Polynomial Profile Approximation for Intraparticle Diffusion

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The parabolic concentration profile approximation for intraparticle diffusion (Do and Rice, 1986; Rice et al., 1983; Liaw et al., 1979) is known to be equivalent to the long-time diffusion result (Jury, 1967) and to the commonly used linear driving force approximation for particle mass transfer (Glueckauf, 1955). The procedure has been used to simplify computations for a variety of problems involving intraparticle diffusion (Rice, 1982; Akulov and Ustinov, 1981). Do and Rice examined the fourth-degree (quartic) polynomial for the intraparticle concentration profile of a particle in a stirred vessel. Liaw et al. referred to the similarity with other polynomial approximations, such as those for boundary layer velocity profiles.

The present objective is to examine further the consequences of the polynomial approximations, including the special cases of parabolic and uniform profiles, for linear adsorption and reaction processes in spherical particles. These polynomial approximations appreciably simplify moment calculations, as shown below, especially when both reversible adsorption and irreversible surface reaction are included in the kinetics. Two special cases are also treated here: reversible adsorption (no irreversible reaction), and no adsorption or reaction (i.e., intraparticle diffusion only). The results are applicable to intraparticle heat conduction as well as to intraparticle diffusion.

We show that as the degree of the polynomial increases indefinitely, the polynomial profile, a power-series expansion in the reaction-diffusion modulus, equates to the exact solution. The linear driving force is a consequence of truncating the polynomial to the parabolic profile; higher degree polynomials yield more complex expressions for mass transfer. The parabolic approximation for intraparticle diffusion applied to a chromatographic response for fixed-bed or agitated-slurry systems with reversible adsorption (no irreversible reaction) provides exact expressions for temporal moments including the second. For the same systems with an added irreversible first-order reaction, the approximation provides a good estimate for lower moments if the reaction-diffusion modulus is not large (<2). The approximation should be useful in generating moments for a variety of reactor and adsorber problems.

The mass balance equation inside the particle is

$$\beta \partial c_i/\partial t = D_i \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial c_i}{\partial r} - \rho k_a (c_i - c_a/K) \tag{1}$$

and the kinetic expression, for adsorption and surface reaction rate, is considered to be

$$\partial c_a/\partial t = k_a(c_i - c_a/K) - k_r c_a \tag{2}$$

This rate expression, Eq. 2, more general than assuming that either adsorption or reaction controls the process, has been used to study various aspects of reactions at the liquid-solid interface in stirred slurry reactors (Ahn et al., 1985, 1986; Recasens et al., 1984). Suzuki and Smith (1971) also utilized the rate expression of Eq. 2 to develop the exact zero, first, the second moment expressions for the packed-bed reactor. Schneider and Smith (1968), using moments, studied the case of reversible adsorption in a packed column.

For the spherically symmetric profile, the particle boundary conditions are

$$D_i(\partial c_i/\partial r)_R = k_p[c - c_i(R)] \tag{3}$$

and

$$(\partial c_i/\partial r)_{r=0} = 0 \tag{4}$$

The initial conditions, which as we will show can be made more general, are

$$c_i(t = 0, r) = 0 \quad \text{and}$$
$$c_a(t = 0, r) = 0 \tag{5}$$

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The polynomial profile approximation is written

$$c_i(r, t) = \sum_{n=0}^{N} a_{2n}(t) r^{2n} \tag{6}$$

If $N = 1$, Eq. 6 is the parabolic profile. If coefficients beyond $a_o(t)$ are zero (i.e., for $N = 0$), we have the simple special case of the uniform intraparticle profile. The quartic approximation (Do and Rice, 1986) is obtained if terms through $a_4(t)r^4$ are included in Eq. 6 (i.e., $N = 2$). When the polynomial expression of Eq. 6 is Laplace-transformed and substituted into the transform of the mass balance, Eq. 1, one obtains using Eq. 2:

$$\sum_{n=1}^{N+1} 2n(2n+1)\bar{a}_{2n} r^{2n-2} = [\beta g(s)/D_i] \sum_{n=0}^{N} \bar{a}_{2n} r^{2n} \tag{7}$$

where $g(s)$ is defined in the Notation. Since this equation must be valid for any value of r, the separate coefficients of any power of r must vanish; this yields

$$\begin{aligned} \bar{a}_{2n} &= \bar{a}_{2n-2}\beta[g(s)/D_i]2n(2n+1) \\ &= \bar{a}_o[\beta g(s)/D_i]^n/(2n+1)! \end{aligned} \tag{8}$$

where the last equality is the result of sequential elimination of the coefficients $\bar{a}_{2n-2}$. Thus the polynomial in r is shown to be also an expansion in powers of $\beta g(s)/D_i$. When the expression for $\bar{a}_{2n}$ is substituted into the Laplace transform of Eq. 6, in the limit as $N \rightarrow \infty$ we have the result

$$\bar{c}_i(r) = (\bar{a}_o/\phi_r) \sinh \phi_r \tag{9}$$

in terms of

$$\phi_r^2 = r^2 \beta g(s)/D_i \tag{10}$$

It is straightforward to show that Eq. 9 is the exact solution to Eqs. 1–5 when the boundary conditions are applied to determine

$$\bar{a}_o = \frac{\phi}{\sinh \phi} \frac{Bi\,\bar{c}}{A(s) + Bi} \tag{11}$$

in terms of the Biot number,

$$Bi = k_p R/D_i \tag{12}$$

and

$$\begin{aligned} A(s) &= \phi \coth \phi - 1 \\ &= \tfrac{1}{3}\phi^2[1 - \phi^2/15 + 2\phi^4/315 + \cdots] \end{aligned} \tag{13}$$

The parameter $\phi(s)$ is $\phi_r(r = R)$, which becomes, when $s = 0$, the reaction-diffusion modulus. Thus, the polynomial profile approximates the exact profile arbitrarily closely as more terms in the polynomial are considered. This result seems not to have been discussed previously.

Next, we consider the consequences of the polynomial profile for mass transfer at the particle surface. The volume average of the Laplace-transformed intraparticle concentration, Eq. 9, is given by

$$\langle \bar{c}_i \rangle = \frac{3}{R^3} \int_0^R \bar{c}_i(r) r^2 \, dr = 3\bar{a}_o[\phi \cosh \phi - \sinh \phi]/\phi^3 \tag{14}$$

It is easy to show that

$$\bar{c}_i(R)/\langle \bar{c}_i \rangle = \phi^2/3[\phi \coth \phi - 1] \tag{15}$$

Now the Laplace transform of the volume-averaged mass balance, Eq. 1, is

$$g(s)\beta\langle \bar{c}_i \rangle = (3D_i/R)(\partial \bar{c}_i/\partial r)_R = (3k_p/R)[\bar{c} - \bar{c}_i(R)] \tag{16}$$

where the boundary condition Eq. 3, has been utilized. Eliminating $\bar{c}_i(R)$ in Eq. 16 with Eq. 15 yields

$$\beta g(s)\langle \bar{c}_i \rangle = (3k_p/R)[\bar{c} - \langle \bar{c}_i \rangle]/(1 + 3BiP) \tag{17}$$

where

$$\begin{aligned} P &= \frac{1}{\phi^2}\left[\frac{\phi^2/3}{\phi(\coth \phi - 1)} - 1\right] \\ &= 1/15 - \phi^2/525 + 2\phi^4/23{,}526 - \cdots \end{aligned} \tag{18}$$

when the expansion for coth ϕ is applied.

The uniform intraparticle concentration profile is equivalent to setting $Bi = 0$ in Eq. 17. The parabolic profile is equivalent to keeping only the first term in the expansion for P, Eq. 18; for this condition one obtains after inverting Eq. 17,

$$\beta d\langle c_i \rangle/dt = \kappa[c - \langle c_i \rangle] - \rho k_a[\langle c_i \rangle - \langle c_a \rangle/K] \tag{19}$$

in which κ is the effective transfer coefficient, given by

$$\kappa = (15k_p/R)/(5 + Bi) \tag{20}$$

the expression derived by Liaw et al. (1979). For $Bi \gg 5$, we have $\kappa = 15\,D_i/R^2$, the expression due to Glueckauf (1955). For $Bi \ll 5$, applicable to heat conduction, we have $\kappa = 3k_p/R$, the expression consistent with the uniform profile.

For the quartic profile, two terms in P, Eq. 18, are retained and the mass transfer term becomes the inverse Laplace transform,

$$M = \mathcal{L}^{-1}\{(3k_p/R)[\bar{c} - \langle \bar{c}_i \rangle]/[1 + Bi/5 - Bi\phi^2/175]\} \tag{21}$$

For the case where adsorption and reaction are negligible, the mass transfer term replacing the first term on the righthand side of Eq. 19 is the convolution,

$$M = -\frac{525D_i^2}{R + \beta} \int_o^t e^{-\gamma(t'-t)}[c(t') - \langle c_i \rangle(t')] \, dt' \tag{22}$$

in which

$$\gamma = (5/Bi + 1)D_i/\beta R^2 \tag{23}$$

For polynomial approximations beyond the parabolic profile, therefore, the linear driving force model for mass transfer does not apply. Thus, if the intraparticle concentration profile cannot be expressed in the parabolic form, for example for short times, the linear driving force model is replaced by a more complex expression.

The use of Eqs. 19 and 20 is appropriate to implement the computational simplifications of the parabolic profile. The equation for the volume-averaged concentration inside the particle can be combined with mass balance equations for the fluid in a reactor of any configuration (under the condition that the concentration at the particle surface is uniform). For example, computations for packed-column or agitated-slurry reactors and absorbers are simplified by use of the approximation. The intraparticle concentration is coupled to the external fluid concentration for all reactors by the surface flux expression $D_i(\partial c_i/\partial r)$ evaluated at $r = R$. We therefore are justified in restricting our attention to the intraparticle concentration to determine the effect of the polynomial profile assumption on temporal moments.

Temporal moments are computed from the Laplace transform of the fluid concentration in a reactor. This requires having the relationship between the Laplace transform of $\bar{c}_i$ and $\bar{c}$, given by the following expression:

$$D_i\left(\frac{\partial \bar{c}_i}{\partial r}\right)_{r=R} = \frac{D_i Bi}{R}\left[1 - \frac{Bi}{A(s) + Bi}\right]\bar{c} \qquad (24)$$

Since the accuracy of the intraparticle concentration profile is increased by taking more terms in the polynomial, Eq. 6, the accuracy of moments for c is likewise increased. For the kinetics expression, Eq. 2, the parabolic profile yields the following results; that is, $A(s)$ in Eq. 13 is replaced with $A'(s)$

$$A'(s) = (\phi^2/3)/(1 + \phi^2/15)$$
$$= (\phi^2/3)[1 - \phi^2/15 + \phi^6/225 + \cdots] \qquad (25)$$

The deviation of the value of $A'(s)$ from $A(s)$ increases with ϕ. As a consequence, the condition for accuracy of $A'(s = 0)$ is that $\phi(s = 0) < 2$, for which the magnitudes of $A'(s = 0)$ and $A(s = 0)$ differ by 2%. Because of the small particles used by Ahn et al. (1985, 1986) in their studies of oxidation of sulfur dioxide and hydrogenation of α-methyl styrene, the values of the modulus $\phi(s = 0)$ in both cases are less than unity. The parabolic expression would therefore be justified for these systems.

The important case of reversible adsorption with no irreversible reaction, $k_r = 0$ in Eq. 2, demonstrates different behavior. Due to the vanishing of ϕ in the limit $s = 0$ for this case, the zero, first, and second moments are *identical* for the exact and parabolic-approximate treatments of intraparticle diffusion with reversible absorption. The third moments differ in that the coefficient 12/945 in the exact expression for a packed column (McCoy and Carbonell, 1978) is replaced by 2/225 in the approximate expression.

When the uniform intraparticle profile approximation is used for the calculation of moments for reversible adsorption, the first moment is given exactly, and the second moment is slightly in error, except in the limit $Bi = 0$. If, on the other hand, the quartic approximation is applied (keeping terms of order r^4), moments are exact through the third. A higher degree polynomial therefore provides better accuracy for higher moments. In other words, the hierarchy of moments, each moment providing further details of pulse-response structure compared to lower moments, reflects the successive approximations in the concentration profile.

Hills (1986) has considered the linear driving force approximation for several reversible adsorption processes. In all his examples the initial condition is nonzero. It is not difficult to generalize Hills' model to include irreversible reaction and to show that all of our conclusions regarding the polynomial expansion apply to the cases presented by Hills.

We examined the possibility that the polynomial approximation could simplify the Laplace transform inversion to obtain analytical solutions for reactors or adsorbers with intraparticle diffusion. While there is some reduction of complexity in applying the procedures of Haynes (1975), Rasmuson and Neretnieks (1980), and Rasmuson (1981, 1985), the integral form of these solutions is unchanged, and the approximation does not significantly simplify the procedure for Laplace transform inversion.

Notation

$A(s), A'(s)$ = functions of $\phi(s)$, Eqs. 10, 13, 25
a_{2n} = coefficients of polynomial concentration profile, Eq. 6, mol/m^{3+2n}
Bi = Biot number, Rk_p/D_i
c = concentration in interparticle fluid, mol/m^3
c_a = concentration of adsorbed species per unit weight of adsorbent, mol/kg
c_i = concentration of adsorbable species in pore space, mol/m^3
$c_i(R)$ = c_i at particle surface, mol/m^3
$\bar{c}_i$ = Laplace transform of c_i, $\text{s} \cdot \text{mol/m}^3$
$\langle c_a \rangle$ = average concentration of c_a, mol/kg
$\langle c_i \rangle$ = average concentration of c_i, mol/m^3
D_i = effective diffusivity in fluid-filled pores of adsorbent sphere, m^2/s
F = function, $F = [\beta g(s)/D_i]^{1/2}$, 1/m
$g(s)$ = function, $g(s) = s + (\rho/\beta)/[(1/k_a) + 1/K(s + k_r)]$, 1/s
K = adsorption equilibrium constant, m^3/kg
k_a = adsorption rate constant, Eq. 2, $\text{m}^3/\text{s} \cdot \text{kg}$
k_p = fluid-to-particle mass transfer coefficient, m/s
k_r = surface reaction rate constant, 1/s
P = quantity, Eq. 18
$q(s)$ = $1 + \rho k_a/\beta(s + k_r + k_a/K)$
R = radius of adsorbent particle, m
r = radial distance from center of particle, m
s = Laplace transform variable, 1/s
t = time, s
v = velocity in a column, m/s

Greek letters

β = internal porosity of particles
γ = parameter, Eq. 23, 1/s
ϕ = function, $\phi(s) = RF$
ϕ_r = rF
κ = $15\, k_p D_i/[R(k_p R + 5D_i)]$, 1/s
ρ = particle density, kg/m^3

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