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Diffusion-Dependent Peak Broadening in Pore Gradient Electrophoresis

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Summary

An earlier theory of the kinetics of pore gradient electrophoresis has been extended and generalized to include diffusion broadening of peaks. If D and D_0 represent the diffusion coefficient of a molecular species in the gel and in the absence of a gel, respectively, and M and M_0 the respective mobilities, and these variable are assumed to satisfy

$$D/D_0 = M/M_0 = \exp(-x/L)$$

where x is distance, then an exact solution is obtained for the resulting model. Further, an approximate theory has been developed for the determination of diffusion broadening when diffusion coefficient and mobility are allowed to have any more general dependence on distance, provided that diffusion is a small effect. A comparison of the exact and approximate solutions shows that the error due to the approximation is usually smaller than measurement error.

INTRODUCTION

Rodbard, Kapadia, and Chrambach have recently reviewed the theory and presented some relevant experimental information on the use of pore gradient electrophoresis (PGE) for the separation of proteins (*1*). The theory presented by these authors assumes that the material to be analyzed travels through a gel gradient that is not necessarily linear, but that diffusion can be neglected entirely. Some brief remarks on diffusion in PGE were made in an appendix of Ref. *1*, but a solution to the underlying equations was not given, making it difficult to assess quantitative effects of diffusion. Since resolution depends both on position and peak dispersion (bandwidth), it is obviously desireable to have either an exact solution to the underlying equations or some approximate means of calculating bandwidth as is available for many systems in chromatography (*2*) and ultracentrifugation (*3*).

The purpose of this paper is twofold: (a) to derive an exact expression for the development of the molecular distribution in a linear gel gradient under the assumption that the gradient affects the diffusion coefficient exactly as it does the mobility, and (b) to present a modification of an approximate theory previously developed for ultracentrifugation (*4*) which can describe the effects of diffusion in a more general case.

EXACT ANALYSIS

In this section we present an exact analysis of a particular model for mobility and diffusion dependence on gradient parameters. The results are useful in two respects: The principal assumptions have been verified for several systems (*1*), and the exact solution can also be used to check the approximate theory developed in the next section. The assumptions underlying the theory in both this section and the next are:

(1) The column can be regarded to be one dimensional and infinitely long, with space parameter x.

(2) The gel concentration is a function of x only.

(3) The voltage gradient within the gel is constant and is unaffected by gel concentration.

(4) Endosmosis, charge effects, and joule heating can be ignored.

(5) Mobility is a function of gel concentration only and is independent of sample concentration.

(6) The diffusion coefficient is a function of gel concentration only and is independent of sample concentration.

(7) The effects of pH or voltage discontinuities in the region of the protein band due to the Donnan effect can be ignored (*5*).

The assumptions specific to the exact analysis in the next section are:

(8) Gel concentration is a linear function of x.

(9) The Ferguson relation applies, so that if M denotes mobility, M_0 the free mobility, T the gel concentration, and K_R the retardation coefficient, we can write $M = M_0 \exp(-K_R T)$ (*1*).

(10) The diffusion coefficient satisfies $D/D_0 = M/M_0 = \exp(-K_R T)$ (*6, 7*).

If we denote protein concentration at position x at time t by $c(x,t)$ and let $v = MV$ and $v_0 = M_0 V$, be the entrained and free velocities, respectively, where V is the voltage gradient, then Fick's equation can be written

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D(x)\frac{\partial c}{\partial x}\right) - \frac{\partial}{\partial x}[v(x)c] \qquad (1)$$

where v = velocity = mobility × (voltage gradient). We assume that the tube is initially loaded with a delta function pulse of concentration c_0 so that the initial condition for Eq. (1) is

$$c(x,0) = c_0\delta(x) \qquad (2)$$

In what follows it will prove convenient to work with the normalized concentration $\theta(x,t)$ which also obeys Eq. (1) but with the initial condition

$$\theta(x,0) = \delta(x) \qquad (3)$$

We first discuss the general theory in the absence of diffusion. Then the solution to the resulting equation

$$\frac{\partial \theta}{\partial t} = -\frac{\partial}{\partial x}[v(x)\theta] \qquad (4)$$

can be found by the method of characteristics (*8*). If we let $x = H(\rho)$ be the solution to the equation

$$\int_0^x \frac{dy}{v(y)} = \rho \qquad (5)$$

then the general solution can be written (*8*),

$$\theta(x,t) = \frac{1}{v(x)}\, v\left[H\left(\int_0^x \frac{dy}{v(y)} - t\right)\right] \theta\left[H\left(\int_0^x \frac{dy}{v(y)} - t\right), 0\right] \qquad (6)$$

where $\theta(x,0)$ is the initial normalized concentration. In order to appreciate the significance of this formula, let us assume the conditions appropriate to a linear gel gradient which, together with the Ferguson relation, implies that

$$M(x) = M_0 \exp(-x/L) \tag{7}$$

where L is a parameter that can be determined as that position at which the mobility falls to $e^{-1} = 0.368$ of its initial value. For this case

$$H(\rho) = L \ln\left(1 + \frac{v_0\rho}{L}\right) \tag{8}$$

$$\theta(x,t) = \left(1 - \frac{v_0 t}{L} e^{-x/L}\right)^{-1} \theta[L \ln(e^{x/L} - v_0 t/L), 0] \tag{9}$$

Thus for the initial condition in Eq. (3), i.e., an initial sharp pulse, we find

$$\theta(x,t) = \left(1 + \frac{v_0 t}{L}\right) \delta[L \ln(e^{x/L} - v_0 t/L)] \tag{10}$$

This represents a pulse located at

$$x^*(t) = L \ln\left(1 + \frac{v_0 t}{L}\right) \tag{11}$$

as previously reported in Ref. *1*, the pulse being modulated by a linear function of time. A somewhat more interesting situation is one in which the initial distribution is uniform,

$$\begin{aligned} \theta(x,0) &= 1/L_1 \qquad \text{for} \quad 0 \le x \le L_1 \\ &= 0 \qquad\qquad \text{otherwise} \end{aligned} \tag{12}$$

that is to say, a finite initial concentration spread over the interval $(0,L_1)$. This initial distribution becomes

$$\begin{aligned} \theta(x,t) &= L_1^{-1}\left(1 - \frac{v_0 t}{L} e^{-x/L}\right)^{-1} \qquad \text{for} \quad x_1^*(t) \le x \le x_2^*(t) \\ &= 0 \qquad\qquad\qquad\qquad\qquad \text{otherwise} \end{aligned} \tag{13}$$

where

$$x_1^*(t) = L \ln\left(1 + \frac{v_0 t}{L}\right)$$

$$x_2^*(t) = L \ln\left[\exp\left(\frac{L_1}{L}\right) + \frac{v_0 t}{L}\right] \tag{14}$$

Thus the initial distribution has a width L_1, and after time $t > 0$ has a width $W(t)$ given by

$$W(t) = L \ln\left(\frac{\exp\left(\frac{L_1}{L}\right) + \frac{v_0 t}{L}}{1 + \frac{v_0 t}{L}}\right) \tag{15}$$

Since

$$\frac{dW}{dt} = -\frac{v_0\left[\exp\left(\frac{L_1}{L}\right) - 1\right]}{\left(1 + \frac{v_0 t}{L}\right)\left[\exp\left(\frac{L_1}{L}\right) + \frac{v_0 t}{L}\right]} \tag{16}$$

we see that the gel gradient causes the initial bandwidth to decrease asymptotically to zero in the absence of diffusion. This result is to be expected since the leading edge of the distribution travels more slowly than the trailing edge. Furthermore the original flat profile is changed to one that has a positive slope between $x_1^*(t)$ and $x_2^*(t)$.

Let us now consider the effect of diffusion. For the purpose of the analysis we use a normalized space variable $z = x/L$, and the following expression for mobility and diffusion coefficients

$$M = M_0 \exp(-z), \qquad D = D_0 \exp(-z) \tag{17}$$

If we further define a dimensionless time variable τ and dimensionless diffusion coefficient ϵ by

$$\tau = V_0 t/L = M_0 V t/L \qquad \epsilon = D_0/(V_0 L) = D_0/(M_0 V L) \tag{18}$$

then Fick's equation becomes

$$\frac{\partial \theta}{\partial \tau} = \epsilon \frac{\partial}{\partial z}\left(e^{-z} \frac{\partial \theta}{\partial z}\right) - \frac{\partial}{\partial z}\left(e^{-z}\theta\right) \tag{19}$$

and the initial condition given in Eq. (3) becomes

$$\theta(z,0) = \delta(Lz) \tag{20}$$

For a representative case we might have

$$\begin{aligned} D_0 &= 2 \times 10^{-7} \text{ cm}^2/\text{sec} \\ L &= 2 \text{ cm} \\ M_0 &= 1 \times 10^{-5} \text{ cm}^2/\text{sec/volt} \\ V &= 5 \text{ volts/cm} \end{aligned}$$

in which case $\epsilon = 2 \times 10^{-3}$ and the τ corresponding to $t = 1$ hr is 0.09. The range of possible values of ϵ for realistic systems is approximately $5 \times 10^{-4} < \epsilon < 5 \times 10^{-2}$ using polyacrylamide gels (*1*).

The solution to Eq. (19) under the initial condition of Eq. (3) is shown in Appendix A to be

$$\theta(z,\tau) = \frac{1}{L\epsilon\tau} \exp\left[\frac{z}{2}\left(\frac{1+\epsilon}{\epsilon}\right) - \frac{1+e^z}{\epsilon\tau}\right] I_{(1/\epsilon)-1}\left(\frac{2e^{z/2}}{\epsilon\tau}\right) \tag{21}$$

in which $I_{(1/\epsilon)-1}(y)$ is a Bessel function of the first kind, of imaginary argument (*9*). Since ϵ is generally quite small, both the order and the argument of the Bessel function are large, rendering a direct numerical calculation of the Bessel function very difficult. However, an asymptotic analysis given in full in Appendix B leads to a useful approximation that is accurate to within terms of order ϵ. If we define a parameter λ by $\lambda = (2/\tau) \exp(z/2)$, then the expression for protein concentration is approximated by

$$\begin{aligned} \theta(z,\tau) = {} & \frac{1}{L\tau(2\pi\epsilon)^{1/2}} \frac{\lambda}{(\lambda^2+1)^{1/4}} \frac{1}{(1+\lambda^2)^{1/2}-1} \\ & \times \exp\left[\frac{(\lambda^2+1)^{1/2}}{\epsilon} + \frac{1}{\epsilon}\ln\left(\frac{(\lambda^2+1)^{1/2}-1}{\lambda}\right) + \frac{z}{2}\left(\frac{1+\epsilon}{\epsilon}\right) - \frac{1+e^z}{\epsilon\tau}\right] \end{aligned} \tag{22}$$

Some typical curves of $L\theta(z,\tau)$ calculated for $\epsilon = 0.001$ are shown in Fig. 1. The vertical dashed lines indicate the position of the peak pre-

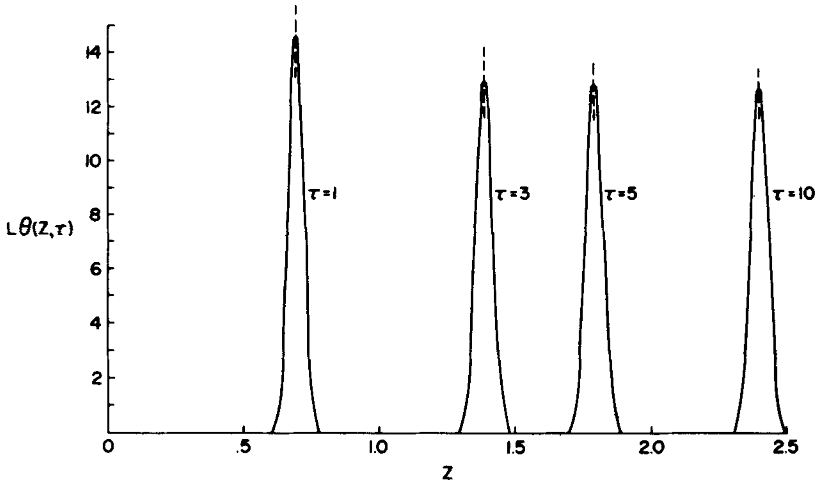

FIG. 1. Curves of normalized concentration as a function of z, for $\epsilon = 0.001$ and several values of dimensionless τ.

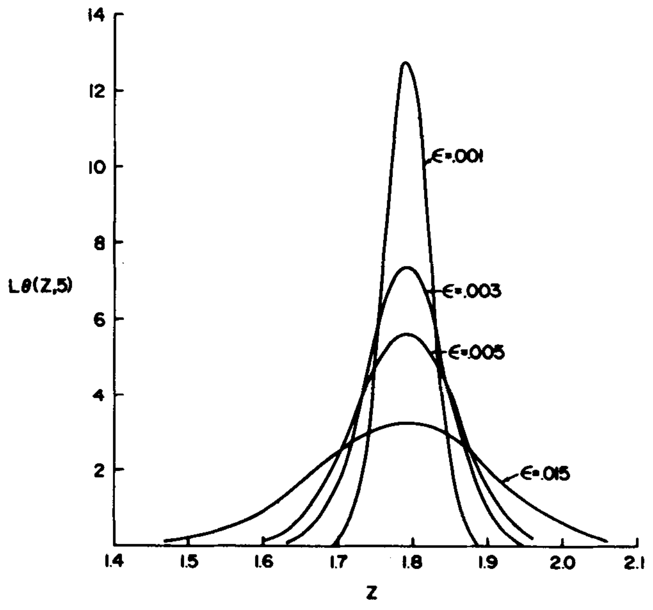

FIG. 2. Curves of normalized concentration as a function of ϵ, the diffusion parameter, for $\tau = 5$.

dicted by the zero diffusion theory ($\epsilon = 0$). As can be observed from the curves, there is no detectable shift due to diffusion. It can be demonstrated analytically that the peak occurs at $z^* = \ln(1 + \tau)$ correct to terms proportional to ϵ. This is the position predicted by the zero diffusion theory. Figure 2 shows some typical bands for $\tau = 5$ for different values of ϵ. There is a slight asymmetry around the maximum.

In Figure 3 we have plotted two curves of the width at half height $W_{1/2}$ as a function of dimensionless time τ. The curves corresponding to $\epsilon = 0.001$ and 0.005, respectively, both approach an asymptotic value. This behavior is reasonable since the diffusion coefficient $D_0 \exp(-z)$ goes to zero as z increases. Even at very early times $W_{1/2}(\tau)$ is not

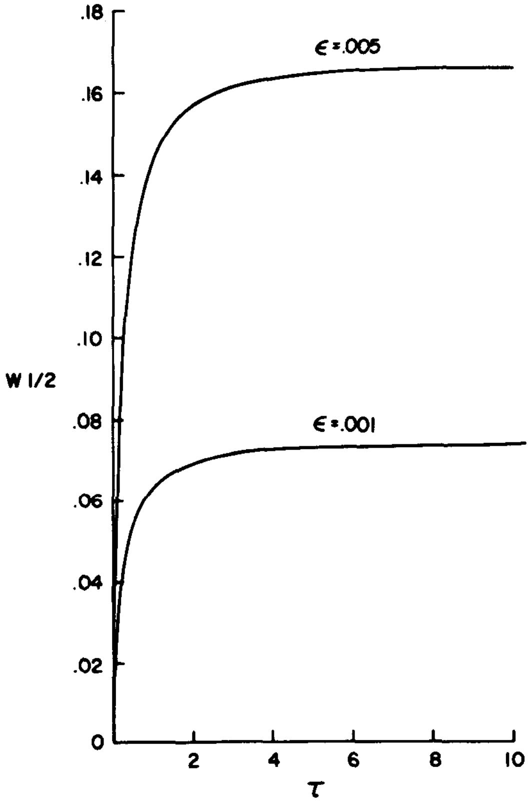

FIG. 3. Curves for $W_{1/2}(\tau)$, the peak width at half height, as a function of τ for $\epsilon = 0.001$ and 0.005.

proportional to $\tau^{1/2}$ as would be characteristic of peak spreading in ordinary diffusion.

APPROXIMATE SOLUTION FOR ARBITRARY MOBILITY AND DIFFUSION COEFFICIENT

Although the solution given in Eq. (21) is a useful one, it depends critically on Assumption (10) that mobility and diffusion coefficient are influenced in the same way by the gel gradient. It is useful, therefore, to have an approximate solution that will allow us to examine the effect of different spatial dependence of mobility and diffusion coefficient. The theory to follow is closely analogous to that developed by Weiss and Dishon (*4*) for ultracentrifugation.

Let us begin by defining a dimensionless space variable $z = x/L'$, where L' can be chosen arbitrarily* but for convenience is chosen so that z is a number of the order of unity. Let

$$D = D_0 f(z), \qquad v = v_0 g(z), \qquad \tau = v_0 t/L', \qquad \epsilon = D_0/(v_0 L') \quad (23)$$

analogous to the variables of the last section. Then Ficks' equation can be written

$$\frac{\partial\theta}{\partial\tau} = \epsilon\frac{\partial}{\partial z}\left(f(z)\frac{\partial\theta}{\partial z}\right) - \frac{\partial}{\partial z}[g(z)\theta] \quad (24)$$

We assume that $f(z)$ and $g(z)$ are the order of unity and that ϵ is small (again, as in the last section, we assume $\epsilon < 10^{-2}$). As a matter of convenience, and without loss of generality, we define $f(z)$ and $g(z)$ so that $f(0) = g(0) = 1$. We also change the space variable x so that the origin in the new set of coordinates is at the position of the peak predicted by the nondiffusion theory. This variable will be denoted by ζ and is

$$\zeta = \int_0^z \frac{dy}{g(y)} - \tau \quad (25)$$

so that in the absence of diffusion the peak is specified by $\zeta = 0$. Let the solution to Eq. (25) for z in terms of ζ and τ be denoted by

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* For example, L' can be the length of the tube, as in Ref. *1*.

$z = H(\zeta + \tau)$ and define

$$f[H(\zeta + \tau)] = F(\zeta + \tau)$$
$$g[H(\zeta + \tau)] = G(\zeta + \tau)$$
$$\psi(z,\tau) = \theta(z,\tau)g(z)$$

In terms of these variables Eq. (24) becomes an equation for $\psi(\zeta,\tau)$, viz.

$$\frac{\partial\psi}{\partial\tau} = \epsilon\frac{\partial}{\partial\zeta}\left[\frac{F(\zeta+\tau)}{G(\zeta+\tau)}\frac{\partial}{\partial\zeta}\left(\frac{\psi}{G(\zeta+\tau)}\right)\right] \tag{26}$$

This last equation is still exact, no approximations having been made. The approximation that we will make to reduce it to a simpler equation is to assume that because of the smallness of ϵ, only the region of $\zeta = 0$ will make an important contribution. This amounts to replacing the exact equation for $\psi(z,\tau)$ by an equation for an approximate $\psi_0(z,\tau)$:

$$\frac{\partial\psi_0}{\partial\tau} = \epsilon\frac{F(\tau)}{G^2(\tau)}\frac{\partial^2\psi_0}{\partial\zeta^2} \tag{27}$$

That is to say we replace $F(\zeta + \tau)$ and $G(\zeta + \tau)$ by $F(\tau)$ and $G(\tau)$, respectively. It can be shown that the neglect of terms in $\partial\psi/\partial\zeta$ and ψ in passing from Eq. (26) to Eq. (27) is of higher order in ϵ than the terms retained (*4*). If we define a new time variable $\Delta(\tau)$ by

$$\Delta = \Delta(\tau) = \int_0^\tau \frac{F(u)}{G^2(u)}\,du \tag{28}$$

then Eq. (27) becomes

$$\frac{\partial\psi_0}{\partial\Delta} = \epsilon\frac{\partial^2\psi_0}{\partial\zeta^2} \tag{29}$$

This equation is the classical diffusion equation, and is to be solved subject to the initial condition

$$\psi_0(z,0) = \delta(L'z)g(z) \tag{30}$$

when the initial concentration is a delta function pulse. The solution to Eq. (29) is (*10*)

$$\psi_0(\zeta,\Delta) = \frac{1}{(4\pi\epsilon\Delta)^{1/2}}\int_{-\infty}^{\infty} g[H(\zeta')]\delta[L'H(\zeta')]\exp\left(-\frac{(\zeta-\zeta')^2}{4\epsilon\Delta}\right)d\zeta' \tag{31}$$

in which the function $H(x)$ has been defined above. But the integral is easily evaluated because of the delta function, leading to the expression

$$\psi_0(\zeta,\Delta) = \frac{1}{L'(4\pi\epsilon\Delta)^{1/2}} \exp\left(-\frac{\zeta^2}{4\epsilon\Delta}\right) \tag{32}$$

Thus the normalized concentration can be approximated by

$$\theta_0(z,\Delta) = \frac{1}{L'g(z)\,(4\pi\epsilon\Delta)^{1/2}} \exp\left(-\frac{\zeta^2}{4\epsilon\Delta}\right). \tag{33}$$

Although this expression includes a Gaussian term, the space variable appearing in the exponent is ζ rather than z so that the Gaussian term is not necessarily symmetric in z.

In order to derive some of the consequences of Eq. (33), let us consider the case characterized by

$$f(z) = \exp(-\alpha z), \qquad g(z) = \exp(-z) \tag{34}$$

The preceding section was devoted to the case $\alpha = 1$. When $\alpha > 1$ the

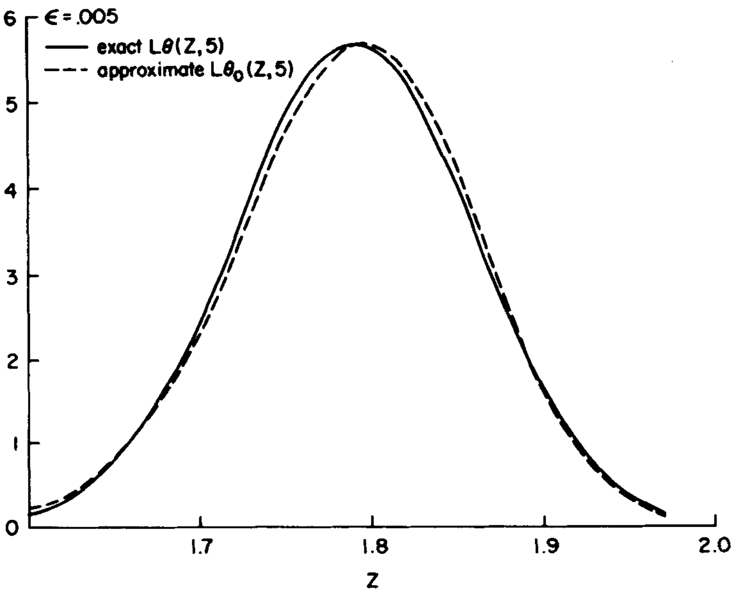

FIG. 4. Comparison of the approximate Eq. (22) and exact Eq. (21) concentration profiles for $\epsilon = 0.005$ and $\tau = 5$.

rate of diffusion decreases more quickly with the gel gradient than does the mobility, while when $\alpha < 1$ it decreases more slowly. For the choice of space dependence in Eq. (34) we find, simply, that

$$H(y) = \ln(1+y) \tag{35}$$

so that the functions $F(\tau)$ and $G(\tau)$ that appear in Eq. (28) are $F(\tau) = (1+\tau)^{-\alpha}$, $G(\tau) = (1+\tau)^{-1}$. But this leads to the following expression for $\Delta(\tau)$:

$$\begin{aligned} \Delta(\tau) &= \frac{1}{3-\alpha}[(1+\tau)^{3-\alpha} - 1] \qquad && \alpha \neq 3 \\ &= \ln(1+\tau) && \alpha = 3 \\ \zeta &= \exp(z) - 1 - \tau \end{aligned} \tag{36}$$

The first problem to be considered is the accuracy of the approximation. For this purpose we set $\alpha = 1$ and compare the approximate $L\theta_0(z,\tau)$ with the more accurate values of $L\theta(z,\tau)$ obtained from Eq. (22). Figure 4 shows two curves for $\epsilon = 0.005$ and $\tau = 5$. There is a slight shift in the peak between the two curves. Accurate calculation shows that the difference in z values between the two peaks is 0.0043, so that if $L = 2$ cm the actual peak shift would be less than 0.09 cm out of a total distance traveled of 3.6 cm. A more accurate theory can be developed to partially compensate for the shift but the resulting expressions are quite unwieldly, and the error resulting from the use of Eq. (33) is probably smaller than experimental error. The relative error $E(z,\tau)$, defined by

$$E(z,\tau) = 1 - \frac{\theta_0(z,\tau)}{\theta(z,\tau)} \tag{37}$$

for $\epsilon = 0.005$ and $\tau = 5$ is approximately 4.6% or less except in the tails of the curve, where $\theta(z,\tau)$ is small in consequence of which relative errors tend to be magnified.

In Fig. 5 we have plotted several curves of $L\theta_0(z,5)$ for the model specified in Eq. (34). The curves given are for $\epsilon = 0.001$ and $\alpha = 0.5$, 1, 1.5, 2. The curves are slightly asymmetric, but the asymmetry does not appear to depend very strongly on the parameter α. If $z_m(\tau)$ denotes the position of the maximum, then it is easy to show from Eq. (33) that

$$z_m(\tau) = \ln\left(\tfrac{1}{2}\{1 + \tau + [(1+\tau)^2 + 8\epsilon\Delta(\tau)]^{1/2}\}\right) \tag{38}$$

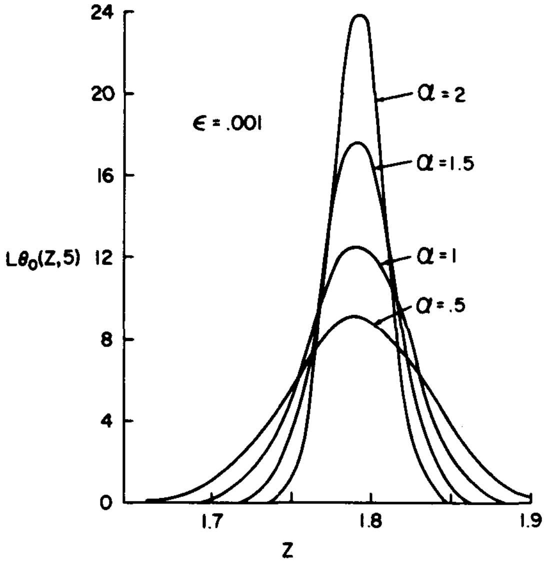

FIG. 5. A comparison of concentration profiles for the case characterized by $M = M_0 \exp(-z)$, $D = D_0 \exp(-\alpha z)$. The curves given are for $\epsilon = 0.001$ and $\tau = 5$, for various values of α.

This depends only weakly on α through the term $8\epsilon\Delta(\tau)$ appearing in the square root Both the half-width and the maximum of concentration have a significant dependence on α, although it would be very difficult to distinguish experimentally between effects that depend on changes in α and those that depend on changes in ϵ.

In future investigations we shall examine the problem of optimizing gel gradients for resolution of multicomponent systems. The mathematical apparatus developed in this paper allows us to consider diffusion effects, at least in an approximate way. The errors in the mathematical approximation appear to be no greater than experimental error so that our theory should be useful in many similar applications in separation systems.

APPENDIX A: SOLUTION TO THE FICK EQUATION (19)

In order to solve Eq. (19), let us first transform the independent and dependent variables, z and $\theta(z,\tau)$ to y and $\psi(y,\tau)$ by

$$y = \exp(z), \qquad \theta(z,\tau) = y\psi(y,\tau) \tag{A-1}$$

These variables transform Eq. (19) into

$$\frac{\partial\psi}{\partial\tau} = \epsilon\frac{\partial}{\partial y}\left(y\frac{\partial\psi}{\partial y}\right) + (\epsilon - 1)\frac{\partial\psi}{\partial y} = \epsilon y\frac{\partial^2\psi}{\partial y^2} + (2\epsilon - 1)\frac{\partial\psi}{\partial y} \tag{A-2}$$

We next apply a separation of variables to this equation in the form $\psi(y,\tau) = T(\tau)U(y)$. These functions then satisfy

$$\frac{T'(\tau)}{T(\tau)} = \epsilon y\frac{U''(y)}{U(y)} + (2\epsilon - 1)\frac{U'(y)}{U(y)} \tag{A-3}$$

Setting both sides of this equation equal to $-\lambda^2$, we find that

$$T(\tau) = \exp(-\lambda^2\tau), \qquad U(y) = y^{1/2[(1-\epsilon)/\epsilon]}J_{(1-\epsilon)/\epsilon}\left[2\lambda\left(\frac{y}{\epsilon}\right)^{1/2}\right] \tag{A-4}$$

where $J_r(x)$ is a Bessel function of the first kind, of order r and argument x (*9*). Hence a general solution to Eq. (A-2) can be written

$$\psi(y,\tau) = y^{1/2[(1-\epsilon)/\epsilon]}\int_0^\infty A(\lambda)J_{(1-\epsilon)/\epsilon}\left[2\lambda\left(\frac{y}{\epsilon}\right)^{1/2}\right]\exp(-\lambda^2 t)\,d\lambda \tag{A-5}$$

where $A(\lambda)$ is to be determined from the initial condition, i.e.,

$$\psi(y,0) = y^{1/2[(1-\epsilon)/\epsilon]}\int_0^\infty A(\lambda)J_{(1-\epsilon)/\epsilon}\left[2\lambda\left(\frac{y}{\epsilon}\right)^{1/2}\right]d\lambda \tag{A-6}$$

This integral equation can be solved by making use of the fact that if (*10*)

$$f^*(\rho) = \int_0^\infty \lambda J_n(\lambda\rho)f(\lambda)\,d\lambda \tag{A-7}$$

then $f(\lambda)$ can be written in terms of $f^*(\rho)$ as

$$f(\lambda) = \int_0^\infty \rho J_n(\lambda\rho)f^*(\rho)\,d\rho \tag{A-8}$$

Equation (A-6) can be put in the form of Eq. (A-7) by setting $f(\lambda) = A(\lambda)/\lambda$. When the initial condition corresponds to an initial pulse at $x = x'$, i.e.,

$$\theta(z,0) = \delta[L(z - z')] \tag{A-9}$$

then

$$\psi(y,0) = \frac{1}{y}\delta\left[L\ln\left(\frac{y}{y'}\right)\right] \tag{A-10}$$

where $y' = \exp(z')$. Combining Eqs. (A-6) through (A-10) we find that

$$A(\lambda) = \frac{2\lambda}{L\epsilon} \exp\left[-\frac{1}{2}\left(\frac{1-\epsilon}{\epsilon}\right)z'\right] J_{(1-\epsilon)/\epsilon}\left(\frac{2\lambda e^{z'/2}}{(\epsilon)^{1/2}}\right) \qquad \text{(A-11)}$$

Therefore the normalized concentration $\theta(z,\tau)$ can be written

$$\theta(z,\tau;z') = \frac{2}{L\epsilon} \exp\left[z - \left(\frac{1-\epsilon}{\epsilon}\right)z'\right]$$

$$\times \int_0^\infty \lambda J_{(1-\epsilon)/\epsilon}\left(\frac{2\lambda e^{z'/2}}{(\epsilon)^{1/2}}\right) J_{(1-\epsilon)/\epsilon}\left(\frac{2\lambda e^{z/2}}{(\epsilon)^{1/2}}\right) \exp(-\lambda^2\tau)\, d\lambda \qquad \text{(A-12)}$$

in which we have explicitly displayed the dependence on z'. But the integral has been evaluated *(9)*, with the result that

$$\theta(z,\tau;z') = \frac{2}{L\epsilon} \exp\left[z + \frac{1}{2}\left(\frac{1-\epsilon}{\epsilon}\right)(z - z') - \frac{e^z + e^{z'}}{\epsilon\tau}\right]$$

$$\times I_{(1-\epsilon)/\epsilon}\left(\frac{2e^{1/2(z+z')}}{\epsilon\tau}\right) \qquad \text{(A-13)}$$

The result corresponding to a pulse at $z' = 0$ is $\theta(x,\tau;0)$. However, if one wishes to discuss a more general initial distribution, say $\theta(z,0) = \rho(z)$, then the corresponding solution is

$$\theta(z,\tau) = \int_0^\infty \rho(z')\theta(z,\tau;z')\, dz' \qquad \text{(A-14)}$$

in terms of the solution just derived.

APPENDIX B: ASYMPTOTIC ANALYSIS OF THE EXACT SOLUTION IN EQ. (21)

We will reduce Eq. (21) by starting with the known properties of the Bessel function *(9)*

$$I_{(1/\epsilon)-1}(\eta) = \frac{d}{d\eta} I_{1/\epsilon}(\eta) + \frac{1}{\epsilon\eta} I_{1/\epsilon}(\eta)$$

$$= I_{1/\epsilon}(\eta)\left\{\frac{1}{\epsilon\eta} + \frac{d}{d\eta} \ln I_{1/\epsilon}(\eta)\right\} \qquad \text{(B-1)}$$

The Bessel function appearing in Eq. (21) is of the form $I_{(1/\epsilon)-1}(\lambda/\epsilon)$ where $\lambda = (2/\tau) \exp(z/2)$ will be considered to be of the order of unity. But by a result of Montroll (*11*) we can write for small ϵ,

$$I_{1/\epsilon}\left(\frac{\lambda}{\epsilon}\right) \sim \frac{(\epsilon)^{1/2}}{(2\pi\rho)^{1/2}}\left[\frac{(\rho - 1)}{\lambda} e^{\rho}\right]^{1/\epsilon} \qquad \text{(B-2)}$$

where $\rho = (\lambda^2 + 1)^{1/2}$. The combination of Eqs. (B-1) and (B-2) leads to the final result given in Eq. (22). One can show that the error terms in Montroll's expansion of the Bessel function are negligible.

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