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ON AMUNDSON'S MODEL OF THE UNSTEADY COMBUSTION OF A SLAB OF CARBON*

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1. Model and equations. A carbon particle in combustion is a complex system involving mainly: the diffusion of temperature and oxygen, the production and diffusion of carbon monoxide, and the production and subsequent diffusion of carbon dioxide. The relative importance of these and other factors and the exact details of various models are discussed in Caram and Amundson [4], Sundaresan and Amundson [12, 13], and Amundson [2]. As far as we know, no time-dependent case has been analyzed in the literature, although these papers contain very interesting results for the "quasi-steady equations". They suggest a hierarchy of models of which we have studied the simplest.

This (Amundson, [2], p. 5) disregards the production of carbon dioxide; oxygen is consumed at the surface of the carbon, and the carbon monoxide thus formed diffuses away. The diffusion is confined to a stagnant boundary layer about the carbon particle. Outside the boundary layer the ambient temperature and oxygen density are known.

Geometrically simplest is a semi-infinite slab of carbon burning homogeneously on the exposed face, in effect a 1-dimensional problem with the coal occupying the initial domain $x \geqslant R$ at $t = 0$. Let $w(x, t)$ and $z(x, t)$ be the oxygen density and temperature, and $y(t)$ be the position of the burning surface. The boundary layer occupies $0 < x < y(t)$ and ambient conditions are applied at $x = 0$. We then consider the following free (moving) boundary problem:

$$\left.\begin{aligned} w_t &= D_1 w_{xx} \\ z_t &= D_2 z_{xx} \end{aligned}\right\} \quad 0 < x < y(t) \qquad \left.\begin{aligned} w_x &= -c_1 w \exp(-c_4/z) \\ z_x &= c_2 w \exp(-c_4/z) \\ dy/dt &= c_3 w \exp(-c_4/z) \end{aligned}\right\} \quad \text{at } x = y(t)$$
$$\begin{aligned} w(x,0) &= A_1 \\ z(x,0) &= A_2 \\ w(0,t) &= w_a \\ z(0,t) &= z_a \end{aligned} \qquad y(0) = R. \tag{1A}$$

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We also consider a slightly simpler model which leads to neater a priori estimates. For aesthetic reasons the existence and uniqueness proofs are carried out in this case. Every step can be suitably modified to fit the first model, though with messier details.

The simplification is to replace the boundary layer by the entire exterior of the carbon. There are no ambient conditions to match. Instead solutions w and z are assumed to satisfy certain spatial bounds. The carbon occupies initially the domain $x \geqslant 0$.

$$
\left.\begin{aligned} w_t &= D_1 w_{xx} \\ z_t &= D_2 z_{xx} \end{aligned}\right\} \quad -\infty < x < y(t)
$$
$$
w(x,0) = A_1
$$
$$
z(x,0) = A_2
$$
$$
\left.\begin{aligned} w_x &= -c_1 w \exp(-c_4/z) \\ z_x &= c_2 w \exp(-c_4/z) \\ dy/dt &= c_3 w \exp(-c_4/z) \end{aligned}\right\} \quad \text{at } x = y(t) \tag{1B}
$$
$$
z, w, z_x, w_x = O\left(\exp(|x|^\delta)\right) \text{ as } x \to -\infty, \text{ for some } \delta < 2
$$
$$
y(0) = 0.
$$

These two models will be called the bounded and unbounded models respectively.

We remark that the unbounded model is related to the one-phase Stefan problem (see, for example, Cannon [3], p. 281). The Stefan problem results from the singular perturbation $c_4 = 0$, $c_1 \to \infty$.

A slab of finite length L can be handled by stopping the solution when $y(t)$ reaches a certain level. In the bounded model, if ambient conditions are the same on both sides, the slab will burn to extinction when $y(t) = L/2$.

Using Green's functions we convert (1A) and (1B) to systems of integral equations in the time variable for the unknown functions $w(t) := w(t, y(t))$ and $z(t) := z(t, y(t))$. A degree-theoretic proof is given that the equations have a solution. It is then shown that this solution is unique and is in turn a solution of (1A) or (1B). The integral equations, though mildly singular, can be solved numerically with extreme efficiency and accuracy by the method given in Kershaw, [6]. These numerical calculations show that, asymptotically,

$$
\begin{aligned} w(t) &\sim ct^{-1/2}, \\ y(t) &\sim kt^{1/2}, \\ z(t) &\to Z \end{aligned}
$$

for constants c, k, Z. The integral equations enable us to calculate these constants explicitly. These expressions are given in Sec. 5.

The method of lines can also be applied to prove the existence of solutions and to compute them. This has been explained by Meyer, [9], for a general class of problems. On the other hand this approach does not yield our simple a priori estimates or exact asymptotic results.

2. Integral equations. Consider the unbounded model. For any smooth $u = u(x_0, t_0)$ and $v = v(x_0, t_0)$ and any T and D,

$$\int_0^T dt_0 \int_{-\infty}^{y(t_0)} \left\{ v\left(u_{t_0} - Du_{x_0x_0}\right) - u\left(-v_{t_0} - Dv_{x_0x_0}\right)\right\} dx_0$$

$$= \int_0^T dt_0 \left\{ \partial/\partial t_0 \int_{-\infty}^{y(t_0)} uv\, dx_0 - (uv)\big|_{x_0 = y(t_0)} y'(t_0)\right\} \quad (2)$$

$$+ D\int_0^T dt_0 \int_{-\infty}^{y(t_0)} \partial/\partial x_0 (uv_{x_0} - vu_{x_0})\, dx_0.$$

For $t > 0$ let $x = y(t)$ and let v be the "causal" free space Green's function

$$\begin{cases} -v_{t_0} - Dv_{x_0x_0} = \delta(x_0 - x)\delta(t_0 - t), & -\infty < t_0 < \infty, -\infty < x_0 < \infty \\ v = 0 \quad \text{for } t_0 > t, -\infty < x_0 < \infty \\ v \text{ regular at } x_0 = \pm\infty, \end{cases}$$

(see Stakgold, [11], Vol. II, p. 197). We recall that v is related to v^*: $v^*_{t_0} - Dv^*_{x_0x_0} = \delta(x - x_0)\delta(t - t_0)$, $v^* = 0$ for $t_0 < t$, by $v^* = v \circ \pi$ where π is the permutation $x \to x_0 \to x$, $t \to t_0 \to t$. Hence

$$v = \frac{\exp\left\{-\dfrac{(x - x_0)^2}{4D(t - t_0)}\right\}}{\sqrt{4\pi D(t - t_0)}} H(t - t_0);$$

$H(x)$ is the Heaviside function.

Thus if u is a solution to $u_{t_0} = Du_{x_0x_0}$ and $T > t$, the left side of (2) is

$$-\int_{-\infty}^{y(t)} u(x_0, t)\delta(x - x_0)\, dx_0 = \begin{cases} 0 & y(t) < x \\ -\frac{1}{2}u(x, t) & y(t) = x \\ -u(x, t) & y(t) > x \end{cases}$$

$$= -\tfrac{1}{2}u(y(t), t)$$

$$= -\tfrac{1}{2}u(t).$$

The right side of (2) is easily computed and the result after simplification is

$$u(t) = (\pi Dt)^{-1/2} \int_{-\infty}^0 u(x_0, 0) e^{-(y(t) - x_0)^2/(4Dt)}\, dx_0$$

$$+ (\pi D)^{-1/2} \int_0^t \frac{\exp\left\{-\dfrac{(y(t) - y(t_0))^2}{4D(t - t_0)}\right\}}{\sqrt{t - t_0}}$$

$$\times \left\{ u(t_0)\left[y'(t_0) - \frac{1}{2}\frac{y(t) - y(t_0)}{t - t_0}\right] + Du_{x_0}(y(t_0), t_0)\right\} dt_0.$$

For given initial data, this is an integral relation satisfied by u and u_x on any smooth curve $x = y(t)$. Applying the boundary data from (1B) for $u = w$ and then $u = z$ and using the evaluation

$$(\pi D t)^{-1/2}\int_{-\infty}^{0} e^{-(y(t)-x_0)^2/(4Dt)}\,dx_0 = 1 - \operatorname{erf}\left(y(t)/(4Dt)^{1/2}\right)$$

$$\equiv \operatorname{erfc}\left(y(t)/(4Dt)^{1/2}\right),$$

$$\operatorname{erf}(x) \equiv \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}\,dt,$$

we obtain a coupled system of equations for

$$w(t) = \text{oxygen density at the front,}$$

$$z(t) = \text{temperature at the front,}$$

$$y(t) = \text{position of the front.}$$

Integral equations for unbounded model.

$$w(t) = A_1\operatorname{erfc}\left(y(t)/(4D_1 t)^{1/2}\right) + \frac{1}{\sqrt{\pi D_1}}\int_0^t \frac{\exp\left\{\dfrac{-(y(t)-y(s))^2}{4D_1(t-s)}\right\}}{\sqrt{t-s}}\left\{w(s)y'(s) - \frac{1}{2}w(s)\frac{y(t)-y(s)}{t-s} - c_1 D_1 w(s)e^{-c_4/z(s)}\right\}ds \tag{4B}$$

$$z(t) = A_2\operatorname{erfc}\left(y(t)/(4D_2 t)^{1/2}\right) + \frac{1}{\sqrt{\pi D_2}}\int_0^t \frac{\exp\left\{-\dfrac{(y(t)-y(s))^2}{4D_2(t-s)}\right\}}{\sqrt{t-s}} \times\left\{z(s)y'(s) - \frac{1}{2}z(s)\frac{y(t)-y(s)}{t-s} + c_2 D_2 w(s)e^{-c_4/z(s)}\right\}ds \tag{5B}$$

$$y(t) = \int_0^t c_3 w(s)e^{-c_4/z(s)}\,ds.$$

The **integral equations for the bounded case** are derived in a similar way but using v = the Green's function of $(0, \infty)$. The analogue of (3) with integrals explicitly evaluated where possible is

$$u(t) = A\left\{2\operatorname{erf}\left(\frac{y(t)}{2\sqrt{tD}}\right) - \operatorname{erf}\left(\frac{y(t)-R}{2\sqrt{tD}}\right) - \operatorname{erf}\left(\frac{y(t)+R}{2\sqrt{tD}}\right)\right\}$$
$$+2\int_0^t\left[y'(s)u(s)v - Du(s)v_{x_0} + Dvu_{x_0}(s)\right]ds + 2u_a\operatorname{erfc}\left(\frac{y(t)}{2\sqrt{tD}}\right).$$

This assumes $u(s) = u(y(s), s)$, $u(x,0) \equiv A$, $u(0,t) \equiv u_a$, and $u_t = Du_{xx}$ in $0 < x < y(t)$. The expression for v is

$$v = \frac{1}{\sqrt{4\pi(t-s)D}}(e_- - e_+),$$

$$e_- = \exp\left\{-\frac{(y(t)-y(s))^2}{4D(t-s)}\right\},$$

$$e_+ = \exp\left\{-\frac{(y(t)+y(s))^2}{4D(t-s)}\right\};$$

hence

$$v_{x_0} = \frac{1}{4\sqrt{\pi D(t-s)}}\left\{\frac{y(t)-y(s)}{D(t-s)}e_- + \frac{y(t)+y(s)}{D(t-s)}e_+\right\}.$$

We successively take $u = w$ and $u = z$, with the expressions for $w_{x_0}(s)$ and $z_{x_0}(s)$ taken from (1A), i.e.,

$$w_{x_0}(s) = -c_1 w(s)\exp(-c_4/z(s)),$$

$$z_{x_0}(s) = c_2 w(s)\exp(-c_4/z(s)).$$

This results in two integral equations which we call (4A) and (5A). The equation for y is

$$y(t) = R + \int_0^t c_3 w(s)\exp(-c_4/z(s))\,ds. \tag{6A}$$

3. A priori bounds for the unbounded model. We assume the existence of continuous solutions $w(t)$ and $z(t)$ and smooth solution $y(t)$. As will be explained in Sec. 4, the parabolic system (1) has a corresponding solution.

THEOREM 1. $0 < w(t) \leqslant A_1$, $z(t) \geqslant A_2$, $dy/dt > 0$.

Proof. These all follow from the "boundary point" theorem of the maximum principle (see Protter and Weinberger, [10], p. 170). For if $w(x,t)$ were to have a nonpositive minimum on the front $x = y(t)$, the boundary conditions would imply $w_x \geqslant 0$ there while the boundary point theorem requires $w_x < 0$. Hence $w(t) > 0$.

If the maximum of $w(x,t)$ were to occur on the front then $w_x > 0$ there, which together with $w(t) > 0$ contradicts the boundary condition. Hence $w(t) \leqslant A_1$.

Likewise the minimum of $z(x,t)$ cannot occur on the front, for $z_x < 0$ at a point on the front would be incompatible with the boundary condition. Hence $z(t) \geqslant A_2$.

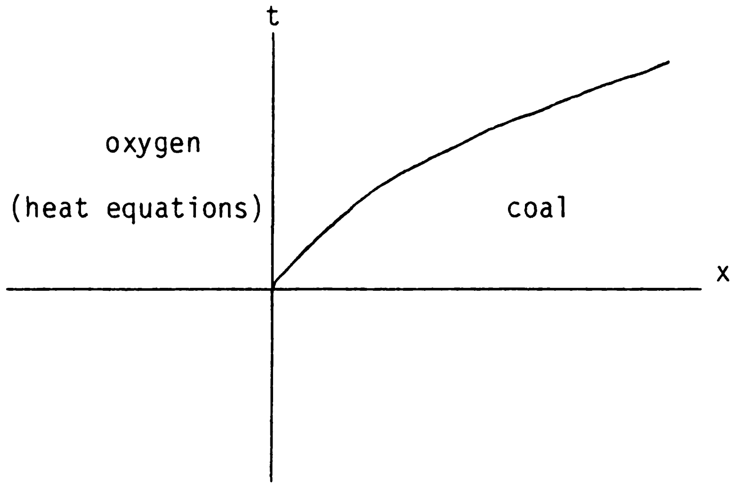

FIG. 1.

LEMMA. For any continuous function F,

$$\frac{1}{\sqrt{\pi D}}\int_0^t \frac{\exp\left\{-\frac{(y(t)-y(s))^2}{4D(t-s)}\right\}}{\sqrt{t-s}} F(s)\left\{y'(s)-\frac{1}{2}\frac{y(t)-y(s)}{t-s}\right\} ds$$

$$\leqslant \max_{s\leqslant t} F(s)\times \operatorname{erf}\left(\frac{y(t)}{\sqrt{4Dt}}\right).$$

Proof. Define $v=(y(t)-y(s))/\sqrt{4D(t-s)}$. Then

$$\frac{dv}{ds}=\frac{1}{\sqrt{4D(t-s)}}\left\{-y'(s)+\frac{1}{2}\frac{y(t)-y(s)}{t-s}\right\} ds$$

so that the integral can be rewritten

$$\frac{2}{\sqrt{\pi}}\int_0^{y(t)/\sqrt{4Dt}} e^{-v^2}F(s)\, dv,$$

which leads immediately to the result.

THEOREM 2. For each t, $y(t)\leqslant Y(t)$ where

$$\begin{cases} \dfrac{dY}{dt}=A_1c_3-c_1D_1\operatorname{erf}\left(\dfrac{Y(t)}{\sqrt{4D_1t}}\right) & t>0, \\ Y(0)=0. \end{cases} \tag{8}$$

Proof.

$y'(t) \leqslant c_3 w(t)$ from (6)

$$= A_1 c_3 \operatorname{erfc}\left(\frac{y(t)}{\sqrt{4D_1 t}}\right) + \frac{1}{\sqrt{\pi D_1}} \int_0^t \frac{\exp\left\{-\dfrac{(y(t)-y(s))^2}{4D_1(t-s)}\right\}}{\sqrt{t-s}}$$

$$\times \left\{c_3 w(s)\left[y'(s) - \frac{1}{2}\frac{y(t)-y(s)}{t-s}\right] - c_1 D_1 y'(s)\right\} ds$$

$$\leqslant A_1 c_3 \operatorname{erfc}\left(\frac{y(t)}{\sqrt{4D_1 t}}\right) + \frac{1}{\sqrt{\pi D_1}} \int_0^t \frac{\exp\left\{-\dfrac{(y(t)-y(s))^2}{4D_1(t-s)}\right\}}{\sqrt{t-s}} (c_3 w(s) - c_1 D_1)$$

$$\times \left(y'(s) - \frac{1}{2}\frac{y(t)-y(s)}{t-s}\right) ds$$

$$\leqslant A_1 c_3 \operatorname{erfc}\left(\frac{y(t)}{\sqrt{4D_1 t}}\right) + (A_1 c_3 - c_1 D_1) \operatorname{erf}\left(\frac{y(t)}{\sqrt{4D_1 t}}\right) \quad \text{by the Lemma}$$

$$= A_1 c_3 - c_1 D_1 \operatorname{erf}\left(\frac{y(t)}{\sqrt{4D_1 t}}\right).$$

The result then follows from [Hartman, [5], p. 26, Theorem 4.1].

REMARK. Thus an upper bound for the front position can be rapidly computed by solving a single differential equation.

COROLLARY. If $\eta_B = A_1 c_3/(c_1 D_1) < 1$ then $y(t)/\sqrt{4D_1 t} \leqslant \operatorname{erf}^{-1}(\eta) < \infty$.

THEOREM 3. If $\eta_B < 1$ then for $t \leqslant T$,

$$A_2 + \frac{c_2 D_2}{c_3} \operatorname{erf}\left(\frac{y(t)}{\sqrt{4D_2 t}}\right) \leqslant z(t) \leqslant \frac{A_2 + 2T^{1/2} c_2 D_2^{1/2} A_1 \pi^{-1/2}}{1 - \operatorname{erf}\left(\sqrt{D_1/D_2}\, \operatorname{erf}^{-1}(\eta)\right)}.$$

Proof. From (5) and the Lemma

$$z(t) \leqslant A_2 + \max_{s \leqslant t} Z(s) \cdot \operatorname{erf}\left(\frac{y(t)}{\sqrt{4D_2 t}}\right) + \frac{c_2 D_2 A_1}{\sqrt{\pi D_2}} \times 2t^{1/2}.$$

Now apply the Corollary and take max over $t \leqslant T$. Likewise from (5) and the Lemma but with $\geqslant \min F$ replacing $\leqslant \max F$,

$$z(t) \geqslant A_2 \operatorname{erfc}\left(\frac{y(t)}{\sqrt{4D_2 t}}\right) + A_2 \operatorname{erf}\left(\frac{y(t)}{\sqrt{4D_2 t}}\right) + \frac{c_2 D_2}{c_3} \operatorname{erf}\left(\frac{y(t)}{\sqrt{4D_2 t}}\right).$$

REMARKS. If η_B is not < 1 we can still derive bounds adequate for the existence proofs but not as close to the sharp results of Sec. 5. We do not bother to do this. The Corollary suggests $w < Kt^{-1/2}$ as $t \to \infty$ and this will be formally substantiated in Sec. 5. Were we to take this as a hypothesis in Theorem 3, instead of the $O(t^{1/2})$ term in the bound for $z(t)$ we would have a bound independent of t. A sharper result will be formally derived in Sec. 5.

If it is known that $z(t) \leqslant M$ for all t and $\int xz(x,0)\,dx < \infty$ then choosing $v \equiv x_0$ and $u = z$ in (2) we find

$$\int_{-\infty}^{0} z(x_0,0)|x_0|\,dx_0 + D_2\int_0^T z(t_0)\,dt_0 = \int_{-\infty}^{y(T)} z(T,x_0)|x_0|\,dx_0$$
$$+\int_0^T z(t_0)y(t_0)y'(t_0)\,dt_0 + D_2\int_0^T y(t_0)z_{x_0}(t_0)\,dt_0.$$

The right side is $\geqslant D_2c_2c_3^{-1}y(T)^2/2$ while the left side is $\leqslant D_2MT + O(1)$ as $T \to \infty$. Hence, under the assumptions made,

$$\limsup_{T\to\infty} \frac{y(T)^2}{2T} \leqslant Mc_3/c_2.$$

4. Existence and uniqueness for the unbounded model. Equations (4), (5), (6) are not strictly speaking a system of integral equations for unknowns w, z, y—at least as the term is normally used—because $y(t)$ occurs explicitly in the right side; hence the system needs an additional (implicit) elimination, after which it can no longer be written down explicitly by formulae involving integrals. If $y(t)$ were replaced on the right side by a parameter, we would have a nonlinear system of Urysohn equations (Krasnoselskii, [7], p. 32) which could be analyzed by use of Leray–Schauder degree. We rapidly sketch out a proof from scratch.

Thus we consider equations (4), (5), (6), interpreted as the problem of finding a fixed point of a map F,

$$X = F(X),$$
$$F\colon B \to B,$$

where $X = (w, z, y)$ and

$$B = C[0,T] \times C[0,T] \times C'[0,T] \cap \{y\colon y(0) = 0\}$$

with norm taken as the maximum of the usual norms of the three factors. We observe the following.

- F is a compact map depending upon parameters c_3, c_4. The proof is routine and is omitted.
- $c_3 \downarrow 0$, $c_4 \downarrow 0$ is a homotopy of these maps.
- If X is a solution then an upper bound for its norm is obtained from the results of Sec. 3, *and this upper bound itself remains bounded by some constant M in the course of the homotopy.*
- The limiting equation $X = F_0(X)$ is simply an Abel integral equation followed by two quadratures.

Hence, given $\varepsilon > 0$, any and all solutions to $X = F(X)$ lie in the ball of radius $M + \varepsilon$ about 0 in B and none lie on the boundary. So the Leray–Schauder degree deg($id - F$, ball, 0) (see Lloyd, [8]) is defined and independent of c_3, c_4. But deg($id - F_0$, ball, 0) is easily seen to be ± 1. Hence deg($id - F$, ball, 0) $\neq 0$ and on this account there must be a solution in the ball of radius M itself. Since the reasoning holds for any T we have proved this theorem.

THEOREM 4. The system of integral equations (4), (5), (6) possesses a continuous solution w, z for $t > 0$.

It remains to be shown why the original system of partial differential equations has a solution. We take the front $y(t)$ computed from (6) as a given smooth boundary and let $\bar{w}$ be the unique solution (see Cannon, [3], Ch. 14) to the problem

$$\bar{w}_t = D_1 \bar{w}_{xx},$$
$$\bar{w}(0, x) = A_1,$$
$$\bar{w}(y(t), t) = w(t)$$

and let $\bar{z}$ be defined similarly. We must show that (le) and (lf) are satisfied, that is,

$$\bar{w}_x(y(t), t) = -c_1 w(t) \exp(-c_4/z(t)),$$
$$\bar{z}_x(y(t), t) = c_2 w(t) \exp(-c_4/z(t)).$$

The existence of these derivatives is proved in [ibid., pg. 247, Theorem 14.4.1.]. We write down equation (3) for $u = \bar{w}$ and compare it to (4). Five of the six terms are identical. Subtracting these equations we find

$$\int_0^t \frac{\exp\left\{-\dfrac{(y(t)-y(s))^2}{4D_1(t-s)}\right\}}{\sqrt{t-s}} \left\{ w_x(y(s), s) + c_1 w(s) \exp(-c_4/w(s)) \right\} ds = 0 \quad \text{all } t > 0$$

and a similar equation related to (1f), and obtained by taking $u = z$ and comparing to (5).

It is quite obvious that if F is continuous a relation

$$\int_0^t \frac{\exp\left\{-\dfrac{(y(t)-y(s))^2}{4D_1(t-s)}\right\}}{\sqrt{t-s}} F(s)\, ds = 0$$

cannot hold for all $t > 0$ unless F is identically zero. For if F had isolated zeros at T_1, $T_2, \ldots$ then by taking successively $t = T_1, T_2, \ldots$ we find successively F to be zero for $s \leqslant T_1$, $s \leqslant T_2, \ldots$, etc. We have proved:

THEOREM 5. The free boundary problem (1) has a solution.

We now prove uniqueness. Suppose w_1, z_1, y_1 and w_2, z_2, y_2 are each solutions of (4)–(6) and temporarily let $w(t) = w_1(t) - w_2(t)$, $z(t) = z_1(t) - z_2(t)$, $y(t) = y_1(t) - y_2(t)$. By subtracting equations, adding and subtracting terms, and applying the mean-value theorem we find with new c's,

$$w(t) \leqslant \frac{c_1(t) y(t)}{\sqrt{t}} + \int_0^t \frac{c_2 w(s) + c_3 z(s) + c_4 (y(t) - y(s))/(t-s)}{\sqrt{t-s}}\, ds,$$

$$z(t) \leqslant \text{similar expression with different } c\text{'s},$$

$$|y'(t)| \leqslant c_9 |w(t)| + c_{10} |z(t)|,$$

and

$$|y(t)| \leqslant \int_0^t c_9|w(s)| + c_{10}|z(s)|\,ds,$$

where $c_j = c_j(s, t)$ and by the a priori estimates of Sec. 3 each $c_j \leqslant C$, a constant independent of s, t but depending on the parameters A_1, A_2, etc. From now on the value of C can change from line to line.

We observe that

$$\begin{aligned}\left|\int_0^t c_4(s,t)\frac{(y(t)-y(s))/(t-s)}{\sqrt{t-s}}\,ds\right| &= \left|\int_0^t c_4(s,t)(t-s)^{-3/2}\int_s^t y'(r)\,dr\,ds\right| \\ &= \left|\int_0^t y'(r)\int_0^r c_4(s,t)(t-s)^{-3/2}\,ds\,dr\right| \\ &\leqslant C\int_0^t |y'(r)|\left[(t-r)^{-1/2} - t^{-1/2}\right]dr \\ &\leqslant C\int_0^t (|w(s)| + |z(s)|)\frac{ds}{\sqrt{t-s}}\end{aligned}$$

and since $(t-s)^{-1/2} \geqslant t^{-1/2}$,

$$\frac{|y(t)|}{\sqrt{t}} \leqslant \text{similar expression with different } C.$$

Thus

$$|w(t)| \leqslant C\int_0^t (|w(s)| + |z(s)|)\frac{ds}{\sqrt{t-s}},$$

$$|z(t)| \leqslant C\int_0^t (|w(s)| + |z(s)|)\frac{ds}{\sqrt{t-s}}.$$

So with $\phi(t) = |w(t)| + |z(t)|$,

$$\phi(t) \leqslant C\int_0^t \phi(s)\frac{ds}{\sqrt{t-s}} \equiv CK[\phi].$$

However, K is the operator of integration of order 1/2 [Cannon, [3], Theorem 8.1.1], i.e.,

$$K^2[\phi] = C\int_0^t \phi(s)\,ds.$$

Applying K to both sides we find

$$K[\phi] \leqslant C\int_0^t \phi(s)\,ds$$

which implies

$$\phi(t) = C\int_0^t \phi(s)\,ds,$$

so clearly $\phi(t) \equiv 0$. We have proved

Theorem 6. Both the integral equations (4B), (5B), (6B) and also the free boundary problem (1B) have unique solutions.

5. Asymptotic properties. The integral equations possess *formal* asymptotic solutions as $t \to \infty$,

$$\begin{aligned} w(t) &= \alpha t^{-1/2} + \alpha_1 t^{-1} + \cdots, \\ z(t) &= Z + \gamma_1 t^{-1/2} + \gamma_2 t^{-1} + \cdots, \\ y(t) &= 2k(D_1 t)^{1/2} + \delta_1 \log t + \delta_2 t^{-1/2} + \cdots. \end{aligned} \tag{9}$$

We do not prove (but do not doubt) that these series are asymptotic; we do calculate the leading coefficients. First consider the unbounded case.

On the basis of these expressions a short calculation in (4B) shows that only two of the five terms are dominant and they are

$$A_1 \operatorname{erf}\left(\frac{y(t)}{\sqrt{4D_1 t}}\right) - c_1 D_1^{1/2}\pi^{-1/2}\int_0^t \frac{\exp\left\{-\dfrac{(y(t)-y(s))^2}{4D_1(t-s)}\right\}}{\sqrt{t-s}} w(s)\exp(-c_4/z(s))\,ds \tag{10}$$
$$= O\left(\frac{\log t}{\sqrt{t}}\right).$$

Assuming (9), the error we commit by integrating in (10) over $T < s < t$ rather than $0 < s < t$ is $O(t^{-1/2})$. Therefore (10) is also correct when the shifted functions

$$\begin{aligned} w_+(s) &= w(T+s), \\ z_+(s) &= z(T+s), \\ y_+(s) &= y(T+s) \end{aligned}$$

replace w, z, y. This justifies the insertion of the *asymptotic* expressions (9) into (10). The result will be a relation between α, k, and Z. Two more relations are obtained from (5B) and (6B). Two definite integrals are required.

LEMMA.

$$\int_0^1 \frac{\exp\left\{\dfrac{-k^2(1-s^{1/2})^2}{1-s}\right\}}{\sqrt{s(1-s)}}\,ds = e^{k^2}\left(1-(\operatorname{erf}(k))^2\right),$$

$$\int_0^1 \frac{\exp\left\{\dfrac{-k^2(1-s^{1/2})^2}{1-s}\right\}}{\sqrt{1-s}}\,\frac{1-s^{1/2}}{1-s}\,ds = \pi e^{k^2}\left(1-(\operatorname{erf}(k))^2\right) - \frac{\sqrt{\pi}}{k}\operatorname{erf}(k).$$

Proof. Substitute $x^2 = (1-s^{1/2})^2/(1-s)$ and refer to [Abramowitz–Stegun, [1], p. 302, #7.4.12].

From (10) with $t \to \infty$, recalling $\eta_B = A_1 c_3/(c_1 D_1)$, we find after some simplification and reference to the lemma,

$$\eta_B = \sqrt{\pi}\, k e^{k^2}(1 + \operatorname{erf}(k)) \equiv h_B(k).$$

Proceeding to (5B) and (6B), we note each term has a limit as $t \to \infty$, straightforwardly but lengthily computable using the lemma where necessary. The result is an expression for Z. We summarize.

Asymptotic behavior of the unbounded model.

$$\lim_{t\to\infty} \frac{y(t)}{\sqrt{4D_1 t}} = h_B^{-1}(\eta_B),$$

$$\lim_{t\to\infty} z(t) = A_2 + \frac{c_2 D_2}{c_3} h_B\left(\sqrt{D_1/D_2}\, h_B^{-1}(\eta_B)\right) \equiv Z,$$

$$\lim_{t\to\infty} t^{1/2} w(t) = c_3^{-1} D_1^{1/2} \exp(-c_4/Z) h_B^{-1}(\eta_B).$$

COROLLARY. If $D_1 = D_2$ then $Z = A_2 + A_1 c_2/c_1$.

The calculations for the bounded model are much more lengthy and will also be omitted. The results are quite similar. We define

$$h_A(k) = \sqrt{\pi}\, k e^{k^2} \operatorname{erf}(k),$$

$$\eta_A = \frac{c_3 w_a}{c_1 D_1}.$$

Asymptotic behavior of the bounded model.

$$\lim_{t\to\infty} \frac{y(t)}{\sqrt{4D_1 t}} = h_A^{-1}(\eta_A),$$

$$\lim_{t\to\infty} z(t) = z_a + \frac{c_2 D_2}{c_3} h_A\left(\sqrt{D_1/D_2}\, h_A^{-1}(\eta_A)\right) \equiv Z,$$

$$\lim_{t\to\infty} t^{1/2} w(t) = c_3^{-1} D_1^{1/2} \exp(-c_4/Z) h_A^{-1}(\eta_A).$$

COROLLARY. If $D_1 = D_2$ then $Z = z_a + w_a c_2/c_1$.

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