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Numerical investigation of a dynamical model for emulsion pseudo-homopolymerization

Thibaut Besson, Cheng-Zhong Xu, Nida Sheibat-Othman, Hassan Hammouri

Université Lyon1, LAGEP, 69622 VILLEURBANNE, FRANCE, besson@lagep.cpe.fr

Abstract

A computationally efficient technique is presented to compute the dynamical behavior of an emulsion polymerization process based on a strongly nonlinear model with non-local couplings taken into account. We propose a numerical study adapted to the population balance equation (PBE). This numerical investigation is based on an academic example of hyperbolic type. The partial differential equation (PDE) is discretized by the methods of finite differences and orthogonal collocations. Via simulations, the analytical and numerical solutions are compared. Finally, it seems that the method of orthogonal collocations is the most appropriate for numerical investigations of such process.

Keywords

Population balance equation, finites differences, orthogonal collocations, method of characteristics.

1. Introduction

Emulsion polymerization is a chemical reaction in which the main reacting are the monomer (butyl acrylate), the surfactant (dodecyl sulphate) and the initiator (persulfate potassium). We consider a batch reactor in which the monomer is dispersed in the aqueous phase thanks to the surfactant. Conventional emulsion polymerization starts in the aqueous phase where the soluble water initiator decomposes and generates primary radicals. These radicals propagate and then

nucleate new particles by entering in micelles. The polymer chains continue to propagate inside the particles causing the particles to grow in size. We denote by $F(r,t)$, the particle size distribution function (PSD). The size and time evolution of F is influenced by physical and chemical processes like particle growth and particle nucleation, and is described by a population balance equation (PBE). We adopt the general structure of the pseudo-homopolymerization of Salvidar et al. [1] and rounded out by Immanuel et al. [2]. Finally, the pseudo-homopolymerization model is described by two nonlinear partial differential equations coupled with a system of nonlinear ordinary differential equations (given by the balance equations for the monomer and other components). The PSD is strongly correlated with the end product properties of the latex. It influences the rheological properties, adhesion and film-forming properties of final products.

2. Problem Statement, background

Given the system complexity, our main interest is to build a reliable algorithm to make an efficient prediction for the dynamical behavior of emulsion polymerization processes. The numerical simulations are very useful for the design of experimental reactors and sate observers. We can also consider control laws to track a goal trajectory stated according to the properties of the required product. To approximate the PBE, we must use a method of discretization which guaranties a fast and accurate algorithm. The most popular method is that of finite differences. Using this technique, the r-domain is divided into N points regularly spaced with a step of discretization Δr and the derivative with respect to r is approximated using limited Taylor developpment. Fig. 1 represents the profile of $F(r,t)$ with $r = 100\ nm$, for different N:

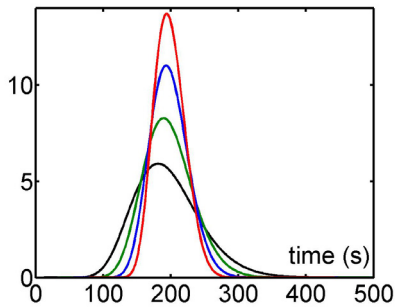

Figure 1 : Profile of $F(r,t)$ for N =100 (—), N =200 (—), N =400 (—) and N =800 (—)

In spite of a major decrease of Δr, the consistent of the method of finite differences is never satisfied. Obviously we could decrease again the step of

discretization but penalizing the algorithm fastness. Thus, given the initial aim, the method of finite differences is badly adapted to simulate efficiently the emulsion polymerization model.

3. Paper approach

We study a second method of discretization namely the method of orthogonal collocations. In this technique, $F(r,t)$ is expressed in terms of Lagrange polynomials with resepct to r within the domain $[r_{nuc}, r_{\max}]$.

3.1. Methodology

The methods of finite differences and orthogonal collocations have been implemented on a hyperbolic system in which an analytical solution has been worked out by the method of characteristics. Analytical and numerical solutions will be compared by simulations.

3.2. Case study

In order to study methods of discretization, the proposed system is a population balance equation of the form:

$$\begin{cases} \dfrac{\partial F(r,t)}{\partial t} + \dfrac{\partial}{\partial r}\big(G(r,t)F(r,t)\big) = 0, \ \forall (r,t) \in \Omega \\ G(r_{nuc},t)F(r_{nuc},t) = R_{nuc}(t) \end{cases} \quad 1.$$

with $F(0,t) = 0$ and Ω denotes $[r_{nuc}, r_{max}] \times [0,+\infty[$. The growth and nucleation terms denoted respectively by $G(r,t)$ and $R_{nuc}(t)$ are radius and time well-known functions such as $G(r,t) = \dfrac{G_0}{r^2}(1 - e^{-t/T})$, $G_0 > 0$, $T > 0$ and $R_{nuc}(t) = \dfrac{\alpha}{\sigma\sqrt{2\pi}} e^{\left(\frac{-(t-\mu)^2}{2\sigma^2}\right)}$, $\alpha > 0$, $\sigma > 0$ and $\mu > 0$. Moreover, taking $\overline{F} = \dfrac{F}{r^2}$, Eq. (1) takes the following form:

$$\begin{cases} \dfrac{\partial \overline{F}(r,t)}{\partial t} + G(r,t)\dfrac{\partial \overline{F}(r,t)}{\partial r} = 0 \\ r_{nuc}^2 G(r_{nuc},t)\overline{F}(r_{nuc},t) = R_{nuc}(t) \end{cases} \quad 2.$$

with $\overline{F}(0,t) = 0$. Now, from Eq. (2) we can use the method of characteristics to work out an analytical solution of Eq. (1). The characteristic curves are defined by $(x(\tau),\tau)$ where $x(\tau)$ is the solution of the ordinary differential equation (ODE):

$$\begin{cases} \dfrac{dx}{d\tau} = \dfrac{G_0(1-e^{-\tau/T})}{x^2}, \quad \forall (r,t) \in \Omega \\ x(\tau)\big|_{\tau=t} = r \end{cases}$$

By integrating, we get:

$$x(\tau) = \sqrt[3]{r^3 + 3G_0[\tau - t + T(e^{-\tau/T} - e^{-t/T})]}$$

So, the characteristics are increasing and parallel curves passing through the plan Ω from left to right. Finally, using directly the method of characteristics, the analytical solutions of Eq.1 are :

$$F(r,t) = \begin{cases} 0 & \text{if } r \geq \phi(t) \\ \dfrac{r^2}{r_{nuc}^2}\dfrac{R_{nuc}(\tau^*)}{G(r_{nuc},\tau^*)} & \text{if } r \leq \phi(t) \end{cases} \quad 3.$$

with $\phi(t) = \sqrt[3]{r_{nuc}^3 + 3G_0[t + T(e^{-t/T} - 1)]}$ and τ^* solution of $0 = r^3 - r_{nuc}^3 + 3G_0[\tau^* - t + T(e^{-\tau^*/T} - e^{-t/T})]$. τ^* is the intersection point with $\tau-$axis and the characteristic passing through $(r,t) \in \Omega$. Now, we discretize Eq. (1) using the methods of finite differences and orthogonal collocations. Discretizing Eq. (1) by the finites differences, yields the following system of ODE:

$$\begin{cases} \dot{F}_1 = -\dfrac{G_1 F_1 - R_{nuc}}{\Delta r} \\ \dot{F}_i = -\dfrac{G_i F_i - G_{i-1} F_{i-1}}{\Delta r}, \ \forall\ i = 2,\ldots,N \end{cases} \quad 4.$$

where $\dot{F}_i = \left.\frac{\partial F(r,t)}{\partial t}\right|_{r=r_i}$, $F_i = F(r_i,t)$ and $G_i = G(r_i,t)$. Using the method of orthogonal collocations, $F(r,t)$ is approximated by a Lagrange polynomial of degree N. The support of interpolation composed by $\{r_0, r_1, \ldots, r_N\}$, with $r_0 = r_{nuc}$ and $r_N = r_{max}$, is constitued of $N+1$ roots of a Jacobi polynomial $0 = z_0 < z_1 < \cdots < z_N = 1$ such as $r = \delta z + \lambda$, with $\delta = r_{max} - r_{nuc}$ and $\lambda = r_{nuc}$. Finally ,with respect to $z \in [0,1]$ Eq. (1) becomes the following system of ODE:

$$\dot{F}_j = \frac{-1}{\delta}\left(\sum_{i=1}^{N} X_i \frac{dL_i}{dz}(z_j) + R_{nuc}\frac{dL_0}{dz}(z_j)\right), \ \forall\, j = 1,\ldots,N \qquad 5.$$

where $X_j = \sum_{i=1}^{N} L_i(z_j)X_i + L_0(z_j)R_{nuc} = F(r_j,t)G(r_j,t)$. $L_i(z_j) = 1$ if $i = j$ else 0 and $\frac{dL_i}{dz}(z_j)$ is computed using [4].

3.3. Results & discussions

Taking $G_0 = 2{,}11e^{-22}$, $T = 50$, $\alpha = 1e^{-6}$, $\sigma = 15$ and $\mu = 66$, Fig. 2 represents the solutions of Eq. (3) (—) , Eq. (4) (—) and Eq. (5) (o), for $r = 213\,nm$.

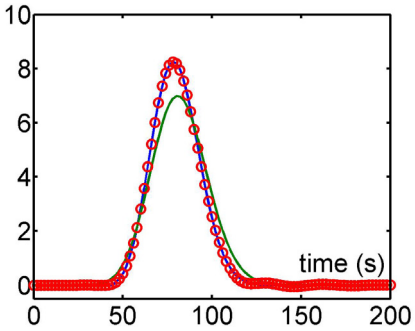

Figure 2 : Analytical and numerical solutions of Eq.1

For both techniques, we have chosen 20 points of discretization. Fig. 2 exhibits the accuracy of the method of orthogonal collocations which is confused with

the analytical solution. Moreover only 20 ODE have been integrated. Finally, the method of orthogonal collocations is fast and precise and satisfies the initial aim : to develop a reliable numerical algorithm. In conclusion we propose a simulation of the emulsion polymerization process using the method of orthogonal collocations.

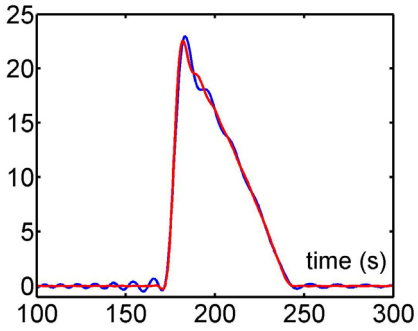

Figure 3 : Numerical solution of $F(r,t)$ using the method of orthogonal collocations

Fig. 3 represents the profile of $F(r,t)$ with $r = 100\ nm$, for 200 (—) and 300 (—) points of collocations. The consistent is checked since both solutions are equal.

4. Conclusions and future works

Thanks to the method of collocations, we have developed a fast and precise numerical algorithm to simulate particularly a model of emulsion polymerization. Others techniques as fast and precise as the method of orthogonal collocations, have been employed to solve numerically a hyperbolic PDE [4]. Our numerical investigation based on an academic system can be extended to other processes like crystallization. In future works, we will use the numerical model to design state observers and to study control laws in order to improve the product quality in emulsion pseudo-homopolymerization processing.

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