Perturbation Solution and Moment Expansion for Nonlinear Adsorption in a CSTR

Regular perturbation theory is applied to determine the response to an impulse input in a continuous-flow stirred-tank reactor (CSTR) with nonlinear adsorption. A series expansion for temporal moments is a result of the procedure. This moment expansion allows the usual restriction of linearity in analysis of experimental data by moments to be waived. The response at each order can be expressed as an expansion in Laguerre polynomials involving moments, which, in the present example, converges to the exact solution.

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Analytical solutions have obvious advantages over numerical solutions, not the least of which is that they are easier to compare with experiments. Regular perturbation solutions to nonlinear problems are conceptually straightforward (Bender and Orszag, 1978), but higher order terms in the procedure can involve much tedious algebra. However, symbolic manipulation (computer algebra) systems are now available to relieve the human effort and ensure accuracy (Pavelle et al., 1981). The objective of the present study is to apply regular perturbation theory to an example problem for response to an impulse with nonlinear adsorption in a well-stirred vessel. For this problem Laplace transforms provide exact solutions at each order. Since for many problems inversion of the Laplace transform expressions may not be feasible, a method of expansion in Laguerre polynomials is introduced. Temporal moments are shown to be expansions in the perturbation parameter, because the concentration is such an expansion. The Laguerre polynomial expansions, which contain the temporal moments, are shown to sum to the exact solution.

Consider a CSTR charged with an impulse of adsorbate at the scaled time θ' The dimensionless equations governing the process are

$$dc/d\theta = \delta(\theta - \theta') - c - dq/d\theta \tag{1}$$

$$q = \kappa c(1 - \epsilon c) \tag{2}$$

$$c(\theta = 0) = 0 \tag{3}$$

Equation 2 is an expression for a nonlinear isotherm that approximates a Langmuir isotherm for small $\epsilon > 0$. For $\epsilon < 0$ the isotherm is concave upward. We expand both $c(\theta)$ and $q(\theta)$ in perturbation series:

$$c = \sum_{k=0}^{\infty} \epsilon^k c_k \tag{4}$$

$$q = \sum_{k=0}^{\infty} \epsilon^k q_k \tag{5}$$

Substitution into Eqs. 1 and 2 and collection of like powers of ϵ yield the sequence of equations for $k = 0, 1, 2, \ldots$.

$$dc_k/d\theta = \delta_{ko}\delta(\theta - \theta') - c_k - dq_k/d\theta \tag{6}$$

$$q_k = \kappa c_k - \kappa \sum_{i=0}^{k-1} c_i c_{k-1-i} \tag{7}$$

$$c_k(\theta = 0) = 0 \tag{8}$$

Applying Laplace transformation, $\mathcal{L}\{\ \}$, to Eqs. 6 and 7 gives the Laplace domain solution

$$\bar{c}_k = \frac{a}{s + a}\left[\delta_{ko}e^{-\theta' s} + s\kappa\mathcal{L}\left\{\sum_{i=0}^{k-1} c_i c_{k-1-i}\right\}\right] \tag{9}$$

where $a = 1/(1 + \kappa)$. The sequential Laplace inversions of Eq. 9 for $k = 0, 1, 2, 3, 4$ yield

$$c_0(\theta) = ae^{-a(\theta-\theta')}H(\theta - \theta') \tag{10}$$

$$c_1(\theta) = \kappa a^3[-e^{-a(\theta-\theta')} + 2e^{-2a(\theta-\theta')}]H(\theta - \theta') \tag{11}$$

$$c_2(\theta) = 2\kappa^2 a^5 [-2e^{-2a(\theta-\theta')} + 3e^{-3a(\theta-\theta')}]H(\theta - \theta') \tag{12}$$

$$c_3 = \frac{1}{3}\kappa^3 a^7[-e^{-a(\theta-\theta')} + 6e^{-2a(\theta-\theta')} - 54e^{-3a(\theta-\theta')} + 64e^{-4a(\theta-\theta')}]H(\theta - \theta') \tag{13}$$

$$c_4 = \frac{2}{3}\kappa^4 a^9[-e^{-a(\theta-\theta')} - 2e^{-2a(\theta-\theta')} + 27e^{-3a(\theta-\theta')} - 128^{-4a(\theta-\theta')} + 125e^{-5a(\theta-\theta')}]H(\theta - \theta') \tag{14}$$

The limiting case of $\kappa = 0$ corresponds to no adsorption

$$\lim_{\kappa \to 0} c = e^{-(\theta-\theta')}H(\theta - \theta') \tag{15}$$

and the case of $\epsilon = 0$ corresponds to linear adsorption

$$\lim_{\epsilon \to 0} c = ae^{-a(\theta-\theta')}H(\theta - \theta') = c_0 \tag{16}$$

The temporal moments of the individual order solutions may be calculated from the expressions for $\bar{c}_k$. To simplify the moment expressions, consider an impulse introduced at $\theta' = 0$. The dimensionless moments, defined by

$$m_n = \int_0^{\infty} \theta^n c(\theta) d\theta \tag{17}$$

are expansions in ϵ, since $c(\theta)$ is an expansion in ϵ, Eq. 4. Thus we may write

$$m_n = \sum_{k=0}^{\infty} \epsilon^k m_{nk} \tag{18}$$

in terms of the kth approximation to the nth moment:

$$m_{nk} = \int_0^{\infty} \theta^n c_k(\theta) d\theta \tag{19}$$

The moments are calculated from the identity

$$m_{nk} = (-1)^n \left(\frac{d^n \bar{c}_k}{ds^n}\right)_{s=0} \tag{20}$$

The algebra associated with these differentiation and limit operations can be extensive and tedious. To ensure accuracy we have utilized REDUCE 2, a symbolic manipulation (computer algebra) system (Hearn, 1982; Brown and Hearn, 1979) to calculate the moments. The results are as follows:

$$m_0 = 1 \tag{21}$$

$$m_1 = \frac{1}{a} - \frac{1}{2}\epsilon\kappa a - \frac{1}{3}\epsilon^2\kappa^2 a^3 - \frac{1}{2}\epsilon^3\kappa^3 a^5 + \dots \tag{22}$$

$$m_2 = \frac{2}{a^2} - \frac{3}{2}\epsilon\kappa - \frac{5}{9}\epsilon^2\kappa^2 a^2 - \frac{5}{6}\epsilon^3\kappa^3 a^4 + \dots \tag{23}$$

$$m_3 = \frac{6}{a^3} - \frac{21}{4}\frac{\epsilon\kappa}{a} - \frac{19}{18}\epsilon^2\kappa^2 a - \frac{25}{12}\epsilon^3\kappa^3 a^3 + \dots \tag{24}$$

$$m_4 = \frac{24}{a^4} - \frac{45}{2}\frac{\epsilon\kappa}{a^2} - \frac{65}{27}\epsilon^2\kappa^2 - \frac{70}{9}\epsilon^3\kappa^3 a^2 + \dots \tag{25}$$

$$\vdots$$

The zeroth moment, which must be unity because of the unit mass input, can be independently derived by integrating Eq. 1 from 0 to ∞. The power series expressions for the higher moments will converge well, because ϵ and a are less than 1. The convergence can be speeded up by applying the Shanks transformation (Bender and Orszag, 1978). The moment analysis of experimental data has been limited to linear systems in the past; the use of perturbation theory can, as just shown, overcome this limitation.

In the present case, the Laplace transform expressions at each order in ϵ can be inverted to get exact expressions for $c_k(\theta)$. For more complicated systems, e.g., where mass transfer steps are involved, inverting the Laplace transforms may be impossible. In this event an approximation to $c_k(\theta)$ may be formulated by an expansion in Laguerre polynomials, in which temporal moments play a fundamental role. The method of expansion in terms of temporal moments and Laguerre polynomials for linear differential equations was proposed by Greco et al. (1975). They calculated the moments by numerically differentiating the transfer function, whereas in the present work we have calculated moments analytically with a computer algebra system. Linek and Dudukovic (1982) have also applied moments and Laguerre polynomials to represent solutions for linear systems.

The Laguerre polynomials, defined by (Courant and Hilbert, 1953)

$$L_n(\theta) = e^{\theta} \frac{d^n}{d\theta^n} (\theta^n e^{-\theta}) \tag{26}$$

are given by

$$L_0(\theta) = 1 \tag{27}$$

$$L_1(\theta) = -\theta + 1 \tag{28}$$

$$L_2(\theta) = \theta^2 - 4\theta + 2 \tag{29}$$

$$L_3(\theta) = -\theta^3 + 9\theta^2 - 18\theta + 6 \tag{30}$$

$$L_n(\theta) = \sum_{j=0}^{n} \theta^j l_{nj} \qquad (3$$

in terms of

$$l_{nj} = \frac{n!}{j!}\binom{n}{j}(-1)^j \qquad (3$$

The coefficients in the expansion

$$c(\theta) = e^{-\theta} \sum_{n=0}^{\infty} b_n L_n(\theta) \qquad (3$$

have the expression

$$b_n = \frac{1}{(n!)^2} \sum_{j=0}^{n} l_{nj} m_j \qquad (3$$

because of the orthogonality relation

$$\int_0^{\infty} e^{-\theta} L_n(\theta) L_m(\theta) d\theta = \delta_{nm}(n!)^2 \qquad (3$$

Therefore if one has the moments m_{nk} at any order in ϵ, the expression for $c_k(\theta)$ can be written as in Eq. 33.

For the zeroth approximation the moments are by inductio given simply by

$$m_{jo} = j!/a^j \qquad (36$$

Substituting m_{jo} into Eq. 34 and using the binomial expansio formula gives

$$b_{no} = \frac{1}{n!}(1 - 1/a)^n \qquad (37$$

The generating function for Laguerre polynomials is (Courant an Hilbert, 1953)

$$\psi(\theta,x) = \frac{1}{1-x} e^{-\theta x/(1-x)} = \sum_{n=0}^{\infty} \frac{x^n}{n!} L_n(\theta) \qquad (38$$

which yields, with the substitution $x = 1 - 1/a$ into 38, from 33 th exact solution $c_0(\theta)$ given by Eq. 10. Thus at the zeroth order in th perturbation scheme an expansion in Laguerre polynomials wit temporal moments gives the same exact solution obtained by Laplace transform inversion. A similar procedure, utilizing the generating formula 38, works for $j = 0$ to 4 at the orders $n = 1$ to 4. Fo this problem the Laguerre polynomial expansions converge precisely to the exact solutions.

As shown in this work, the method of regular perturbation series can be applied to nonlinear adsorption problems to obtain solutions to a high order. A series expansion of moments is a natural consequence of the perturbation method. The solution at each order can be expressed as an expansion in Laguerre polynomials, which in the present example, converges to the exact solution.

The expansion of the concentration response in terms of ϵ has possibilities for describing experimental data for real reactor systems. The expansion of temporal moments in ϵ is potentially of even greater importance. Analysis of lower moments for experimental responses has a good record of success, but has been limited to linear systems. The present work shows how this limitation can be overcome.

NOTATION

a	$= 1/(1 + \kappa)$, used in Eq. 10 ff
b_n	= expansion coefficient in Eq. 33
c	= dimensionless concentration in fluid
$H(\theta)$	$= 1$ if $\theta > 0$, 0 if $\theta < 0$

l_{nj} = coefficient in the expression for Laguerre polynomial, Eq. 31
$L_n(\theta)$ = Laguerre polynomial, Eq. 26 ff
m_n = dimensionless nth temporal moment, Eq. 17
m_{nk} = coefficient in power series expansion of m_n, Eq. 18
s = Laplace transform parameter
q = dimensionless concentration of adsorbed species

Greek Letters

κ = dimensionless parameter in isotherm expression, Eq. 2
ϵ = small dimensionless parameter in isotherm expression, Eq. 2, and expansion parameter, Eqs. 4 and 5
θ = dimensionless time
θ' = dimensionless time for impulse input
ψ = generating function for Laguerre polynomials, Eq. 38

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