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CONCENTRATION-DEPENDENT DIFFUSION*

BY

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1. Introduction. Classical treatments of the one-dimensional diffusion or heat equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x}\right)$$

assume that the diffusion coefficient D is a constant. For heat conduction this is ordinarily a good assumption, though for large variations in temperature one must take into account a dependence of D on the temperature. For most diffusion problems the assumption is not nearly so good and often one cannot regard D as constant at all. There is a substantial literature on problems in which D depends only on the concentration c. Friedmann [1] surveys the subject in the context of heat flow. *The Mathematics of Diffusion* by Crank [2] surveys the literature in the more general context. Much of this text is devoted to the class of problems we treat. Other smaller but useful surveys are section 13.3 of the text [3] and several sections in the text [4].

Much of the study of concentration-dependent diffusion is concerned with the problem of a semi-infinite medium initially at a concentration c_0 after the concentration at the face is instantaneously changed to c_1 and held at this value thereafter. There are two reasons for this. This physical problem is used often to describe the experimental conditions prevailing when one attempts to measure $D(c)$. Secondly, by using a similarity transformation the problem becomes one for an ordinary differential equation. This permits a more detailed analysis, both theoretically and computationally, than does the general problem. An interesting recent paper [5] shows that in some circumstances solutions of problems with more general boundary conditions converge to similarity solutions.

There are few papers analyzing existence and uniqueness for concentration dependent diffusion. Seyferth [6] proves a very general result about uniqueness for the partial differential equation. He considers coefficients $D(c)$ which are positive and continuously differentiable. It is not apparent that the very complex proof is applicable in the circumstances we discuss or that it can be carried out directly for the ordinary differential equation at all. Peletier [5] has established both existence and uniqueness for the similarity solution with the strong additional hypothesis $D'(c) < 0$. (His excellent work is marred by an oversight which we rectify below.) We prove both existence and uniqueness for all positive $D(c)$ which are piecewise continuously differentiable. This seems a natural class physically, but there are some problems of physical interest approximated by D

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which vanish. There is a considerable difference in the behavior of solutions between the two cases, so our assumption is a convenient mathematical one as well as being the more important physical case. Our proofs are quite elementary and rather simple. In addition we sketch a second existence proof requiring more technical arguments.

Another aim of this paper is to support theoretically the use of shooting methods to solve problems of this type. The theory is complemented by numerical examples. Some of the results derived are also computationally useful in the context of perturbation solutions and we briefly discuss this matter.

2. Existence. We are interested in the diffusion of a substance into a semi-infinite medium initially at a concentration c_0 after the concentration at the face is changed to c_1 and maintained thereafter. The diffusion coefficient D is to depend only on the concentration level. This problem is described by

$$\begin{aligned}
&\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D(c)\,\frac{\partial c}{\partial x}\right) && 0 \le x < \infty, && t > 0,\\
&c = c_0 && 0 \le x < \infty, && t = 0,\\
&c = c_0 && x \to \infty, && t \ge 0,\\
&c = c_1 && x = 0, && t > 0,
\end{aligned}$$

where $c = c(x, t)$. The two constants c_0, c_1 can always be taken to be 0, 1 by a change of dependent variable to $\tilde{c} = (c - c_0)/(c_1 - c_0)$, as may be easily verified. We shall suppose this has been done.

It is the similarity solution of the problem that is our sole concern. In terms of the Boltzmann similarity variable $\eta = x/\sqrt{t}$ the problem is

$$\frac{d}{d\eta}\left(D(c)\,\frac{dc}{d\eta}\right) + \frac{\eta}{2}\frac{dc}{d\eta} = 0, \tag{1}$$

$$c(0) = 1, \qquad c(\infty) = 0. \tag{2}$$

The diffusion coefficient $D(c)$ will be presumed positive for $0 \le c \le 1$ and piecewise continuously differentiable with right- and left-hand limits at discontinuities. The diffusion coefficient is to be continuous at $c = 0$ and $c = 1$. This is more smoothness than is mathematically necessary, but is convenient and physically reasonable. At points of discontinuity of $D(c)$ we add the requirements that the concentration $c(\eta)$ and the flux $D(c(\eta))c'(\eta)$ be continuous. If $D(c)$ is continuous everywhere, it is clear that initial-value problems for Eq. (1) are well defined and have unique solutions. In a moment we shall clear up the case of discontinuities.

It may not be clear why we allow discontinuities in $D(c)$. In problems with phase changes this may be an appropriate physical assumption [7]. Generalizing the approach of Neumann to phase change problems, Philip [8] writes equations for the use of piecewise constant diffusion coefficients to approximate problems with continuous coefficients. Several authors [1, 7, 9] report successful computations with the approach. Our analysis will apply to these approximating problems whether their origin is physical or numerical.

On physical grounds one would anticipate that $c(\eta)$ strictly decreases from 1 at $\eta = 0$ to 0 as $\eta \to \infty$. This turns out to be true, so it is unnecessary to say anything about $D(c)$ for c outside the interval [0, 1]. It is convenient for our purposes to define $D(c) = D(0)$ for $c < 0$. Any solution of (1) with initial conditions $c(\eta_0) = \gamma$, $c'(\eta_0) = m$

with $\eta_0 \geq 0$, $\gamma \leq 1$, and D continuous at γ is either strictly increasing, identically constant, or strictly decreasing. For rewriting (1) as

$$\frac{d}{d\eta}\left(D(c)\,\frac{dc}{d\eta}\right) = -\frac{\eta}{2D(c)}\,D(c)\,\frac{dc}{d\eta}$$

makes it obvious that

$$D(c(\eta))c'(\eta) = D(c(\eta_0))c'(\eta_0)\,\exp\left(-\int_{\eta_0}^{\eta}\frac{\tau\,d\tau}{2D(c(\tau))}\right),$$

whence the statements follow because $D(c) > 0$. These properties cause initial-value problems for Eq. (1) to be well defined and to have unique solutions. As an integral curve $c(\eta)$ crosses a value at which $D(c)$ has a jump, the continuity of concentration and flux uniquely defines the continuation of $c(\eta)$. (Note that $c'(\eta)$ has a jump at such points.) Discontinuities in D cause only minor changes in succeeding arguments and we shall not refer to the matter again.

Let us define constants δ, Δ so that

$$0 < \delta \leq D(c) \leq \Delta$$

for $0 \leq c \leq 1$. In terms of these constants we shall derive bounds on any solution of (1, 2) which might exist. We shall consider solutions of (1) with the initial conditions $c(0) = 1$, $c'(0) = -m < 0$. When it is convenient to remind ourselves that $c(\eta)$ depends on the slope $-m$, we shall write $c(\eta, m)$. The idea is to show there exist m such that $c(\infty, m) = 0$ and hence that there exist solutions of (1, 2). The numerical realization of this approach is called a shooting method. From the observations above,

$$D(c(\eta))c'(\eta) = -mD(1)\,\exp\left(-\int_0^{\eta}\frac{\tau\,d\tau}{2D(c(\tau))}\right); \tag{3}$$

but now the bounds on D assure us that

$$D(c(\eta))c'(\eta) \leq -mD(1)\,\exp\left(-\int_0^{\eta}\frac{\tau\,d\tau}{2\delta}\right)$$

and

$$-c'(\eta, m) \geq \frac{mD(1)}{D(c(\eta))}\exp(-\eta^2/4\delta) \geq \frac{mD(1)}{\Delta}\exp(-\eta^2/4\delta). \tag{4a}$$

In a similar way we prove

$$-c'(\eta, m) \leq \frac{mD(1)}{\delta}\exp(-\eta^2/4\Delta). \tag{4b}$$

By integrating (4b) from η_0 to η we find

$$0 < c(\eta_0) - c(\eta) \leq \frac{mD(1)}{\delta}\int_{\eta_0}^{\eta}\exp(-\tau^2/4\Delta)\,d\tau. \tag{5}$$

If we take $\eta_0 = 0$, this is

$$1 - c(\eta) \leq (mD(1)/\delta)(\pi\Delta)^{1/2}\,\mathrm{erf}\,(\eta/2\sqrt{\Delta})$$

or

$$c(\eta, m) \geq 1 - (mD(1)/\delta)(\pi\Delta)^{1/2} \operatorname{erf}(\eta/2\sqrt{\Delta}). \tag{6a}$$

A complementary bound is derived in the same way:

$$c(\eta, m) \leq 1 - (mD(1)/\Delta)(\pi\delta)^{1/2} \operatorname{erf}(\eta/2\sqrt{\delta}). \tag{6b}$$

The *a priori* bounds (4a, b), (6a, b) assure us that $c(\eta, m)$ can be continued for all η by a standard result for initial-value problems. Since $0 < -c'(\eta, m)$, the inequality (4b) states that $c'(\eta) \to 0$ exponentially fast for all $m \geq 0$.

The bounds (6a, b) are valid for any negative initial slope and all η (because we extended the definition of $D(c)$ to $c < 0$), so a uniform lower bound for $c(\eta, m)$ is obvious:

$$c(\eta, m) \geq 1 - (mD(1)/\delta)(\pi\Delta)^{1/2}.$$

Since $c(\eta, m)$ is strictly decreasing as a function of η and bounded below, the limit $c(\infty, m)$ must exist. If the lower bound is itself positive, then $-m$ cannot be a slope resulting in a solution of (1, 2). We conclude it is necessary that

$$(0 <)\ \delta/D(1)(\pi\Delta)^{1/2} \leq m \tag{7a}$$

if m is to yield a solution of the boundary-value problem. Similarly arguing with (6b), we find

$$c(\infty, m) \leq 1 - (mD(1)/\Delta)(\pi\delta)^{1/2}$$

and the necessary condition

$$m \leq \Delta/D(1)(\pi\delta)^{1/2}. \tag{7b}$$

This analysis not only gives necessary conditions on the initial slope but also shows that $c(\infty, m)$ assumes both positive and negative values. If we can prove $c(\infty, m)$ depends continuously on m, we obviously have the existence of an m such that $c(\infty, m) = 0$ and the existence of solutions of (1, 2).

Let us return to the inequality (5) and use it in a different way. Passing to the limit, we see

$$0 < c(\eta_0, m) - c(\infty, m) \leq \frac{mD(1)}{\delta} \int_{\eta_0}^{\infty} \exp(-\tau^2/4\Delta)\, d\tau,$$

or

$$0 < c(\eta_0, m) - c(\infty, m) \leq mD(1)[(\pi\Delta)^{1/2}/\delta] \operatorname{erfc}(\eta_0/2\sqrt{\Delta}). \tag{8}$$

This is a very useful result. The numerical realization of this approach requires the numerical construction of the integral curve $c(\eta, m)$. Of course, one cannot integrate numerically to $\eta = \infty$. This inequality tells us when we may terminate the integration because we have reached the limiting value to within a specified accuracy. Since m must satisfy (7a, b) if $c(\eta, m)$ is to be a solution of (1, 2), we can combine it with (8) to get an inequality easier to use,

$$0 < c(\eta_0, m) - c(\infty, m) \leq (\Delta/\delta)^{3/2} \operatorname{erfc}(\eta_0/2\sqrt{\Delta}).$$

Further useful information can be gleaned. If m is such that $c(\eta, m)$ is a solution of (1, 2), then since $c(\infty, m) = 0$ we have

$$0 < c(\eta_0) \leq -c'(0)D(1)\,\frac{(\pi\Delta)^{1/2}}{\delta}\,\mathrm{erfc}\,(\eta_0/2\sqrt{\Delta}) \leq (\Delta/\delta)^{3/2}\,\mathrm{erfc}\,(\eta_0/2\sqrt{\Delta}).$$

With numerical methods like that of Crank and Henry [10] one replaces the condition $c(\infty) = 0$ with $c(N) = 0$ for a suitable number N; hitherto there has been no means for choosing N. The upper bound is asymptotically

$$2(\Delta/\delta)^{3/2}(\Delta/\pi)^{1/2}\,\frac{\exp\,(-\eta_0^2/4\Delta)}{\eta_0},$$

so we have a result about the rate at which $c(\eta)$ tends to zero. It is sufficiently fast that the integral $\int_0^\infty c(\eta)d\eta$ exists and is finite; this is a result we require later. The total amount of diffusing substance which has crossed $x = 0$ at time t, M_t, is given by

$$M_t = \int_0^\infty c(x,\,t)\,dx = \sqrt{t}\int_0^\infty c(\eta)\,d\eta$$

(cf. Crank [2, p. 151]). We have proven the physically reasonable property that this amount is finite.

To return to the existence question, we need to show for any $\epsilon > 0$ and $m > 0$ that if m' is sufficiently close to m, then $|c(\infty, m) - c(\infty, m')| < \epsilon$. In (8) choose η_0 so large that

$$(mD(1)(\pi\Delta)^{1/2}/\delta)\,\mathrm{erfc}\,(\eta_0/2\sqrt{\Delta}) < \epsilon/4.$$

Now take m' sufficiently close to m that

$$|c(\eta_0\,,\,m) - c(\eta_0\,,\,m')| < \epsilon/4,$$

which can be done because at finite points the solutions depend continuously on the initial data. If necessary, take m' closer to m so that

$$(m'D(1)(\pi\Delta)^{1/2}/\delta)\,\mathrm{erfc}\,(\eta_0/2\sqrt{\Delta}) < \epsilon/2.$$

Then

$$|c(\infty,\,m) - c(\infty,\,m')| \leq |c(\eta_0\,,\,m) - c(\infty,\,m)| + |c(\eta_0\,,\,m) - c(\eta_0\,,\,m')| + |c(\eta_0\,,\,m') - c(\infty,\,m')| < \frac{\epsilon}{4} + \frac{\epsilon}{4} + \frac{\epsilon}{2} = \epsilon.$$

This completes the existence proof.

If we combine the bounds (6a, b) on $c(\eta, m)$ with the necessary conditions on the initial slope (7a, b), we arrive at *a priori* bounds for any solution of (1, 2) which may exist:

$$c(\eta) \leq 1 + (\delta/\Delta)^{3/2}\,\mathrm{erf}\,(\eta/2\sqrt{\delta}), \tag{9a}$$

$$c(\eta) \geq 1 - (\Delta/\delta)^{3/2}\,\mathrm{erf}\,(\eta/2\sqrt{\Delta}). \tag{9b}$$

An alternative existence proof can be given which produces bounds like (9a, b) except that the bounds actually satisfy both boundary conditions of (2). One changes the dependent variable by a Kirchoff transformation

$$\varphi(c) = \int_0^c D(\lambda)\,d\lambda.$$

Let F denote the inverse function of this transformation (which must exist because $D(c)$ is positive). Then (1, 2) become

$$\frac{d^2\varphi}{d\eta^2} + \frac{\eta}{2D(F(\varphi))}\frac{d\varphi}{d\eta} = 0, \tag{10}$$

$$\varphi(0) = \varphi_1, \qquad \varphi(\infty) = 0 \tag{11}$$

where $\varphi_1 = \int_0^1 D(\lambda)\, d\lambda$.

It is an easy matter to produce functions satisfying (10) as an inequality and (11) with equality. For

$$v(\eta) = \varphi_1 \operatorname{erfc}(\eta/2\sqrt{\delta})$$

satisfies

$$\frac{d^2v}{d\eta^2} + \frac{\eta}{2D(F(v))}\frac{dv}{d\eta} \geq 0, \qquad v(0) = \varphi_1, \qquad v(\infty) = 0$$

and

$$u(\eta) = \varphi_1 \operatorname{erfc}(\eta/2\sqrt{\Delta})$$

satisfies the complementary inequality. Now let $\varphi(\eta, m)$ be the solution of (10) with initial values $\varphi(0) = \varphi_1$, $\varphi'(0) = -m$. An elegant result of Nagumo [11] implies there are initial slopes $-m$ with $v'(0) \geq -m \geq u'(0)$ such that for any η, $\varphi(\eta, m)$ assumes any value in $[u(\eta), v(\eta)]$. A simple argument as in Theorem 7.3 of [12] then implies that (10, 11) has a solution $\varphi(\eta)$ such that $v(\eta) \geq \varphi(\eta) \geq u(\eta)$ for all η. Returning to the original variables, we find there is a solution $c(\eta)$ with

$$F(\varphi_1 \operatorname{erfc}(\eta/2\sqrt{\Delta})) \leq c(\eta) \leq F(\varphi_1 \operatorname{erfc}(\eta/2\sqrt{\delta})). \tag{12}$$

Instead of introducing the Kirchoff transformation, one could argue directly with (1, 2). However, it is no longer trivial to generate functions $u(\eta)$, $v(\eta)$ satisfying appropriate differential inequalities. Peletier [5] did this for the special case of $D(c)$ being strictly decreasing and differentiable everywhere, which leads to bounds sharper than (12). He relied upon the theorem cited above from the text [12], but his argument is incomplete. A similar incomplete argument is found in example 7.3 of that text which is a particular diffusion problem of the sort we are now examining. The theorems of the text assume the differential equation is Lipschitzian, but here

$$\frac{d^2c}{d\eta^2} = -\frac{D'(c)}{D(c)}\left(\frac{dc}{d\eta}\right)^2 - \frac{\eta}{2D(c)}\frac{dc}{d\eta}.$$

The quadratic growth in c' is too strong. Nevertheless, it is easy to modify the equation to make it Lipschitzian because of the *a priori* bounds on the slope $c'(\eta)$. So, bounds like (4a, b) and a modification of the equation are necessary if one is to use directly the theorems of [12]. Use of Nagumo's theorem is an easy way to avoid modification and get existence, but uniqueness is another matter. Peletier relied upon a general uniqueness result of [12] which also requires the modification of the equation so as to be Lipschitzian. Even then one only gets uniqueness for his special class. In the next section we prove uniqueness is generally true.

3. Uniqueness. The boundary-value problem (1, 2) has a unique solution if $m \neq m'$ implies that $c(\infty, m) \neq c(\infty, m')$. Our proof of this actually establishes rather more.

For any $\eta > 0$ it is true that $c(\eta, m) \neq c(\eta, m')$. In graphical terms this means that integral curves of the initial-value problem (1) and $c(0) = 1$, $c'(0) = -m \leq 0$ cannot intersect at $\eta > 0$. This property can be very useful in the solution of (1, 2) by numerical methods (cf. [12, Ch. 8]). The proof breaks into two parts. First we prove the inequality for finite η, and second we show uniqueness by proving it for $\eta = \infty$. The hypotheses are the same as for existence.

Suppose $0 > c_1'(0) > c_2'(0)$, so that initially $c_1(\eta) > c_2(\eta)$. We want to prove this is true for all $0 < \eta < \infty$. These functions are the solutions of

$$(d/d\eta)(D(c)c') + (\eta/2)c' = 0, \quad c(0) = 1, \quad c'(0) \text{ given.}$$

Let $f(\eta) = D(c(\eta))c'(\eta)$ be the flux. Then we write the differential equation as the system

$$dc/d\eta = f/D(c), \quad c(0) = 1 \quad df/d\eta = -(\eta f/2D(c)), \quad f(0) = D(1)c'(0) \text{ given.}$$

We already know $c(\eta)$ strictly decreases from its initial value of 1, so it is permissible to introduce the new independent variable $u = 1 - c$. Then

$$\frac{d\eta}{du} = \frac{d\eta}{dc}\cdot\frac{dc}{du} = -1\Big/\frac{dc}{d\eta} = -\frac{D(1-u)}{f},$$

$$\frac{df}{du} = \frac{df}{d\eta}\,\frac{d\eta}{du} = -\frac{\eta f}{2D(1-u)}\cdot -\frac{D(1-u)}{f} = \frac{\eta}{2},$$

which is an equivalent system. The initial conditions become

$$\eta(u = 0) = \eta(c = 1) = 0, \qquad f(u = 0) = f(\eta = 0) = D(1)c'(0) \text{ given.}$$

We are interested in the two solutions $\eta_i(u)$, $f_i(u)$ with $i = 1$ or 2 and

$$\eta_i(0) = 0, \qquad 0 > f_1(0) = D(1)c_1'(0) > f_2(0) = D(1)c_2'(0).$$

We know that from continuity and the fact that

$$\eta_1'(0) = -1/c_1'(0) > \eta_2'(0) = -1/c_2'(0) > 0$$

that for some interval $(0, \delta)$ we have

$$\eta_1(u) > \eta_2(u)(>0), \qquad (0>)f_1(u) > f_2(u).$$

We claim this holds for all $\delta < 1 - c_1(\infty)$. For there are only three possibilities as $u \to \delta$:

(i) $f_1(\delta) = f_2(\delta)$, $\eta_1(\delta) = \eta_2(\delta)$. This is impossible because the system has unique solutions to initial-value problems.

(ii) $f_1(\delta) = f_2(\delta)$, $\eta_1(\delta) > \eta_2(\delta)$. From the differential equations

$$\lim_{u\to\delta} (d/du)(f_1(u) - f_2(u)) = \tfrac{1}{2}(\eta_1(\delta) - \eta_2(\delta)) > 0,$$

which contradicts the assumption that $f_1(u) - f_2(u) > 0$ for $u < \delta$.

(iii) $f_1(\delta) > f_2(\delta)$, $\eta_1(\delta) = \eta_2(\delta)$. As in (ii),

$$\lim_{u\to\delta} \frac{d}{du}(\eta_1(u) - \eta_2(u)) = D(1 - \delta)\left[-\frac{1}{f_1(\delta)} + \frac{1}{f_2(\delta)}\right] > 0$$

is a contradiction.

Returning to the original variables, this result says that if $0 > c_1'(0) > c_2'(0)$ and if η_i is defined by $c = c_i(\eta_i)$, $i = 1$ or 2, then

$$\eta_1 > \eta_2 , \; D(c)c_1'(\eta_1) > D(c)c_2'(\eta_2).$$

In particular, there cannot be a point η_3 where $c_1(\eta_3) = c_2(\eta_3)$; hence for $0 < \eta < \infty$, $c_1(\eta) > c_2(\eta)$.

Uniqueness can be shown by integrating (1) from 0 to η. This gives

$$D(c(\eta))c'(\eta) - D(1)c'(0) + \int_0^\eta \frac{\tau}{2} c'(\tau)\, d\tau = 0$$

or, on integrating by parts,

$$D(c(\eta))c'(\eta) - D(1)c'(0) + \frac{\eta}{2} c(\eta) = \frac{1}{2} \int_0^\eta c(\tau)\, d\tau.$$

Suppose now that $c(\eta)$ is a solution of (1, 2). We have already examined the convergence of $c'(\eta)$ and $c(\eta)$ to zero as $\eta \to \infty$ and so justified a passage to the limit in this equation:

$$-D(1)c'(0) = \frac{1}{2} \int_0^\infty c(\tau)\, d\tau.$$

Physically, this equation represents the conservation of the diffusing substance (cf. Crank [2, p. 151]). Suppose there are two solutions $c_1(\eta)$, $c_2(\eta)$ with $0 > c_1'(0) > c_2'(0)$. Our preceding argument implies $c_1(\eta) > c_2(\eta)$ for all $\eta > 0$, so

$$-c_1'(0) = \frac{1}{2D(1)} \int_0^\infty c_1(\tau)\, d\tau > \frac{1}{2D(1)} \int_0^\infty c_2(\tau)\, d\tau = -c_2'(0)$$

or

$$c_1'(0) < c_2'(0),$$

which is a contradiction. We conclude there is precisely one solution to (1, 2).

4. Solution bounds and perturbation methods. Apparently the only previous attempt to determine simple techniques for bounding the effects of property changes for general problems is due to Friedmann [1]. He derived the bounds (12) above by working directly with the parabolic partial differential equation and assuming existence and uniqueness. Peletier's [5] bounds previously alluded to are quite useful, but one must have a $D(c)$ which is strictly decreasing. We want to discuss the general problem so we shall not refer to this special case again. The bounds (12) are often difficult to use directly because unless $D(c)$ is rather simple, we cannot obtain the inverse function $F(\varphi)$ analytically. One can without difficulty, though, derive bounds on F and then cruder but more easily applied bounds on c. In any event, the upper and lower bounds are not close unless $D(c)$ is nearly constant. This suggests they are most useful in connection with perturbation methods.

Friedmann was interested in heat conduction problems. A conductivity $D(c)$ nearly constant is an extremely important practical class, since only for quite high or low temperatures do most materials show much variation in conductivity (cf. Ozisik [13] p. 37ff.). Perturbation methods have been widely applied to such problems [3, 14, 15; an especially useful formulation is 16]. They are well suited for some methods of measuring the diffusion coefficient [17, 18]. Even when $D(c)$ cannot be regarded as constant the methods may still be applicable. The original problem posed in Sec. 2 is for concentrations ranging from c_0 to c_1. The coefficient $D(c)$ we have been discussing is that after a change of dependent variable. In terms of the original variables, we are concerned only with the variation of the diffusion coefficient over the range $[c_0, c_1]$. For any continuous diffusion coefficient, perturbation methods are applicable if the initial and final concentrations are sufficiently close. An example of this is Kidder's [15] perturbation solution of the flow of a gas through a porous medium. For this problem $D(c) = c$ in the original variables, but the perturbation process is applicable because c_0 and c_1 are close.

One difficulty in using perturbation methods is knowing when they are valid. The bounds (9a, b) lead to a very simple criterion for the applicability of perturbation methods. If $\Delta = \delta + 0(\epsilon)$, then the upper and lower bounds are $0(\epsilon)$ apart. They bound the error in the constant-coefficient approximation. For suppose we use $D(c) \doteq D_0$, $\delta \leq D_0 \leq \Delta$, and the zero-order perturbation solution $y_0(\eta)$ defined by

$$\frac{d}{d\eta}\left(D_0 \frac{dy_0}{d\eta}\right) + \frac{\eta}{2}\frac{dy_0}{d\eta}, \qquad y_0(0) = 1, \qquad y_0(\infty) = 0.$$

The bounds (9a, b) apply to $y_0(\eta)$ as well as $c(\eta)$; hence

$$|c(\eta) - y_0(\eta)| \leq (\Delta/\delta)^{3/2} \operatorname{erf}(\eta/2\sqrt{\Delta}) - (\delta/\Delta)^{3/2} \operatorname{erf}(\eta/2\sqrt{\delta}).$$

The right-hand side is an increasing function of η, so we have the uniform bound

$$|c(\eta) - y_0(\eta)| \leq (\Delta/\delta)^{3/2} - (\delta/\Delta)^{3/2}.$$

This is, of course, an extremely easy bound to apply. To get some feeling for it, suppose $\Delta/\delta = 1 + \epsilon$; then the bound is approximately 3ϵ.

5. Shooting methods. With the analysis developed, the use of shooting methods is straightforward and effective. The equations are integrated as a system

$$\frac{dc}{d\eta} = \frac{f}{D(c)}, \qquad c(0) = 1, \qquad \frac{df}{d\eta} = -\frac{\eta f}{2D(c)}, \qquad f(0) \text{ given}.$$

Using the constants δ, Δ we derived *a priori* bounds on the initial flux

$$-\Delta/(\pi\delta)^{1/2} \leq f(0) \leq -\delta/(\pi\Delta)^{1/2}$$

for the solution of the boundary-value problem. Because of the fact that if $f_1(0) > f_2(0)$, then $c_1(\infty) > c_2(\infty)$, we can use bisection to find the correct initial flux. We actually used the ZEROIN code of Dekker [19] which combines bisection with the secant rule for increased efficiency. We attempted to compute the initial flux to a relative accuracy of 10^{-7}. The inequality

$$0 < c(\eta_0, m) - c(\infty, m) \leq (\Delta/\delta)^{3/2} \operatorname{erfc}(\eta_0/2\sqrt{\Delta})$$

was used to terminate the integration. Before beginning shooting one can step η_0 from 0 until an η_0 is found which makes this bound sufficiently small; this value of η_0 is used for "infinity" in all the shots. This is suitable for integration codes which integrate to a given endpoint without reporting intermediate results, but is rather conservative. If one monitors the results at each step, one can terminate when all figures of $c(\eta)$ become fixed.

The basic danger in using shooting methods is that one is trying to follow integral curves numerically and inevitably one drifts off the desired curves onto neighbors. If neighboring curves behave very differently, then shooting methods are unsatisfactory. Near some argument τ and $\gamma = c(\tau)$ the differential equations are approximately

$$dc/d\eta = f/D(\gamma), \qquad df/d\eta = -\eta f/2D(\gamma)$$

which have the general solutions

$$c(\eta) = A + B \operatorname{erfc}\,(\eta/2(D(\gamma))^{1/2}),$$

$$f(\eta) = -B\left(\frac{D(\gamma)}{\pi}\right)^{1/2} \exp\,(-\eta^2/4D(\gamma)).$$

All solution curves behave the same way with one significant exception. We are trying to follow a curve $c(\eta)$ which is strictly decreasing, equivalently $f(\eta) < 0$. If we drift to a value $f(\tau) \geq 0$, then we are on curves $c(\eta)$ which are constant or strictly increasing. If our differential equation solver is using a relative error test, we cannot drift from a correct value $f(\tau) < 0$ to a value $f(\tau) \geq 0$ unless $f(\tau) \doteq 0$, that is, the shot is essentially completed. If we are careful to use a relative error criterion and monitor $f(\eta)$ so that we terminate the integration when $f(\eta) \geq 0$, we need not fear any particular difficulty with the stability of the shooting method. A simple way to handle this computationally is to replace values of $c'(\eta)$ by zero if they become positive.

Crank [2, p. 267] gives eight examples of typical diffusion coefficients. We solved (1, 2) for all. A library Runge–Kutta code was used with a requested relative error of less than 10^{-8}. The value of η_0 was chosen to make the bound less than 10^{-8}. A valuable and sensitive check is the conservation relation

$$-f(0) = \frac{1}{2}\int_0^\infty c(\tau)\, d\tau.$$

So along with the system we integrated

$$dI/d\eta = c/2, \qquad I(0) = 0$$

and on returned we compared $f(0)$ to

$$I(\eta_0) = \frac{1}{2}\int_0^{\eta_0} c(\tau)\, d\tau.$$

A FORTRAN program implementing this procedure was written for the PDP-10 which has a working precision of about eight decimal digits. Two test problems were used to check out the code. Problem (i) has $D(c) \equiv 0.25$ and the analytic solutions $c(\eta) = \operatorname{erfc}\,(\eta)$, $-f(0) = .28209479$. Five shots were needed to get convergence. The results for the initial flux and the conservation test are in Table 2. The maximum absolute error in the computed concentration was about 1.4×10^{-6}. The error increased steadily from its minimum at $\eta = 0$ to this value as η increased.

To get a nontrivial test problem we generated a family of nonlinear problems with simple analytical solutions. If we choose $D_0 > 0$, $\eta_0 > 0$ and then define

$$\alpha = (\pi D_0)^{1/2} \exp\,(\eta_0^2/4D_0), \quad \beta = \alpha \operatorname{erfc}\,(\eta_0/2\sqrt{D_0}), \quad c_0 = \beta/(\beta + \eta_0),$$

we find that $0 < c_0 < 1$. Furthermore, if we define

TABLE 1

The Problems

Number	$D(c)$	δ	Δ
i	0.25	exp(−2.303)	1
ii	$\begin{cases} 8 - 7.605858829(1-c)^2 \\ \text{if } c \geq .2748032226, \\ 4 \text{ otherwise} \end{cases}$	4	8
1	$1 + 10(1 - \exp(-2.303c))$	1	10
2	$1 + 50 \ln(1 + .5136c)$	1	10
3	$1 + 9c$	1	10
4	$\exp(2.303c)$	1	10
5	$\exp(-2.303c)$	exp(−2.303)	1
6	$1/(1 - 3.292c + 2.877c^2)$	1	18
7	$1/(1 - .6838c)^2$	1	11
8	$1/(1 - .9c)$	1	10

$$D(c) = D_0 + 0.25\eta_0^2\left[1 - \left(\frac{1-c}{1-c_0}\right)^2\right] \qquad c \geq c_0 ,$$

$$= D_0 \qquad c \leq c_0 ,$$

the solution of (1, 2) is

$$c(\eta) = 1 - \eta((1 - c_0)/\eta_0) \qquad 0 \leq \eta \leq \eta_0 ,$$

$$= (\alpha/(\beta + \eta_0)) \operatorname{erfc}(\eta/2\sqrt{D_0}) \qquad \eta_0 \leq \eta.$$

These statements may be verified easily. Test problem (ii) takes $\eta_0 = D_0 = 4$. Eleven shots were required for convergence. The maximum absolute error in the concentration was about 3.7×10^{-6} with the error steadily increasing from its minimum at $\eta = 0$.

All of Crank's typical problems were solved. Each required nine shots with the exception of problem 2 which required eight. There were no apparent numerical difficulties.

TABLE 2

Some Numerical Results

Number	$-f(0)$	$\frac{1}{2}\int_0^{\eta_0} c(\tau)\,d\tau$
i	.28209519	.28208911
ii	1.4503982	1.4503436
1	1.6063233	1.6062375
2	2.1533009	2.1532498
3	1.4497852	1.4497697
4	1.2525323	1.2526087
5	.29177820	.29178078
6	1.4338576	1.4336833
7	1.1329485	1.1328898
8	1.0173323	1.0172385

Tables of the solutions $c(\eta)$ may be obtained from the author. Tables of solutions computed on a CDC 6600 for diffusion coefficients depending linearly, exponentially and in a few other ways on the concentration may be obtained from the author.

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