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The axial dispersion model and orthogonal collocation

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INTRODUCTION

Models for packed bed chemical reactors and chromatographic columns frequently include an axial dispersion term to account for deviations from ideal flow. The inclusion of axial dispersion leads to a differential equation model of second order in the spatial variable. It is common practice to solve this model with the "Danckwerts boundary conditions" (Danckwerts, 1953), where the spatial derivative of the dependent variables are required to be zero at the bed exit, even though the boundary condition is questionable under non-steady state conditions (Froment and Bischoff, 1979; van Cauwenberghe, 1966).

When the axial dispersion coefficient is small, use of the Danckwerts boundary conditions can create numerical problems, since concentration and temperature gradients are required to change very rapidly in the vicinity of the bed exit. As a result the bed profiles are more difficult to approximate numerically than the corresponding profiles in the absence of axial dispersion.

The aim of this note is to demonstrate a numerical solution procedure based on the method of orthogonal collocation (Finlayson, 1972; Villadsen and Michelsen, 1978), where the problems associated with the Danckwerts boundary conditions are avoided by treating the bed as a section in an infinitely long system. The procedure is illustrated for a steady-state chemical reactor as well as for a non-steady-state model of chromatographic column.

STEADY STATE

The model for the concentration profile in an isothermal tubular reactor can be written as

$$-\frac{1}{Pe}\frac{d^2y}{dx^2}+\frac{dy}{dx}+r(y)=0 \tag{1}$$

where the dimensionless parameters x and y represent the distance from the reactor inlet and the reactant concentration, respectively. The rate of the chemical reaction is $r(y)$, and the Peclet number Pe, which is inversely proportional to the axial dispersion coefficient, is assumed to be much larger than 1. At the reactor inlet, the boundary condition is

$$x=0 \Rightarrow y-\frac{1}{Pe}\frac{dy}{dx}=y_{in} \tag{2}$$

and at the exit, the Danckwerts boundary condition is

$$x=1 \Rightarrow \frac{dy}{dx}=0. \tag{3}$$

Integration of eq. (1) over the reactor volume, combined with the boundary conditions, eqs (2) and (3), yields

$$y_{out}=y_{x=1}=y_{in}-\int_0^1 r(y)\,dx. \tag{4}$$

We shall compare the solution $y(x)$ with the solution $y^*(x)$ to the same model, where the reactor is assumed to be infinitely long. The exit boundary condition, eq. (3), is thus replaced by

$$y^* \text{ is finite for } x \to \infty. \tag{5}$$

It is readily shown that the first approximation to the difference between the two solutions is given by the term

$$y(x)-y^*(x)=-\frac{1}{Pe}\left(\frac{dy^*}{dx}\right)_{x=1}\exp\left[Pe(x-1)\right]+O(Pe^{-2}). \tag{6}$$

Substitution of this expression yields

$$\int_0^1 r(y)\,dx=\int_0^1 r(y^*)\,dx-\frac{1}{Pe^2}\left(\frac{dy^*}{dx}\right)_{x=1}\left(\frac{\partial r}{\partial y^*}\right)_{x=1}+O(Pe^{-3}) \tag{7}$$

or

$$\int_0^1 r(y)\,dx=\int_0^1 r(y^*)\,dx+O(Pe^{-2}). \tag{8}$$

When Pe is large the term proportional to Pe^{-2} can be neglected, and the outlet concentration can therefore be determined from

$$y_{out}=y_{in}-\int_0^1 r(y^*)\,dx=\left(y^*-\frac{1}{Pe}\frac{dy^*}{dx}\right)_{x=1}. \tag{9}$$

Solution by orthogonal collocation

The method of orthogonal collocation approximates the solution $y(x)$ of eqs (1)–(3) by

$$y(x)=\sum_{i=0}^{N+1} y_i l_i(x) \tag{10}$$

where the $l_i(x)$ are the Lagrange interpolation polynomials derived from the nodal polynomial

$$p_{N+1}(x)=\prod_{i=0}^{N+1}(x-x_i) \tag{11}$$

with $x_0=0$, $x_{N+1}=1$ while $x_1, x_2, \ldots, x_N$ are chosen as the zeroes of the Nth degree shifted Legendre polynomial. The unknown ordinates y_i are determined from the requirement that the expansion, eq. (10), must satisfy the boundary conditions eqs (2) and (3) and that the residual of the differential equations must be zero at the N interior collocation points.

The corresponding solution for y^* is obtained similarly by means of the expansion

$$y^*(x)=\sum_{i=0}^{N} y_i l_i(x) \tag{12}$$

Table 1.

Approx order	Error in y_{out}	
	Danckwerts BC	Open BC
2	5.3×10^{-3}	5.4×10^{-4}
3	4.2×10^{-4}	3.8×10^{-6}
4	2.4×10^{-5}	1.5×10^{-8}
5	1.1×10^{-6}	3.7×10^{-11}

and in this case only satisfaction of the boundary condition at $x = 0$ is required. Optionally, the interval endpoint $x = 1$ can be included in the expansion with the requirement that the residual must also be equal to zero at the endpoint.

The advantage of solving for $y^*(x)$ is that a lower approximation order, N, is required to obtain a specified accuracy, as can be seen from Table 1, where the error in y_{out} is given in dependence of the approximation order in the limiting case of an infinite Peclet number for $r(y) = y$.

NON-STEADY STATE

Equilibrium chromatography with a linear adsorption isotherm is frequently modeled with the partial differential equation (Suwondo *et al.*, 1991; Ma and Guichon, 1991)

$$\frac{\partial y}{\partial t} + \frac{\partial y}{\partial x} - \frac{1}{Pe}\frac{\partial^2 y}{\partial x^2} = 0 \tag{13}$$

with boundary conditions

$$t = 0 \Rightarrow y = 0 \tag{14}$$

$$x = 0 \Rightarrow y - \frac{1}{Pe}\frac{\partial y}{\partial x} = y_{\mathrm{in}}(t) \tag{15}$$

and the Danckwerts exit condition

$$x = 1 \Rightarrow \frac{\partial y}{\partial x} = 0. \tag{16}$$

A value of Pe of the order 10^4 is not uncommon in chromatographic columns, and for a perfect pulse input, $y_{\mathrm{in}}(t) = \delta(t)$, the numerical simulation of the sharp pulse progressing through the column can be very demanding. Global collocation is infeasible, and as an alternative many authors have used "spline collocation", where the column is divided into a number of subsections, tied together with the condition that y and $\partial y/\partial x$ must be continuous at the section boundaries. The dependent variables in the ith section are thus coupled to the variables in the previous and in the following section through the continuity conditions.

A computationally much more convenient formulation is obtained if the 'infinite system" boundaries are used. The condition of continuity of y as well as of its spatial derivative is now replaced with the single condition that the axial flux, $y - (1/Pe)\,\partial y/\partial x$, must be continuous at the section boundaries. In essence this condition implies that the "output" from section i acts as "input" to section $i + 1$. The backwards coupling inherent in the traditional approach is completely avoided, since the time integration of the ith section is unaffected by the state of all subsequent sections.

Equation (13) was discretized using the collocation method, and the resulting set of coupled ordinary differential equations were integrated using a 4th order Runge–Kutta method. Results for a pulse input, a Peclet number of 10^4, and an integration time step of 0.001 and using 80 subsections with four interior collocation points in each is shown in Fig. 1. The response curve can be compared with the analytic result:

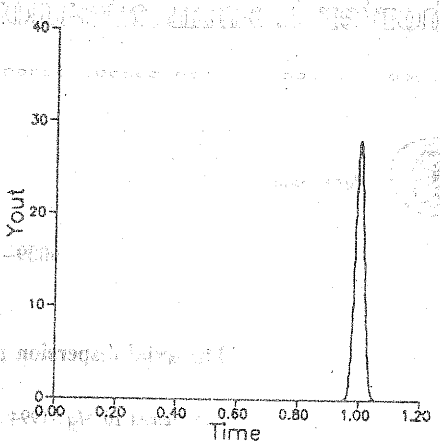

Fig. 1. Output from column.

$$\left(y - \frac{1}{Pe}\frac{\partial y}{\partial x}\right)_{x=1} = \frac{1}{2}\sqrt{\frac{Pe}{\pi t^3}}\exp\left[-\frac{Pe}{4}\frac{(t-1)^2}{t}\right]. \tag{17}$$

The park value of 28.20 at $t = 1$ is in error by less than 0.01, and the difference between the analytical and the numerical solution is at all times smaller than 0.015.

MICHAEL L. MICHELSEN

Institut for Kemiteknik
Bygning 229, DTU 2800 Lyngby
Denmark

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