CONCENTRATION-DEPENDENT DIFFUSION*
II. SINGULAR PROBLEMS

BY

L. F. SHAMPINE

Sandia Laboratories, Albuquerque

1. Introduction. In the paper [1], hereafter referred to as I, we discussed the similarity solution of the one-dimensional diffusion equation

$$\partial c/\partial t = (\partial/\partial x)(D\ \partial c/\partial x)$$

when the diffusion coefficient D is a function of the concentration c. Only positive D were considered although we remarked that there are problems of physical interest approximated by D which vanish. Ames [2, Sec. 1.2] discusses a variety of physical situations leading to such problems, as do [3–6]. The ordinary differential equation resulting from the use of the similarity variable $\eta = x/\sqrt{t}$,

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

is singular if D vanishes. This interesting mathematical behavior is reflected in the interesting physical phenomenon that there is a nonlinear wave solution. We shall use the analysis of I to prove that a singular problem has one and only one solution. Moreover, it can be regarded as the limit of solutions of non-singular problems in accord with physical derivations and intuition.

The computational solution of singular problems presents new difficulties. We shall derive bounds on the initial flux which are independent of whether or not the problem is singular; indeed, in the nonsingular case the new bounds are better than those derived in I. We briefly discuss the numerical solution in connection with some examples and show how to avoid some of the difficulties.

2. Existence and uniqueness. The physical problem that concerns us is the diffusion of a substance into a semi-infinite medium after the substance is introduced at the face at a given concentration level which is maintained. As in I, normalizing and introducing the similarity variable $\eta = x/\sqrt{t}$ leads to

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

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

In addition to (1, 2) a solution must also have a continuous flux $f(\eta) = D(c(\eta))c'(\eta)$. To avoid unnecessary complications let us suppose $D(c) \in C^1[0, 1]$. If $D(c) > 0$ for

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$c > 0$ but $D(0) = 0$, singular behavior consisting of $c(\eta)$ vanishing at some finite point η_0 and then $c(\eta)$ vanishing identically for $\eta \geq \eta_0$ is possible. A family of examples which will prove useful later depends on two positive parameters α, β:

$$D(c) = \frac{\beta c^\beta}{2\alpha^2}\left[1 - \frac{c^\beta}{1+\beta}\right]$$

and

$$\begin{aligned} c(\eta) &= (1 - \alpha\eta)^{1/\beta}, \qquad 0 \leq \eta \leq 1/\alpha, \\ &= 0, \qquad \eta > 1/\alpha. \end{aligned}$$

Singular behavior of this kind represents a nonlinear wave with a "front" at η_0. Returning from the similarity variable $\eta = x/\sqrt{t}$ to the original ones shows that at time t the diffusant has penetrated to $x = \eta_0\sqrt{t}$ but no further. Physical problems described by singular $D(c)$ apparently represent idealized limits of problems with positive diffusion coefficients. We shall prove there still exists a unique solution in the singular case. The proof reflects the limit process and shows that non-singular diffusion problems can "look" like nonlinear wave problems.

We shall consider a family of problems (1) and

$$c(0) = 1, \qquad c(\infty) = \epsilon \tag{3}$$

for $0 < \epsilon < 1$. It is convenient to regard the limit process by which we approximate singular problems in two ways.

As we pointed out in I, the problem (1, 3) is equivalent to the problem

$$\frac{d}{d\eta}\left(D_\epsilon(\tilde{c})\,\frac{d\tilde{c}}{d\eta}\right) + \frac{\eta}{2}\frac{d\tilde{c}}{d\eta} = 0 \tag{4}$$

$$\tilde{c}(0) = 1, \qquad \tilde{c}(\infty) = 0 \tag{5}$$

with $D_\epsilon(\tilde{c}) = D((1-\epsilon)\tilde{c} + \epsilon)$ and $\tilde{c}(\eta, \epsilon) = (c(\eta, \epsilon) - \epsilon)/(1 - \epsilon)$. The problem (4, 5) is nonsingular since $D_\epsilon(0) = D(\epsilon) > 0$; hence the analysis of I shows that $c(\eta, \epsilon)$ exists and is unique. As $\epsilon \to 0^+$ the problem (4, 5) tends to the problem (1, 2). We might anticipate that $\lim \tilde{c}(\eta, \epsilon) = \lim c(\eta, \epsilon)$ will be a solution of (1, 2).

The other point of view is similar to that adopted in the first physical paper [3] known to the author which used a singular diffusion coefficient. The idea is that when the concentration falls to a sufficiently low level one loses interest in its precise value. It may be that one does not know the mechanism for diffusion in these circumstances. One is willing to accept a solution of (1, 3) as being a physically adequate approximation to a solution of (1, 2) if ϵ is sufficiently small. The paper [4] extends the analysis of [3] to give a formal series solution for $D(c) = c^n$. In addition, Figs. 4 and 5 of that paper show numerical solutions for $n = 1$ and 1.5 with various ϵ. It is quite interesting to see how the solutions with small $\epsilon > 0$ approach the singular solution. In particular one sees how nonsingular diffusion problems can have solutions which "look" singular since a sharp increase in the concentration of the diffusant moves into the material with a finite speed. The aim of this section is to prove the following theorem:

THEOREM. Suppose $D(c) \in C^1[0, 1]$, $D(c) > 0$ for $c > 0$ but $D(0) = 0$. Then (1, 2) has one and only one solution $c(\eta)$ with a continuous flux $f(\eta) = D(c(\eta))c'(\eta)$.

In I we showed that solutions of the initial-value problems (1) and

$$c(0) = 1, \qquad c'(0) < 0 \text{ given} \tag{6}$$

cannot intersect, at least as long as they remain positive. The analysis also shows (1, 3) has a unique solution $c(\eta, \epsilon)$ which is strictly decreasing and if $\epsilon > \epsilon'$, then

$$c(\eta, \epsilon) > c(\eta, \epsilon') > 0 \quad \text{for} \quad \eta > 0. \tag{7}$$

The inequalities of (7) imply that there is a pointwise limit

$$\lim_{\epsilon \to 0^+} c(\eta, \epsilon) = V(\eta).$$

Indeed, the limit curve is continuous because the monotonicity implies the convergence is uniform on any finite interval. The limit curve $V(\eta)$ is either positive for all η or else vanishes at some point η_0. Since $c(\eta, \epsilon)$ is strictly decreasing in η we must then have $V(\eta) \equiv 0$ for all $\eta \geq \eta_0$.

We shall now show that a particular solution $c(\eta)$ of (1, 6) vanishes at a finite point η_1. This has several important implications. Since the solutions of initial-value problems cannot cross, we must have $c(\eta, \epsilon) > c(\eta)$ for $0 < \eta \leq \eta_1$ and all ϵ. This in turn implies $V(\eta) \geq c(\eta)$ for $0 < \eta \leq \eta_1$ so that $\eta_0 > 0$. In addition, the limit $m = \lim c'(0, \epsilon)$ must exist. The solution of (1, 6) with $c'(0) = m$ must coincide with $V(\eta)$ as long as $V(\eta) > 0$ since then (1) is Lipschitzian and solutions of initial-value problems depend continuously on their initial slope. If the limit curve $V(\eta)$ is positive for all η, we see now that it is a solution of (1) for all η and an easy argument shows that $V(\infty) = 0$. In this case we have found a solution of (1, 2) which does not exhibit singular behavior. If η_0 is finite, the curve $V(\eta)$ still satisfies (1, 2) and we need only prove the flux is continuous at η_0, i.e., $f(\eta_0-) = 0$.

LEMMA. If $c(\eta)$ is the solution of (1, 6) with $c'(0) = f(0)/D(1)$ and

$$-f(0) = \tfrac{1}{2} + \max_{0 \leq c \leq 1} D(c),$$

then there is an $\eta_1 < 1$ such that $c(\eta_1) = 0$.

Proof. We have already used in I the system equivalent to (1),

$$\begin{aligned} d\eta/du &= -D(1-u)/f, \qquad \eta(0) = 0 \\ df/du &= \eta/2, \qquad 0 > f(0) \quad \text{given} \end{aligned} \tag{8}$$

where $u = 1 - c$. We claim that with $f(0)$ as specified,

$$f(u) < -\max D < 0, \qquad \eta(u) < 1$$

for $0 \leq u \leq 1$. The statement about η is the conclusion of the lemma in terms of these new variables.

The inequalities certainly hold strictly in some interval $0 \leq u < u_0$. Let $u_0 \leq 1$ be the first point at which equality holds in either function. But then

$$f(u_0) = f(0) + \frac{1}{2}\int_0^{u_0} \eta(\tau)\, d\tau < f(0) + \frac{u_0}{2} \leq -\max D$$

and

$$\eta(u_0) = \int_0^{u_0} \frac{D(1-\tau)}{-f(\tau)}\, d\tau < \frac{u_0 \max D}{\max D} \le 1.$$

We see that strict inequality must hold for $0 \le u \le 1$.

To complete the proof of existence we must show $f(\eta_0-) = 0$ when η_0 is finite. Our earlier analysis in I shows that $c'(\eta) < 0$ as long as $c(\eta) > 0$ so that $f(\eta) = D(c(\eta))c'(\eta) < 0$ for $\eta < \eta_0$ and $f(\eta_0-) \le 0$. Suppose that $f(\eta_0-) < 0$. Then in a suitable region about $\eta(u)$, $f(u)$ the system (8) is Lipschitzian and solutions must accordingly depend continuously on the initial value $f(0)$. But they do not. Any solution of (1, 6) with $c'(0) > V'(0) = \lim c'(0, \epsilon)$ is positive at $\eta = \infty$. This is because for some $\epsilon > 0$, $c'(0) \ge c'(0, \epsilon)$ with the consequence that $c(\eta) \ge c(\eta, \epsilon) \ge \epsilon$ for all η. In the variables of (8) this says that for any $f(0) > D(1)V'(0)$, $\eta(u)$ is unbounded as u tends to 1 whereas if $f(0) = D(1)V'(0)$, then $\eta(1) = \eta_0 < \infty$ by definition.

Uniqueness is established just as in the nonsingular case. Integration by parts of (1) shows $f(\eta) - f(0) = \frac{1}{2} \int_0^{\eta} c(\tau) - c(\eta)\, d\tau$, so if $c(\eta_0) = 0$ and $f(\eta_0) = 0$, we have

$$-f(0) = \frac{1}{2} \int_0^{\eta_0} c(\tau)\, d\tau$$

for a solution of the boundary-value problem. Using the fact that solutions of initial-value problems cannot cross, we easily prove uniqueness as in I.

3. Bounds on the initial flux. For numerical purposes it is valuable to bound the initial flux for a solution of the boundary-value problem. We shall now develop bounds independent of whether or not the problem is singular. A specific bound which is always applicable is better than that derived for the nonsingular case in I. We want to compare solutions of the initial-value problem (1) and

$$c(0) = 1, \qquad 0 > f(0) \text{ given}$$

where it is convenient to work with the initial flux instead of $c'(0)$ since we actually work with the equivalent system (8). Specifically, we compare solutions associated with two diffusion coefficients $D_1(c) > D_2(c)$ for $0 < c \le 1$; subscripts 1 or 2 will be used to denote corresponding solutions.

LEMMA. If $D_1(c) > D_2(c)$ for $0 < c \le 1$ and $0 > f_1(0) \ge f_2(0)$, then

$$\eta_1(u) > \eta_2(u) > 0 \quad \text{for} \quad 0 < u < 1. \tag{9}$$

$$0 > f_1(u) > f_2(u) \tag{10}$$

Proof. We find

$$(\eta_1 - \eta_2)'(0) = -D_1(1)/f_1(0) + D_2(1)/f_2(0) > 0$$

and either $(f_1 - f_2)(0) > 0$ or else

$$(f_1 - f_2)'(0) = \tfrac{1}{2}(\eta_1 - \eta_2)'(0) > 0.$$

In any event there is a $\delta > 0$ such that (9) and (10) hold for $0 < u < \delta$.

Case (i). What if $f_1(\delta) = f_2(\delta)$, $\eta_1(\delta) > \eta_2(\delta)$? Since

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

contradicts (10), this case is impossible.

Case (ii). What if $f_1(\delta) \geq f_2(\delta)$, $\eta_1(\delta) = \eta_2(\delta)$? Since

$$\lim (\eta_1 - \eta_2)' = -D_1(1 - \delta)/f_1(\delta) + D_2(1 - \delta)/f_2(\delta) > 0$$

contradicts (9), this case is also impossible.

We conclude that (9, 10) must hold for $0 < u < 1$ as long as both quantities in the expressions exist.

THEOREM. If $f_1(0)$ is the initial flux for the solution of (1, 2) with $D(c) = D_1(c)$ and $f_2(0)$ is the initial flux with $D(c) = D_2(c)$ and if $D_1(c) > D_2(c)$ for $0 < c \leq 1$, then $0 > f_2(0) > f_1(0)$.

Proof. Let $c_1(\eta)$, $c_2(\eta)$ be the respective solutions and suppose $0 > f_1(0) \geq f_2(0)$. Equation (9) of the lemma implies that $c_1(\eta) > c_2(\eta)$ for $\eta > 0$. However, the conservation law leads to a contradiction as follows:

$$-f_1(0) = \frac{1}{2}\int_0^\infty c_1(\tau)\, d\tau > \frac{1}{2}\int_0^\infty c_2(\tau)\, d\tau = -f_2(0).$$

As an easy consequence of this theorem we find that if

$$\Delta = \max_{0 \leq c \leq 1} D(c),$$

then the initial flux of the solution of (1, 2) is bounded by

$$0 > f(0) \geq -\sqrt{\Delta/\pi} \tag{11}$$

whether or not $D(c)$ is singular. If D is not singular so that

$$0 < \delta = \min_{0 \leq c \leq 1} D(c),$$

we also find

$$-\sqrt{\delta/\pi} \geq f(0).$$

These bounds are considerably better than the corresponding ones derived in I.

An upper bound on the initial flux for a singular D can be derived by using the singular family given earlier. Choose α, β positive so that $D(c) \geq \beta c^\beta/2\alpha^2$, for then

$$D(c) > \beta c^\beta/2\alpha^2[1 - (c^\beta/(1 + \beta))]$$

and the comparison problem yields the bound

$$-\beta/2\alpha(1 + \beta) > f(0). \tag{12}$$

4. Computational matters. In I we integrated the system

$$dc/d\eta = f/D(c), \qquad c(0) = 1,$$

$$df/d\eta = -(\eta f/2D(c)), \qquad 0 > f(0) \quad \text{given},$$

and adjusted $f(0)$ until we obtained $c(\infty) = 0$. For singular problems we must proceed more carefully because the derivative of c with respect to η may well become infinite (and along with it $df/d\eta$). A good way to avoid difficulties of this nature is to write the system in autonomous form and then introduce arc length s as independent variable

[7, p. 59]. This leads to the system

$$\begin{aligned} d\eta/ds &= F_1(\eta, c, f, I)/\Sigma, & \eta(0) &= 0, \\ dc/ds &= F_2(\eta, c, f, I)/\Sigma, & c(0) &= 1, \\ df/ds &= F_3(\eta, c, f, I)/\Sigma, & 0 &> f(0) \quad \text{given}, \\ dI/ds &= F_4(\eta, c, f, I)/\Sigma, & I(0) &= 0, \end{aligned}$$

where $F_1 \equiv 1$, $F_2 = f/D(c)$, $F_3 = -\eta f/2D(c)$, $F_4 = c/2$, $\Sigma = (F_1^2 + F_2^2 + F_3^2 + F_4^2)^{1/2}$. Then no derivative becomes larger than 1 in magnitude. When actually computing one must monitor F_2 and on its becoming large, evaluate the right-hand sides with $|F_2|$ removed as a factor from numerator and denominator to prevent overflow.

The boundary conditions are satisfied by obtaining the unique root of $F(z) = 0$ where z is the initial flux $f(0)$ and each integration proceeds to a point $s = \zeta$ where either
(i) $c(\zeta) \leq 0$ and we define $F(z) = f(\zeta)$,
(ii) $f(\zeta) \geq 0$ and we define $F(z) = c(\zeta)$.
If z is too low, case (i) occurs and $F(z) \leq 0$. If z is too high, case (ii) occurs and $F(z) \geq 0$. The function $I(s)$ specified above is

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

so comparing its value for $s = \zeta$ to that of the initial flux tests the conservation law. This is valuable in assessing the numerical results.

The root solver we use requires upper and lower bounds on the root. The lower bound (11) is easy to apply but an upper bound from (12) is not routine. We have preferred another approach to the upper-bound difficulty. There is an interesting paper of Macey [5] which uses physical reasoning to approximate the solutions of diffusion problems of the form which concerns us. It is especially interesting in this context because it amounts to approximating a nonsingular problem by a singular one with a known solution. In our notation his approximations are

$$f(0) \doteq -\left(\frac{1}{2} \int_0^1 \tau D(\tau)\, d\tau\right)^{1/2}$$

$$\eta(c) \doteq \left(\int_c^1 D(\tau)\, d\tau\right)\left(\frac{1}{2} \int_0^1 \tau D(\tau)\, d\tau\right)^{-1/2}.$$

He observes that the approximation to $f(0)$ is always high and that this is plausible. We have found it to be high for all the cases solved in I and moreover for the singular family we have been using it is easily shown to be always high. This approximation is easy to compute and in every case its error has proved roughly 8%. We have used it in our codes as a heuristic upper bound of good accuracy.

The numerical computations were made on a CDC 6600 which works with roughly 14 decimal figures. The integrator is a classical Runge–Kutta code which attempts to control its local error by varying the step size. It attempted a pure absolute error bound of 10^{-8}. The root solver is the code ZEROIN referenced in I; it attempted a pure relative error bound of 5×10^{-8}. The code was tested on the problem $D(c) = 0.5c(1 - 0.5c)$ with the solution $c = 1 - \eta$. The maximum difference $|1 - (c(\eta) + \eta)|$ was 9.8×10^{-5}. The concentration was found to vanish numerically at 0.99991. The true initial flux of -0.25 was approximated by -0.250001. $I(\zeta)$ was found to be 0.249997 so the conservation law was well satisfied.

The problems $D(c) = c^n$ with $n = 1$ and 1.5 were chosen to illustrate our computations since some checks are available. The formal series solution of Heaslet and Alksne [4] says that η_0 is 1.616 and 1.210 respectively (our similarity variable differs by a constant from theirs). They report the straightforward numerical integration of (1) to obtain initial fluxes of -0.444 and -0.406 respectively. The latter computation seems questionable since in the variables they use both the concentration and flux are infinite at η_0 and the integration is not straightforward. Our results are

n	η_0	$f(0)$	$I(\eta_0)$
1	1.61636	-0.44375	0.44375
1.5	1.28121	-0.40621	0.40592

which is in reasonable agreement with their results.

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