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On the Solution of Linear Chemical Separation Equations with Weak Diffusion Effects

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Abstract

We indicate how successive approximations to the solution of equations of the form

$$\frac{\partial c}{\partial \tau} = \epsilon \frac{\partial}{\partial x}\left(f(x) \frac{\partial c}{\partial x}\right) - \frac{\partial}{\partial x}[g(x)c]$$

can be derived. The resulting theory is applied to accurate solutions to equations arising in pore gradient electrophoresis and to ultracentrifugation with pressure effects. The second approximation decreases errors by at least 25% over the first approximation, and leads to substantial improvement in the application to the Lamm equation that describes ultracentrifugation.

INTRODUCTION

We have recently reported on an approximate method for the solution of equations that commonly arise in the analysis of biochemical separation systems (*1*). Although the original application was made to pressure dependence on velocity sedimentation experiments, (*2–4*), subsequent applications have been made to equations arising from pore gradient electrophoresis (*5*) and GPC with a varying gel density (*6*). In view of the many potential uses of such approximations in the analysis of chemical separation systems, it is of some interest to indicate how to obtain corrections to the original approximation. It is the purpose of this paper to derive the first correction term to the original approximation, and to indicate how higher order correction terms can be derived.

Many equations describing chemical separation systems can be reduced to the dimensionless form

$$\frac{\partial \theta}{\partial \tau} = \epsilon \frac{\partial}{\partial x}\left(f(x)\frac{\partial \theta}{\partial x}\right) - \frac{\partial}{\partial x}[g(x)\theta] \tag{1}$$

where $\theta(x, \tau)$ is the concentration of a single substance, x is the distance, τ the time, and ϵ is a parameter proportional to the diffusion constant. The term $g(x)$ is the transport term, and $f(x)$ expresses the spatial dependence of the diffusion coefficient. It is generally assumed that boundary effects can be neglected, so that Eq. (1) is to be solved subject to an initial condition $\theta(x,0)$. The systems in which we will be interested are characterized by a diffusion effect small compared to the transport force. More precisely, we assume that $\epsilon \ll 1$ while $f(x)$ and $g(x)$ are of the order of 1 for relevant values of x. For example, in ultracentrifugation the parameters τ, x, and ϵ are defined by

$$\tau = 2\omega^2 s_0 t, \qquad x = r^2/r_a^2, \qquad \epsilon = 2D/(s_0\omega^2 r_a^2) \tag{2}$$

where t is time, ω the angular velocity, s_0 the reference sedimentation coefficient, r_a the radial position of the meniscus, and D the diffusion constant. The parameter ϵ for velocity sedimentation experiments on typical protein molecules is generally less than 5×10^{-3}. When pressure has a significant effect on sedimentation, but diffusion is unaffected by pressure, $f(x) = x$ is a term due to the cylindrical geometry, and $g(x) = x(1 + m - mx)$ is a typical representation of the effect of pressure on sedimentation (*7*). For ultracentrifuges in current use, x varies from 1 to approximately 1.5, and no value of m greater than 0.95 has been found, (*8, 9*). A similar set of parameters can be defined for pore gradient electrophoresis with values of ϵ equal to 5×10^{-2} or less (*6*).

A common method for the solution to Eq. (1) is to set $\epsilon = 0$ and to solve the resulting first-order equation by the method of characteristics (*10*). While this method is sufficiently good for most single solute experiments, broadening of the concentration profile due to diffusion can be important when many substances are to be separated, as is commonly the case in chromatography. The remainder of this paper is devoted to a systematic perturbation development of the solution to Eq. (1) valid for small ϵ.

MATHEMATICAL DEVELOPMENT

Let us begin by assuming an initial condition $\theta(x,0) = \delta(x - x_0)$, where $\delta(x)$ is a delta function corresponding to a pulse injection at $t = 0$ at position x_0. Then, if $\epsilon = 0$, the solution to Eq. (1) corresponds to a modulated pulse traveling down the column, where the position at time t is the solution to the equation

$$\int_{x_0}^{x} \frac{du}{g(u)} = \tau \tag{3}$$

The initial condition $\theta(x,0) = U(x - 1)$, where $U(y)$ is a step function defined by

$$\begin{aligned} U(y) &= 0 \qquad y < 0 \\ &= 1 \qquad y > 0 \end{aligned} \tag{4}$$

leads to a solution with a traveling discontinuity located at the value of x specified by Eq. (3). Since small ϵ implies a slight broadening of the peak either in concentration or concentration gradient, it is plausible that we should be interested in the behavior of $\theta(\zeta,\tau)$ for small $|\zeta|$ where ζ is a running coordinate defined by

$$\zeta = \int_{x_0}^{x} \frac{du}{g(u)} - \tau \tag{5}$$

For later use we define the solution of this equation for x in terms of ζ to be

$$x = H(\zeta + \tau) \tag{6}$$

so that in the absence of diffusion the position of a peak initially at $x = 0$ will be $x_+ = H(\tau)$.

Since we will be interested in small $|\zeta|$, it is clearly desireable to transform the space variable x in Eq. (1) to ζ using Eqs. (5) and (6). Furthermore it is convenient but not necessary to treat the two cases corresponding to the two initial conditions $\theta(x,0) = \delta(x)$ and $\theta(x,0) =$

$U(x-1)$ in slightly different ways. Let us first consider the pulse initial condition $\theta(x,0) = \delta(x)$. For this case we define functions $F(u)$ and $G(u)$ by

$$F(u) = f[H(u)], \qquad G(u) = g[H(u)] \tag{7}$$

and we define a new independent variable $\psi(x,\tau)$ by

$$\psi(x,\tau) = g(x)\theta(x,\tau) \tag{8}$$

When the transformation of x to ζ and θ to ψ is made, the transport equation can be written

$$\frac{\partial\psi}{\partial\tau} = \epsilon A(\zeta,\tau)\frac{\partial^2\psi}{\partial\zeta^2} + \epsilon B(\zeta,\tau)\frac{\partial\psi}{\partial\zeta} + \epsilon C(\zeta,\tau)\psi \tag{9}$$

where

$$A(\zeta,\tau) = F(\zeta+\tau)/G^2(\zeta+\tau)$$

$$B(\zeta,\tau) = \frac{\partial A}{\partial\zeta} - \frac{A}{G}\frac{\partial G}{\partial\zeta}$$

$$C(\zeta,\tau) = -\frac{\partial}{\partial\zeta}\left(\frac{A}{G}\frac{\partial G}{\partial\zeta}\right) \tag{10}$$

Equation (9) is to be solved subject to the initial condition

$$\psi(\zeta,0) = G(\zeta)\delta[H(\zeta)] \tag{11}$$

The equation corresponding to the initial condition $\theta(x,0) = U(x-1)$ is most conveniently handled by defining a new dependent variable $\psi(x,\tau)$ by

$$\theta(x,\tau) = \frac{G(\zeta)}{G(\zeta+\tau)}\psi(\zeta,\tau) \tag{12}$$

in which, now, $\psi(x,0)$ satisfies the initial condition

$$\psi(\zeta,0) = U[H(\zeta)-1] \tag{13}$$

Notice that the factor $G(\zeta)/G(\zeta+\tau)$ is just the modulating factor in the solution to the transport equation in the absence of diffusion. Thus the solution to the diffusion free ($\epsilon = 0$) equation can be written

$$\theta(x,\tau) = \frac{G(\zeta)}{G(\zeta + \tau)} U[H(\zeta + \tau) - 1] \tag{14}$$

where ζ is to be expressed in terms of x to return to original variables. When the transformation to ψ is made by means of Eq. (5), and the space variable is transformed to ζ, then an equation for ψ is obtained exactly in the form of Eq. (9), except that the functions $A(\zeta,\tau)$, $B(\zeta,\tau)$, and $C(\zeta,\tau)$ are now given in terms of the function $S(\zeta,\tau) = G(\zeta)/G(\zeta + \tau)$ by

$$\begin{aligned} A(\zeta,\tau) &= F(\zeta + \tau)/G^2(\zeta + \tau) \\ B(\zeta,\tau) &= A \frac{\partial}{\partial \zeta} \ln \frac{FS^2}{G} \\ C(\zeta,\tau) &= \frac{1}{SG} \frac{\partial}{\partial \zeta} \left(\frac{F}{G} \frac{\partial S}{\partial \zeta} \right) \end{aligned} \tag{15}$$

Since the equations for ψ for both initial conditions are formally the same, the analysis to follow can be applied to both problems.

Up to this point the analysis has been exact and no approximations have been made. In order to derive a systematic perturbation solution to Eq. (9), we use the terminology of singular perturbation theory (*11*) to assume the existence of a "stretched" coordinate which will be denoted by ρ and defined by

$$\rho = \zeta/\varphi(\epsilon) \tag{16}$$

and an expansion of ψ in the form

$$\psi(\zeta,\tau) = \psi_0[\rho\varphi(\epsilon), \tau] + h_1(\epsilon)\psi_1[\rho\varphi(\epsilon), \tau] + h_2(\epsilon)\psi_2[\rho\varphi(\epsilon), \tau] + \cdots \tag{17}$$

where $\varphi(\epsilon)$, $h_1(\epsilon)$, $h_2(\epsilon)$, . . . , are arbitrary functions at our disposal with the properties

$$\lim_{\epsilon \to 0} \varphi(\epsilon) = 0, \qquad \lim_{\epsilon \to 0} h_n(\epsilon) = 0, \qquad \lim_{\epsilon \to 0} \frac{h_{n+1}(\epsilon)}{h_n(\epsilon)} = 0 \tag{18}$$

The intuitive idea behind the calculations is that ρ is a coordinate that will remain of the order of 1 as $\epsilon \to 0$, and that a series of successive approximations can be derived in which the ψ_n at each order satisfy an equation that involves only $\psi_0, \psi_1, \ldots, \psi_n$ and no higher order terms and in which all coefficients are of order equal to one. We will assume further, that the $\psi_n(\zeta,\tau)$ satisfy the initial conditions

$$\psi_0(\zeta,0) = \psi(\zeta,0), \qquad \psi_1(\zeta,0) = \psi_2(\zeta,0) = \cdots = 0 \tag{19}$$

Although the $\varphi(\epsilon)$, $h_1(\epsilon)$, $h_2(\epsilon)$, . . . , are arbitrary, we shall see that there is a natural way to choose them.

For the purpose of the calculation we require the assumption that $A(u)$, $B(u)$, and $C(u)$ are analytic functions of u, i.e., that expansions of the form

$$A(\zeta,\tau) = A(\tau) + \zeta \left.\frac{\partial A}{\partial \zeta}\right|_{\zeta=0} + \frac{\zeta^2}{2} \left.\frac{\partial^2 A}{\partial \zeta^2}\right|_{\zeta=0} + \cdots \tag{20}$$

are valid. If we now substitute Eqs. (7) and (20) into Eq. (9), we find

$$\begin{aligned}
&\frac{\partial \psi_0}{\partial \tau} + h_1(\epsilon)\frac{\partial \psi_1}{\partial \tau} + h_2(\epsilon)\frac{\partial \psi_2}{\partial \tau} + \cdots \\
&\quad = \frac{\epsilon}{\varphi^2(\epsilon)}\left[A(0,\tau) + \rho\varphi(\epsilon)\frac{\partial A}{\partial \zeta}(0,\tau) + \frac{[\rho\varphi(\epsilon)]^2}{2}\frac{\partial^2 A}{\partial \zeta^2}(0,\tau) + \cdots\right] \\
&\quad\quad \times \left[\frac{\partial^2 \psi_0}{\partial \rho^2} + h_1(\epsilon)\frac{\partial^2 \psi_1}{\partial \rho^2} + \cdots\right] \\
&\quad\quad + \frac{\epsilon}{\varphi(\epsilon)}\left[B(0,\tau) + \rho\varphi(\epsilon)\frac{\partial B}{\partial \zeta}(0,\tau) + \cdots\right] \\
&\quad\quad \times \left[\frac{\partial \psi_0}{\partial \rho} + h_1(\epsilon)\frac{\partial \psi_1}{\partial \rho} + \cdots\right] \\
&\quad\quad + \epsilon\left[C(0,\tau) + \rho\varphi(\epsilon)\frac{\partial C}{\partial \zeta}(0,\tau) + \cdots\right][\psi_0 + h_1(\epsilon)\psi_1 + \cdots]
\end{aligned} \tag{21}$$

Since the first term on the left, $\partial\psi_0/\partial\tau$, has no associated factor of ϵ, we require the same of the lowest order term on the right-hand side. This can be achieved by setting $\varphi(\epsilon) = \sqrt{\epsilon}$. A consideration of the next higher order term shows that $h_1(\epsilon) = \sqrt{\epsilon}$, and it is then easy to see that $h_n(\epsilon)$ should be $\epsilon^{n/2}$.

The hierarchy of equations that results from these calculations then reads

$$\frac{\partial \psi_0}{\partial \tau} = A(\tau)\frac{\partial^2 \psi_0}{\partial \rho^2}$$

$$\frac{\partial \psi_1}{\partial \tau} - A(\tau)\frac{\partial^2 \psi_1}{\partial \rho^2} = \rho A'(\tau)\frac{\partial^2 \psi_0}{\partial \rho^2} + B(0,\tau)\frac{\partial \psi_0}{\partial \rho}$$

$$\frac{\partial \psi_2}{\partial \tau} - A(\tau)\frac{\partial^2 \psi_2}{\partial \rho^2} = \rho A'(\tau)\frac{\partial^2 \psi_1}{\partial \rho^2} + \frac{\rho^2}{2}A''(\tau)\frac{\partial^2 \psi_0}{\partial \rho^2}$$

$$+ \rho\frac{\partial B(0,\tau)}{\partial \zeta}\frac{\partial \psi_0}{\partial \rho} + B(0,\tau)\frac{\partial \psi_1}{\partial \rho} + C(0,\tau)\psi_0 \quad (22)$$

since $A(\zeta, \tau) = A(\zeta + \tau)$ from Eq. (15). All of these equations take the form

$$\frac{\partial \psi}{\partial \tau} - A(\tau)\frac{\partial^2 \psi}{\partial \rho^2} = V(\rho,\tau) \quad (23)$$

where the $V(\rho,\tau)$ are calculated from lower order terms of the hierarchy, and can therefore be considered to be known. The first of these equations is

$$\frac{\partial \psi_0}{\partial \tau} = A(\tau)\frac{\partial^2 \psi_0}{\partial \rho^2} \quad (24)$$

or, defining a new dimensionless time, $\Delta(\tau)$, by

$$\Delta(\tau) = \int_0^\tau A(u)\,du \quad (25)$$

it becomes

$$\frac{\partial \psi_0}{\partial \Delta} = \frac{\partial^2 \psi_0}{\partial \rho^2} \quad (26)$$

The solutions to this equation for the two initial conditions of interest are

$$\theta(x,0) = \delta(x): \qquad \psi_0(x,\tau) = [4\pi\epsilon\Delta(\tau)]^{-1/2}\exp\left(-\frac{\zeta^2}{4\epsilon\Delta(\tau)}\right) \quad (27a)$$

$$\theta(x,0) = U(x-1): \qquad \psi_0(x,\tau) = \Phi\{\zeta/[2\epsilon\Delta(\tau)]^{1/2}\} \quad (27b)$$

where $\Phi(x)$ is the error function defined by

$$\Phi(x) = (2\pi)^{-1/2} \int_{-\infty}^{x} \exp(-u^2/2)\, du.$$

Expressions for $\theta_0(x,\tau)$ appropriate for the two initial conditions are obtained by inserting the appropriate values of ζ in terms of x, and by multiplying, in the first case by $1/g(x)$, and in the second by $G(\zeta)/G(\zeta+\tau)$.

We next turn our attention to the solution of the equations for $\psi_n(x,\tau)$, where $n > 1$, i.e., equations for which $V(\rho,\tau) \neq 0$ in Eq. (23). If we define Fourier transforms $\Gamma(\omega,\Delta)$ and $W(\omega,\Delta)$ by

$$\Gamma(\omega,\Delta) = \int_{-\infty}^{\infty} \psi(\rho,\Delta) \exp(i\omega\rho)\, d\rho$$

$$W(\omega,\Delta) = \int_{-\infty}^{\infty} V(\rho,\Delta) \exp(i\omega\rho)\, d\rho \tag{28}$$

then the Fourier transformation of Eq. (23) yields

$$\frac{\partial\Gamma}{\partial\tau} + A(\tau)\omega^2\Gamma = W \tag{29}$$

Since $\Gamma_1(\omega,0) = \Gamma_2(\omega,0) = \cdots = 0$ from Eq. (19), we can express the solution to Eq. (29) as

$$\Gamma(\omega,\tau) = \int_0^{\tau} W(\omega,u) \exp\{-\omega^2[\Delta(\tau) - \Delta(u)]\}\, du \tag{30}$$

Applying the inverse transform and interchanging the orders of integration, we find

$$\begin{aligned}\psi(\rho,\tau) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} \Gamma(\omega,\Delta) \exp(-i\omega\rho)\, d\omega \\ &= \frac{1}{2\pi}\int_0^{\tau} du \int_{-\infty}^{\infty} \exp\{-i\omega\rho - \omega^2[\Delta(\tau) - \Delta(u)]\} W(\omega,u)\, d\omega\end{aligned} \tag{31}$$

But the integral over ω is the Fourier transformation of a product (*12*) and can therefore be written as a convolution integral, leading to a final result

$$\psi(\rho,\tau) = \frac{1}{(4\pi)^{1/2}} \int_0^{\tau} \frac{du}{[\Delta(\tau) - \Delta(u)]^{1/2}} \times \int_{-\infty}^{\infty} V(v,u) \exp\left[- \frac{(\rho - v)^2}{4[\Delta(\tau) - \Delta(u)]}\right] dv \tag{32}$$

DETAILED EVALUATIONS OF THE FIRST CORRECTION

In this section we calculate in detail the expressions for $\psi_1(\rho,\tau)$. Let us first consider the initial pulse condition, for which $\psi_0(\rho,\tau)$ is given by the expression in Eq. (27a). In this case one finds that $V(\rho,\tau)$ can be expressed as

$$V(\rho,\tau) = \frac{1}{[4\pi\epsilon\Delta(\tau)]^{1/2}} [\rho^3 J(\tau) - \rho K(\tau)] \exp\left(- \frac{\rho^2}{4\epsilon\Delta(\tau)}\right) \tag{33}$$

in which

$$J(\tau) = \frac{A'(\tau)}{4\Delta^2(\tau)}, \qquad K(\tau) = \frac{1}{2\Delta(\tau)} [A'(\tau) + B(0,\tau)] \tag{34}$$

When this expression is substituted into Eq. (22) we can evaluate the v integral in closed form, the integrals needed for the evaluation being:

$$\int_{-\infty}^{\infty} v \exp\left[- \frac{v^2}{4\Delta(\tau)} - \frac{(\rho - v)^2}{4[\Delta(\tau) - \Delta(u)]}\right] dv = \rho \left(\frac{\Delta(u)}{\Delta(\tau)}\right)^{3/2} \{4\pi[\Delta(\tau) - \Delta(u)]\}^{1/2} \exp\left(- \frac{\rho^2}{4\Delta(\tau)}\right)$$

$$\int_{-\infty}^{\infty} v^3 \exp\left[- \frac{v^2}{4\Delta(\tau)} - \frac{(\rho - v)^2}{4[\Delta(\tau) - \Delta(u)]}\right] dv = \left(\frac{\Delta(u)}{\Delta(\tau)}\right)^{5/2} \{4\pi[\Delta(\tau) - \Delta(u)]\}^{1/2} \left[6\rho[\Delta(\tau) - \Delta(u)] + \rho^3 \frac{\Delta(u)}{\Delta(\tau)}\right] \times \exp\left(- \frac{\rho^2}{4\Delta(\tau)}\right) \tag{35}$$

The final expression for the first correction term $\sqrt{\epsilon}\psi_1(\rho,\tau)$ is:

$$\sqrt{\epsilon}\psi_1(\rho,\tau) = \frac{\exp\{-[\rho^2/4\Delta(\tau)]\}}{(16\pi)^{1/2}}\left\{\frac{3\rho}{4\Delta^{5/2}(\tau)}\int_0^\tau A'(u)[\Delta(\tau)-\Delta(u)]\,du\right.$$

$$\left.+\frac{\rho^3}{8\Delta^{7/2}(\tau)}\int_0^\tau A'(u)\Delta(u)\,du-\frac{\rho}{4\Delta^{3/2}(\tau)}\int_0^\tau[A'(u)+B(0,u)]\,du\right\} \tag{36}$$

for the initial pulse concentration.

Analogous calculations can be made for the unit step input function for which the initial approximation is shown in Eq. (27b). The expression for $V(\rho,\tau)$ is, in this case,

$$V(\rho,\tau) = \frac{1}{[4\pi\Delta(\tau)]^{1/2}}\left[B(0,\tau)-\frac{\rho^2A'(\tau)}{2\Delta(\tau)}\right]\exp\left(-\frac{\rho^2}{4\Delta(\tau)}\right) \tag{37}$$

and the final expression is found, after some manipulation, to be

$$\sqrt{\epsilon}\psi_1(\rho,\tau) = \frac{1}{[4\pi\Delta(\tau)]^{1/2}}\left\{\int_0^\tau B(0,u)\,du+1-A(\tau)\right.$$

$$\left.+\frac{1}{\Delta(\tau)}\left(1-\frac{\rho^2}{2\Delta(\tau)}\right)\int_0^\tau \Delta(u)A'(u)\,du\right\}\exp\left(-\frac{\rho^2}{4\Delta(\tau)}\right) \tag{38}$$

Values of $\psi_n(\rho,\tau)$ can be calculated from Eq. (22); the resulting expression will consist of sums of terms of the form

$$\rho^kM(\tau)\exp\left(-\frac{\rho^2}{4\Delta(\tau)}\right).$$

However, for the purpose of assessing the usefulness of higher order correction terms, we will confine ourselves to comparing the approximate values of $\theta_0(x,\tau)$ and $\theta_0(x,\tau)+\sqrt{\epsilon}\theta_1(x,\tau)$ with more accurate numerical evaluations of the solutions to Eq. (1).

COMPARISON BETWEEN APPROXIMATE AND EXACT SOLUTIONS

Our first example is taken from the theory of pore gradient electrophoresis (*13*, *5*). The transport equation can be written

$$\frac{\partial\theta}{\partial\tau} = \epsilon\frac{\partial}{\partial z}\left(e^{-z}\frac{\partial\theta}{\partial z}\right)-\frac{\partial}{\partial z}(e^{-z}\theta) \tag{39}$$

and the variable ζ is easily shown to be

$$\zeta = e^z - \tau - 1 \tag{40}$$

so that $H(u) = \ln(u + 1)$. Consequently the functions $A(\tau)$, $B(0,\tau)$ and $\Delta(\tau)$, needed for the expression in Eq. (36), are

$$A(\tau) = 1 + \tau, \qquad B(0,\tau) = 2, \qquad \Delta(\tau) = \tau + \tau^2/2 \tag{41}$$

The resulting integrals are elementary and the final expression for $\sqrt{\epsilon}\psi_1(\rho,\tau)$ is

$$\sqrt{\epsilon}\psi_1(\rho,\tau) = \frac{1}{(16\pi)^{1/2}}\left\{\frac{3\rho\tau^2}{\Delta^{5/2}(\tau)}\left(\frac{1}{2}+\frac{\tau}{3}\right)+\frac{\rho^3\tau^2}{4\Delta^{7/2}(\tau)}\left(1+\frac{\tau}{3}\right) - \frac{3\rho\tau}{\Delta^{3/2}(\tau)}\right\}\exp\left(-\frac{\rho^2}{4\Delta(\tau)}\right) \tag{42}$$

with $\Delta(\tau)$ as shown in Eq. (41). The exact solution has been given by Weiss and Rodbard (*5*) as

$$\theta(z,\tau) = \frac{1}{\tau(2\pi\epsilon)^{1/2}}\,\frac{1}{(\lambda^2+1)^{1/4}}\left(\frac{1}{(\lambda^2+1)^{1/2}-1}\right)^{1-1/\epsilon} \times \exp\left[\frac{1}{\epsilon}\left((\lambda^2+1)^{1/2}+\frac{z}{2}(1+\epsilon)+\frac{1+e^z}{\tau}\right)\right] \tag{43}$$

where $\lambda = (2/\tau)\exp(z/2)$.

In Fig. 1 we have plotted the relative errors defined in terms of the exact and approximate concentration profiles, $\theta_{\text{ex}}(x,\tau)$ and $\theta_{\text{app}}(x,\tau)$ by

$$R = 1 - (\theta_{\text{app}}/\theta_{\text{ex}}) \tag{44}$$

for the following set of parameters: M_0 = free mobility = 5×10^{-5} cm^2/sec/V; D_0 = free diffusion constant = 1×10^{-6} cm^2/sec; V = voltage gradient = 10 V/cm; L = column length = 10 cm.

The value of ϵ can be calculated in terms of these parameters as

$$\epsilon = D_0/(M_0VL) = 2 \times 10^{-4} \tag{45}$$

and the value of τ corresponding to 1 hr in real time is 0.18. The solid curves in Fig. 1 give the relative error corresponding to the approximation of concentration by $\theta_0(x,\tau)$. The abscissa of these curves is plotted so that the point $z = 0$ corresponds to the peak, and $z = \pm 0.035$ corresponds roughly to the concentration equal to 0.01 or less of the

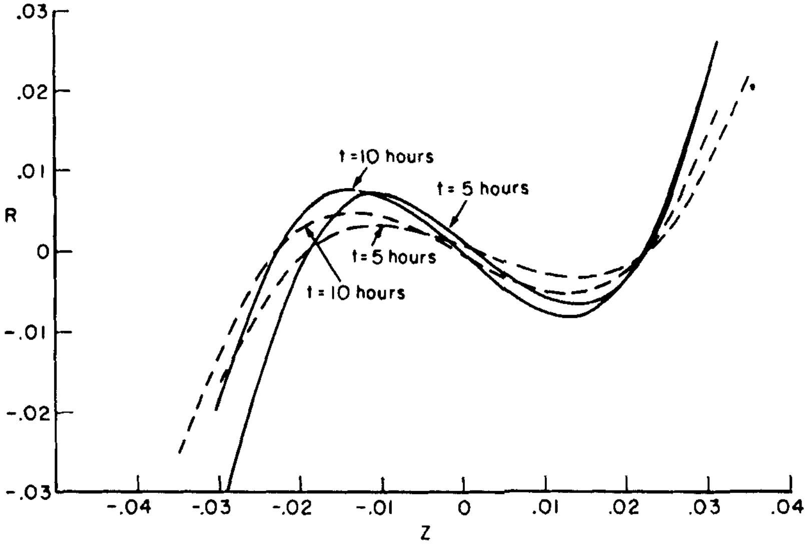

FIG. 1. Relative errors for uncorrected and corrected approximations as a function of dimensionless space coordinates z, for pore gradient electrophoresis, for $\epsilon = 2 \times 10^{-4}$ and $t = 5$ and 10.

peak maximum. The dashed curves give the relative error corresponding to the choice of $\theta_{\text{app}} = \theta_0 + \sqrt{\epsilon}\theta_1$. Although it is not evident from the curves, this second approximation yields a relative error that is very nearly a constant fraction of the relative error for the first approximation. The fraction involved is roughly 0.47 at $t = 5$ hr, 0.64 at $t = 10$ hr, and 0.77 at $t = 20$ hr. Similar results have been obtained for other parameter sets.

As a second example we consider results for the ultracentrifuge, in which pressure effects are important (*7*). For this model, using the parameters defined in Eq. (2), we have

$$f(x) = x, \qquad g(x) = x(1 + m - mx) \tag{46}$$

where m is a parameter proportional to compressibility that describes the effects of pressure. We have used the program described by Dishon, Weiss, and Yphantis (*14*) to generate accurate solutions to the Lamm equation with pressure effects, and with the initial condition $\theta(x,0) = U(x - 1)$. Numerical calculations were made for $m = 0.3$, $\epsilon = 2.4461 \times 10^{-3}$, and $\tau = 0.2$ and 0.3. In Fig. 2a we have plotted curves of the relative error as defined in Eq. (44) to approximate the concentration using θ_0 (denoted by R_0) and $\theta_0 + \sqrt{\epsilon}\theta_1$ (denoted by R_1). The relevant formulas required for numerical evaluation of Eq. (38) can be written in terms of the quantity $\alpha(\tau) = \exp[(1+m)\tau]$ as

$$\Delta(\tau) = \frac{1}{(1+m)^4}\left[1 - \frac{1}{\alpha} + 3m(m+1)\tau + 3m^2(\alpha - 1) + \frac{m^3}{2}(\alpha^2 - 1)\right]$$

$$\int_0^\tau B(0,u)\,du = \frac{m}{(m+1)^3}\left[\frac{m^2(m+5)}{2}(\alpha^2 - 1) + 2m(5-m)(\alpha - 1) + (5-7m)(m+1)\tau + 4\left(\frac{1}{\alpha} - 1\right)\right]$$

$$A(\tau) = \left(\frac{m\alpha + 1}{m+1}\right)^2$$

$$\int_0^\tau \Delta(u)A'(u)\,du = \Delta(\tau)A(\tau) - \frac{1}{(m+1)^7}\left[\frac{m^6}{4}(\alpha^4 - 1) + 2m^5(\alpha^3 - 1) + \frac{15}{2}m^4(\alpha^2 - 1) + 20m^3(\alpha - 1) + 15m^2(m+1)\tau + \frac{6m}{\alpha}(\alpha - 1) + \frac{1}{2\alpha^2}(\alpha^2 - 1)\right] \tag{47}$$

Figure 2a shows curves of R_0 and R_1 at $\tau = 0.3$ as a function of a distance z, where $z = 0$ is defined to be the position of the discontinuity in a diffusion free ($\epsilon = 0$) theory. The dotted curve represents the concentration profile. As can be seen from the curves the approximation generated by R_1 is considerably more accurate than R_0 except in the leading and trailing edges of the concentration profile. The absolute error remains small throughout the profile; large values of $|R|$ in the trailing edge are magnified by the small denominator θ_{exp} and the errors

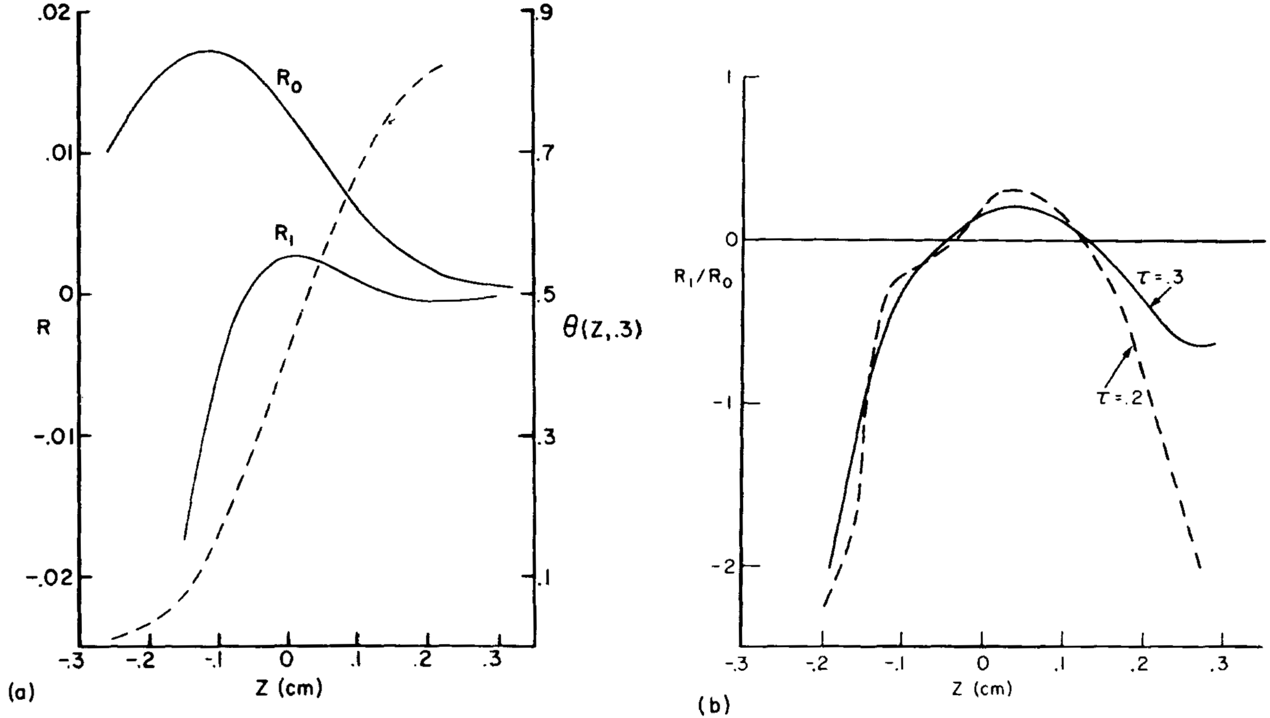

FIG. 2a. Relative errors for uncorrected and corrected approximations plotted against distance from the maximum concentration gradient. The dotted curve shows the concentration profile, with ordinate variables on the right. The parameters are $\epsilon = 2.4461 \times 10^{-3}$ and $\tau = 0.3$.

FIG. 2b. The ratio of relative errors of corrected and uncorrected approximations for $\tau = 0.2$ and 0.3 and $\epsilon = 2.4461 \times 10^{-3}$.

at the leading edge are very small for either approximation. Another way of looking at this data is shown in Fig. 2b where we have plotted the ratio R_1/R_0 for $\tau = 0.2$ and 0.3. The patterns of both curves are roughly similar indicating a considerable gain in the use of the corrected approximation from roughly $z = -0.1$ to $+0.15$ cm.

In summary, we have presented a second approximation in the singular perturbation theory of chemical separation equations, with a systematic procedure for generating higher approximations. Whether such corrections to the first approximation are required depends on the experimental accuracy of measuring concentration profiles. Most present experiments are adequately described by the first approximation, that is, experimental errors exceed the magnitude of mathematical errors. However, the recent interest in, and development of, new analytic procedures (*15*) indicates that there are and will be situations in which the higher corrections are important.

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