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A Comparison of Two Methods for Solving Transport Equations with Weak Diffusion

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ABSTRACT

The equations that describe the transport of material through a separation system often take the form of diffusion-convection equations in which diffusion plays a minor role. It is possible to derive approximate solutions to such equations using singular perturbation theory. At least two such theories have been developed, one by van Kampen and the second by Weiss and Dishon. We compare results generated by the two theories on two exactly solvable equations, one equivalent to the Lamm equation and the second related to electrophoresis in a gradient. In both cases the van Kampen approximation proved to be more accurate in a neighborhood of the peak for a pulse-loaded system.

INTRODUCTION

A determination of the kinetic behavior of separation systems that either employ gradients or because of geometric effects have nonuniform properties generally requires the solution of a diffusion equation with nonconstant coefficients. Most such equations cannot be solved in closed form, but in a large number of instances diffusion is small in some dimensionless sense compared to convection, which suggests the possibility of some form of perturbation theory to develop approximate solutions to the relevant equations. One such version of perturbation theory was originally developed in Ref. 1 and has been applied to a number of problems related to ultracentrifugation and other separation techniques (2–7). It is the purpose of this note to examine a second type of perturbation theory which has been widely applied in statistical physics but has not yet been used to analyze problems in separation science. The technique to be discussed was first proposed and analyzed by van Kampen (8, 9). Although the formalism was developed to establish a relation between a master equation and a diffusion approximation, it is not difficult to adapt it to produce a singular perturbation theory for diffusion equations with nonconstant coefficients. It should be noted that both the theory of Refs. 1–7 and the van Kampen analysis are mainly useful when there are no boundaries. Neither technique is easily modified to produce readily computable approximations to the solution of diffusion equations that describe systems in the presence of boundaries.

ANALYSIS

The Method of Moving Peaks

We briefly outline the two techniques and later compare the results obtained with both of them when applied to exactly solvable equations that typify those in separation science. Our analysis will be restricted to the case of one dimension, the extension to higher dimensions being quite straightforward. The most general form of a linear diffusion-convection equation with nonconstant coefficients can be written as

$$\frac{\partial p}{\partial t} = \epsilon \frac{\partial}{\partial x}\left(f(x)\frac{\partial p}{\partial x}\right) - \frac{\partial}{\partial x}(g(x)p) \tag{1}$$

where the coordinates x and t are assumed to be dimensionless, $f(x)$ is a dimensionless function describing the variation of the diffusion coefficient with x, and $g(x)$ similarly describes that of the convective term. The parameter ϵ is a constant that sets the scale of the problem. It will be assumed small in the sense that $\epsilon \ll 1$.

Approximate solutions to Eq. (1) will be developed subject to the initial condition

$$p(x, 0) = \delta(x - x_0) \tag{2}$$

which is equivalent to pulse loading and a unit initial concentration. The formalism outlined in Ref. 6 replaces the variable x by a new coordinate

ξ depending both on x and t which has the property that the motion of the delta function peak in the absence of diffusion is given by ξ = constant. We will refer to this technique as the moving peak method because $\xi = 0$ corresponds to the peak position in a purely convective system, i.e., when $\epsilon = 0$. If we set $\epsilon = 0$ in Eq. (1), then the use of a standard technique for the solution of first-order partial differential equations (the method of characteristics) gives as one possible definition of ξ:

$$\xi = \int_{x_0}^{x} \frac{d\alpha}{g(\alpha)} - t \tag{3}$$

A useful observation is that not only is ξ a permissible definition of the moving coordinate, but any arbitrary function of ξ can play the same role, each choice generating a different approximate solution to Eq. (1). Our analysis is based on the choice of ξ by itself as the moving coordinate since, although one has the flexibility of choosing a transformation of this parameter to define the moving coordinate, it is not clear how best to take advantage of this capability to maximize the accuracy as discussed at greater length in Ref. 10.

Let the solution to Eq. (3) for x in terms of t and ξ be denoted by

$$x = H(\xi + t) \tag{4}$$

and define the functions $f(H(u)) = \mathcal{F}(u)$ and $g(H(u)) = \mathcal{G}(u)$. Since $\xi = 0$ corresponds to the case $\epsilon = 0$, we expect that when $\epsilon \ll 1$ the peak will be reasonably well described by the equation $\xi = 0$, at least for some initial period of time. We further redefine a new dependent variable, $\psi(\xi, t)$,

$$\psi(\xi, t) = \mathcal{G}(\xi)p(\xi, t) \tag{5}$$

The equivalent of Eq. (1) in terms of these new variables is

$$\frac{\partial \psi}{\partial t} = \epsilon \frac{\partial}{\partial \xi}\left\{\frac{\mathcal{F}(t+\xi)}{\mathcal{G}(t+\xi)} \frac{\partial}{\partial \xi}\left[\frac{\psi}{\mathcal{G}(t+\xi)}\right]\right\} \tag{6}$$

which is exact.

An equation for the lowest order approximation to the solution $\psi_0(\xi, t)$ is obtained by simply setting ξ equal to 0 in the functions $\mathcal{F}(t + \xi)$ and $\mathcal{G}(t + \xi)$ that appear in this last form of the equation. The function $\psi_0(\xi, t)$ therefore satisfies

$$\frac{\partial \psi_0}{\partial t} = \epsilon \frac{\mathcal{F}(t)}{\mathcal{G}^2(t)} \frac{\partial^2 \psi_0}{\partial \xi^2} \tag{7}$$

which is readily transformed to a diffusion equation in which the time variable is to be replaced by

$$\Delta(t) = \int_0^t \frac{\mathcal{F}(\tau)}{\mathcal{G}^2(\tau)}\, d\tau \tag{8}$$

and the diffusion constant is equal to ϵ. The approximation furnished by this sequence of steps can be expressed in terms of $\psi_0(\xi, t)$ which is a Gaussian:

$$\psi_0(\xi, t) = \frac{1}{\sqrt{4\epsilon\Delta(t)}} \exp\left(-\frac{\xi^2}{4\epsilon\Delta(t)}\right) \tag{9}$$

from which the lowest order approximation to $p(x, t)$ can be generated by making use of Eq. (5). To transform $\psi_0(\xi, t)$ to the lowest order approximation to $p(x, t)$, we make use of the conservation of material by writing

$$p_0(x, t)dx = \psi_0(\xi, t)d\xi \tag{10}$$

But since $d\xi/dx = 1/g(x)$ we have

$$p_0(x, t) = \frac{1}{g(x)} \psi_0(\xi, t) \tag{11}$$

where, as a last step, we must express $\psi_0(\xi, t)$ in terms of x.

The van Kampen Approximation

Consider next the van Kampen approximation which in general gives a slightly different approximation than does the method of moving peaks. This is based on an elimination of the factor ϵ from Eq. (1) through the introduction of a new independent variable y by

$$y = \frac{x - H(t)}{\sqrt{\epsilon}} \tag{12}$$

and a function $\mathcal{H}(t)$ by

$$\mathcal{H}(t) = \left.\frac{dg}{dx}\right|_{x=H(t)} \tag{13}$$

Then, following this formalism, one can write an equation for the lowest order approximation to $p(y, t)$ directly as

$$\frac{\partial p_0}{\partial t} = \mathcal{F}(t)\frac{\partial^2 p_0}{\partial y^2} - \mathcal{H}(t)\frac{\partial}{\partial y}(y p_0) \tag{14}$$

When $\mathcal{F}(t)$ and $\mathcal{H}(t)$ are constants, this is known in the literature of statistical physics as the Ornstein–Uhlenbeck equation (11). It is also solvable when these functions depend on time, as we now show.

The solution of the Ornstein–Uhlenbeck equation in free space can be found by taking the Fourier transform of Eq. (14). Define this transform by

$$\hat{p}_0(\omega, t) = \int_{-\infty}^{\infty} p_0(y, t)e^{i\omega y}\, dy \tag{15}$$

which satisfies the equation

$$\frac{\partial \hat{p}_0}{\partial t} = -\omega^2 \mathcal{F}(t)\hat{p}_0 + \omega \mathcal{H}(t)\frac{\partial \hat{p}_0}{\partial \omega} \tag{16}$$

This equation is to be solved subject to the initial condition equivalent to Eq. (2)

$$\hat{p}_0(\omega, 0) = \exp(i\omega y_0) \tag{17}$$

Rather than solving Eq. (16) ab initio, we will assume that it has a Gaussian form in ω which we write

$$\hat{p}_0(\omega, t) = \exp[i\omega A(t) - \omega^2 B(t)] \tag{18}$$

where the functions $A(t)$ and $B(t)$ are found by substituting this formula into Eq. (16). Doing this leads to two easily solved differential equations for $A(t)$ and $B(t)$. These are found to be

$$\frac{dA}{dt} = \mathcal{H}(t)A, \qquad \frac{dB}{dt} = \mathcal{F}(t) + 2\mathcal{H}(t)B \tag{19}$$

These must be solved with the initial condition $A(0) = y_0$ and $B(0) = 0$ and can be expressed in terms of a function $\Gamma(t)$ which is defined by

$$\Gamma(t) = \exp\left\{\int_0^t \mathcal{H}(\tau)\, d\tau\right\} \tag{20}$$

The solution to the set of equations in Eq. (19) can be expressed as

$$A(t) = y_0\Gamma(t), \qquad B(t) = \Gamma^2(t)\int_0^t \frac{\mathcal{F}(\tau)}{\Gamma^2(\tau)}\, d\tau \tag{21}$$

Finally, an evaluation of the inverse transform of Eq. (18) yields

$$p_0(y, t) = \frac{1}{\sqrt{4\pi B(t)}} \exp\left[-\frac{(y - A(t))^2}{4B(t)}\right] \tag{22}$$

or, in terms of the original spatial coordinate x,

$$p_0(x, t) = \frac{1}{\sqrt{4\pi\epsilon B(t)}} \exp\left[-\frac{\{x - x_0\Gamma(t)\}^2}{4\epsilon B(t)}\right] \tag{23}$$

In this approximation the profile is seen to be Gaussian in which the mean peak position and variance of the position are, respectively,

$$\langle x(t)\rangle_0 = x_0\Gamma(t), \qquad \sigma_0^2(t) = 2\epsilon B(t) \tag{24}$$

Thus we have shown that both the method of moving peaks and the van Kampen approximation can be expressed in terms of Gaussian functions.

TWO EXAMPLES

Having derived the lowest order terms in the two approximations, we next compare results obtained using them in the context of two exactly solvable equations which describe the kinetics of separation processes. The first of these is the Lamm equation which applies to separation in an ultracentrifuge (12). This equation can be expressed in terms of dimensionless variables as

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial x}\left[x\left(\epsilon\frac{\partial p}{\partial x} - p\right)\right], \qquad x \gtrsim 1 \tag{25}$$

where for sedimentation velocity experiments on typical proteins the dimensionless ϵ values fall in the range 10^{-2} to 10^{-6}. The restriction on x is because only flow at radii greater than that of the meniscus is of physical interest. An exact solution to the equation in Eq. (25) can be expressed in terms of the reduced time variable $\Delta(t) = 1 - e^{-t}$ as

$$p(x, t) = \frac{e^{-t}}{\epsilon\Delta(t)} \exp\left\{-\frac{x_0 + xe^{-t}}{\epsilon\Delta(t)}\right\} I_0\left(\frac{2\sqrt{x_0x}\, e^{-t/2}}{\epsilon\Delta(t)}\right) \tag{26}$$

Because the factor ϵ appears in the denominator of the argument of the Bessel function and because $\Delta(t)$ is bounded, the denominator will remain small compared to the numerator except at very large t where it is most likely that the following approximation will not be useful. This implicitly restricts the validity of the formula to be derived to values of x and t that satisfy $x \gg \epsilon[\cosh(t) - 1]$. In evaluating the expression for $p(x, t)$ given in the last equation we therefore make use of the asymptotic form of $I_0(u)$ for $u \gg 1$ which is

$$I_0(u) \sim \frac{e^u}{\sqrt{2\pi u}} \tag{27}$$

This substitution leads to a representation of $p(x, t)$ which is somewhat easier to compute than the rigorously correct Eq. (26),

$$p(x, t) \sim \frac{e^{-3t/4}}{(4\pi\epsilon\Delta(t))^{1/2}(x_0x)^{1/4}} \exp\left\{-\frac{(\sqrt{xe^{-t}} - \sqrt{x_0})^2}{\epsilon\Delta(t)}\right\} \tag{28}$$

Consider the formalism based on the method of moving peaks discussed in the last section. The first step required in the calculation is to find the moving peak ξ. In the present example this is easily seen to be

$$\xi = \ln\left(\frac{x}{x_0}\right) - t \tag{29}$$

where the factor x_0 has been inserted to adjust the value of ξ on the diffusion-free trajectory at the value $\xi = 0$. It follows from this definition of ξ that the method of moving peaks based on the combination of Eqs. (5) and (7) yields an approximation which, to lowest order, can be written

$$p_{0,mp}(x, t) = \frac{1}{x\sqrt{4\pi\epsilon\Delta(t)}} \exp\left[-\frac{1}{4\epsilon\Delta(t)}\left\{\ln\left(\frac{x}{x_0}\right) - t\right\}^2\right] \tag{30}$$

The van Kampen approximation to the solution to Eq. (25) is also readily computable and is, in lowest order,

$$p_{0,vK}(x, t) = \frac{e^{-t}}{\sqrt{4\pi\epsilon\Delta(t)}} \exp\left[-\frac{(xe^{-t} - x_0)^2}{4\epsilon\Delta(t)}\right] \tag{31}$$

In Fig. 1 we compare the relative error obtained from both of these approximations when applied to Eq. (25) for the parameters $\epsilon = 0.001$, $x_0 = 1$, and $t = 1$. The extreme values of x are at the points at which $p(x, t)$ falls to approximately 1% of the peak value. The value $x = 1$ corresponds to the peak at which both approximation techniques give a zero error. A glance at the figure, which is typical for data found for other values of ϵ and t, indicates that the van Kampen approximation gives more accurate results in the neighborhood of the peak than does the method of moving peaks, but the latter is slightly more accurate further out in the tails of the peak. The accuracy of both approximations decreases with increasing time.

A second example is suggested by a model for diffusion-dependent peak broadening in electrophoresis (5). An exactly solvable diffusion equation that describes this system is

$$\frac{\partial p}{\partial t} = \epsilon\frac{\partial}{\partial x}\left(e^{-x}\frac{\partial p}{\partial x}\right) - \frac{\partial}{\partial x}(e^{-x}p) \tag{32}$$

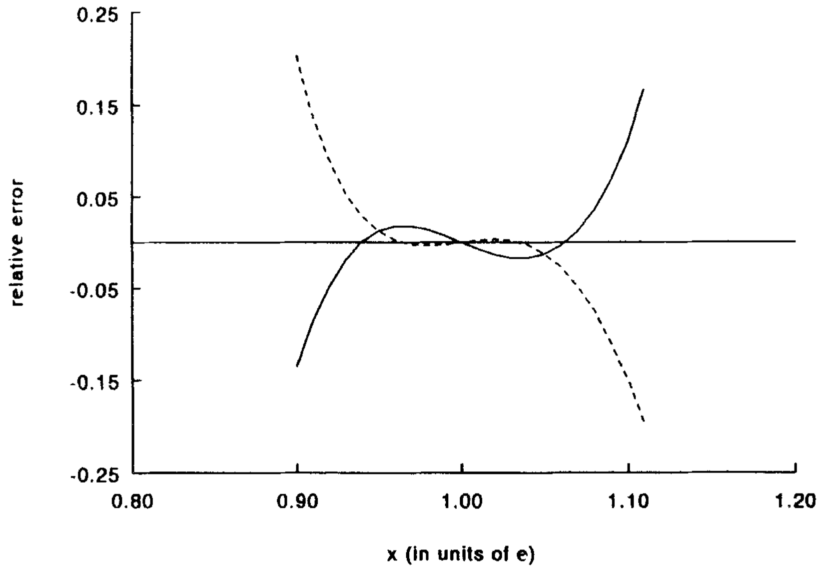

FIG. 1 A comparison of the relative error using the two approximations applied to Eq. (25). The parameters used to generate the figure are $\epsilon = 0.001$ and $t = 1$. The dashed curve gives the relative error with the van Kampen approximation, and the solid curve corresponds to the method of moving peaks. The value $x = 1$ corresponds to the peak maximum.

The exact solution of this equation with the initial condition $p(x, 0) = \delta(x)$ has been shown to be (5)

$$p(x, t) = \frac{1}{\epsilon t} \exp\left[\frac{x}{2\epsilon}(1 + \epsilon) - \frac{1 + e^x}{\epsilon t}\right] I_{1/\epsilon - 1}\left(\frac{2e^{x/2}}{\epsilon t}\right) \tag{33}$$

Since physically realistic values of ϵ are expected to be of the order of 10^{-3}, the Bessel function in this last equation will be quite large, so we can use an asymptotic form for the Bessel function (13). Doing so leads to a quite accurate approximation without the necessity of evaluating a special function. Define a parameter β by $\beta = (2/t) \exp(x/2)$. In terms of this we can express $p(x, t)$ as

$$\begin{aligned} p(x, t) \sim \frac{1}{t\sqrt{2\pi\epsilon}} \frac{\beta}{(\beta^2 + 1)^{1/4}} \frac{1}{(\beta^2 + 1)^{1/2} - 1} \exp\Bigg[\frac{1}{\epsilon}\Bigg\{&(\beta^2 + 1)^{1/2} \\ &+ \ln\left(\frac{(\beta^2 + 1)^{1/2} - 1}{\beta}\right) + \frac{x}{2}\left(\frac{1 + \epsilon}{\epsilon}\right) - \frac{e^x + 1}{t}\Bigg\}\Bigg] \end{aligned} \tag{34}$$

The leading term of the approximation given by van Kampen's method has the form

$$p_{0,vK}(x, t) = \frac{1}{\sigma_1(t)\sqrt{2\pi\epsilon}} \exp\left\{-\frac{[x - \ln(1 + t)]^2}{2\epsilon\sigma_1^2(t)}\right\} \tag{35}$$

in which the variance $\sigma_1^2(t)$ is

$$\sigma_1^2(t) = 1 - \frac{1}{(t + 1)^2} \tag{36}$$

In contrast, the moving peak method peaks gives

$$p_{0,mp}(x, t) = \frac{e^x}{\sqrt{2\pi\epsilon(2t + t^2)}} \exp\left\{-\frac{(e^x - t - 1)^2}{2\epsilon(2t + t^2)}\right\} \tag{37}$$

Figure 2 shows the relative errors resulting from the use of both approximation schemes plotted as a function of x for the parameters $\epsilon = 0.001$ and $t = 1$. Here again the van Kampen technique gives a more accurate approximation to the exact result than does the method of moving peaks. Qualitative features of the curves are quite similar to those in Fig. 1. It is natural to ask whether this is, in fact, always the case since we have

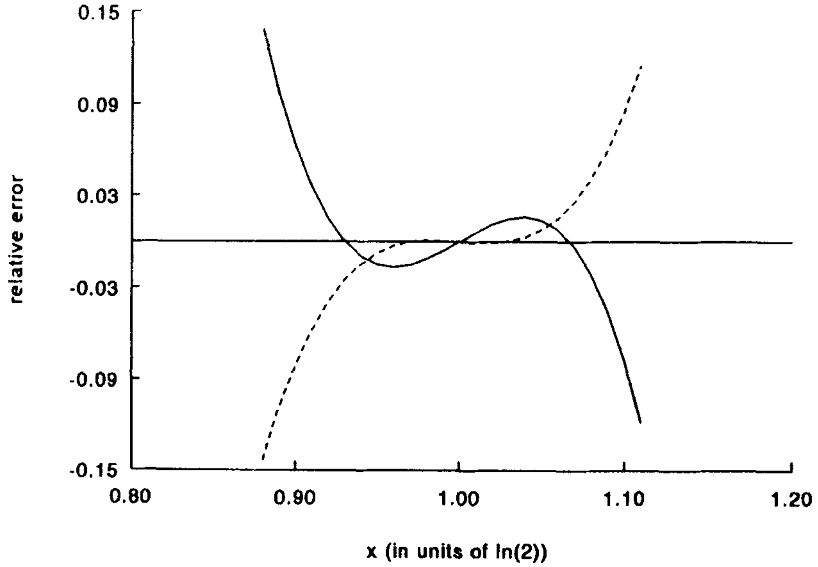

FIG. 2 A comparison of relative error for the two approximations applied to Eq. (32). The parameters used to generate the curve are again $\epsilon = 0.001$ and $t = 1$.

not actually proved the superiority of the method. As a first point we can observe that the van Kampen approximation is not uniformly more accurate than the method of moving peaks, but is less accurate in the leading edge of the profile. We have also shown in Ref. 10 that slightly modified versions of the two methods can be proved to be equivalent to one another. Further, it is possible to replace the coordinate ξ defined in Eq. (3) by an arbitrary function of ξ which can sometimes be used to advantage to improve the accuracy of the moving peak approximation. However, we have been unable to develop a way to find a reasonable way to define an optimal functional relationship for this parameter given only a knowledge of the form of the original diffusion equation. The present work therefore seems to suggest that the van Kampen method should be the technique of choice for the solution of equations in which diffusion is weak although the relative differences, even in the neighborhood of the peak position, tend to be quite small.

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