Section 2.

Starting with

$$l_{-1}^\alpha := 0, \quad l_0^\alpha := 1, \quad (1.10.a)$$

the whole set of the $l_k^\alpha(s; \rho)$, $k = 1, 2, \dots$, can be built up by means of the *three-term recurrence relation*

$$(k+1)l_{k+1}^\alpha(s; \rho) = [(k-\alpha+1)\rho + k - (1-\rho)(s-1)]l_k^\alpha(s; \rho) - (k-\alpha)\rho l_{k-1}^\alpha(s; \rho). \quad (1.10.b)$$

In view of (1.2) we define the inner product

$$(f, g)_\alpha := \sum_{s=1}^{\infty} f(s)g(s)\Psi(s; \rho, \alpha). \quad (1.11)$$

Then the *orthogonality relations* can be written as

$$\left(l_j^\alpha, l_k^\alpha \right)_\alpha = \gamma_k^\alpha \delta_{jk}, \quad \gamma_k^\alpha := \rho^k \binom{k-\alpha}{k}. \quad (1.12)$$

Sometimes the following *series representation* is useful :

$$l_k^\alpha(s; \rho) = \rho^k \sum_{\nu=0}^k \binom{k-\alpha}{k-\nu} \left(\frac{\rho-1}{\rho} \right)^\nu \binom{s-1}{\nu}. \quad (1.13)$$

which can be obtained by regarding $l_k^\alpha(s; \rho)$ as a hypergeometric function [9] :

$$l_k^\alpha(s; \rho) = \rho^k \binom{k-\alpha}{k} {}_2F_1\left(-k, -s+1, 1-\alpha; 1-\frac{1}{\rho}\right).$$

In Section 2, mutual representations of $\{l_k^0\}$ and $\{l_k^\alpha\}$ will play a role :

$$l_k^\alpha(s) = \sum_{\nu=0}^k b^{k,\nu}(\alpha) l_\nu^0(s), \quad 0 \leq \alpha < 1, \quad (1.14)$$

and, in reverse direction

$$l_k^0(s) = \sum_{\nu=0}^k b^{k,\nu}(-\alpha) l_\nu^\alpha(s), \quad 0 \leq \alpha < 1, \quad (1.15)$$

with

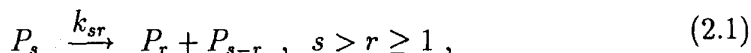
$$b^{k,\nu}(\alpha) := (-1)^{k-\nu} \rho^{k-\nu} \binom{\alpha}{k-\nu}, \quad k \geq \nu \geq 0. \quad (1.16)$$

The transformation formulas (1.14) and (1.15) can be proven by use of a general relation for Meixner polynomials, which can be found in [9].

2. Analytic Preprocessing of a Polymer Degradation Model

The basic idea of Section 1 is now applied to the special example of polymer degradation – compare [7], (1.7) and (1.8.b).

In a degradation reaction of the type



a polymer P_s of chain length s breaks at position r into two polymers of length r and length $s-r$. Following [2] the reaction rate coefficients k_{sr} depend on the degree of the polymer s and the location r of the breaking bond in the polymer chain. Modeling hydrolytic cleavage of dextrane leads, under special assumptions (Model II in [2]), to the following countable system of ordinary differential equations:

$$N'_s(t) = -k_p \frac{(s-1)}{(s-1)^{(\alpha)}} N_s(t) + 2k_p \sum_{r=s+1}^{\infty} \frac{1}{(r-1)^{(\alpha)}} N_r(t), \quad s = 1, 2, \dots, \quad (2.2)$$

where $N_s(t)$ denotes the number of polymers of degree s at time t . Herein the original rate coefficient $k_{sr} = k_s = k_p/s^\alpha$, k_p constant, $\alpha = 1/3$, from [2] has been substituted by $k_s = k_p/(s-1)^{(\alpha)}$ in view of the considerations of Section 1. An initial distribution $N_s(0)$ is given.

In the framework of the discrete Galerkin method [7] one will represent the number chain length distribution (NCLD) of the polymer, here also denoted by $N_s(t)$, by the series

$$N_s(t) = \Psi(s) \sum_{k=0}^{\infty} a_k(t) l_k(s), \quad (2.3)$$

wherein Ψ is a probability density function to be chosen on the basis of chemical insight and analytical convenience. The $\{l_k\}$ are the set of orthogonal polynomials generated by Ψ . Special attention must be paid to the fact that the series in (2.3) converges (with good approximations already for few terms), which means that the sequence $\{N_s(t)/\Psi(s)\}$ is contained in the Hilbert space H_Ψ spanned by the $\{l_k\}$. The theoretical verification of this requirement for the present model will be given elsewhere in a more general setting.

As demonstrated in the earlier paper [7], one can derive a differential equation for each expansion coefficient $a_j(t)$ by use of the orthogonality and certain properties of the polynomials $\{l_k\}$ after insertion of the representation (2.3) into the countable system, multiplication of each equation by the basis element $l_j(s)$ and summation over s – this is called *analytic preprocessing*. For the first right-hand term of the

degradation system (2.2) this yields the expression

$$T_1 := \sum_{k=0}^{\infty} a_k(t) k_p \sum_{s=1}^{\infty} \frac{(s-1)}{(s-1)^{(\alpha)}} l_k(s) l_j(s) \Psi(s) . \quad (2.4)$$

At this point, the choice

$$\Psi(s) = \Psi(s; \rho, 0) = (1 - \rho) \rho^{s-1} , \quad 0 < \rho < 1 .$$

turns out to be the only efficient one for two reasons: First, as shown in [7], the (experimental) initial distributions $N_s(0)$ considered in [2] and the solutions of (2.2) for $\alpha = 0$ can be approximated very well with discrete Laguerre polynomials $l_k^0(s; \rho)$ generated by $\Psi(s; \rho, 0)$. Second, with this choice T_1 can be rewritten as

$$T_1 = \frac{k_p}{C(\rho, \alpha)} \sum_{k=0}^{\infty} a_k(t) \left((s-1) l_k^0, l_j^0 \right)_\alpha , \quad (2.5)$$

by using the modified scalar product (1.11). After insertion of the three-term recurrence relation (1.10) for $\alpha = 0$, essentially terms of the form

$$d_{\rho, \alpha}^{k,j} := \left(l_k^0, l_j^0 \right)_\alpha = \left(l_k^0 l_j^0, l_0^\alpha \right)_\alpha \quad (2.6)$$

need to be calculated. The above reformulation motivates the representation of the products $l_k^0 l_j^0$, $k, j, \geq 0$, as a series in terms of the polynomials $\{l_i^\alpha\}$. Since a similar strategy successfully applies to the second term of the right-hand side in (2.2) as well, the remaining task is the calculation of the coefficients $d_{\rho, \alpha}^{k,j}$.

Lemma 2 *The terms $d_{\rho, \alpha}^{k,j}$ from (2.6) can be expressed as*

$$d_{\rho, \alpha}^{k,j} = (-1)^{k+j} \sum_{i=0}^{k+j} \binom{-\alpha}{i} \sum_{\nu \in I(k,j,i)} \frac{\nu! \rho^\nu (1 + \rho)^{k+j+i-2\nu}}{(\nu - k)! (\nu - j)! (\nu - i)! (k + j + i - 2\nu)!} , \quad (2.7)$$

where the index set $I(k, j, i)$ is defined by

$$I(k, j, i) := \{ \nu \in \mathbf{N} \mid \nu \geq \max\{k, j, i\} \wedge 2\nu \leq k + j + i \} . \quad (2.8)$$

Proof. In a first step the coefficients $C(k, j, i; \rho)$ of the *product linearization*

$$l_k^0(s; \rho) l_j^0(s; \rho) = \sum_{i=0}^{k+j} C(k, j, i; \rho) l_i^0(s; \rho)$$

are required. With a result of ASKEY/GASPER in [1] for Meixner polynomials one can find:

$$C(k, j, i; \rho) = (-1)^{k+j+i} \sum_{\nu \in I(k,j,i)} \frac{\nu! \rho^{\nu-i} (1 + \rho)^{k+j+i-2\nu}}{(\nu - k)! (\nu - j)! (\nu - i)! (k + j + i - 2\nu)!} \quad (2.9)$$

Then the transformation (1.15) connecting the sets $\{l_i^0\}$ and $\{l_i^\alpha\}$ is inserted. This leads to the expansion

$$l_k^0(s; \rho) l_j^0(s; \rho) = \sum_{i=0}^{k+j} C(k, j, i; \rho) \sum_{\nu=0}^i b^{i,\nu}(-\alpha) l_\nu^\alpha(s; \rho) . \quad (2.10)$$

Due to the orthogonality of the $\{l_i^\alpha\}$ the calculation of the scalar product in (2.6) only requires the knowledge of the l_0^α -part of the representation (2.10). Thus one has

$$d_{\rho,\alpha}^{k,j} = \sum_{i=0}^{k+j} C(k, j, i; \rho) b^{i,0}(-\alpha) .$$

This is the assertion. Finally, noting that the factorials in the inner sum of (2.7) are only defined for ν in the index set (2.8), the proof is complete. ■

Let $f_1(s)$ and $f_2(s)$ now denote the series of the s -components of the two terms on the right-hand side of the countable ODE system (2.2). Then the analytic preprocessing can be described as the evaluation of the relations

$$\frac{1}{\gamma_j^0} \langle N'_s, l_j^0(s; \rho) \rangle = \frac{1}{\gamma_j^0} \langle f_1 + f_2, l_j^0(s; \rho) \rangle , \quad j \geq 0 ,$$

in terms of the *Euclidian inner product*

$$\langle f, g \rangle := \sum_{s=1}^{\infty} f(s) g(s) .$$

The result for the left-hand side can be taken from [7], formula (4.3). The parameter ρ is assumed to be time dependent in such a way that $\Psi(s; \rho(t), 0)$ is a *moving weight function*. This can be used for an adaptive control of ρ by the algorithm. For the first right-hand term f_1 one obtains with (1.10):

$$\frac{1}{\gamma_j^0} \langle f_1, l_j^0 \rangle = \frac{k_p \rho^{-j}}{(1-\rho)C(\rho, \alpha)} \sum_{k=0}^{\infty} a_k(t) \left[(k+1) d_{\rho,\alpha}^{k+1,j} + k \rho d_{\rho,\alpha}^{k-1,j} - ((k+1)\rho + k) d_{\rho,\alpha}^{k,j} \right] \quad (2.11)$$

For the treatment of f_2 , the relation (3.12) from [7] and proper reordering of the summations over s and r are employed:

$$\frac{1}{\gamma_j^0} \langle f_2, l_j^0 \rangle = \frac{2 k_p \rho^{-j}}{(1-\rho)C(\rho, \alpha)} \sum_{k=0}^{\infty} a_k(t) \left[\rho d_{\rho,\alpha}^{k,j} - d_{\rho,\alpha}^{k,j+1} \right] \quad (2.12)$$

Thus one ends up with the countable ODE system ($a_{-1} := 0$):

$$a'_j + \frac{j\rho'}{(1-\rho)\rho} (a_j - a_{j-1}) = \frac{k_p \rho^{-j}}{(1-\rho)C(\rho, \alpha)} \sum_{k=0}^{\infty} a_k(t) g_{\rho,\alpha}^{k,j} , \quad j \geq 0 , \quad (2.13)$$

$$g_{\rho,\alpha}^{k,j} = (k+1) d_{\rho,\alpha}^{k+1,j} + k \rho d_{\rho,\alpha}^{k-1,j} - 2 d_{\rho,\alpha}^{k,j+1} - ((k-1)\rho + k) d_{\rho,\alpha}^{k,j} ,$$

with initial values $a_j(0)$, $j \geq 0$. At first glance, this new system might look more horrible than the original system (2.2). However, unlike (2.2), the new system (2.13) can be truncated after a few terms (see below).

For numerical computations one replaces the infinite sum in the ansatz (2.3) by the Galerkin approximation

$$N_s^{(n,m)}(t) := \Psi(s; \rho, 0) \sum_{k=0}^n a_k^{(m)}(t) l_k^0(s; \rho) \quad (2.14)$$

with a projection index n and a truncation index $m \geq n$ controlling the *projection* error and the *truncation* error, respectively. The (relative) projection error $\bar{\epsilon}_P^{(n)}(t)$ arises from the termination of the series (2.3) after $n + 1$ terms. This can be regarded as a orthogonal projection of $N_s(t)/\Psi \in H_\Psi$ to the subspace $\text{span}\{l_0^0, \dots, l_n^0\} \subset H_\Psi$. It is well known that

$$\bar{\epsilon}_P^{(n)}(t)^2 = \frac{\sum_{k=n+1}^{\infty} a_k(t)^2 \gamma_k^0}{\sum_{k=0}^{\infty} a_k(t)^2 \gamma_k^0}, \quad (2.15)$$

using the norm in H_Ψ induced by the scalar product (1.11) for $\alpha = 0$. In what follows the *theoretical* approximation errors will be indicated by a bar, *computational* estimates of these errors without the bar. After the truncation (*closure*) of an *open* system such as (2.13) by setting $a_k(t) \equiv 0$, $k \geq m + 1$, the projection described above is no longer an orthogonal projection. The introduced truncation error for a Galerkin approximation with projection index n then reads:

$$\bar{\epsilon}_T^{(n,m)}(t)^2 = \frac{\sum_{k=0}^n (a_k^{(m)}(t) - a_k(t))^2 \gamma_k^0}{\sum_{k=0}^{\infty} a_k(t)^2 \gamma_k^0}. \quad (2.16)$$

Recall that for *closed* systems one has $a_k^{(m)}(t) = a_k(t)$. In order to estimate the total error of the Galerkin approximation $N_s^{(n,m)}(t)$, the principle error term is computed (compare (2.20) in [7]). The *estimated relative approximation error* $\epsilon^{(n,m)}(t)$ is then given by:

$$\epsilon^{(n,m)}(t)^2 := \frac{\sum_{k=0}^n (a_k^{(m)}(t) - a_k^{(m+1)}(t))^2 \gamma_k^0 + (a_{n+1}^{(m+1)})^2 \gamma_{n+1}^0}{\sum_{k=0}^n (a_k^{(m+1)}(t))^2 \gamma_k^0} \quad (2.17)$$

In order to justify a truncation of the system, an examination shows that the factors $g_{\rho,\alpha}^{k,j}$ in (2.13) decay rapidly for $k > j$, the leading term of $|d_{\rho,\alpha}^{k,j}|$ being approximately $\rho^k \binom{-\alpha}{k-j} \binom{j-k-\alpha}{j}$. In actual computations even the choices $m = n$ or $m = n + 1$ turn out to be sufficient. The dependence of the truncation error on m will be illustrated in Section 3.

Initial values. For a general initial NCLD $N_s(0)$ the coefficients $a_j(0)$, $j \geq 0$, with respect to the basis $\{l_j^0(s; \rho)\}$ can be computed by

$$a_j(0) = \frac{1}{\gamma_j^0} \sum_{s=1}^{\infty} N_s(0) l_j^0(s; \rho). \quad (2.18)$$

For the models treated in this paper, initial distributions of the form

$$N_s(0) = \frac{s}{r} \bar{\rho}^s, \quad \bar{\rho} := e^{-1/r}, \quad s \geq 1, \quad r \text{ given}, \quad (2.19)$$

are in sufficient accordance with realistic data [2]. The maximum of the distribution $N_s(0)$ roughly occurs at chain length $s = r$, the number average is $2r$. For $\rho(0)$ according to the moving weight function condition (3.15) in [7]:

$$\rho(t) = 1 - \frac{\mu_0(t)}{\mu_1(t)} \quad (2.20)$$

in terms of the statistical moments

$$\mu_k(t) := \sum_{s=1}^{\infty} s^k N_s(t)$$

one obtains $\rho(0) = 2\bar{\rho}/(1 + \bar{\rho})$ and

$$a_j(0) = \frac{\bar{\rho}}{(1 - \bar{\rho})^2 r} 2^{-j} (1 - j), \quad j \geq 0. \quad (2.21)$$

It has been demonstrated in [7], that $\bar{\epsilon}_p^{(n)} \leq 1.2 \cdot 10^{-2}$ for $n \geq 8$. With the preprocessing being complete now, the system (2.13) can be integrated numerically for given n, m, r by an ODE solver. In the sense of a moving weight function an ODE for the variable ρ substitutes the ODE for the variable a_1 .

3. Numerical Results

In this section numerical results obtained by application of the above ideas to degradation processes will be presented. In particular, the following items will be addressed:

- the *modeling error* introduced substituting fractional powers by factorial powers
- the behavior of the *truncation error*
- the *approximation error* of the Galerkin method
- the numerical results in a *realistic degradation example*.

The first three items will be discussed by means of a reduced toy-like example, small enough to allow a direct numerical integration of the truncated original countable system. Recall the countable ODE arising from a general degradation process

$$N'_s(t) = -(s-1)k_{sr}N_s(t) + 2 \sum_{r=s+1}^{s_{\max}} k_{rs}N_r(t) \quad , \quad s = 1, 2, \dots, s_{\max} \quad , \quad (3.1)$$

with either reaction coefficients from the original modeling [2]

$$k_{sr} = k_{sr}^\alpha := k_p/s^\alpha$$

or coefficients as suggested in Section 1

$$k_{sr} = k_{sr}^{(\alpha)} := k_p/(s-1)^{(\alpha)} .$$

Due to [2], throughout this section $\alpha = 1/3$ is set. System (3.1) can be closed by choosing the maximum polymer degree s_{\max} as a finite number. The initial distribution $N_s(0)$ used in this paper is given by (2.19).

For the time being, consider the model problem with

$$k_p = 1 \quad , \quad r = 100 \quad s_{\max} = 1000 .$$

With this choice the maximum of the initial distribution arises at polymer degree $r = 100$. As $N_{s_{\max}}(0)$ is small compared to that maximum, a truncation of system (3.1) at s_{\max} will lead to a reasonable approximation of the infinite system [5]. With the choice of $k_p = 1$ the degradation is essentially finished after one second .

The numerical programs applied herein include an automatic adaptation of the parameter $\rho(t)$ as described in [7], Section 4. The integrations in time are performed by nonstiff and stiff extrapolation codes due to [6] written in FORTRAN. The results were obtained on a SUN 4/60 workstation, leading to computing times of about 10 sec (CPU) in the most time-consuming cases.

Modeling error. In order to examine the influence of replacing fractional by factorial powers, solutions for both types of reaction coefficients are computed in the case of the model problem. If one denotes by $N_s^\alpha(t)$ the solution of (3.1) with coefficients k_{sr}^α and by $N_s^{(\alpha)}$ the solution with $k_{sr} = k_{sr}^{(\alpha)}$ the *modeling error* can be estimated by

$$\epsilon_M^\alpha(t)^2 := \frac{\sum_{s=1}^{s_{\max}} \left(N_s^\alpha(t) - N_s^{(\alpha)}(t) \right)^2 \Psi(s; \rho, 0)}{\sum_{s=1}^{s_{\max}} N_s^\alpha(t)^2 \Psi(s; \rho, 0)}, \quad (3.2)$$

where $\rho = \rho(t)$ is computed via the moving weight function condition (2.20). In this way the modeling error can be compared with the approximation error $\epsilon^{(n,m)}(t)$ of the Galerkin method. Table 1 shows the evolution of $\epsilon_M^\alpha(t)$ in time.

time [sec]	$\epsilon_M^\alpha(t)$
$1 \cdot 10^{-3}$	$2 \cdot 10^{-4}$
$1 \cdot 10^{-2}$	$1 \cdot 10^{-3}$
$1 \cdot 10^{-1}$	$1 \cdot 10^{-2}$
$1 \cdot 10^{-0}$	$7 \cdot 10^{-2}$

Table 1: Modeling error $\epsilon_M^\alpha(t)$ replacing $1/s^\alpha \rightarrow 1/(s-1)^{(\alpha)}$.

It can be seen that $\epsilon_M^\alpha(t)$ increases strongly between $t = 10^{-2}$ and $t = 10^{-1}$. A detailed examination shows, that the chain length N_{\max} of the maximum of the distribution $N_s^\alpha(t)$ decreases from about 40 to 1 in the time interval $[10^{-2}, 2 \cdot 10^{-2}]$. As shown in Section 1, the approximation of fractional powers by factorial powers is sufficiently good for polymer degrees $s \geq 10$. Obviously the modeling error is larger, whenever polymer degrees smaller than 10 play a role in the process. For the realistic problem treated below, N_{\max} will be between 10^3 and 10^5 depending on the reaction time. So one can expect that there the modeling error will be negligible for technical accuracies.

Truncation error. The heuristic argument for the truncation of system (2.13) given in Section 2 will be backed now by numerical experiments (with $r = 200$ here). Fixing the projection error at a given n , the computation of the expansion coefficients $a_k^{(m)}(t)$, $k = 0, \dots, n$, was performed. In Figure 2, the true and estimated truncation errors are plotted for $t = 10^{-3}$, $n = 5$ and increasing m . The estimated relative truncation error is given by the first term of (2.17) by means of the coefficients $a_k^{(m+1)}(t)$, $k = 0, \dots, n$. The true errors were determined by comparison with a high order approximation.

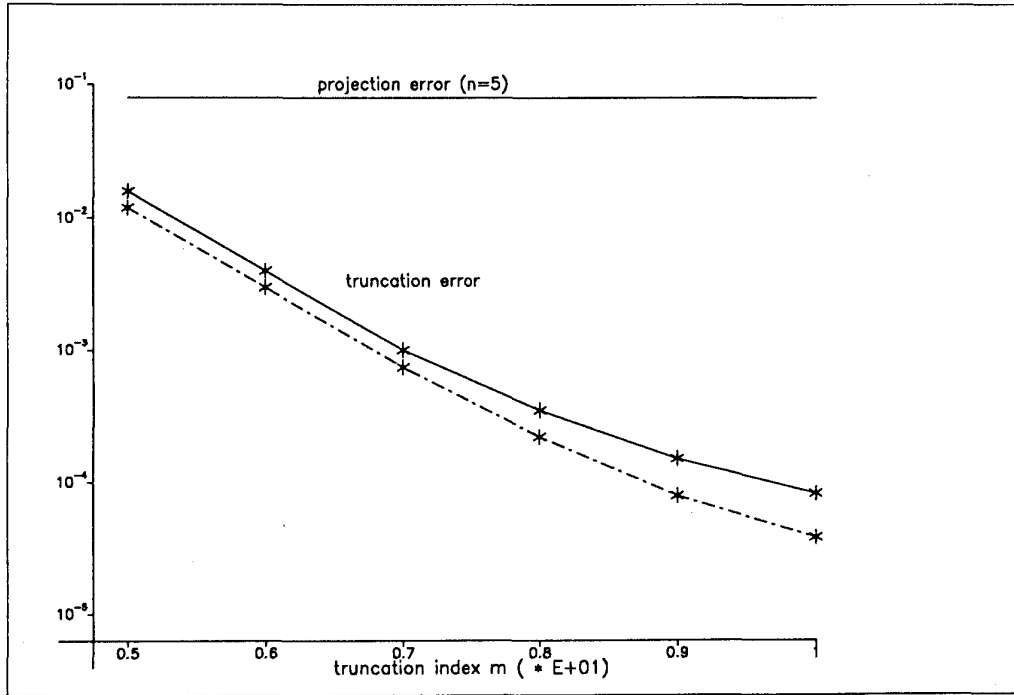


Figure 2: Behavior of the truncation error $\epsilon_T^{(n,m)}(t)$, $t = 10^{-3}$, for $n = 5$, $m \geq n$. Dashed lines denote true errors, broken lines denote estimated errors.

It can be seen that the estimation of the truncation error works in a satisfactory manner and that the truncation error is significantly smaller than the projection error for $m \geq n$. So for this example even the choice $m = n$ appears to be possible. In all numerical tests $m = n + 1$ has been found to be large enough so that

$$\epsilon_P^{(n)} \approx \epsilon_T^{(n,m)},$$

which is optimal in order to minimize the approximation error. In the light of this observation, the following strategy seems to be promising for the numerical treatment of open countable systems and will be used for the realistic example:

- choice of a truncation index \bar{m}
- computation of $a_k^{(m)}(t)$, $k = 0, \dots, m$, for $m = \bar{m}$ and $m = \bar{m} + 1$.
- estimation of the truncation errors $\bar{\epsilon}_T^{(n,m)}(t)$ for $n = \bar{m}, \bar{m} - 1, \dots$.
- estimation of the projection errors $\bar{\epsilon}_P^{(n)}(t)$ for $m = \bar{m} + 1$, $n = \bar{m}, \bar{m} - 1, \dots$
- choice of the projection index \bar{n} as the largest index such that $\epsilon_P^{(\bar{n})}(t) \geq \epsilon_T^{(\bar{n},\bar{m})}(t)$.

Approximation error. Looking at Figure 2 one can expect that the Galerkin approximations $N_s^{(n,m)}(t)$ will approach the solution of (3.1) ($s_{\max} = \infty$, $k_{sr} = k_{sr}^{(\alpha)}$) for reasonable choices of n and m . Table 2 shows the estimated approximation error $\epsilon^{(n,m)}(t)$ combining projection and truncation error for different $n = m$.

n	$\epsilon^{(n,m)}(t)$
3	$7 \cdot 10^{-2}$
4	$4 \cdot 10^{-2}$
5	$2 \cdot 10^{-2}$
8	$4 \cdot 10^{-3}$
10	$1 \cdot 10^{-3}$

Table 2: Approximation error $\bar{\epsilon}^{(n,m)}(t)$, $t = 10^{-2}$, for $n = m = 3, 4, 5, 8, 10$.

The table nicely reflects the good approximation behavior of the discrete Laguerre polynomials. This fact is illustrated in Figure 3, where Galerkin approximations for the weight chain length distribution (WCLD) $\{P_s(t)\} = \{s \cdot N_s(t)\}$ are compared with the direct solution of the truncated original system (3.1).

Realistic degradation process. After the encouraging tests described above, an impression of the real power of the method is given now. The degradation process modeled in [2] starts with an experimental distribution having a number average \bar{M}_N of about 120 000 and a maximum of the WCLD at about $M_{\max} = 100\,000$. The constant reaction coefficient k_p is estimated to be $k_p = 2.11 \cdot 10^{-7}$ in [2]. For the presentation in Figure 4, a maximum polymer degree of $s_{\max} = 400\,000$ is chosen. In case one would try to solve the truncated countable system (3.1), one

may expect $s_{\max} \geq 800\,000$ to be necessary. Thus a direct solution is impossible. For illustration purposes, the initial distribution $N_s(0)$ as in (2.19) is selected to show the features of the method. Taking $r = 60\,000$ leads to $M_{\max} = 123\,000$ and $\bar{M}_N = 120\,000$.

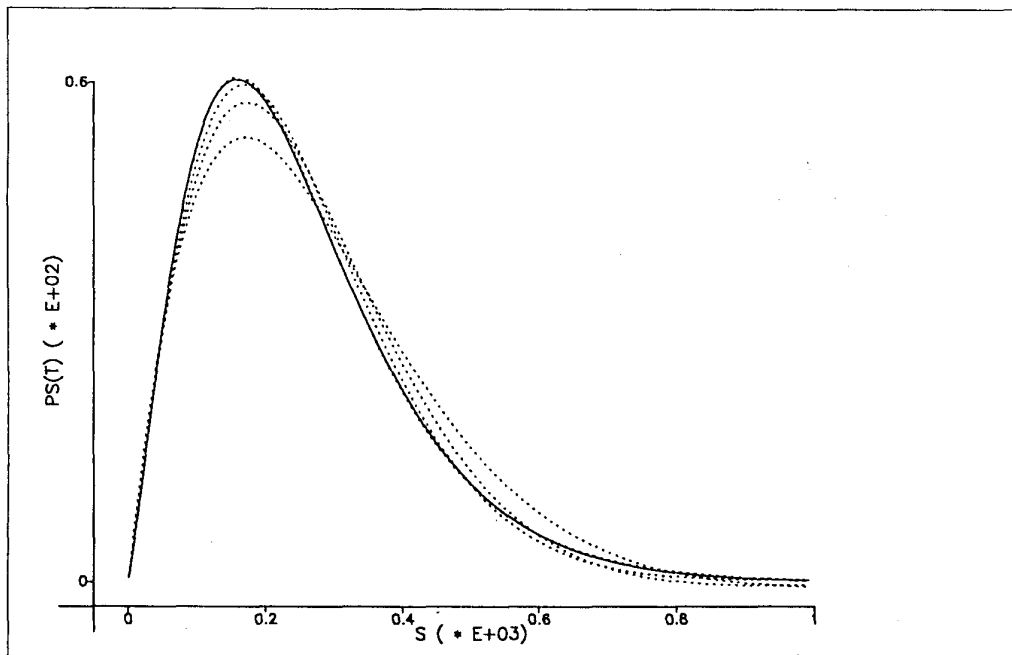


Figure 3: Galerkin approximations $P_s^{(n,m)}(t)$, $n = m = 3, 4, 5, 8$ and direct solution for the test problem at $t = 10^{-2}$ for $r = 100$.

The expansion coefficients $a_k^{(m)}(t)$ have been computed for $m = 8, m = 9$. Then the strategy suggested above was applied to determine the projection index n . Table 3 shows the time evolution of the process up to 120 minutes reaction time for the number average \bar{M}_N , the maximum M_{\max} , the estimated approximation error $\epsilon^{(n,m)}(t)$ and the truncation indices n and m . Comparing \bar{M}_N and M_{\max} with the data from [2], one can see that the results are in good qualitative agreement. The values of $\epsilon^{(n,m)}(t)$ have been verified by high order approximations and turned out to be reliable.

time [min]	\bar{M}_N	M_{\max}	$\epsilon^{(n,m)}(t)$	n	m
0	120000	120000	$1.2 \cdot 10^{-2}$	8	8
15	82000	88000	$2.6 \cdot 10^{-3}$	7	8
30	61000	65000	$3.5 \cdot 10^{-3}$	8	8
60	39000	37000	$4.8 \cdot 10^{-3}$	8	8
90	28000	24000	$6.6 \cdot 10^{-3}$	8	8
120	21000	18000	$3.8 \cdot 10^{-3}$	8	8

Table 3: Time evolution of number average \bar{M}_N , weight maximum M_{\max} , approximation error $\epsilon^{(n,m)}(t)$ and truncation indices n and m .

In Figure 4, the weight chain length distributions $P_s(t)$ are shown.

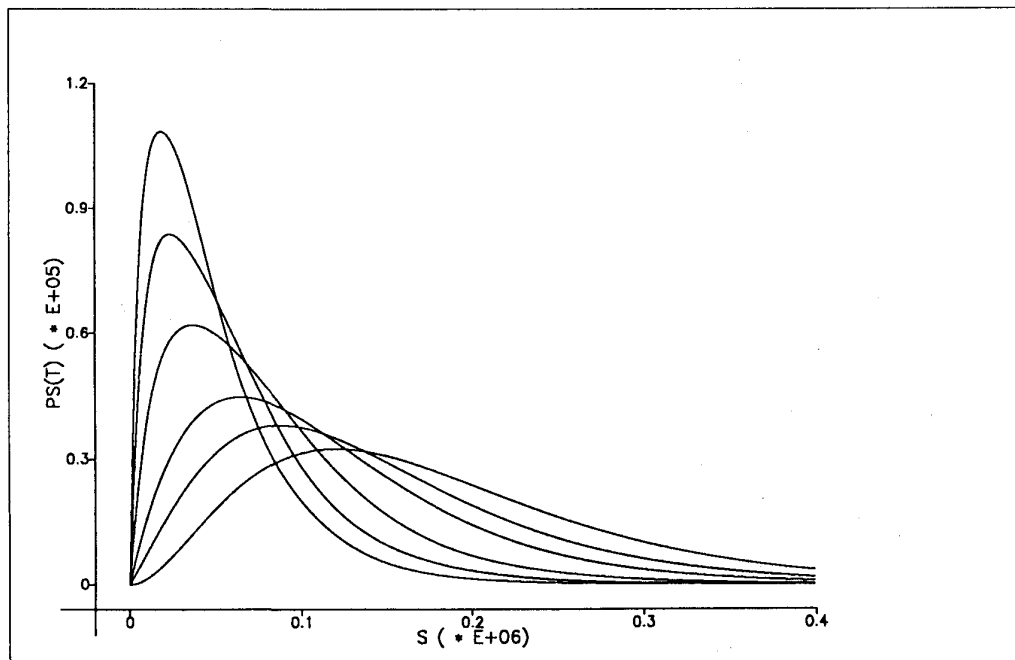


Figure 4: Time evolution of the degradation model due to [2],
 $t = 15, 30, 60, 90, 120$ min, $s_{\max} = 400\,000$.
 Computing time: 9 sec (CPU) on a SUN 4/60.

Conclusion

The paper discussed a variant of the discrete Galerkin method [7] for the case of heterogeneous polymer reaction models, where fractional powers of the polymer degree arise in the reaction rate coefficients. The main idea is the suggestion to replace fractional by factorial powers in order to utilize already available know-how from special functions about a discrete variable (here: modified discrete Laguerre polynomials). For illustration the method was successfully applied to a degradation process involving the treatment of polymer degrees up to 400 000 by only a few Galerkin coefficients.

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