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Abstract

The paper presents a new approach to the computational treatment of polyreaction kinetics. This approach is characterized by a Galerkin method based on orthogonal polynomials of a discrete variable, the polymer degree (or chain length). In comparison with the known competing approaches (statistical moment treatment, Galerkin methods for continuous polymer models), the suggested method is shown to avoid the disadvantages and preserve the advantages of either of them. The basic idea of the method is the construction of a discrete inner product associated with a reasonably chosen probability density function. For the so-called Schulz-Flory distribution one thus obtains the discrete Laguerre polynomials, whereas the Poisson distribution leads to the Charlier polynomials. Numerical experiments for selected polyreaction mechanisms illustrate the efficiency of the proposed method.

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Contents

0. Introduction

In recent years, numerical *simulation* of chemical reaction systems has reached a level of sophistication, which makes it interesting even for chemical engineering. Mathematically speaking, simulation involves the numerical solution of systems of ordinary differential equations — possibly large, usually nonlinear and "stiff". In principle, these systems can be efficiently treated by chemical kinetics packages such as LARKIN, which is especially designed for *large* systems (compare DEUFLHARD/NOWAK [9] for a recent survey).

However, as soon as *polyreactions* arise and each individual polymer must be computed up to technical accuracy, then both storage requirements and computing times tend to increase beyond a tolerable level. In special situations, the actual computation of *statistical moments* is a sufficient alternative — see e.g. recent work by FRENKLACH [12, 13]. If the total polymer distribution function is needed, then the moment treatment will appear to be unsatisfactory. As a further alternative, *continuous* polyreaction models are often recommended with the polymer degree as a continuous non-negative variable — see e.g. RAY [18]. This kind of modeling leads to partial differential equations, which might be attacked by a Galerkin method based on Laguerre polynomials — see GAJEWSKI/ZACHARIAS [14] for a description and approximation study. However, making the discrete polymer degree a continuous variable is somewhat artificial — a feature, which shows up in poor approximations for small polymer degree. Details are presented in Section 1 below.

In order to avoid this artificial modeling, the present paper proposes a different approximation scheme, which preserves the discrete structure of the polymer degree. This method is a Galerkin method based on orthogonal polynomials of a discrete variable, the polymer degree. Such polynomials are generated by a discrete inner product in terms of a weight function, which may be interpreted as a probability distribution function. The basic approach and its connection with the statistical moments are given in Section 2. For the Schulz-Flory distribution, one obtains the so-called *discrete* Laguerre functions, whereas the Poisson distribution leads to the Charlier polynomials — see Section 3. In Section 4, the Galerkin scheme is applied to a selection of typical polyreaction mechanisms. Finally, in Section 5, numerical experiments are given that nicely illustrate the attractive features of the approach advocated herein.

1. Mathematical Polyreaction Models

1.1 Kinetic Equations for Selected Mechanisms

Let $P_s(t)$ denote the concentration of polymers of *chain length* s (also: *polymer degree* s) at time t, and $N_s(t)$ the number of polymers of length s at time t. For ease of writing, the notation does not distinguish between the chemical species P_s and its concentration $P_s(t)$ — the notation will be clear enough from the context. If a polyreaction mechanism is known in sufficient detail, then the associated system of ordinary differential equations can be generated, in principle. Throughout the paper, attention is focussed on simple model problems to illustrate the special features of the new method to be proposed.

Chain addition polymerization. Examples of this mechanism are e.g. *anionic polymerization* or *free radical polymerization.* Let M denote a monomer and P_s the polymer. Then the associated reaction mechanism is:

$$P_s + M \xrightarrow{k_p} P_{s+1} \quad s = 1, 2, \ldots \quad , \tag{1.1}$$

where $k_p > 0$ denotes the reaction rate coefficient. The kinetics of the reaction (1.1) is modelled by a system of ordinary differential equations of the form:

$$\begin{aligned} P_1' &= -k_p M P_1 \\ P_s' &= -k_p M (P_s - P_{s-1}) \qquad s = 2, 3, \ldots \\ M' &= -k_p M \sum_{s=1}^{\infty} P_s \end{aligned} \tag{1.2.a}$$

with the given initial values

$$\begin{aligned} P_1(0) &= P_{10} \\ P_s(0) &= 0 \ , \qquad\qquad s = 2, 3, \ldots \\ M(0) &= M_0 \ . \end{aligned} \tag{1.2.b}$$

Following RAY [18], the time variable t may be rescaled according to

$$t \rightarrow \int_0^t k_p M(\tau) d\tau \ . \tag{1.3}$$

In terms of this scaled time, also denoted by t here for simplicity, one obtains

$$\begin{array}{llll} \text{a)} & P_1' & = & -P_1 \\ & P_s' & = & -P_s + P_{s-1} \qquad s = 2, 3, \ldots \\ \text{b)} & P_1(0) & = & P_{10} \\ & P_s(0) & = & 0 \qquad s = 2, 3, \ldots \end{array} \tag{1.4}$$

For the methods to be discussed and proposed herein, the treatment of the model problem (1.4) is sufficient.

Reversible polymerization [19]. With the notation as above, this reaction mechanism reads

$$P_s + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P_{s+1} \quad , \qquad s = 1, 2, \ldots \tag{1.5}$$

with reaction coefficients $k_1 > k_2 \geq 0$. The associated simplified model equations (analogous to (1.4)) are

$$\begin{array}{llll} \text{a)} & P_1' & = & k_2 P_2 - k_1 P_1 \\ & P_s' & = & k_1(P_{s-1} - P_s) + k_2(P_{s+1} - P_s) \qquad s = 2, 3, \ldots \\ \text{b)} & P_1(0) & = & P_{10} \\ & P_s(0) & = & 0 \qquad s = 2, 3, \ldots \end{array} \tag{1.6}$$

Polymer Degradation [11]. In the present notation, this process leads to the model equations

$$N_s' = -\left(\sum_{r=1}^{s-1} k_{sr}\right) N_s + 2 \sum_{r=s+1}^{\infty} k_{rs} N_r \qquad s = 1, 2, \ldots \tag{1.7}$$

Let the initial distribution $N_s(0)$ be given. In [2], the following additional specifications are discussed:

$$\begin{array}{llll} \text{a)} & k_{sr} & = & k_p \\ \text{b)} & k_{sr} & = & \bar{k}_s := k_p \cdot s^{\alpha} \ , \quad \alpha = -\dfrac{1}{3} \\ \text{c)} & k_{sr} & = & \bar{k}_r + \bar{k}_{s-r} \end{array} \tag{1.8}$$

An example described by such models is the *acid hydrolysis of dextrane.* The specifications (1.8.a,b) permit a formal analytic solution of (1.7), which is quite simple in case a), but prohibitively complicated in case b) — compare [2].

Coagulation [12] and irreversible polycondensation [18]. These processes can be modelled by the following system of nonlinear ordinary differential equations:

$$N_s' = \frac{1}{2}\sum_{r=1}^{s-1} k_{r,s-r} N_r N_{s-r} - N_s \sum_{r=1}^{\infty} k_{sr} N_r \quad , \qquad s = 1, 2, \ldots . \tag{1.9}$$

Let an initial distribution $N_s(0)$ be given. With the additional specification

$$k_{sr} = k_p \tag{1.10}$$

this model is also referred to as *Smoluchowski coagulation model.* At the same time, RAY [18] uses (1.9) with (1.10) to model the *polycondensation of A–B type monomer.* As an example of this mechanism, [18] mentions the *production of polyesters from hydroxy acids* in a well-stirred batch reactor. Note that under the specification (1.10) the nonlinear system (1.9) can be solved in closed analytic form.

In the case of *heterogeneous* reactions, fractional powers like in (1.8.b,c) may also arise in model (1.9) — e.g. in soot formation [13].

Mass conservation. For the first two models, (1.4) and (1.6), one easily verifies that

$$\sum_{s=1}^{\infty} P_s'(t) = 0 \quad , \quad t > 0 , \tag{1.11}$$

which means mass conservation:

$$\sum_{s=1}^{\infty} P_s(t) = \sum_{s=1}^{\infty} P_s(0) \quad , \quad t > 0 . \tag{1.11'}$$

For the other two models, (1.7) and (1.9), mass conservation shows up in the form

$$\sum_{s=1}^{\infty} s N_s'(t) = 0 \quad , \quad t > 0 , \tag{1.12}$$

which is equivalent to

$$\sum_{s=1}^{\infty} s N_s(t) = \sum_{s=1}^{\infty} s N_s(0) \quad , \quad t > 0 . \tag{1.12'}$$

1.2 Standard Computational Approaches

Large scale stiff integration. On the basis of chemical insight into a specific polyreaction process, the infinite system of differential equations may be truncated. The arising finite systems are usually still large and stiff — with a rather full Jacobian matrix. As a consequence, this kind of simulation leads to prohibitive array storage and computing time.

Lumping. A popular method to reduce the large number of (stiff) ordinary differential equations is the so-called lumping technique. In this approach, polymer species of chain lengths within certain prescribed intervals are "lumped" together to certain superspecies. It is clear that an appropriate interval definition requires a lot of a-priori insight into the chemical process (cf. [11]). Nevertheless, even in the best cases, this lumping technique introduces a modeling error of unknown size — which may be totally unacceptable especially in nonlinear models.

Statistical moment treatment. The classical statistical moments are defined as

$$\mu_k(t) := \sum_{s=1}^{\infty} s^k P_s(t) \,, \quad k = 0, 1, \ldots \tag{1.13}$$

Insertion of this definition into the kinetic models (cf. Section 1.1) leads to a system of ordinary differential equations for $\mu_0, \mu_1, \ldots$.

Mathematically speaking, the (bounded) *infinite* sequence $\mu_0, \mu_1, \ldots$ essentially determines the distribution density P_s — which is the well-known Stieltjes problem of mathematical statistics [20]. If, however, only a *finite* number of moments $\mu_0, \ldots, \mu_N$ is known, then associated approximations $P_s^{(N)}$ of the exact distribution P_s may vary within an extremely wide range! A detailed theoretical discussion of this fact and its consequences will be given in Section 2.2 below, a numerical illustration in Section 5.

For the sake of completeness, recall that *mass conservation* shows up in this treatment as

$$\mu_0(t) = \textit{const.} \,,$$

if (1.11) holds, or as

$$\mu_1(t) = \textit{const.} \,,$$

if (1.12) holds. (Herein, $P_s(t)$ in (1.13) must be replaced by $N_s(t)$, of course).

Continuous Models. In this kind of model, the polymer degree appears as a continuous real variable $s \geq 0$. The polymer distribution $P_s(t) \equiv P(s, t)$ is then determined by a *partial integro-differential equation.* For example, the kinetic equations (1.4) are transformed to (see RAY [18]):

$$\begin{aligned} \text{a)} \quad \frac{\partial}{\partial t} P(s, t) &= -\frac{\partial}{\partial s} P(s, t) + \frac{1}{2} \left(\frac{\partial}{\partial s} \right)^2 P(s, t) \\ \text{b)} \quad P(s, 0) &= P_{10} \cdot \delta(s - 1) \,, \end{aligned} \tag{1.14}$$

where δ means the Dirac-distribution. However, RAY already indicates that the number of terms used in the Taylor expansion of the above right-hand side needs

subtle consideration. A comparison of the analytic results of (1.4) and (1.7) shows that the continuous model introduces significant *errors for small degree s*. In the polymer degradation model (1.9), a short examination demonstrates that

$$\lim_{t\to\infty} N_s(t) = \frac{1}{s}\delta(s)\,. \tag{1.15}$$

Hence, asymptotically a nasty singularity is introduced by this kind of continuous modeling.

In [14], GAJEWSKI and ZACHARIAS study the continuous analogue of the coagulation equation (1.7), which reads (dropping the convection term):

$$\begin{aligned} \text{a)}\quad \frac{\partial}{\partial t}N(s,t) &= \frac{1}{2}\int_{r=0}^{s} k(r,\,s-r)N(r,\,t)N(s-r,\,t)dr \\ &\quad -N(s,\,t)\int_{r=0}^{\infty} k(s,\,r)N(r,\,t)dr \\ \text{b)}\quad N(s,\,0) &:= N_0(s) \end{aligned} \tag{1.16}$$

In order to solve this nonlinear partial integro-differential equation, these authors suggest a *Galerkin method* based, for example, on finite elements or on modified Laguerre polynomials L_k^α. In the latter approach (see [15]), the distribution density $P(s,\,t)$ is approximated by

$$P^{(N)}(s,\,t) := \sigma^\alpha e^{-\sigma}\sum_{k=0}^{N} a_k(t)L_k^\alpha(\sigma) \tag{1.17}$$

with σ defined by

$$\sigma := \beta(t)s \tag{1.18}$$

for suitably chosen $\beta(t)$. For example, BAMFORD and TOMPA [1] suggest to use

$$\beta(t) := \frac{\mu_0(t)}{\mu_1(t)}\,. \tag{1.19}$$

The artificial nature of modeling the discrete length s by a continuous variable shows up in the depth of the convergence analysis in [14]: for $s = 0$, a singularity arises, which needs special regularization. Moreover, even though [14] analyse the *approximation error* introduced by the Galerkin method in detail, the beforehand introduced *modeling error* is overlooked. For these reasons, the continuous Galerkin approach seems to be not sufficiently reliable for real life scientific and engineering computations.

2. Discrete Galerkin Method

The method to be proposed herein aims at preserving the advantages of both the statistical moment treatment and the continuous Galerkin method (Section 1.2) and, at the same time, to avoid the intrinsic disadvantages of these approaches. Starting point is the fact that, after all, the polymer degree (or chain length) s is a *discrete variable.*

2.1 Basic Approximation Scheme

The key to the construction of the basic scheme is the introduction of a *discrete inner product*

$$(f,\, g) := \sum_{s=1}^{\infty} f(s)\, g(s)\, \Psi(s) \tag{2.1}$$

where f, g are grid functions defined only on the grid $\{1, 2, \ldots\}$ and Ψ is a given *weight function* with

$$\Psi(s) > 0 \qquad s = 1, 2, \ldots < \infty \tag{2.2}$$

which characterizes the inner product $(\cdot\,,\,\cdot)$. This inner product induces the *norm*

$$\| f \|_{\Psi} := (f,\, f)^{1/2} \tag{2.3}$$

and an associated Hilbert space H_{Ψ}. In H_{Ψ}, there exists an orthogonal polynomial basis $\{l_j(s)\}$ $j = 0, 1, \ldots$ satisfying

$$(l_i,\, l_j) = \gamma_j\, \delta_{ij}\,, \quad \gamma_j > 0\,, \qquad i, j = 0, 1, 2, \ldots \tag{2.4}$$

with δ_{ij} the Kronecker symbol. For ease of the subsequent presentation, the (Euclidean) inner product

$$\langle u,\, v\rangle := \sum_{s=1}^{\infty} u(s)\, v(s)\,, \tag{2.5}$$

will also be used, where u, v are grid functions such that $\langle u,\, v\rangle$ is bounded. Assume that

$$\bar{P}_s(t) := \frac{P_s(t)}{\Psi(s)} \in H_{\Psi}\,. \tag{2.6}$$

Then there exists a unique representation

$$P_s(t) = \Psi(s) \sum_{k=0}^{\infty} a_k(t)\, l_k(s)\,. \tag{2.7}$$

With this notation, (2.6) is readily seen to be equivalent to

$$\sum_{k=0}^{\infty} a_k^2(t)\,\gamma_k \;<\; \infty\,. \tag{2.6'}$$

For given $P_s(t)$, the coefficients $\{a_j\}$ can be obtained from the relation

$$a_j(t) = \frac{1}{\gamma_j}\langle l_j,\, P_s(t)\rangle \;, \qquad j = 0,\, 1\, \ldots\,. \tag{2.8}$$

This means that the $\{a_j\}$ may be interpreted as *generalized moments* with respect to the orthogonal basis $\{l_j\}$.

In passing, one may note that *mass conservation* in the form (1.11′) can be written as

$$\langle 1,\, P_s(t)\rangle \;=\; \langle 1,\, P_s(0)\rangle\;. \tag{2.9}$$

This directly implies

$$\begin{aligned} a_0(t) \;&=\; \frac{1}{\gamma_0}\langle l_0,\, P_s(t)\rangle \;=\; \frac{l_0}{\gamma_0}\langle 1,\, P_s(t)\rangle \\ &=\; \frac{l_0}{\gamma_0}\langle 1,\, P_s(0)\rangle \;=\; a_0(0)\,. \end{aligned} \tag{2.10}$$

The alternative condition (1.12′) in terms of $N_s(t)$ does not lead to a comparably simple condition, if $N_s(t)$ has a representation of the form (2.7).

Appropriate treatment of the kinetic equations (Section 1.1) by means of the above formalism leads to a system of ordinary differential equations for the generalized moments — as worked out in Section 4 for the special functions to be derived in Section 3. Truncation of the expansion (2.7) after N terms will lead to a *Galerkin approximation* of the type

$$P_s^{(N)}(t) := \Psi(s)\sum_{k=0}^{N} a_k(t)\, l_k(s) \tag{2.11}$$

for *self-closing systems* or of the type

$$P_s^{(N)}(t) := \Psi(s)\sum_{k=0}^{N} a_k^{(N)}(t)\, l_k(s) \tag{2.12}$$

for *open systems* — see Section 4 for examples of both types.

For the type (2.11), a *minimization property* is known to hold: let Π_N denote the space of polynomials in s of maximum degree N over the grid $\{1,\, 2,\, \ldots\}$ and define

$$\bar{P}_s^{(N)}(t) := \frac{P_s^{(N)}(t)}{\Psi(s)} \in \Pi_N\,. \tag{2.13}$$

Then (2.11) implies

$$\|\bar{P}_s^{(N)} - \bar{P}_s\|_\Psi = \min_{\tilde{P}\in\Pi_N} \|\tilde{P} - \bar{P}_s\|_\Psi \,. \tag{2.14}$$

In this case, the associated *approximation error* can be represented by

$$\|\bar{P}_s^{(N)} - \bar{P}_s\|_\Psi = \left[\sum_{k=N+1}^{\infty} a_k^2(t)\gamma_k\right]^{1/2} \tag{2.15}$$

For any Ψ such that (2.6) holds, one thus obtains for self-closing systems:

$$\lim_{N\to\infty} P_s^{(N)}(t) = P_s(t) \,. \tag{2.16}$$

For open systems, however, the situation is much more complicated. On the basis of (2.12), there the associated approximation error is

$$\|\bar{P}_s^{(N)} - \bar{P}_s\|_\Psi = \left[\sum_{k=0}^{N}\left(a_k^{(N)} - a_k\right)^2\gamma_k + \sum_{k=N+1}^{\infty} a_k^2\gamma_k\right]^{1/2} . \tag{2.17}$$

A theoretical convergence analysis for this kind of approximation is beyond the scope of the present paper. A rather general scheme for such a convergence analysis may be found in DEIMLING [6]. In view of an algorithmic control of the truncation index N, the *truncation error estimates*

$$\|\bar{P}_s^{(N)} - \bar{P}_s^{(N+1)}\|_\Psi \doteq \left(a_{N+1}^2\,\gamma_{N+1}\right)^{1/2} \tag{2.18}$$

in the case (2.11) or

$$\|\bar{P}_s^{(N)} - \bar{P}_s^{(N+1)}\|_\Psi \doteq \left[\sum_{k=0}^{N}\left(a_k^{(N)} - a_k^{(N+1)}\right)^2\gamma_k + \left(a_{N+1}^{(N+1)}\right)^2\gamma_{N+1}\right]^{1/2} \tag{2.19}$$

in the case (2.12) might be useful.

2.2 Connection with Statistical Moments

Recall the definition (1.13) for the statistical moments $\mu_k(t)$, which is also based on the assumption of a *discrete* variable s. For given orthogonal basis $\{l_j(s)\}$, the following expansion is easily established:

$$s^k = \sum_{m=0}^{k} b_{km}\, l_m(s) \quad , \quad k = 0, 1, \ldots \,. \tag{2.20}$$

By definition, one knows that

$$b_{kk} \neq 0 \qquad , \qquad k = 0, 1, \ldots . \tag{2.21}$$

Upon inserting (2.20) and (2.7) into the definition (1.13), one obtains

$$\mu_k(t) = \langle s^k, P_s(t) \rangle = \sum_{m=0}^{k} b_{km} \sum_{r=0}^{\infty} a_r(t)(l_m, l_r) = \sum_{m=0}^{k} b_{km} a_m(t) \gamma_m \, .$$

This leads to an infinite-dimensional recursive linear system of the form

$$\begin{aligned} \mu_0 &= b_{00}\, \gamma_0\, a_0 \\ \mu_1 &= b_{10}\, \gamma_0\, a_0 + b_{11}\, \gamma_1\, a_1 \\ &\vdots \end{aligned} \tag{2.22}$$

Because of

$$b_{kk}\, \gamma_k \neq 0 \, , \tag{2.21'}$$

the generalized moments $a_0, a_1, \ldots$ can be recursively computed from the statistical moments $\mu_0, \mu_1, \ldots$. This fact nicely reflects the basic structure of the Stieltjes problem already mentioned in Section 1.2. If the *infinite* sequence $\{\mu_k\}$ is bounded and given, then the infinite sequence $\{a_k\}$ can be obtained, which, in turn, defines the polymer distribution $P_s(t)$ via the representation (2.7) — for *any* choice of weight function Ψ subject to the condition (2.6). If, however, only a *finite* number N of statistical moments is given, then only N generalized moments are determined — which, in turn, define associated Galerkin approximations $P_s^{(N)}$. However, variation of the weight function may produce a possibly rather wide variation of $P_s^{(N)}$ — this fact is illustrated in Section 5 below.

Summarizing, the mere computation of just a few statistical moments will only be useful in special situations such as:

(a) investigations concerning physical properties that only depend on, say, μ_0, μ_1, or μ_2,

(b) comparisons with experimental data, which anyway arise in the form of statistical moments,

(c) estimation of relaxation times — as in [12].

Even in these cases, the statistical moment treatment appears to be unsatisfactory, if one of the following situations occurs:

(a) fractional powers of s arise in the reaction rate coefficients (compare (1.8)) — here approximation techniques of unclear domain of applicability are in common use [11, 13],

(b) open systems.

Summarizing, it is computationally more reliable to determine a truncation index N in the discrete Galerkin method than in the statistical moment method. Of course, a sophisticated choice of the weight function Ψ will help to decrease the number of terms needed.

Moving weight functions. The weight functions of special interest typically contain at least one free parameter — compare Section 4. A proper choice of this parameter will also help to keep the truncation index N small. For this purpose, define the statistical moments of Ψ by

$$\nu_k := \sum_{s=1}^{\infty} s^k \Psi(s) \;=\; \langle s^k,\, \Psi \rangle \;\equiv\; (s^k,\, 1)\,. \tag{2.23}$$

Note that a sufficient condition for the existence of an orthogonal polynomial basis for Ψ is that all the ν_k are bounded.

Throughout the paper, the normalization

$$\nu_0 := 1 \tag{2.24}$$

will be imposed — thus making Ψ a probability density function. Then a sophisticated choice of Ψ will aim at certain similarities between $P_s(t)$ and $\mu_0(t)\,\Psi(s)$. With (2.24), both distributions have $\mu_0(t)$ in common. The free parameter can then be determined from the natural condition

$$\mu_1(t) = \mu_0(t)\,\nu_1\,. \tag{2.25}$$

Example: Moving exponential weight function in the continuous model (Section 1.2).

In this case, one starts from the *continuous* inner product

$$(f,\, g) := \int_{s=0}^{\infty} f(s)\, g(s)\, \Psi(s)\, ds \tag{2.26}$$

where Ψ, in view of (2.24) and (1.17), is defined as

$$\Psi(s) := \beta\, e^{-\beta s} \quad , \quad \beta > 0\,. \tag{2.27}$$

From this, one concludes that

$$\nu_1 = \frac{1}{\beta}\,. \tag{2.28}$$

Upon combining (2.25) and (2.28) one ends up with

$$\beta(t) = \frac{\mu_0(t)}{\mu_1(t)} \,. \tag{2.29}$$

This is just (1.19), the relation given by BAMFORD and TOMPA [1]. At the same time, the above derivation explains the observations of these authors that "the more closely the molecular weight distribution approximates to the simple exponential distribition, the smaller the number of moments required" [1].

Finally, note that (2.24), (2.25) and (2.22) directly imply

$$\begin{aligned} &\text{a)} \quad a_0(t) \equiv \mu_0(t) \\ &\text{b)} \quad a_1(t) \equiv 0 \end{aligned} \tag{2.30}$$

3. Orthogonal Polynomials of a Discrete Variable

In this Section, the discrete Galerkin method derived in Section 2 above is exemplified in terms of special choices of the weight function Ψ. As it turns out, the first orthogonal polynomials of discrete variables have already been discussed by CHEBYSHEV [3] in 1855 and by STIELTJES [20] in 1894. Even though many of their properties can meanwhile be found in textbooks on special functions [17, 5], a summary of some properties seems to be justified — in view of the special application in mind. As a consequence of this application, most definitions in the literature must be rewritten for the grid $\{1, 2, \ldots\}$ instead of $\{0, 1, \ldots\}$. Moreover, some necessary properties had to be newly derived.

3.1 Discrete Laguerre Polynomials

As shown above, the exponential weight function in connection with the continuous inner product (2.26) defines the classical Laguerre polynomials $\{L_k\}$. For discrete variable s, the identification

$$\rho := e^{-\beta} \quad , \quad \beta > 0 \quad , \tag{3.1}$$

transforms (2.27) to the discrete weight function

$$\Psi(s) := (1-\rho)\rho^{s-1} \, , \; 0 < \rho < 1 \, , \; s = 1, 2, \ldots \, . \tag{3.2}$$

Herein, the normalization (2.24) has been observed. In the chemical literature, (3.2) is also known as the *Schulz-Flory distribution.* With Ψ from (3.2), the inner product (2.1) generates a set of orthogonal polynomials — to be naturally called discrete Laguerre polynomials, say $\{l_k\}$. These polynomials have been considered briefly by STIELTJES [20] in 1894 and in more detail by GOTTLIEB [16] in 1938.

The simplest representation of the discrete Laguerre polynomials $l_k(s)$ is via their *three-term recurrence relation* ($k = 0, 1, \ldots$):

$$(k+1)\, l_{k+1} = [(k+1)\rho + k - (1-\rho)(s-1)]\; l_k - k\rho\, l_{k-1} \quad , \tag{3.3.a}$$

to be started with

$$l_{-1} := 0 \quad , \quad l_0 := 1 \, . \tag{3.3.b}$$

The associated *orthogonality relation* is

$$(l_i, \; l_k) = \rho^k \cdot \delta_{ik} \quad i, \, k = 0, 1, \ldots \, . \tag{3.4}$$

Comparison with (2.4) shows that

$$\gamma_k = \rho^k \qquad k = 0, 1, \ldots \, . \tag{3.5}$$

As in the continuous case, a *Rodrigues-formula* can be proved

$$l_k(s) = \rho^{-s}\Delta^k \left[\binom{s-1}{k} \rho^s \right] \tag{3.6}$$

where Δ denotes the *forward difference operator*

$$\Delta f(s) := f(s+1) - f(s)\,. \tag{3.7}$$

In lieu of (3.3.a, b), the following direct representation is sometimes useful:

$$l_k(s) = \rho^k \sum_{\nu=0}^{k} \binom{k}{\nu} \left(\frac{\rho-1}{\rho}\right)^{\nu} \binom{s-1}{\nu}\,. \tag{3.8}$$

From this, one readily verifies

$$\begin{aligned} \text{a)}\quad l_k(0) &= 1 \\ \text{b)}\quad l_k(1) &= \rho^k \end{aligned} \tag{3.9}$$

For the treatment of the polyreaction model problems (Section 1.1 and Section 4), the following selection of properties are selected:

$$l_k(s+1) - l_k(s) = (\rho-1)\sum_{\nu=0}^{k-1} \rho^{k-1-\nu} l_\nu(s) \tag{3.10}$$

$$l_k(s-1) - l_k(s) = (1-\rho)\sum_{\nu=0}^{k-1} l_\nu(s) \tag{3.11}$$

$$\sum_{r=1}^{s} l_k(r) = \frac{1}{1-\rho}\left[l_k(s) - l_{k+1}(s)\right] \tag{3.12}$$

$$\sum_{r=1}^{s-1} l_k(r) l_j(s-r) = \frac{1}{1-\rho}\left(\rho\, l_{k+j}(s) - l_{k+j+1}(s)\right)\,. \tag{3.13}$$

In order to adapt the free parameter ρ according to (2.25), one needs that

$$\nu_1 = (1-\rho)^{-1} \tag{3.14}$$

which, in turn, leads to

$$1 - \rho = \frac{\mu_0}{\mu_1}\,. \tag{3.15}$$

Remark. This representation avoids cancellation of leading digits in the numerical evaluation, if $1 - \rho(t) \to 0^+$.

By definition, one has

$$\mu_1 \geq \mu_0 \quad , \tag{3.16}$$

which implies

$$\rho \geq 0 \ . \tag{3.16'}$$

Note that equality in (3.16) and (3.16′) holds, if and only if

$$P_s = P_1 \cdot \delta_{s,1} \ . \tag{3.17}$$

In the limiting case $\rho = 0$, the weight function (3.2) degenerates to the discrete distribution

$$\Psi(s) = \delta_{s,1} \ . \tag{3.18}$$

For the variation of ρ, one needs the relation

$$\frac{\partial l_k}{\partial \rho} = \frac{k}{1-\rho}(l_{k-1} - l_k) \ . \tag{3.19}$$

The discrete Laguerre polynomials permit a natural extension to the heterogeneous case — which will be presented in a forthcoming paper.

3.2 Charlier Polynomials

Consider the *Poisson distribution*

$$\Psi(s) := e^{-\lambda} \cdot \frac{\lambda^{s-1}}{(s-1)!} \quad , \qquad s = 1, 2, \ldots \tag{3.20}$$

with normalization (2.24). The associated discrete inner product (2.1) generates a set of orthogonal polynomials — the so-called *Charlier polynomials* $\{c_k(s)\}$, which have already been treated by CHARLIER [3] in 1905.

Their *three-term recurrence relation* is

$$\lambda\, c_{k+1} = (k + \lambda + 1 - s)\, c_k - k\, c_{k-1} \tag{3.21.a}$$

to be started with

$$c_{-1} := 0, \qquad c_0 := 1 \ . \tag{3.21.b}$$

Orthogonality in the form (2.4) holds with

$$\gamma_k := \frac{k!}{\lambda^k} \qquad k = 0, 1, \ldots \ , \tag{3.22}$$

which directly implies

$$\gamma_k = \gamma_{k-1} \cdot \frac{k}{\lambda} \ , \quad \gamma_0 := 1 \quad , \quad k = 1, 2, \ldots \tag{3.22'}$$

The discrete *Rodrigues formula* reads

$$c_k(s) = \frac{(s-1)!}{\lambda^s} \Delta^k \left[\frac{\lambda^s}{(s-1-k)!} \right] . \tag{3.23}$$

As direct representation one obtains

$$c_k(s) = \sum_{\nu=0}^{k} \binom{k}{\nu} \nu! \, (-1)^\nu \lambda^{-\nu} \binom{s-1}{\nu} \ , \tag{3.24}$$

which readily yields

$$\begin{aligned} \text{a)} \quad c_k(0) &= \sum_{\nu=0}^{k} \binom{k}{\nu} \nu! \, \lambda^{-\nu} \\ \text{b)} \quad c_k(1) &= 1 \ . \end{aligned} \tag{3.25}$$

In analogy to (3.10) – (3.12), the following selection of properties is given:

$$c_k(s+1) - c_k(s) = -\frac{k}{\lambda} c_{k-1}(s) \qquad [17] \tag{3.26}$$

$$c_k(s-1) - c_k(s) = k! \sum_{\nu=0}^{k-1} \frac{\lambda^{\nu-k}}{\nu!} c_\nu(s) \tag{3.27}$$

$$\sum_{r=1}^{s} c_k(r) \frac{\lambda^{r-1}}{(r-1)!} = \frac{\lambda^{s-1}}{(s-1)!} c_{k-1}(s) \tag{3.28}$$

Adaptation of the free parameter λ according to (2.25) requires

$$\nu_1 = \lambda + 1 \ , \tag{3.29}$$

which, in turn, leads to

$$\lambda = \frac{\mu_1 - \mu_0}{\mu_0} . \tag{3.30}$$

As in Section 3.2, equality arises exactly in the case (3.17), which, in turn, then produces the representation (3.18) for the weight function Ψ.

For the variation of λ, one needs the relation

$$\frac{\partial c_k}{\partial \lambda} = \frac{k}{\lambda} \left(c_{k-1} - c_k \right) \ . \tag{3.31}$$

4. Analytic Preprocessing of Kinetic Equations

Application of the discrete Galerkin method as derived in Section 2 will lead to a system of ordinary differential equations for the associated generalized moments $\{a_k(t)\}$. This procedure is now exemplified for the two sets of orthogonal polynomials presented in Section 3. The mechanisms to be treated have already been introduced in Section 1.1. In actual computation, these mechanisms will only be part of a large system to be simulated. For the sake of clarity, however, the new approach is demonstrated only for a few isolated model problems. For real life applications, an automated preprocessor will be used, of course.

4.1 Preprocessing by Discrete Laguerre Polynomials

Starting point is the representation (2.7) with Ψ from (3.2)

$$P_s(t) := (1-\rho)\rho^{s-1}\sum_{k=0}^{\infty} a_k(t)\, l_k(s) \quad , \quad 0 < \rho < 1 \ , \tag{4.1}$$

with $\{l_k\}$ the discrete Laguerre polynomials as introduced in Section 3.1.

Moving weight function. The time-dependent adaptation of ρ according to (3.15) is recalled:

$$1-\rho(t) = \frac{\mu_0(t)}{\mu_1(t)} \geq 0 \tag{4.2}$$

which implies (2.30). Upon observing this time dependence in the representation (4.1), the total time derivation reads

$$\begin{aligned} P_s' \;=\; & \sum_{k=0}^{\infty}\{(1-\rho)\,\rho^{s-1}\left[a_k'\, l_k + a_k\frac{\partial l_k}{\partial\rho}\rho'\right] + \\ & +(1-\rho)(s-1)\rho^{s-2}\cdot\rho'\cdot a_k l_k - \rho'\rho^{s-1}a_k\, l_k\} \ . \end{aligned}$$

Upon inserting the relations (3.19) and (3.3.a,b), one ends up with

$$P_s' = (1-\rho)\rho^{s-1}\sum_{k=0}^{\infty}\left[a_k'\, l_k + \frac{a_k\rho'}{(1-\rho)\rho}(kl_k - (k+1)l_{k+1})\right]$$

Projection onto the associated basis yields (with $a_{-1} := 0$):

$$\rho^{-j}\,\langle l_j\,,\,P_s'\rangle \;=\; a_j' + \frac{j\rho'}{(1-\rho)\rho}(a_j - a_{j-1}) \ , \ j = 0,\,1,\,\ldots \tag{4.3}$$

For $j = 0, 1$ and with (2.30.b) one obtains in particular

$$\begin{aligned} \text{a)} \quad \langle l_0 , P_s' \rangle &= a_0' \\ \text{b)} \quad \frac{1}{\rho} \langle l_1 , P_s' \rangle &= -\frac{a_0}{(1-\rho)\rho} \rho' \end{aligned} \tag{4.4}$$

For an individual polyreaction mechanism, the kinetic equations have to be inserted into the left-hand side of (4.3), once more using the representation (4.1). This procedure generates a complete system of ordinary differential equations for the components

$$(a_0(t) , \rho(t) , a_2(t) , \ldots) .$$

Chain addition polymerization. This mechanism is described by the model equations (1.4). In view of (4.3) one has to calculate

$$\begin{aligned} \langle l_j , P_s' \rangle &= \sum_{s=1}^{\infty} l_j(s) P_s' = -l_1(1) P_1 + \sum_{s=2}^{\infty} l_j(s)(-P_s + P_{s-1}) = \\ &= \sum_{s=1}^{\infty} P_s \left(l_j(s+1) - l_j(s) \right) \end{aligned} \tag{4.5}$$

With (3.10), one concludes

$$\rho^{-j} \langle l_j , P_s' \rangle = -\frac{1-\rho}{\rho} \sum_{m=0}^{j-1} a_m \tag{4.6}$$

Combination of (4.3), (4.4), and (4.6) then yields

$$\begin{aligned} \text{a)} \quad a_0' &= 0 \\ \text{b)} \quad \rho' &= (1-\rho)^2 \\ \text{c)} \quad a_j' &= -\frac{1-\rho}{\rho} \left[\sum_{m=0}^{j-1} a_m + j(a_j - a_{j-1}) \right] , \quad j = 2, 3, \ldots \end{aligned} \tag{4.7}$$

For the transformation of the initial values (1.4.b) recall (2.8), (3.17) and (3.18) to obtain

$$\begin{aligned} \text{a)} \quad a_0(0) &= P_{10} \\ \text{b)} \quad \rho(0) &= 0 \end{aligned} \tag{4.8}$$

This is the *degenerate* case of the weight function (3.2). As a consequence, the representation (2.8) cannot directly be applied to yield $a_j(0)$ — just recall that

$$\gamma_j = \rho^j \doteq l_j(1) = 0 . \tag{4.9}$$

Rather, a limiting process

$$a_j(0) := \lim_{t \to 0^+} a_j(t) \tag{4.10}$$

must be performed. Examination of the right-hand side in (4.7.c) shows that a regular solution a_j is only possible under the necessary algebraic conditions

$$a_j(0) = a_{j-1}(0) - \frac{1}{j} \sum_{m=0}^{j-1} a_m(0) \quad , \qquad j = 2, 3, \dots \ , \tag{4.11}$$

which are seen to determine the missing initial values. Under this assumption, (4.7.c) has a *removable singularity*: by means of Taylor expansion around $t = 0$ one easily verifies that the initial right-hand side

$$a_j'(0) = \frac{1}{j+1} \left[j a_{j-1}'(0) - \sum_{m=0}^{j-1} a_m'(0) \right] \tag{4.12}$$

must be used to start the numerical integration.

Coagulation and polycondensation. This mechanism is modelled by the differential equations (1.9) in terms of the number $N_s(t)$ of polymers of length s. Of course, $N_s(t)$ now replaces $P_s(t)$ in the representation (4.1). Moreover, for illustration purposes, the specification (1.10) for the *Smoluchowski model* is made. Once more, the relation (4.3) requires the calculation of

$$\langle l_j \, , N_s' \rangle = \frac{k_p}{2} \left\langle l_j, \sum_{r=1}^{s-1} N_r N_{s-r} \right\rangle - k_p \left\langle l_j, \, N_s \sum_{r=1}^{\infty} N_r \right\rangle$$

Upon using the relations (2.30) and (1.13), rearranging the order of summation and applying the properties of Section 3.1, one obtains

$$\begin{aligned} \langle l_j, \, N_s' \rangle &= \frac{k_p}{2} \sum_{k=0}^{\infty} a_k \sum_{m=0}^{\infty} a_m \sum_{s=1}^{\infty} (1-\rho)^2 \rho^{s-2} l_j(s) \sum_{r=1}^{s-1} l_k(r) \, l_m(s-r) - \\ &\quad - k_p \, a_0 \sum_{k=0}^{\infty} a_k \sum_{s=1}^{\infty} (1-\rho) \rho^{s-1} l_j(s) l_k(s) = \\ &= \frac{k_p}{2} \rho^j \left[\sum_{m=1}^{j-1} a_m \, a_{j-m} - \frac{1}{\rho} \sum_{m=0}^{j-1} a_m \, a_{j-1-m} \right] \end{aligned} \tag{4.13}$$

Combination of (4.13) and (4.3) then leads to the differential equations ($j = 2, 3, \ldots$):

$$
\begin{aligned}
\text{a)}\quad a_0' &= -\frac{k_p}{2} a_0^2 \\
\text{b)}\quad \rho' &= \frac{k_p}{2}(1-\rho) a_0 \\
\text{c)}\quad a_j' &= \frac{k_p}{2}\left[\frac{j\, a_0}{\rho}(a_{j-1} - a_j) + \sum_{m=1}^{j-1} a_m\, a_{j-m} - \frac{1}{\rho}\sum_{m=0}^{j-1} a_m\, a_{j-1-m}\right]
\end{aligned}
\tag{4.14}
$$

For general initial values $N_s(0)$, the representations (4.2) and (2.8) are directly evaluated (compare [7, 8]). In [18], the *degenerate* case

$$N_s(0) = N_{10}\, \delta_{s,1} \tag{4.15}$$

has been prescribed. As in the preceding model problem, a singularity arises in (4.14.c), which can be removed by setting the initial values

$$a_j(0) := a_{j-1}(0) - \frac{1}{j a_0(0)} \sum_{m=0}^{j-1} a_m(0)\, a_{j-1-m}(0) \quad , \quad j = 2, 3, \ldots \tag{4.16}$$

With $a_0(0) = N_{10}$, $a_1(0) = 0$ repeated induction in (4.16) readily yields

$$a_j(0) = 0 \quad , \quad j = 2, 3, \ldots \ . \tag{4.17}$$

In order to start the integration, one needs the right-hand side

$$a_j'(0) = \frac{j-2}{j+1} a_{j-1}'(0) \quad , \quad j = 2, 3, \ldots \ , \tag{4.18}$$

which, with $a_1'(0) = 0$, directly leads to

$$a_j'(0) = 0 \qquad , \qquad j = 2, 3, \ldots \ . \tag{4.19}$$

As it turns out, these initial values imply

$$a_j(t) \equiv 0 \qquad , \qquad j = 1, 2, \ldots \ . \tag{4.20}$$

Summarizing, only *one* generalized moment and a moving Schulz-Flory weight function is sufficient to describe this mechanism! This structure is, of course, modified in the cases, when either the initial values (4.15) are different or the polyreaction mechanism is part of a larger reaction scheme. In any case, the above derivation confirms that the discrete Galerkin-Laguerre method is particularly well-suited for this kind of mechanism.

Polymer degradation. In this paper, only the method for the *homogeneous* model (1.7) with (1.8.a) is presented. The treatment of the heterogeneous cases (1.8.b, c) will be given elsewhere. As in the two preceding model problems, one has to calculate

$$\frac{1}{k_p}\langle l_j\,,\,N_s'\rangle = -\langle (s-1)l_j\,,\,N_s\rangle + 2\left\langle l_j\,,\,\sum_{i=s+1}^{\infty} N_i\right\rangle \;.$$

The first term on the right-hand side just requires the application of the three-term-recurrence (3.3.a, b). For the second term, the relations (3.12) and (3.9.b) together with a proper reordering of summations are employed. This leads to the result

$$\rho^{-j}\langle l_j\,,\,N_s'\rangle = \frac{k_p}{1-\rho}\left[j(a_{j-1}-a_j)+\rho(j-1)(a_{j+1}-a_j)\right] \tag{4.21}$$

Insertion of (4.21) into (4.3) then yields the differential equations

$$\begin{aligned}
&\text{a)}\quad a_0' &&= \frac{k_p\,\rho}{1-\rho}\,a_0 \\
&\text{b)}\quad \rho' &&= -k_p\,\rho \\
&\text{c)}\quad a_j' &&= \frac{k_p\,\rho}{1-\rho}(j-1)\,(a_{j+1}-a_j)\quad,\quad j=2,3,\ldots\;.
\end{aligned} \tag{4.22}$$

Note that the system (4.22) is *open*, which requires a truncation rule such as $a_{N+1} := 0$ for truncation index N.

Initial values $P_s(0) \sim sN_s(0)$ from experimental measurements are plotted in Figure 4, [2], or in Figure 13.6, [11]. In view of these experimental data, the following model initial values seem to be realistic:

$$N_s(0) = \frac{s}{r}\,e^{-s/r}\;. \tag{4.23}$$

With this choice, the maximum of the distribution $N_s(0)$ roughly occurs at $s = r$. From (4.23), the initial value

$$1-\rho(0) := \frac{1-\bar\rho}{1+\bar\rho}\;,\quad \bar\rho := e^{-1/r} \tag{4.24}$$

can be obtained, which then allows to compute the $a_0(0)$, $a_2(0)$, ... from (2.8).

4.2 Preprocessing by Charlier Polynomials.

With the weight function Ψ from (3.20) the associated representation for the polymer distribution reads

$$P_s(t) := e^{-\lambda}\frac{\lambda^{s-1}}{(s-1)!}\sum_{k=0}^{\infty} a_k(t)\,c_k(s)\quad,\quad \lambda>0 \tag{4.25}$$

where $\{c_k\}$ denotes the set of Charlier polynomials as introduced in Section 3.2.

Moving weight function. According to (3.30), the time-dependence of the parameter λ comes out to be

$$\lambda(t) = \frac{\mu_1(t) - \mu_0(t)}{\mu_0(t)} \geq 0 \quad , \tag{4.26}$$

which implies (2.30). Proceeding as in Section 4.1, using (3.21.a,b) and (3.31), one ends up with a representation for the total time derivation

$$P_s' = e^{-\lambda} \frac{\lambda^{s-1}}{(s-1)!} \sum_{k=0}^{\infty} [a_k' \, c_k - a_k \, \lambda' c_{k+1}] \quad . \tag{4.27}$$

This, in turn, generates the result (with $a_1 := 0$):

$$\frac{\lambda^j}{j!} \langle c_j \, , \, P_s' \rangle = a_j' - \lambda' a_{j-1} \quad , \quad j = 0, 1, \ldots \tag{4.28}$$

In particular, for $j = 0, 1$ one has

$$\begin{aligned} \text{a)} \quad \langle c_0, P_s' \rangle &= a_0' \\ \text{b)} \quad \lambda \langle c_1, P_s' \rangle &= -a_0 \cdot \lambda' \end{aligned} \tag{4.29}$$

With these preparations one is now ready to derive the differential equations for various polyreaction mechanisms.

Chain addition polymerization. A short calculation using the model equations (1.4) and the property (3.26) of the Charlier polynomials leads to

$$\frac{\lambda^j}{j!} \langle c_j, P_s' \rangle = -a_{j-1} \quad , \quad j = 0, 1, \ldots \tag{4.30}$$

and to the differential equations

$$\begin{aligned} \text{a)} \quad a_0' &= 0 \\ \text{b)} \quad \lambda' &= 1 \\ \text{c)} \quad a_j' &= 0 \quad , \quad j = 2, 3, \ldots \end{aligned} \tag{4.31}$$

Transformation of the initial values (1.4.b) produces the initial values

$$\begin{aligned} \text{a)} \quad a_0(0) &= P_{10} \\ \text{b)} \quad \lambda(0) &= 0 \\ \text{c)} \quad a_j(0) &= 0 \quad , \quad j = 2, 3, \ldots \end{aligned} \tag{4.32}$$

Note that (4.32.b) is once more the *degenerate* case of the weight function (3.20), which, however, does not induce a singularity in (4.32). Only two components of the expansion turn out to be sufficient for an exact representation — a result derived from general principles without use of the special model structure!

Reversible polymerization. On the basis of the model equations (1.6) the above procedure leads to

$$\frac{\lambda^j}{j!}\langle c_j, P_s'\rangle = -k_1 a_{j-1} + k_2 \cdot (A_{j-1} - \Phi(j)\, A_\infty) \tag{4.33}$$

with the convenient notation

$$\begin{aligned} &\text{a)} \quad A_k \quad := \sum_{m=0}^{k} a_m \\ &\text{b)} \quad \Phi(j) \quad := \sum_{m=1}^{j} \Psi(m) \;\leq\; \Phi(\infty) \;=\; 1 \end{aligned} \tag{4.34}$$

To derive (4.33), the relations (3.26) and (3.27) as well as the representation

$$P_1 = e^{-\lambda} A_\infty \tag{4.35}$$

have been used. Note that the system (4.33) is *open*, which means that a truncation rule needs to be imposed. In Section 5, the truncation

$$A_\infty \longrightarrow A_N \tag{4.36}$$

has been made for varying truncation index N. Of course, such a replacement would require a careful convergence analysis, which is, however, beyond the scope of the present paper. Finally, initial values for this model problem are obtained from (1.4.b) in the same way as described for the other examples.

5. Numerical Experiments

In this section, the approach derived above is now illustrated. Because of the different convergence theory, a splitting between self-closing and open systems is made. On the basis of Section 2.2 it is clear that, whenever the differential equations for the statistical moments are self-closing, then this property is inherited for *any* generalized moments arising in the discrete Galerkin method.

5.1 Self-closing Systems

Among the polyreaction processes treated herein (Section 1.1), the chain addition polymerization and the coagulation (or polycondensation) with the Smoluchowski specification lead to a self-closing differential equation system (compare Section 4).

Chain addition polymerization. The preprocessing of model (1.4) by *Charlier polynomials* showed that the exact analytic solution for the initial values (1.4.b) is just the *moving Poisson distribution* with time dependent amplitude

$$P_s(t) = a_0(t)\, e^{-\lambda(t)}\, \frac{(\lambda(t))^{s-1}}{(s-1)!} \ . \tag{5.1}$$

This means that the discrete Galerkin-Charlier method is exact already for truncation index $N = 1$. (Of course, (5.1) has already been derived otherwise [18].) From (4.31) and (4.32) the direct analytic solution

$$a_0(t) = P_{10} \ , \quad \lambda(t) = t \tag{5.2}$$

can be calculated. Note, however, that for general initial values $P_s(0)$ the truncation index N for a reasonable approximation $P_s^{(N)}$ will be greater than 1. Nevertheless, the Poisson distribution as weight function Ψ seems to fit particularly well with this special polyreaction mechanism.

Things turn out to be different when the *Schulz-Flory distribution* is chosen as weight function Ψ for the discrete Galerkin method (Section 4.1). This fact is illustrated in Figure 1, where the discrete Galerkin-Laguerre approximation for $N = 1$, 10, 30 and $t = 5$ is depicted. At the same time, these Figures visualize the comments about the Stieltjes problem for *finite* truncaton index N, that have been made in Section 2.2: recall that due to the self-closing property of the system (4.7) the first $N + 1$ statistical moments can be correctly computed via (2.22).

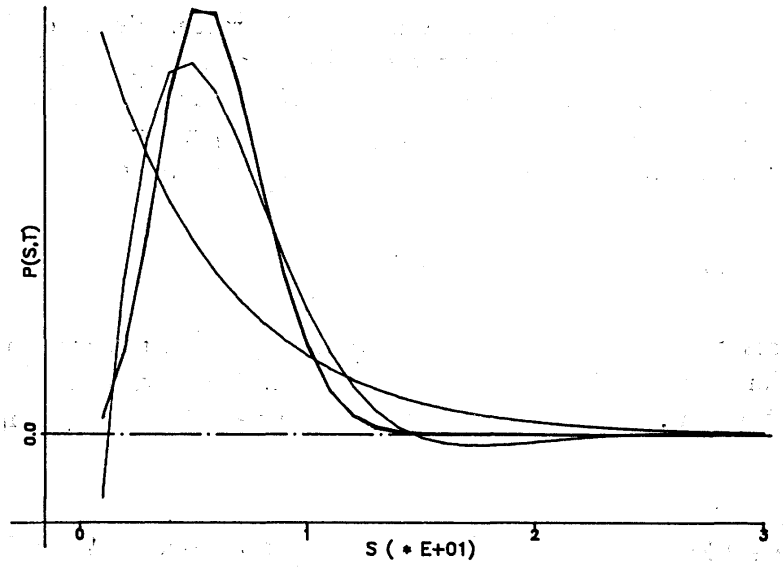

Figure 1: Various discrete Galerkin-Laguerre approximations $P_s^{(N)}$, $t = 5$, for the chain addition polymerization problem. The approximations for $N = 1, 10, 30$ approach the solution from below. Note that, in this model problem, the Galerkin-Charlier approximation is exact already for $N = 1$.

Coagulation/polycondensation. The preprocessing of the Smoluchowski model (1.9)/(1.10) by *discrete Laguerre polynomials* showed that for the special initial values (4.15) the exact solution can be represented already with $N = 1$, which means

$$N_s(t) = a_0(t)\,(1-\rho(t))\,\rho(t)^{s-1}\,. \tag{5.3}$$

The functions a_0, ρ are defined by the 2 coupled differential equations (4.14.a,b), which can be solved in closed analytic form to yield:

$$a_0(t) = \frac{2}{t+2} \quad , \quad \rho(t) = \frac{t}{t+2}\,. \tag{5.4}$$

This example is chosen to demonstrate the importance of the Hilbert space condition (2.6). For this purpose, the analytic solution (5.3) and the weight function Ψ with, for the time being, arbitrary ρ are inserted into (2.6): this means that

the infinite sum

$$S := \sum_{s=1}^{\infty} \frac{N_s^2(t)}{\Psi(s,\, \rho)} \tag{5.5}$$

with Ψ from (3.2) must be bounded. A straightforward calculation shows that

$$S = \frac{4}{(t+2)^2} \cdot \frac{1}{1-\rho} \sum_{s=0}^{\infty} \left(\frac{t^2}{\rho(t+2)^2} \right)^s . \tag{5.6}$$

From this, one obtains the necessary condition

$$\rho > \bar{\rho}(t) = \left(\frac{t}{t+2} \right)^2 . \tag{5.7}$$

Note that $\rho(t)$ from (5.4), which is based on the general adaptation (2.25), actually satisfies the condition (5.7). The question of whether (2.25) *generally* confirms (2.6) is open to further investigation. The importance of condition (2.6) for actual computation is illustrated in Figure 2, where truncated discrete Laguerre expansions with $\rho < \bar{\rho}$ and $\rho > \bar{\rho}$ are compared for increasing N.

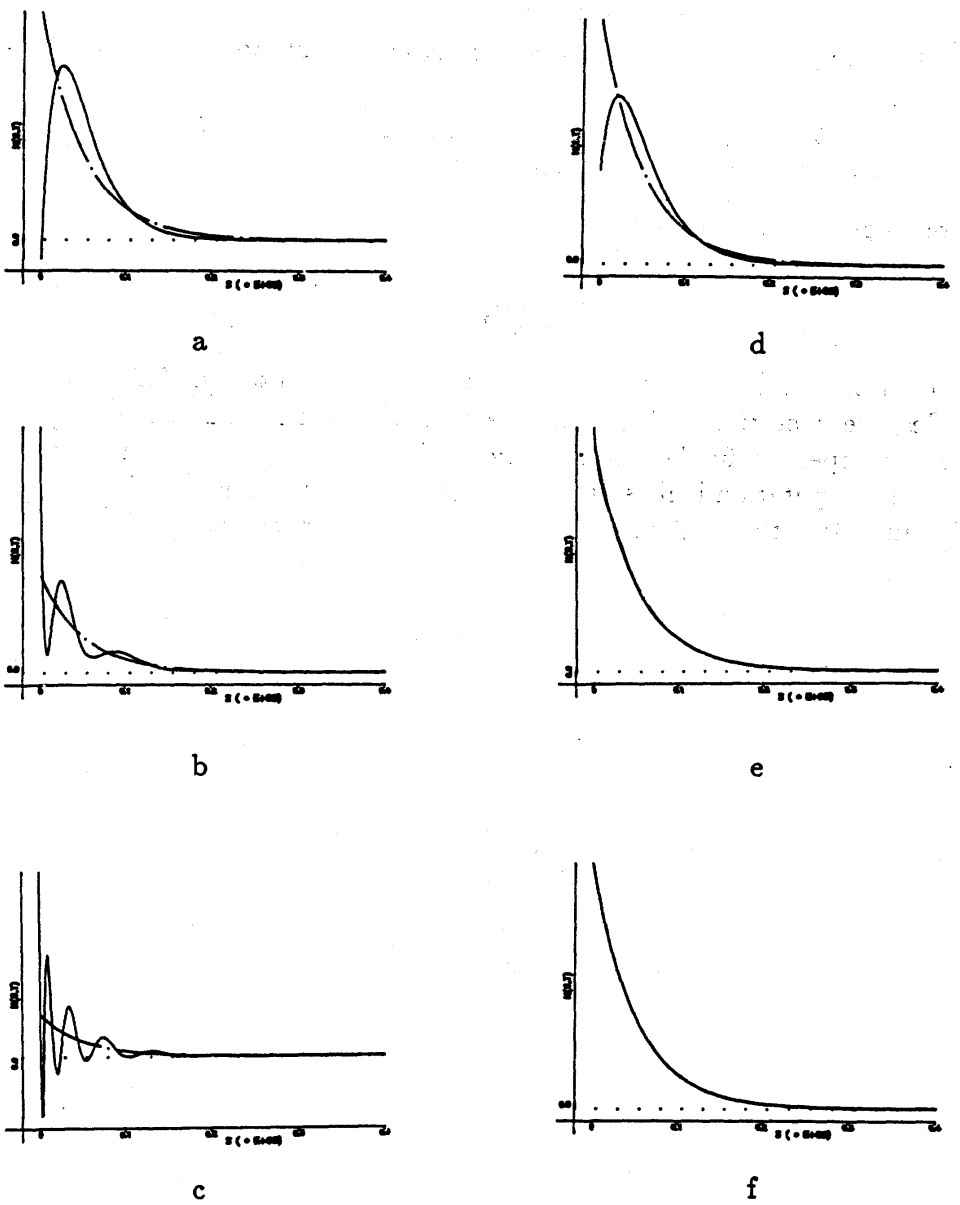

Figure 2: Discrete Galerkin-Laguerre approximation $N_s^{(N)}$, $t = 100$ in the coagulation model problem. The truncation index is selected as $N = 1$ (a, d), $N = 10$ (b, e), and $N = 30$ (c, f). The parameter ρ is chosen as $\rho = 0.960$ (a, b, c) and $\rho = 0.965$ (d, e, f). Threshold value for convergence is $\bar{\rho} = 0.961 \ldots$. Optimal value is $\rho = 0.980 \ldots$, which yields the exact solution with $N = 1$.

5.2 Open Systems

Among the selection of polyreaction processes in Section 1.1, the polymer degradation and the reversible polymerization lead to open differential systems. In these cases, the estimate (2.19) of the Galerkin approximation error needs an additional consideration. Whenever the adapted parameters (here ρ or λ) are independent of the truncation index N, then a reasonable *relative error estimate* will be

$$\epsilon_N := \frac{\|\bar{P}_s^{(N)} - \bar{P}_s^{(N+1)}\|_\Psi}{\|\bar{P}_s^{(N+1)}\|_\Psi} \tag{5.8}$$

in terms of the definition (2.19) and

$$\|\bar{P}_s^{(N+1)}\|_\Psi = \left(\sum_{k=0}^{N+1} \left(a_k^{(N+1)}\right)^2 \gamma_k\right)^{1/2} . \tag{5.9}$$

If, however, the truncation index N affects the value of ρ or λ, then also the normalization factors γ_k and the polynomial basis are affected. In this situation, the estimate (2.19) must be modified replacing

$$a_k^{(N)} - a_k^{(N+1)} \longrightarrow a_k^{(N)} - a_k^{(N+1)} + \frac{j\,\delta\rho}{(1-\rho)\,\rho}\left(a_k^{(N)} - a_{k-1}^{(N)}\right) \tag{5.10.a}$$

with

$$\rho := \rho^{(N)} \quad , \quad \delta\rho := \rho^{(N)} - \rho^{(N+1)} \tag{5.10.b}$$

for the Galerkin-Laguerre approximation and replacing

$$a_k^{(N)} - a_k^{(N+1)} \longrightarrow a_k^{(N)} - a_k^{(N+1)} - \delta\lambda\, a_{k-1}^{(N)} \tag{5.11.a}$$

with

$$\delta\lambda := \lambda^{(N)} - \lambda^{(N+1)} \tag{5.11.b}$$

for the Galerkin-Charlier approximation. In both cases, the factors

$$\gamma_k := \gamma_k^{(N+1)} \tag{5.12}$$

are to be inserted.

Polymer degradation. The preprocessing of model (1.7)/(1.8.a) by *discrete Laguerre polynomials* leads to the differential equations (4.22). The initial values (4.23) with

$$r := 100 \quad , \quad s_{max} = 1000 \tag{5.13}$$

are selected. From (4.22.b) ρ can be seen to be independent from the truncation index N. So the error estimator (5.8) with (2.19) (replacing $P_s(t)$ by $N_s(t)$, of course) is compared with the *true truncation error*

$$\bar{\epsilon}_N := \frac{\|\bar{N}_s^{(N)} - \bar{N}_s\|_\Psi}{\|\bar{N}_s\|_\Psi} \tag{5.14}$$

for varying N. The results are arranged in Table 1 showing that the error estimator is useful.

truncation index N	estimated error ϵ_N	true error $\bar{\epsilon}_N$
1	0.245	0.387
2	0.235	0.295
3	0.170	0.195
4	0.112	0.124
5	0.070	0.074
6	0.043	0.042
7	0.026	0.023
8	0.015	0.012
9	0.008	0.006
10	0.003	0.004

Table 1: Comparison of estimated and true approximation error for the initial values (4.23)/(5.13) in the polymer degradation problem.

In Figure 3, the time evolution of

$$P_s(t) := s\, N_s(t) \tag{5.15}$$

is plotted on the basis of the Galerkin-Laguerre approximation for $N = 10$. The obtained error estimates for $N_s(t)$ were:

$$\begin{aligned} \epsilon_{10}(0) &= 0.003 \\ \epsilon_{10}(0.001) &= 0.002 \\ \epsilon_{10}(0.01) &= 0.0004 \\ \epsilon_{10}(0.1) &= 0.00001 \end{aligned} \tag{5.16}$$

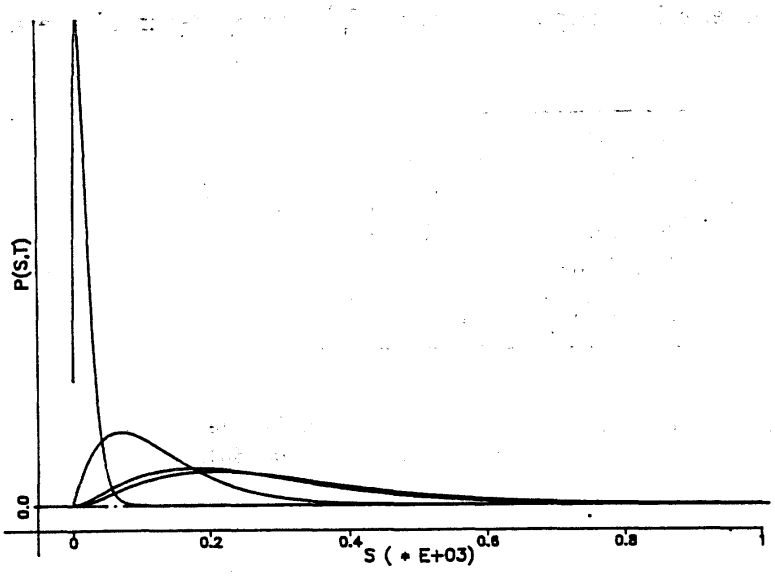

Figure 3: Various polymer distributions $P_s(t)$ for the polymer degradation problem ($N = 10$, $t = 0, 0.001, 0.01, 0.1$). The peaks move from right to left.

Note that the computation of the associated true errors $\bar{\epsilon}_{10}$ would require the solution of 1000 stiff ordinary differential equations with full triangular Jacobian — or a lumping technique, which introduces an unknown approximation error (cf. [11]).

Reversible polymerization. In model problem (1.6), the reaction rate coefficients $k_1 = 1$, $k_2 = 0.2$ have been chosen. Preprocessing by *Charlier polynomials* generates the differential equations based on (4.28) and (4.33). The truncation rule (4.36) is more complicated than in the preceding example — leading to approximations $\lambda^{(N)}$, $\mu_1^{(N)}$ etc. Nevertheless, convergence can be observed: in Table 2, the approximation errors

$$\epsilon_N^{(1)}(t) := \frac{|\,\mu_1^{(N)}(t) - \mu_1^{(N+1)}(t)\,|}{\mu_1^{(N+1)}(t)} \tag{5.17}$$

and $\epsilon_N(t)$ from (5.8) are compared — using the replacement (5.10) in (2.19). Note that the high accuracy of μ_1 does not imply a comparable accuracy of the

polymer distribution. A selection of approximations $P_s^{(N)}$ is depicted in Figure 4.

N	ϵ_N	$\epsilon_N^{(1)}$
1	0.328	$0.108.10^{-3}$
5	0.079	$0.097.10^{-4}$
10	0.033	$0.087.10^{-5}$
15	0.025	$0.091.10^{-6}$

Table 2: Comparison of approximation errors for the reversible polymerization problem ($t = 150$).

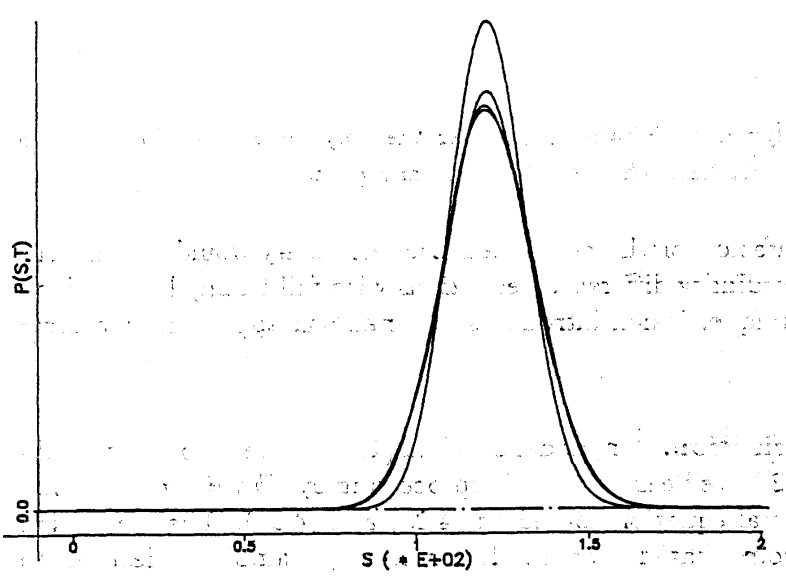

Figure 4: Various Galerkin-Charlier approximations $P_s^{(N)}$ at $t = 150$ for the reversible polymerization problem. The approximations for $N = 1, 5, 10, 15$ approach the solution from above.

Conclusion

The paper presented the basic approximation scheme of the discrete Galerkin method in terms of selected model problems. The theoretical properties of this scheme together with the illustrative numerical experiments back the expectation that the method will also be efficient for more general problems, when further non-polymer species or a mixture of different polymer species arise. Of course, a lot of further work needs to be done in view of extended problem classes. However, the authors regard this paper as a first step towards an efficient, reliable and storage economic simulation of polyreaction kinetics.

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