APPLICATION OF THE POLYNOMIAL CHAOS EXPANSION TO THE NUMERICAL SIMULATION OF A BATCH REACTOR

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Abstract.

The polynomial chaos expansion has become a relative widespread technique to deal with systems with uncertainties. Stochastic linear differential equations can be reduced to deterministic differential equations by projecting this expansion onto the probability space. We use this feature to simulate the decomposition of acetylated castor oil ester in an isothermal batch reactor and to compare the deterministic and stochastic approach.

1 Introduction

For the treatment of uncertainties of model parameters Monte-Carlo evaluations are a state of the art method. If the model is simple in terms of the computation time on a workstation, Monte-Carlo evaluations are a suitable method for computing the moments of the system. For the complex case of reactive flows a probabilistic estimation or optimization of this model with the Monte-Carlo method can be prohibitive.

During the last years *Polynomial Chaos* for the treatment of uncertainties of complex systems has been developed to a cheap and powerful alternative to Monte-Carlo, see [8, 13]. It is based on the assumption that an expansion of a random variable in terms of orthogonal polynomial functions on the probability space of this random variable is possible, and that the convergence to the random variable is fast enough, so that a truncation after few terms of the expansion already offers a good approximation.

Our goal is to use the polynomial chaos expansion to simulate an isothermal batch reactor, reducing the original, stochastic system to a set of deterministic equations, which can be then solved by standard methods, and to illustrate the advantages of considering the stochastic approach in certain situations.

This paper is divided as follows: In section 2 the basics of the chemical kinetics are exposed, along with the derivation of the governing equations for an isothermal batch reactor from simple mass balance assumptions. Section 3 gives a brief overview of the polynomial chaos expansion and applies it to the simulation of an isothermal batch reactor. Finally, in section 4 the decomposition of acetylated castor oil ester in an isothermal batch reactor is simulated and the effect of uncertainties in the temperature is discussed.

2 Governing Equations

2.1 Chemical Kinetics

We consider a chemical system composed of N species and M reactions:

$$\sum_{i=1}^{N} v'_{ij} \mathcal{M}_i \xrightarrow{k_j} \sum_{i=1}^{N} v''_{ij} \mathcal{M}_i \qquad j = 1, ..., M. \tag{1}$$
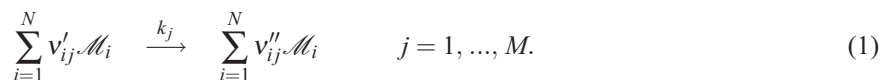
where $\mathcal{M}_i$ represents the i-th species, and v'_{ij}, v''_{ij} are the *molar stoichiometric coefficients* of species i in the reaction j. The *specific reaction rate* of the j-th reaction is given by k_j, and is assumed to follow the Arrhenius law

$$k = A \cdot T^b \cdot exp\left[-\frac{E_a}{RT}\right]. \tag{2}$$

The *activation energy* E_a is the energy threshold for the reaction to occur, R is the gas constant and AT^b the *preexponential factor*. Note the strong dependence of the reaction rate on the temperature T.

The general case (1) yields for the overall reaction rate of a substance $\mathcal{M}_i$

$$R_{\mathcal{M}_i} = \sum_{j=1}^{M} (v''_{ij} - v'_{ij}) k_j \prod_{l=1}^{N} \eta_{\mathcal{M}_l}^{v'_{lj}}, \qquad i = 1, ..., N, \tag{3}$$

with $\eta_{\mathcal{M}_l}$ the molar concentration of $\mathcal{M}_l$.

A deep treatment of chemical kinetics is out of the scope of this work. The reader should consult [1] or [4] for more details.

2.2 Mass Balance Equation

The reactive flows are going to be simulated in chemical reactors. We need a design equation which expresses the time and spatial variation of the concentration for a given substance. This will take into account inflow of the substance in the reactor, outflow and chemical reactions involving it. The following *ansatz* can be made for the mass balance

$$I_X \quad - \quad O_X \quad + \quad G_X \quad = \quad A_X, \tag{4}$$

where I_X is the *Inflow*, O_X the *Outflow* and G_X the overall reaction rate of the substance X. A_X is the change in time of the concentration of X via chemical reaction, the so-called *accumulation*. For the total reaction rate is valid

$$G_X = \int_V R_X dV, \tag{5}$$

with V the total volume of the reactor. I_X is defined as the molar mass per unit time that gets in the reactor. O_X is the molar mass per unit time that exits the reactor.

2.3 Batch Reactor

The classical batch reactor is a perfectly mixed vessel in which reactants are converted to products during a period of time, called *batch cycle*. We suppose a homogeneous reaction mixture of all substances, so that concentration and temperature gradients can be neglected. It is used in a variety of processes, like polymerization and fermentation.

In the batch reactor all variables change dynamically with time. The reactants are charged into the vessel and heat and/or catalyst is added to initiate reaction. In a pure batch operation the reactants are completely fed into the reactor at the beginning. This could result in undesired heating of the reactor, so progresive adddition of the reactants is also a possibility, called fed-batch or semibatch mode. We will only consider the batch mode. Fed-batch mode is treated in [4].

2.3.1 Isothermal Batch Reactor

We study the case of a batch reactor with no change in temperature. This can be justified for reactive flows where no net heat is generated or when the temperature is efficiently controlled during the reaction.

If we look at the design equation (4), operating in batch mode implies that I_X as well as O_X are zero. Remembering the assumption of homogeneity during the chemical reaction process and taking the volume of the reactor as contant we have an equality of two terms, G_X is given by (3) and A_X represents the change in molar mass of X with time. With the homogeneity assumption above we can divide by the volume and finally get

$$\frac{d\eta_i}{dt} = R_i, \qquad i = 1, ..., N. \tag{6}$$

We have thus to deal with a set of N ordinary differential equations.

3 Polynomial Chaos

3.1 Polynomial Chaos Expansion

Due to Wiener [12] homogeneous chaos is defined as a span of Hermite polynomial functionals of a Gaussian process. According to the theorem of Cameron and Martin [2], the Fourier-Hermite series can approximate any functionals in L_2 and converges in the L_2 sense. So second-order random processes can be expanded in terms of orthonormal Hermite polynomials. A general second order random process $x(\theta)$, with θ being the random event, can be represented in the form

$$x(\theta) = \sum_{i=0}^{\infty} a_i \Psi_i(\xi) \tag{7}$$

where there is a one-to-one correspondence between the functions $H_j(\xi)$ and $\Psi_i(\xi)$. The polynomial basis Ψ_i forms a complete orthonormal basis of the Hilbert space H and the coefficients a_i in (7) may be computed very efficiently by a multi-dimensional Gauss-Hermite quadrature [3]

It can be proved, [6], that by truncating the expansion (7) after

$$N+1 = \frac{(n+p)!}{n!p!} \tag{8}$$

terms, we get an approximation of order p for the random variable x. The expectation value and the variance can be then computed as follows

$$E(x) = a_0 \tag{9}$$
$$\sigma^2(x) = \sum_{i=1}^{N} a_i^2 < \Psi_i, \Psi_i > . \tag{10}$$

For normal distributed random variables the exponential convergence of the homogeneous chaos expansion can be shown, [13]. For random variables distributed other than normal, homogeneous chaos expansion still works, but its convergence is no good as it is for the normal distribution.

The same exponential convergence can be achieved when using the *generalized polynomial chaos*. In this generalization not only the Hermite polynomials are used, but a series of orthogonal hypergeometric polynomials grouped in the so called *Askey scheme* can be taken to construct the expansion.

Thus, the expansion for the random process $x(\theta)$ in the generalized expression reads

$$x(\theta) = \sum_{i=0}^{\infty} c_i \Phi_i(\xi). \tag{11}$$

It is shown that for each distributed random variable a polynomial expansion from the Askey-scheme can be found for which the convergence is exponential.

3.1.1   Karhunen-Loève Expansion

When dealing with a model it is usual to have parameters which are of random nature. Thus, it is necessary to introduce these random processes in the model. A way to do that is using the *Karhunen-Loève expansion* [8, 10].

Let $\phi_i(x)$ and λ_i denote the eigenfunctions and eigenvectors respectively of the covariance matrix of the random variable x. Then, x has the representation

$$x(t, \zeta) = E(x(t, \zeta)) + \sigma(x(t, \zeta)) \sum_{i=1}^{\infty} \sqrt{\lambda_i} \phi_i(t) \zeta_i, \tag{12}$$

with $\{\zeta_i\}_{i \in \mathbb{N}}$ a set of uncorrelated random variables which build a basis of L_2. $E(x(t, \zeta))$ and $\sigma(x(t, \zeta))$ have the usual meanings of expectation or mean value and standard deviation.

The truncated version of the Karhunen-Loève expansion reads

$$x(t, \zeta) = E(x(t, \zeta)) + \sigma(x(t, \zeta)) \sum_{i=1}^{N} \sqrt{\lambda_i} \phi_i(t) \zeta_i . \tag{13}$$

3.2   Polynomial Chaos Expansion for the Batch Reactor

We apply now the polynomial chaos expansion to the isothermal batch reactor from section 2. The system of equations consists of n differential equations for n dynamical variables describing the system

$$\eta_i(t), \quad i = 1, ..., N \tag{14}$$

Every variable represents a stochastic process

$$\eta_i(t, \vec{\xi}) \in L_2([0, \tau] \times (\Omega, \mathscr{F}, P)), \qquad \vec{\xi} := (\xi_1, ..., \xi_d)^T, \tag{15}$$

with $\tau \in \mathbb{R}^+$ and $\vec{\xi}$ the vector of the random variables. d is thus the dimension of the probability space.

We assume that the variables are normal distributed, so

$$\eta_i(t,\vec{\xi}) \ \in \ L_2([0,\tau] \times (\mathbb{R}^d, \mathcal{B}^d, N_{m,\sigma^2})). \tag{16}$$

As seen above we can write the stochastic processes with the polynomial chaos expansion. Truncation after term P yields the approximation

$$\eta_i(t,\vec{\xi}) = \sum_{j=0}^{P} a_j^i(t)\Psi_j^d(\vec{\xi}) \tag{17}$$

where Ψ_j^d are the Hermite polynomials, cfr. [13]. The next step is the substitution of the polynomial chaos expansion of the random variables into equation (6)

$$\frac{d}{dt}\left(\sum_{j=0}^{P} a_j^i(t)\Psi_j^d(\vec{\xi})\right) = R\left(\sum_{j=0}^{P}(a_j^i(t))\Psi_j^d(\vec{\xi})\right), \qquad i = 1,...,N. \tag{18}$$

Now the equations (18) are projected on the chaos space $\mathcal{H}^P$ and the result is

$$\left\langle \frac{d}{dt}\left(\sum_{j=0}^{P} a_j^i(t)\Psi_j^d(\vec{\xi})\right), \Psi_m^d \right\rangle = \left\langle R\left(\sum_{j=0}^{P}(a_j^i(t))\Psi_j^d(\vec{\xi})\right), \Psi_m^d \right\rangle, \quad i = 1,...,N, \quad m = 0,...,P. \tag{19}$$

d/dt is a linear operator acting on the temporal coordinate. We can use the orthogonality property of the Hermite polynomials to write

$$\frac{d}{dt}(a_m^i(t))\left\langle (\Psi_m^d(\vec{\xi}))^2 \right\rangle = \left\langle R\left(\sum_{j=0}^{P}(a_j^i(t))\Psi_j^d(\vec{\xi})\right), \Psi_m^d \right\rangle, \quad i = 1,...,N, \quad m = 0,...,P. \tag{20}$$

The integrals $\left\langle (\Psi_m^d(\vec{\xi}))^2 \right\rangle$ for homogeneous chaos are listed up to dimension 4 in [5]. The integrals of the r.h.s. of equation (20) are calculated using a multidimensional *Gauß-Hermite* quadrature.

We see that through projection on the chaos space $\mathcal{H}^P$ the system of stochastic differential equations has been reduced to a system of ordinary differential equations, which can be now solved by standard integration schemes. As a drawback the new system has $(P+1) \times N$ differential equations, that means $P+1$ times more than the original system. Also the multidimensional quadrature. whose complexity increases exponentially with the dimension of the chaos space $\mathcal{H}^p$ is a challenge, which can be overcome by implementing adaptive Gauß quadrature methods.

3.3 Numerical Implementation

Ordinary differential equations arising from chemical kinetics are a paradigmatic example of stiff differential equations, [11]. Hence, care must be taken when choosing the integration scheme.

The code RADAU5 is used to solve the system [7]. It is a 5th order implicit Runge-Kutta technique, offering an efficient and stable performance for stiff differential equations.

Once the solution of the system is computed, mean values and standard deviation for the concentration of the species are given by equations (9), (10). In case some parameters are assumed to be of random nature, e.g. some activation energies, or the temperature, they can be introduced in the equation via the Karhunen-Loève expansion, equation (13).

4 Decomposition of acetylated castor oil ester

We study the case of decomposition on acetylated castor oil (ACO) in an isothermal batch reactor. Treatment of castor oil has a large variety of applications in industry, like cosmetics, inks, or lubricants [9]. Through dehydration drying oil (DO) is obtained, which is extensively used in paints and varnishes. The overall reaction is

$$ACO(l) \ \longrightarrow \ DO(l) + CH_3COOH(g) \tag{21}$$
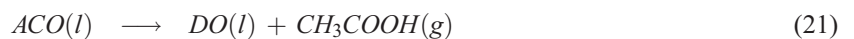
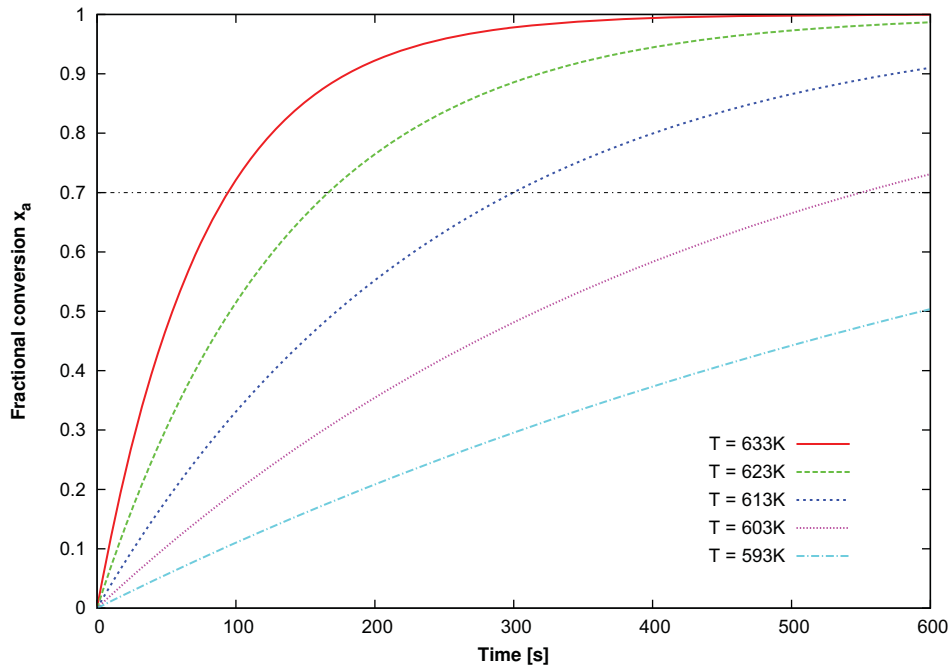and the reaction rate is [4]

Figure 1: Fractional conversion in time for different temperatures.

$$k = \left(\frac{1}{60}\right) \exp\left(35.2 - \frac{22450}{T}\right) s^{-1} \tag{22}$$

The usual operation temperature is $613K$. A final conversion of 70% to drying oil is desired. The fractional conversion is defined as

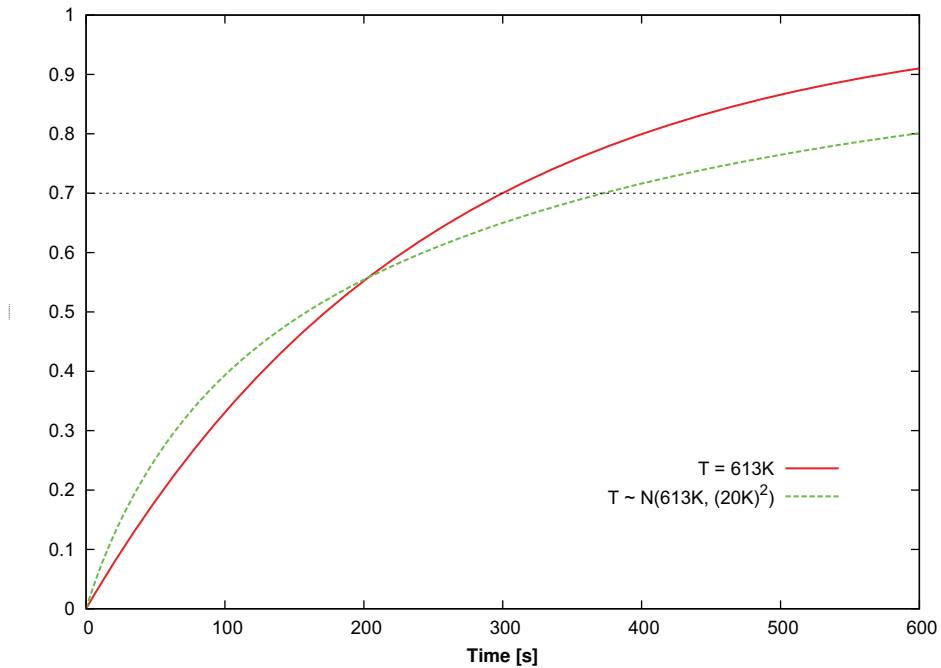$$x_A = \frac{[ACO] - [DO]}{[ACO]}. \tag{23}$$

Figure 2: Comparison of fractional conversion for deterministic and normal distributed temperature.

Fractional conversion progress with time at isothermal conditions for different temperatures is plotted in figure 1. It can be seen that for lower temperatures the time needed to reach 70% conversion explodes, while for temperatures higher than $613K$ the time saved to reach 70% decreases fast.

In the practice, isothermal conditions are not easy to maintain. We assume that the temperature can not be kept constant but varies, following a normal distribution with mean value $\mu = 613K$ and standard deviation $\sigma = 20K$. If we calculate considering a deterministic approach, with no temperature change, an error is being introduced. Plotting the conversion progress for deterministic and for stochastic temperature we get picture 2. The deterministic simulation estimated $298s$ to reach 70% conversion. For the stochastic simulation $371s$ were needed, This amounts to about 20% relative error, showing a clear underestimation of the reaction time for the deterministic computation. This shows that neglection of uncertainties can be a source of relevant misestimation.

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