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Application of Higher-order Discretization to Parametric Dependence of Partial Differential Equations Describing Tubular Flow Reactors

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Abstract−The higher-order discretization for determining the parametric dependence in partial differential equations of diffusion-convection-reaction type is described. For approximation of space differential operators, the Stormer-Numerov formula with the $O(h^4)$ accuracy is used. This method turns out to be useful for investigating the parametric dependence in parabolic diffusion-convection-reaction equations representing the behavior of tubular flow reactors.

Key words: Higher-order Discretization, Stormer-Numerov Formula, Tubular Flow Reactor, Partial Differential Equation, Continuation

INTRODUCTION

The systematic investigation for parametric dependence of steady states, i.e., continuation, in partial differential equations is still a difficult problem. Several methods for continuation in ordinary differential equations have been proposed and developed very extensively. In the meanwhile, the analysis of parametric dependence in partial differential equations is still at the very beginning although some algorithms for locating Hopf-bifurcation points have been published [Hassard and El-Henawy, 1981; Jensen and Ray, 1982; Nandapurkar and Hlavacek, 1984]. A viable strategy for calculating parametric dependence in partial differential equations is to discretize the space differential operator and to apply continuation methods developed in ordinary differential equations. The finite difference approximation of partial differential equations via method of lines may result in a large set of ordinary differential equations, and the calculation of multiplicity and stability in stationary as well as periodic branches may present a formidable task.

The purpose of this paper is to take advantage of the Stormer-Numerov approximation with the $O(h^4)$ accuracy and to apply this method to parabolic partial differential equations of diffusion-convection-reaction type. The Stormer-Numerov approximation is very important for the problems where storage limitation and computer time expenditure preclude standard second-order methods. For the fourth-order approximation, a low number of mesh points can be used for a majority of chemical engineering problems. Nandapurkar and Hlavacek [1984] demonstrated that higher-order discretization methods might provide important improvements of codes in terms of diminishing the required number of mesh points as well as the computer time for desired solution by using the Brusselator model to describe the trimolecular reaction. This approximation can be applied for calculation of parametric dependence in tubular flow reactors.

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GOVERNING EQUATIONS

Consider an irreversible exothermic first-order reaction A → B taking place in tubular flow reactors. Mass and energy balances can be written in the following dimensionless form:

$$\frac{\partial y}{\partial \tau}=\frac{1}{Pe_M}\frac{\partial^2 y}{\partial \xi^2}-\frac{\partial y}{\partial \xi}+Da(1-y)\exp\left(\frac{\theta}{1+\varepsilon\theta}\right) \tag{1}$$

$$\frac{\partial \theta}{\partial \tau}=\frac{1}{Pe_H}\frac{\partial^2 \theta}{\partial \xi^2}-\frac{\partial \theta}{\partial \xi}+DaB(1-y)\exp\left(\frac{\theta}{1+\varepsilon\theta}\right)-\beta(\theta-\theta_C) \tag{2}$$

subject to boundary conditions

$$\xi=0: \quad Pe_M y-\frac{\partial y}{\partial \xi}=0$$

$$Pe_H \theta-\frac{\partial \theta}{\partial \xi}=0 \tag{3}$$

$$\xi=1: \quad \frac{\partial y}{\partial \xi}=\frac{\partial \theta}{\partial \xi}=0. \tag{4}$$

Here y and θ are dimensionless conversion and temperature. Pe_M and Pe_H are Peclet numbers for mass and heat transfer, respectively. Detailed descriptions of the parameters can be found elsewhere [Hlavacek and Hofmann, 1970].

In order to eliminate the first derivatives with respect to ξ in Eqs. (1) and (2), the following transformation of the conversion and the temperature is used:

$$y=Y\exp\left(\frac{Pe_M}{2}\xi\right) \tag{5}$$

$$\theta=\Theta\exp\left(\frac{Pe_H}{2}\xi\right). \tag{6}$$

After simple algebraic manipulation we can get

$$\frac{\partial Y}{\partial \tau}=\frac{1}{Pe_M}\frac{\partial^2 Y}{\partial \xi^2}-\frac{Pe_M}{4}Y$$
$$+Da\left\{\exp\left(-\frac{Pe_M}{2}\xi\right)-Y\right\}\exp\left\{\frac{\Theta}{\exp\left(-\frac{Pe_H}{2}\xi\right)+\varepsilon\Theta}\right\} \tag{7}$$

$$\frac{\partial\Theta}{\partial\tau}=\frac{1}{Pe_H}\frac{\partial^2\Theta}{\partial\xi^2}-\frac{Pe_H}{4}\Theta+DaB\left[\exp\left(-\frac{Pe_H}{2}\xi\right)-\exp\left\{\frac{\xi}{2}(Pe_M-Pe_H)\right\}Y\right]$$
$$\times\exp\left\{\frac{\Theta}{\exp\left(-\frac{Pe_H}{2}\xi\right)+\varepsilon\Theta}\right\}-\beta(\Theta-\Theta_C) \quad (8)$$

subject to boundary conditions

$$\xi=0: \quad \frac{Pe_M}{2}Y-\frac{\partial Y}{\partial\xi}=0$$
$$\frac{Pe_H}{2}\Theta-\frac{\partial\Theta}{\partial\xi}=0 \quad (9)$$

$$\xi=1: \quad \frac{Pe_M}{2}Y+\frac{\partial Y}{\partial\xi}=0$$
$$\frac{Pe_H}{2}\Theta+\frac{\partial\Theta}{\partial\xi}=0. \quad (10)$$

DISCRETIZATION OF SPATIAL OPERATOR

It is obvious that the Stormer-Numerov formula can be applied to Eqs. (7) and (8), which can be rewritten in the following simplified form:

$$\frac{\partial^2\underset{\sim}{X}}{\partial\xi^2}=\underset{\approx}{C}^{-1}\left\{\frac{\partial\underset{\sim}{X}}{\partial\tau}-\underset{\sim}{g}(\underset{\sim}{X},\xi)\right\}=\underset{\sim}{f}(\underset{\sim}{X},\xi). \quad (11)$$

Here the quantities $\underset{\sim}{X}$, $\underset{\approx}{C}$ and $\underset{\sim}{g}$ are defined by

$$\underset{\sim}{X}=\begin{bmatrix}Y\\ \Theta\end{bmatrix} \qquad \underset{\approx}{C}=\begin{bmatrix}\frac{1}{Pe_M} & 0\\ 0 & \frac{1}{Pe_H}\end{bmatrix} \quad (12)$$

$$\underset{\sim}{g}(\underset{\sim}{X},\xi)=\begin{bmatrix}-\frac{Pe_M}{4}Y+Da\left\{\exp\left(-\frac{Pe_M}{2}\xi\right)-Y\right\}\exp\left\{\frac{\Theta}{\exp\left(-\frac{Pe_H}{2}\xi\right)+\varepsilon\Theta}\right\}\\ -\frac{Pe_H}{4}\Theta+DaB\left[\exp\left(-\frac{Pe_H}{2}\xi\right)-\exp\left\{\frac{\xi}{2}(Pe_M-Pe_H)\right\}Y\right]\\ \times\exp\left\{\frac{\Theta}{\exp\left(-\frac{Pe_H}{2}\xi\right)+\varepsilon\Theta}\right\}-\beta(\Theta-\Theta_C)\end{bmatrix}$$

Let us review the Stormer-Numerov formula briefly. For a differential equation

$$\frac{d^2X}{d\xi^2}=R(X) \quad (13)$$

the finite difference approximation of Eq. (13) for N uniform meshes with a spacing h ($0=X_0<X_1<\cdots<X_{N-1}<X_N=1$) can be expressed as

$$X_{i-1}-2X_i+X_{i+1}=\frac{h^2}{12}(R_{i-1}+10R_i+R_{i+1})+O(h^4), \quad i=0, 1, \cdots, N \quad (14)$$

Applying the Stormer-Numerov formula, Eq. (14), to Eq. (11) we can get

$$\underset{\sim}{X}_{i-1}-2\underset{\sim}{X}_i+\underset{\sim}{X}_{i+1}=\frac{h^2}{12}\underset{\approx}{C}^{-1}\left\{\left(\frac{d\underset{\sim}{X}_{i-1}}{d\tau}+10\frac{d\underset{\sim}{X}_i}{d\tau}+\frac{d\underset{\sim}{X}_{i+1}}{d\tau}\right)-(g_{i-1}+10g_i+g_{i+1})\right\}$$
$$i=1, 2, \cdots, N-1. \quad (15)$$

Therefore the resulting set of ordinary differential equations derived from Eq. (15) can be rewritten in the following matrix form:

$$\underset{\approx}{A}\frac{d\underset{\sim}{X}}{d\tau}=\frac{12}{h^2}\underset{\approx}{C}\underset{\approx}{D}\underset{\sim}{X}+\underset{\approx}{A}\underset{\sim}{g} \quad (16)$$

where $\underset{\approx}{A}$ and $\underset{\approx}{D}$ are $(N-1)\times(N-1)$ tridiagonal matrices:

$$\underset{\approx}{A}=\begin{bmatrix}1 & 10 & 1 & 0 & 0 & \cdots & 0\\ 0 & 1 & 10 & 1 & 0 & \cdots & 0\\ 0 & 0 & 1 & 10 & 1 & 0\cdots & 0\\ \vdots & & & \vdots & & & \vdots\\ 0 & \cdots & & 0 & 1 & 10 & 1\end{bmatrix} \quad (17)$$

and

$$\underset{\approx}{D}=\begin{bmatrix}1 & -2 & 1 & 0 & 0 & \cdots & 0\\ 0 & 1 & -2 & 1 & 0 & \cdots & 0\\ 0 & 0 & 1 & -2 & 1 & 0\cdots & 0\\ \vdots & & & \vdots & & & \vdots\\ 0 & \cdots & & 0 & 1 & -2 & 1\end{bmatrix}. \quad (18)$$

In order to express Eq. (16) in an explicit form for $d\underset{\sim}{X}/d\tau$, we must solve the equations with respect to the $d\underset{\sim}{X}/d\tau$ variables. Since the coefficient matrix $\underset{\approx}{A}$ is constant, we can invert the constant matrix $\underset{\approx}{A}$ and hence transform Eq. (16) to a set of ordinary differential equations:

$$\frac{d\underset{\sim}{X}}{d\tau}=\underset{\approx}{A}^{-1}\left(\frac{12}{h^2}\underset{\approx}{C}\underset{\approx}{D}\underset{\sim}{X}+\underset{\approx}{A}\underset{\sim}{g}\right). \quad (19)$$

Then we can easily apply the continuation methods developed for ordinary differential equations to a set of $2(N-1)$ differential equations, Eq. (18). The continuation for tracing out the periodic as well as stationary branches was performed by using the software package AUTO [Doedel, 1980].

It is also necessary to discretize the boundary conditions with the same $O(h^4)$ accuracy. Boundary conditions, Eqs. (9) and (10), can be generalized in the following form:

$$\xi=0: \quad \underset{\sim}{\alpha}_0\underset{\sim}{X}+\underset{\sim}{\beta}_0\frac{\partial\underset{\sim}{X}}{\partial\xi}=\underset{\sim}{\gamma}_0 \quad (20)$$

$$\xi=1: \quad \underset{\sim}{\alpha}_1\underset{\sim}{X}+\underset{\sim}{\beta}_1\frac{\partial\underset{\sim}{X}}{\partial\xi}=\underset{\sim}{\gamma}_1 \quad (21)$$

where the coefficient vectors, $\underset{\sim}{\alpha}_0$, $\underset{\sim}{\beta}_0$, $\underset{\sim}{\gamma}_0$, $\underset{\sim}{\alpha}_1$, $\underset{\sim}{\beta}_1$, and $\underset{\sim}{\gamma}_1$ represent

$$\underset{\sim}{\alpha}_0=\underset{\sim}{\alpha}_1=\begin{bmatrix}\frac{Pe_M}{2}\\ \frac{Pe_H}{2}\end{bmatrix} \quad \underset{\sim}{\beta}_0=\begin{bmatrix}-1\\ -1\end{bmatrix} \quad \underset{\sim}{\beta}_1=\begin{bmatrix}1\\ 1\end{bmatrix} \quad \underset{\sim}{\gamma}_0=\underset{\sim}{\gamma}_1=\begin{bmatrix}0\\ 0\end{bmatrix}. \quad (22)$$

After some algebraic manipulation we can obtain the following approximation formula for the first derivative at boundary ends with the $O(h^4)$ accuracy:

$$\xi=0: \quad \frac{\partial\underset{\sim}{X}}{\partial\xi}\simeq\frac{1}{2h}(\underset{\sim}{X}_0-2\underset{\sim}{X}_1-\underset{\sim}{X}_2+2\underset{\sim}{X}_3)-\frac{h}{18}(7\underset{\sim}{f}_0+29\underset{\sim}{f}_1+15\underset{\sim}{f}_2+2\underset{\sim}{f}_3) \quad (23)$$

$$\xi=1: \quad \frac{\partial \underset{\sim}{X}}{\partial \xi} \simeq \frac{1}{2h}(-2\underset{\sim}{X}_{N-3}+\underset{\sim}{X}_{N-2}+\underset{\sim}{X}_{N-1}-\underset{\sim}{X}_{N}) + \frac{h}{18}(2\underset{\sim}{f}_{N-3}+15\underset{\sim}{f}_{N-2}+29\underset{\sim}{f}_{N-1}+7\underset{\sim}{f}_{N}) \tag{24}$$

Substituting Eqs. (23) and (24) into Eqs. (20) and (21), we can get the approximation formula at both ends with the $O(h^4)$ accuracy. Eq. (19) together with the boundary conditions, Eqs. (21) and (22), results in a set of 2(N+1) ordinary differential equations.

NUMERICAL EXAMPLES

The multiplicity region in "parametric plane" Pe-Da for constant values of B, β, ε, θ_C and N when the Peclet numbers for mass and heat dispersion are the same (Pe_M=Pe_H=Pe), is depicted in Fig. 1. The unique steady state exists in area I while area II is the region of three steady states. There exists a range of Damköhler number (Da_1~Da_2) at the constant Peclet number where the multiplicity can occur. By raising the Peclet number this interval moves to higher values of Da, but the range of Da decreases. Fig. 2 shows parametric dependence of Da on y(1) for the same values of parameters in Fig. 1 where y(1) is the outlet conversion of tubular flow reactors. There exist turning points at Da_1=0.05565 and Da_2=0.09864. In this figure solid and dotted lines represent stable and unstable steady states, respectively. The parametric dependence in Fig. 2 shows the existence of one, three, and one steady states as the value of Da increases. The values of Da (Da_1 =0.05565, Da_2=0.09864) to give turning points in Fig. 2 are in excellent agreement with exact values calculated by numerical simulation of Eqs. (1) to (4) as shown in Table 1. The difference between two methods has maximum 0.6% error because exact values of Da_1 and Da_2 are reported to be 0.056 and 0.098 with two significant digits, respectively [Kim and Park, 1999].

For given parameters in Fig. 3, Hlavacek and Hofmann [1970] found the cycles disappear in the interval of Pe=1.6-1.8. Our calculation shows this Hopf bifurcation occurs at Pe=1.7390. The eigenvalues at this Hopf bifurcation point in Table 2 guarantee the occurrence of limit cycles. The transient behavior in Fig. 3

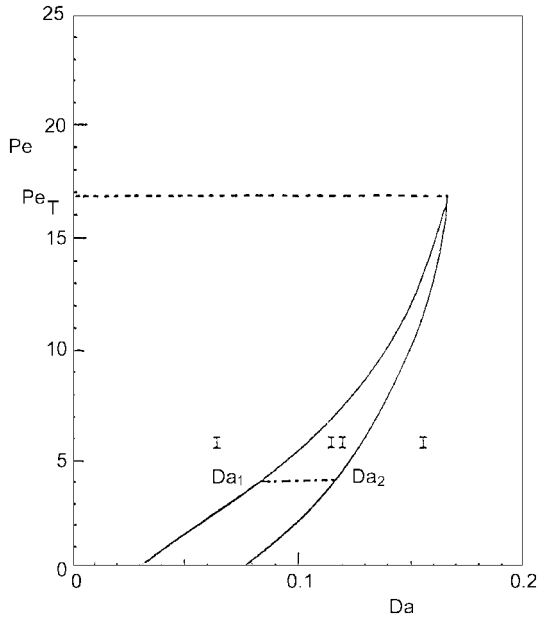

Fig. 1. Multiplicity in tubular flow reactors with A→B reaction (B=6.0, β=0.0, ε=0.0, θ_C=0.0, N=10).

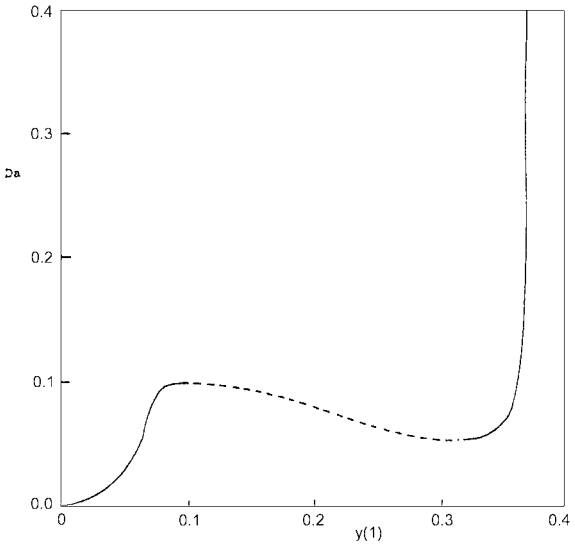

Fig. 2. Bifurcation diagram in tubular flow reactors with A→B reaction at Pe=2.0 (B=6.0, β=0.0, ε=0.0, θ_C=0.0, N=10).

Table 1. A comparison of exact and approximate Damköhler numbers at turning points (B=6.0, β=0.0, ε=0.0, θ_C=0.0, N=10)

Pe	Exact		Approximate		Error (%)	
	Da_1	Da_2	Da_1	Da_2	Da_1	Da_2
2.0	0.056	0.098	0.05565	0.09864	0.6	0.6

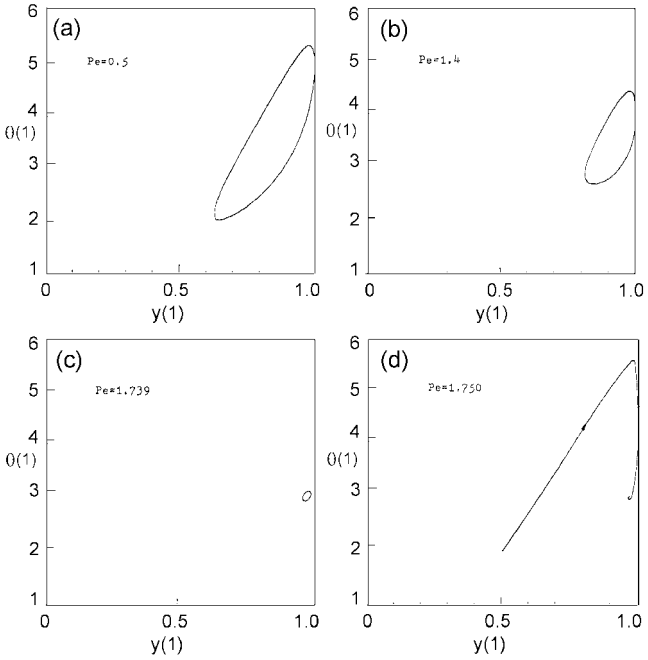

Fig. 3. Transient behavior at the exit of tubular flow reactors with A→B reaction (B=11.0, Da=0.2, β=2.0, ε=0.0, θ_C =0.0, N=10). Pe is: (a) 0.5, (b) 1.4, (c) 1.739 and (d) 1.750.

Table 2. Eigenvalues at Hopf bifurcation point (B=11.0, Da=0.2, β=2.0, ε=0.0, θ_c=0.0, N=10)

±0.4305×10i	$-0.4654\times10^3\pm0.1087\times10$i
$-0.2581\times10^3\pm0.3043\times10^3$	$-0.2020\times10^3\pm0.3954\times10$i
$-0.1433\times10^3\pm0.4241\times10$i	$-0.9347\times10^2\pm0.4343\times10$i
$-0.5455\times10^2\pm0.4300\times10$i	$-0.2645\times10^2\pm0.3929\times10$i
$-0.8609\times10\pm0.2679\times10$i	-0.4607×10^3
-0.4479×10^3	

clearly shows the transition from limit cycles to stable steady states at Pe=1.7390.

CONCLUSIONS

The Stormer-Numerov discretization with the $O(h^4)$ accuracy is adopted to investigate the parametric dependence in partial differential equations of diffusion-convection-reaction type. The continuation algorithms are very sensitive to the accuracy of starting steady states even for moderate Peclet numbers. Our strategy using the low number of mesh points with higher order accuracy represents the most promising approach for calculating parametric dependence in a set of parabolic partial differential equations.

This method may be useful in determining parametric dependence in other systems such as explosion, catalytic reactor, and flames in 1- and 2-dimensional spaces [Nandapurkar and Hlavacek, 1984].

NOMENCLATURE

$\underset{\sim}{A}$: matrix defined by Eq. (17)
B : adiabatic temperature rise
$\underset{\sim}{C}$: matrix defined by Eq. (12)
$\underset{\sim}{D}$: matrix defined by Eq. (18)
Da : Damköhler number
$\underset{\sim}{f}$: defined by Eq. (11)
$\underset{\sim}{g}$: nonlinear source term defined by Eq. (12)
h : spacing
N : total number of mesh points
Pe_M : Peclet number for mass dispersion
Pe_H : Peclet number for heat dispersion
R : defined in Eq. (13)
$\underset{\sim}{X}$: vector defined by Eq. (12)
y, Y : conversion in original and transformed variables
y(1) : exit conversion

Greek Letters

β : heat transfer coefficient between reacting fluids and cooling medium
τ : dimensionless time
θ, Θ : dimensionless temperature in original and transformed variables
ε : dimensionless activation energy
ξ : dimensionless axial length

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