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CONSTANT FRONT SPEED IN WEAKLY DIFFUSIVE NON-FICKIAN SYSTEMS*

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Abstract. In certain polymer-penetrant systems, the effects of Fickian diffusion are dominated by nonlinear viscoelastic behavior. Consequently, such systems often exhibit concentration fronts unlike those seen in classical Fickian systems. These fronts not only are sharper than in standard systems but also propagate at constant speed. The mathematical model presented is a moving boundary-value problem, where the boundary separates the polymer into two distinct states, glassy and rubbery, where different physical processes dominate. The moving boundary condition that results is not solvable by similarity solutions but can be solved by integral equation techniques. In the case under consideration, namely, one where the standard Fickian diffusion coefficient is small, asymptotic solutions where a comparatively sharp front moves with constant speed are obtained.

Key words. integral equations, moving boundary-value problems, non-Fickian diffusion, polymer-penetrant systems

AMS subject classifications. 35B20, 35C15, 35C20, 35K60, 35R35, 73F15, 76R99, 80A22

1. Introduction.

As engineers continue to find new uses for polymers and other synthetic materials [1]–[5], entire industries have been revolutionized and new ones created. Suddenly, materials science has been thrust to the forefront of mathematical applications as engineers and mathematicians alike scramble to understand the dynamics of these new materials. Unfortunately, neither group has come to a full understanding of the exact physical mechanisms involved in such systems. However, all agree that the unusual phenomena these new materials exhibit indicate that the standard Fickian flux $\tilde{\mathbf{J}} = -D(\tilde{C})\nabla\tilde{C}$, where $D(\tilde{C})$ is the second-order diffusion tensor and $\tilde{C}$ is the concentration, is not general enough to model such systems correctly. In addition, there is a growing consensus that some sort of viscoelastic stress plays a major role in the dynamics of many of these materials, sharing dominance with or robbing control from standard Fickian diffusion.

Polymer-penetrant systems are particularly intriguing since much of the observed behavior cannot be explained by a purely Fickian diffusion model. For instance, unless pathological conditions are met, a Fickian front always propagates with speed proportional to $\tilde{t}^{-1/2}$. However, in so-called case II diffusion in polymers, concentration fronts move with constant speed [6], [7]. These fronts are usually sharper than those of the Fickian diffusion model. However, there is no discontinuity in $\tilde{C}$ as can be found in other, more standard chemical systems [8].

The type of polymers that we study are characterized by two distinct phases: *glassy* and *rubbery*. In the glassy state, the polymer has a finite *relaxation time* associated with the length of the polymer in relation to the entanglement network. This nonlocal effect implies that there will be a stress related to the "memory" of the

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polymer with respect to its concentration history. In the rubbery state, the polymer swells, making the relaxation time almost instantaneous. Hence, the "memory" of the polymer in the rubbery state is very faint [9].

To model this unusual behavior, Edwards and Cohen [10] have proposed a much more general model for the flux, which can accomodate many terms. Each term in the expansion represents a flux contribution from a different source, including such effects as molecular diffusion and viscoelasticity. Furthermore, each term can be derived directly from an augmented chemical potential. This form for the flux is general enough to model accurately many more types of anomalous diffusive behavior than simply those associated with polymer-penetrant systems.

In [10]–[18] the authors present specialized forms of the general model to examine several different cases of viscoeleastic diffusion in polymer-penetrant systems. In this paper we will do likewise. We expect to find this unusual behavior in systems where the effects of Fickian diffusion have been swamped by some other effect. Therefore, we will consider the effect of a small diffusion coefficient in a polymer-penetrant system.

In § 2 we enumerate the equations in the general model except for the conditions at the moving boundary, which we describe in § 3. In § 4 we specialize our general model to the case that we wish to consider. Small- and large-time asymptotics are performed in §§ 5 and 6.

2. Governing equations. To have faith in our model, we need to replicate several important properties of polymer-penetrant systems that are generally found in experiments. First, we expect there to be only two dominant processes in our system: molecular diffusion and viscoelasticity. Therefore, we expect our flux expansion to have two terms instead of the one term modeled by Fickian diffusion. In the glassy state, the polymer has a finite relaxation time [19], which indicates the presence of a viscoelastic memory term in our flux. The polymer is affected by past values of the concentration and its time derivative [7], [20], [21].

We wish to reduce our problem to one dimension, so we write the flux as

$$\tilde{J} = -D(\tilde{C})\tilde{C}_{\tilde{x}} - E(\tilde{C})\tilde{\sigma}_{\tilde{x}}, \tag{2.1a}$$

where

$$\tilde{\sigma} = \int_0^{\tilde{t}} [\eta\tilde{C}(\tilde{x},\tilde{t}') + \nu\tilde{C}_{\tilde{t}}(\tilde{x},\tilde{t}')] \exp\left[-\int_{\tilde{t}'}^{\tilde{t}} \beta(\tilde{C}(\tilde{x},z))\,dz\right] d\tilde{t}'. \tag{2.1b}$$

Here $\beta(\tilde{C})$ is the inverse of the relaxation time for the polymer, $E(\tilde{C})$ is a stress coefficient term, and η and ν are constants. Further justification for an expansion such as (2.1) may be found in Edwards and Cohen [10]. We also note that $\tilde{\sigma}$ plays the role of the viscoelastic memory term and can be considered analogous to a stress term. In addition, the definition of $\tilde{\sigma}$ in (2.1b) implies that

$$\tilde{\sigma}(\tilde{x}, 0) = 0. \tag{2.2}$$

The term $\beta(\tilde{C})$ is the inverse of the relaxation time, which corresponds roughly to the time needed for one part of the polymer to respond to changes in neighboring parts. In the polymer-penetrant systems in which we are interested, $\beta(\tilde{C})$ changes greatly as the polymer goes from the glassy state to the rubbery state. Therefore, its dependence on $\tilde{C}$ will be important, although the differences in $\beta(\tilde{C})$ *within* phases are negligible when compared with the differences *between* phases. Hence, we model $\beta(\tilde{C})$ by its average in each phase, yielding the following functional form:

$$\beta(\tilde{C}) = \begin{cases} \beta_g, & 0 \leq \tilde{C} \leq \tilde{C}_* \text{ (glass)}, \\ \beta_r, & \tilde{C}_* < \tilde{C} \leq \tilde{C}_c \text{ (rubber)}, \end{cases} \tag{2.3}$$

where $\tilde{C}_*$ is the concentration at which the rubber–glass transition occurs. Subscripts and superscripts r refer to the rubbery region; subscripts and superscripts g refer to the glassy region. This choice for $\beta(\tilde{C})$ also has the advantage that it makes the problem more tractable analytically.

It has been shown experimentally that the qualitative effects of the variance of $E(\tilde{C})$ on the concentration are essentially negligible. Since we are eventually going to consider the case of a weakly diffusive system, we also conclude that variations in $D(\tilde{C})$ will not contribute qualitatively to the solution. Thus, we approximate $E(\tilde{C})$ and $D(\tilde{C})$ by their averages over the range of concentration and treat them as constants, which we denote by E and D. More discussion of various physically appropriate forms for $D(\tilde{C})$ and $E(\tilde{C})$ can be found in Cohen and White [11].

Substituting (2.1a) and our expressions for $D(\tilde{C})$ and $E(\tilde{C})$ into the standard diffusion operator $\tilde{C}_{\tilde{t}} = -\tilde{J}_{\tilde{x}}$, we have

$$\tilde{C}_{\tilde{t}} = D\tilde{C}_{\tilde{x}\tilde{x}} + E\tilde{\sigma}_{\tilde{x}\tilde{x}}. \tag{2.4a}$$

We also note that equation (2.1b) is the solution to the following equation:

$$\tilde{\sigma}_{\tilde{t}} + \beta(\tilde{C})\tilde{\sigma} = \eta\tilde{C} + \nu\tilde{C}_{\tilde{t}}. \tag{2.4b}$$

We wish to model the penetration of solute imposed at a concentration $\tilde{C}_c$ on the boundary of an initially "dry" and unstressed semi-infinite polymer. Mathematically, we wish to solve equations (2.4) on the interval $\tilde{x} > 0$ subject to (2.2) and the following boundary and initial conditions:

$$\tilde{C}(0, \tilde{t}) = \tilde{C}_c, \qquad \tilde{C}(\tilde{x}, 0) = 0. \tag{2.5}$$

In addition, on physical grounds we expect that as the experiment progresses, the polymer will become totally saturated. The mathematical condition, which we will impose only when warranted, is

$$\tilde{C}(\tilde{x}, \infty) = \tilde{C}_c. \tag{2.6}$$

This condition, which is naturally satisfied by the full problem due to its parabolic nature, is needed when we attempt to use perturbation techniques to solve the complicated moving boundary-value problem.

We wish to incorporate effects of both the glassy and the rubbery phases in our nondimensionalization. We normalize $\tilde{x}$ by our diffusive length scale in the glassy region, since we wish to track front motion on a macroscopic level and the diffusive length scale in the glassy region is the longer length scale. However, it has been seen in experiments and numerical simulations [22] that these fronts move quickly; therefore, we normalize $\tilde{t}$ by the relaxation time in the rubbery region, which is the faster time scale. We normalize $\tilde{C}$ by $\tilde{C}_c$ and $\tilde{\sigma}$ by $\nu\tilde{C}_c$. Summarizing, we have

$$x = \tilde{x}\sqrt{\frac{\beta_g}{D}}, \quad t = \tilde{t}\beta_r, \quad C(x,t) = \frac{\tilde{C}(\tilde{x},\tilde{t})}{\tilde{C}_c}, \quad \sigma(x,t) = \frac{\tilde{\sigma}(\tilde{x},\tilde{t})}{\nu\tilde{C}_c}, \quad C_* = \frac{\tilde{C}_*}{\tilde{C}_c}. \tag{2.7}$$

Then equations (2.2) and (2.4)–(2.6) reduce to

$$C_t = \frac{\beta_g}{\beta_r} C_{xx} + \frac{\nu E \beta_g}{D \beta_r} \sigma_{xx}, \tag{2.8a}$$

$$\sigma_t + \frac{\beta(C)}{\beta_r} \sigma = \frac{\eta}{\nu \beta_r} C + C_t, \tag{2.8b}$$

$$C(0,t) = 1, \qquad C(x,0) = 0, \qquad \sigma(x,0) = 0, \tag{2.9}$$

$$C(x,\infty) = 1. \tag{2.10}$$

Since $\beta(C)$ is constant on either side of the threshold level $C = C_*$, we may differentiate and combine equations (2.8a) and (2.8b) to yield

$$C_{tt} = \frac{\beta_g}{\beta_r} \left(1 + \frac{\nu E}{D}\right) C_{xxt} - \frac{\beta(C)}{\beta_r} C_t + \frac{\beta_g}{\beta_r^2} \left(\beta(C) + \frac{\eta E}{D}\right) C_{xx}. \tag{2.11}$$

3. Front conditions. Due to our choice of a piecewise-constant function to model $\beta(C)$, our problem will involve matching the solutions in the two regions where $\beta = \beta_g$ and $\beta = \beta_r$. Thus, it is necessary to impose conditions at the moving boundary $\tilde{s}(\tilde{t})$ between the two regions. First, it is clear that since $C_* < 1$, our front has an initial condition $\tilde{s}(0) = 0$.

In a moving boundary-value problem, several conditions need to be imposed at the moving front $\tilde{x} = \tilde{s}(\tilde{t})$. In polymer-penetrant systems, one does not see a *jump* in concentration but rather a sharp rise at a moving front [7]. However, the front is still relatively wide when compared with molecular length scales, so the continuum model we use is still valid. Since there is no jump in concentration, $\tilde{C}$ should be continuous at the front at the specified transition value $\tilde{C}_*$:

$$\tilde{C}^r(\tilde{s}(\tilde{t}), \tilde{t}) = \tilde{C}_* = \tilde{C}^g(\tilde{s}(\tilde{t}), \tilde{t}). \tag{3.1}$$

We also need a condition for the stress at the front. Although some models incorporate discontinuities in the stress at the front [23], in our model we require that the stress be continuous:

$$\tilde{\sigma}^r(\tilde{s}(\tilde{t}), \tilde{t}) = \tilde{\sigma}^g(\tilde{s}(\tilde{t}), \tilde{t}). \tag{3.2}$$

This choice is consistent with (3.1) above, which we derived by using the reasoning that although our relevant dependent variables may change quickly near the front, they are still continuous.

Last, we need a relationship between the flux $\tilde{J}$ at the front and the speed at which the front travels. Since the polymer undergoes a phase transition from a glassy to a rubbery phase, we use the flux condition from the Stefan problem [8], which is

$$[\tilde{J}]_{\tilde{s}} = -\tilde{a} \frac{d\tilde{s}}{d\tilde{t}}, \tag{3.3}$$

where $[\cdot]_{\tilde{s}} = \cdot^g(\tilde{s}^+(\tilde{t}), \tilde{t}) - \cdot^r(\tilde{s}^-(\tilde{t}), \tilde{t})$.

In a standard problem, the constant $\tilde{a}$ is related to the latent heat of melting of the substance. However, here we are assuming that a "phase transition" takes place in the polymer as we go from the glassy to the rubbery state. Experimentally, this has been shown to be related to a stretching of the polymer, which reduces the amount of stress quickly, although not discontinuously. In fact, an experiment where $\tilde{a}$ can be measured directly can be designed [10], [18]. The flux used by the polymer in this stretching is directly analogous to the energy used in melting in a standard two-phase heat conduction problem. Using (2.1a) in (3.3), we have the following:

$$[D\tilde{C}_{\tilde{x}} + E\tilde{\sigma}_{\tilde{x}}]_{\tilde{s}} = \tilde{a}\frac{d\tilde{s}}{d\tilde{t}}. \tag{3.4}$$

Since the stretching of the polymer reduces the stress, we expect that as the system reaches a steady state, we should see the stress increasing in the glassy polymer, reaching a continuous maximum in the rubbery polymer near the concentration front and then decaying quickly to 0 in the fully relaxed rubbery polymer. This behavior has been seen in other numerical simulations of the equations of Thomas and Windle [22].

Using our dimensionless variables (2.7) in (3.1), (3.2), and (3.4) and the same length scale for $\tilde{s}$ as for $\tilde{x}$, we have

$$C^r(s(t),t) = C_* = C^g(s(t),t), \tag{3.5}$$

$$\sigma^r(s(t),t) = \sigma^g(s(t),t), \tag{3.6}$$

$$[DC_x + \nu E\sigma_x]_s = \frac{aD\beta_r}{\beta_g}\dot{s}, \tag{3.7}$$

where the dot indicates differentiation with respect to t and $a = \tilde{a}/\tilde{C}_c$.

To simplify our analysis, we now wish to remove σ_x from (3.7). In [10] Edwards and Cohen show how (3.7) may be rewritten as

$$(D + \nu E)[C_x]_s + \nu E\left(\frac{\beta_g}{\beta_r} - 1\right)\frac{\sigma(s(t),t)}{\dot{s}} = \frac{aD\beta_r}{\beta_g}\dot{s} \tag{3.8}$$

by using (2.8b) to solve for σ and then using our front conditions.

Equation (3.8) now replaces (3.7) as the last equation governing our system. Although σ still remains in (3.8), in general practice it is easier to compute σ than σ_x. Experimentally it has been shown that polymers have a near-instantaneous relaxation time in the rubbery state, while in the glassy state these substances are characterized by finite relaxation times. Hence, we assume that $\beta_g/\beta_r = \epsilon$, where $0 < \epsilon \ll 1$. We now wish to solve these equations by using perturbation expansions in the small parameter ϵ to show that in a certain limit these equations lead to constant front speed.

4. The weakly diffusive case. In the weakly diffusive case, we assume that the diffusion coefficient is always small, i.e., $D = D_0\epsilon$. For reasons that will become clear later, we wish to restrict the parameter range that we consider to the following:

$$C_* \leq \frac{1 - (1 + 2a - 2\sqrt{a^2 + a})^2}{4(1 + a)}, \qquad a > 0. \tag{4.1}$$

The second restriction may seem obvious since we have considered a to be analogous to a latent heat, although there are polymer-penetrant systems where this is not the case [10], [18].

Substituting our parameters into (2.11) and (2.8b), we see that for $C > C_*$ we have

$$C^r_{tt} = \frac{\epsilon D_0 + \nu E}{D_0} C^r_{xxt} - C^r_t + \frac{\epsilon}{D_0}\left(D_0 + \frac{\eta E}{\beta_g}\right) C^r_{xx}, \tag{4.2a}$$

$$\sigma^r_t + \sigma^r = \frac{\eta\epsilon}{\nu\beta_g} C^r + C^r_t, \tag{4.2b}$$

while for $C \leq C_*$ we have the following equations:

$$C^g_{tt} = \frac{\epsilon D_0 + \nu E}{D_0} C^g_{xxt} - \epsilon C^g_t + \frac{\epsilon}{D_0}\left(D_0\epsilon + \frac{\eta E}{\beta_g}\right) C^g_{xx}, \tag{4.3a}$$

$$\sigma^g_t + \epsilon\sigma^g = \frac{\eta\epsilon}{\nu\beta_g} C^g + C^g_t. \tag{4.3b}$$

In addition, (3.8) becomes

$$(D_0\epsilon + \nu E)[C_x]_s + \nu E(\epsilon - 1)\frac{\sigma(s(t),t)}{\dot{s}} = aD_0\dot{s}. \tag{4.4}$$

We now construct series for C and σ in ϵ by assuming that $C = C^0 + o(1)$ and $\sigma = \sigma^0 + o(1)$. Doing so, we see that, to leading order, (4.2) and (4.3) become

$$C^{0r}_{tt} = \gamma C^{0r}_{xxt} - C^{0r}_t, \tag{4.5a}$$

$$\sigma^{0r}_t + \sigma^{0r} = C^{0r}_t, \tag{4.5b}$$

$$C^{0g}_{tt} = \gamma C^{0g}_{xxt}, \tag{4.6a}$$

$$\sigma^{0g}_t = C^{0g}_t, \tag{4.6b}$$

where $\gamma = \nu E/D_0$.

Solving (4.6b) subject to (2.9), we see that

$$\sigma^{0g} = C^{0g}, \tag{4.7a}$$

from which (3.5) implies that

$$\sigma(s(t),t) = C_*. \tag{4.7b}$$

Then (4.4) becomes, to leading order,

$$[C^0_x]_s - \frac{C_*}{\dot{s}} = \frac{a\dot{s}}{\gamma}. \tag{4.8}$$

The form of (4.8) immediately indicates that the commonly used method of similarity transformations will not work for this problem. We will have to solve the full partial differential equations and then match these solutions at the moving boundary. To do so, we adopt the integral method used by Boley [24]. In his paper, he extended the equations that held on either side of the front to the entire domain. Then by introducing *fictitious* boundary conditions that held in the extended part of each equation's domain, he was able to construct solutions to the moving boundary-value problem. Following that method, we introduce two new quantities, T^g and T^r, which extend each of (4.5a) and (4.6a) to the full semi-infinite region. We then ensure that each of these solutions satisfies the correct boundary conditions as follows:

$$T^r_{tt} = \gamma T^r_{xxt} - T^r_t, \qquad 0 < x < \infty, \tag{4.9a}$$

$$T^r = C^{0r}, \qquad 0 < x < s(t), \tag{4.9b}$$

$$T^r(0,t) = 1, \qquad T^r(x,0) = 1 - f^i(x), \qquad T^r(x,\infty) = 1, \tag{4.10}$$

$$T^r(s(t),t) = C_*, \tag{4.11}$$

$$T^g_{tt} = \gamma T^g_{xxt}, \qquad 0 < x < \infty, \tag{4.12a}$$

$$T^g = C^{0g}, \qquad s(t) < x < \infty, \tag{4.12b}$$

$$T^g(0,t) = f^b(t), \qquad T^g(x,0) = 0, \tag{4.13}$$

$$T^g(s(t),t) = C_*, \tag{4.14}$$

$$T^g_x(s(t),t) - T^r_x(s(t),t) - \frac{C_*}{\dot{s}} = \frac{a\dot{s}}{\gamma}, \tag{4.15}$$

$$s(0) = 0. \tag{4.16}$$

The new quantities T^r and T^g are simply C^{0r} and C^{0g} extended to the full semi-infinite range. The unknowns f^i and f^b are fictitious initial and boundary conditions introduced to facilitate the solution of the problem.

The first step in the solution of our problem is to integrate (4.9a) with respect to t. Doing so, we see that we need a condition at some point in t. Thus, we use our far-field time condition in (4.10) to yield

$$T^r_t = \gamma T^r_{xx} + (1 - T^r), \qquad 0 < x < \infty. \tag{4.17}$$

Now, if we write $T^r = 1 - e^{-t}T^u$, (4.17) and (4.10) become

$$T^u_t = \gamma T^u_{xx}, \qquad 0 < x < \infty, \tag{4.18a}$$

$$T^u(0,t) = 0, \qquad T^u(x,0) = f^i(x). \tag{4.18b}$$

The solution of (4.18a) and (4.18b) is

$$T^u(x,t) = \frac{1}{2\sqrt{\pi\gamma t}} \int_0^\infty f^i(z) \left\{ \exp\left[-\frac{(x-z)^2}{4\gamma t}\right] - \exp\left[-\frac{(x+z)^2}{4\gamma t}\right]\right\} dz, \tag{4.19}$$

so we have

$$T^r(x,t) = 1 - \frac{e^{-t}}{2\sqrt{\pi\gamma t}} \int_0^\infty f^i(z) \left\{ \exp\left[-\frac{(x-z)^2}{4\gamma t}\right] - \exp\left[-\frac{(x+z)^2}{4\gamma t}\right]\right\} dz. \tag{4.20}$$

Next we solve for T^g. Using (4.13), we may integrate equation (4.12a) once with respect to t to obtain the following:

$$T^g_t = \gamma T^g_{xx}. \tag{4.21}$$

Solving (4.21) subject to (4.13) yields

$$T^g(x,t) = \frac{x}{2\sqrt{\pi\gamma}} \int_0^t \frac{f^b(z)}{(t-z)^{3/2}} \exp\left[-\frac{x^2}{4\gamma(t-z)}\right] dz. \tag{4.22}$$

Now we may substitute (4.20) and (4.22) into (4.11), (4.14), and (4.15) (omitting the dependence of s on t) to yield the following:

$$1 - \frac{e^{-t}}{2\sqrt{\pi\gamma t}} \int_0^\infty f^i(z) \left\{ \exp\left[-\frac{(s-z)^2}{4\gamma t}\right] - \exp\left[-\frac{(s+z)^2}{4\gamma t}\right]\right\} dz = C_*, \tag{4.23}$$

$$\frac{s}{2\sqrt{\pi\gamma}} \int_0^t \frac{f^b(z)}{(t-z)^{3/2}} \exp\left[-\frac{s^2}{4\gamma(t-z)}\right] dz = C_*, \tag{4.24}$$

$$\begin{aligned} &\frac{1}{2\sqrt{\pi\gamma}} \int_0^t \frac{f^b(z)}{(t-z)^{3/2}} \left[1 - \frac{s^2}{2\gamma(t-z)}\right] \exp\left[-\frac{s^2}{4\gamma(t-z)}\right] dz \\ &\quad - \frac{e^{-t}}{4\gamma t\sqrt{\pi\gamma t}} \int_0^\infty f^i(z) \Bigg\{ (s-z)\exp\left[-\frac{(s-z)^2}{4\gamma t}\right] \\ &\qquad\qquad - (s+z)\exp\left[-\frac{(s+z)^2}{4\gamma t}\right]\Bigg\} dz - \frac{C_*}{\dot{s}} = \frac{a\dot{s}}{\gamma}. \end{aligned} \tag{4.25}$$

In addition, we need condition (4.16):

$$s(0) = 0. \tag{4.26}$$

We now seek asymptotic solutions to equations (4.23)–(4.26) for small and large t. These will give expressions for s, f^b, and f^i that we may use to constuct C^{0g} and C^{0r}.

5. Small-time asymptotics. We note that for small t the dominant contribution to the integral in (4.23) is from z near s and hence near 0. Thus, we make the following assumptions about the functional forms of our unknown quantities:

$$f^i(x) \sim f_0^i, \quad x \to 0; \qquad f^b(t) \sim f_0^b, \quad t \to 0. \tag{5.1}$$

Making these substitutions into equations (4.23)–(4.25), we have the following:

$$1 - f_0^i e^{-t} \operatorname{erf}\left(\frac{s}{2\sqrt{\gamma t}}\right) = C_*, \tag{5.2}$$

$$f_0^b \operatorname{erfc}\left(\frac{s}{2\sqrt{\gamma t}}\right) = C_*, \tag{5.3}$$

$$\frac{f_0^i e^{-t} - f_0^b}{\sqrt{\pi \gamma t}} \exp\left(-\frac{s^2}{4\gamma t}\right) - \frac{C_*}{\dot{s}} = \frac{a\dot{s}}{\gamma}. \tag{5.4}$$

Using (4.26), we now postulate that for small t, $s(t) \sim 2s_0 t^p \sqrt{\gamma}$, where $p > 0$. From (5.4), we can see that if $p > 3/2$, the second term on the left-hand side dominates; if $0 < p < 1/2$, the right-hand side dominates. Therefore, solutions of (5.4) exist for the region $1/2 \le p \le 3/2$.

If $1/2 < p \le 3/2$, then (5.2) becomes $C_* = 1$ to leading order in t, which we consider to be a vacuous limiting case. Hence, we conclude that $p = 1/2$, in which case (5.2) becomes

$$f_0^i = \frac{1 - C_*}{\operatorname{erf} s_0}, \tag{5.5}$$

(5.3) becomes

$$f_0^b = \frac{C_*}{\operatorname{erfc} s_0}, \tag{5.6}$$

and (5.4) becomes

$$\frac{f_0^i - f_0^b}{\sqrt{\pi \gamma t}} e^{-s_0^2} = \frac{a s_0}{\sqrt{\gamma t}}. \tag{5.7}$$

Using (5.5) and (5.6) in (5.7), we have the following:

$$e^{-s_0^2}(\operatorname{erfc} s_0 - C_*) = a s_0 \sqrt{\pi} \operatorname{erfc} s_0 \operatorname{erf} s_0. \tag{5.8}$$

Figure 1 shows a graph of the right-hand side and the left-hand side of (5.8). Note that as we increase a or C_*, the value of s_0 at the intersection point (i.e., our velocity coefficient) decreases. This is perfectly consistent with our physical intuition of the problem in this regime, where the solution behaves in a Fickian way. As a increases, the difference in the flux needed to move the front a preset distance increases, so we would expect the speed to slow. As C_* increases, the value of the concentration at which the transition takes place increases, therefore slowing the speed of its advance. This slowing takes place even in the limit $C_* \to 1$, where $s_0 \to 0$. This is perfectly

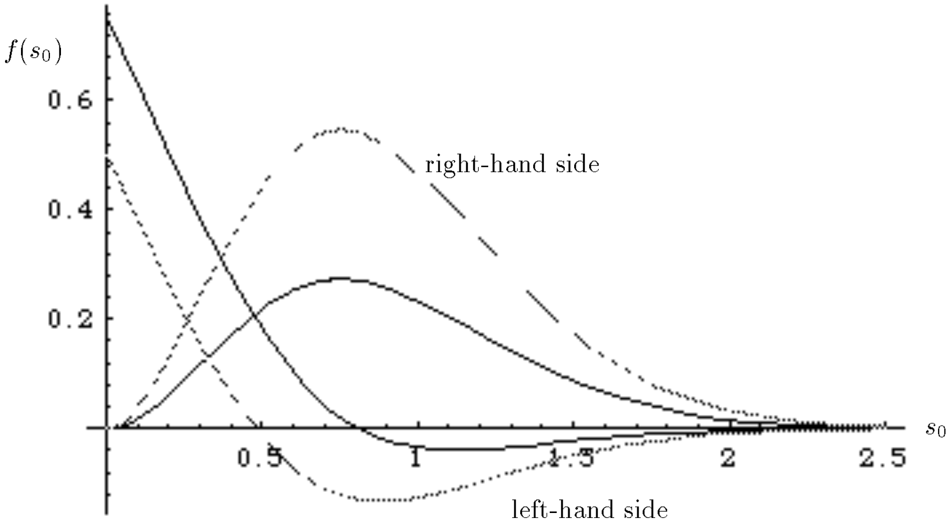

FIG. 1. *Graphs of equation* (5.8). *Dark lines:* $C_* = 1/4$, $a = 1$. *Light lines:* $C_* = 1/2$, $a = 2$.

consistent with our argument earlier, since in that case $1/2 < p \leq 3/2$. Note also that there is a unique positive solution s_0 of (5.8) for all $a > 0$ and $0 < C_* < 1$.

We may now complete our representations for small t:

$$s(t) \sim 2s_0\sqrt{\gamma t}, \quad t \to 0; \qquad e^{-s_0^2}(\operatorname{erfc} s_0 - C_*) = as_0\sqrt{\pi}\operatorname{erfc} s_0 \operatorname{erf} s_0. \tag{5.9}$$

Using (5.6), we may conclude immediately from (4.22) that

$$C^{0g}(x,t) \sim \frac{C_*}{\operatorname{erfc} s_0}\operatorname{erfc}\left(\frac{x}{2\sqrt{\gamma t}}\right), \qquad t \to 0. \tag{5.10}$$

Using (4.7a), we have the following:

$$\sigma^{0g}(x,t) \sim \frac{C_*}{\operatorname{erfc} s_0}\operatorname{erfc}\left(\frac{x}{2\sqrt{\gamma t}}\right), \qquad t \to 0. \tag{5.11}$$

Using (5.5), we see from (4.20) that

$$C^{0r}(x,t) \sim 1 - \frac{1-C_*}{\operatorname{erf} s_0}e^{-t}\operatorname{erf}\left(\frac{x}{2\sqrt{\gamma t}}\right), \qquad x \to 0. \tag{5.12}$$

Using (5.12) in (4.5b), we have that

$$e^t\sigma^{0r} = \frac{1-C_*}{\operatorname{erf} s_0}\left[x\sqrt{\frac{t}{\gamma\pi}}\exp\left(-\frac{x^2}{4\gamma t}\right) + \left(1 - \frac{x^2}{2\gamma}\right)\operatorname{erfc}\left(\frac{x}{2\sqrt{\gamma t}}\right) + t\operatorname{erf}\left(\frac{x}{2\sqrt{\gamma t}}\right)\right] + f(x), \tag{5.13}$$

where we use $f(x)$ to satisfy our boundary condition (4.7b). Our final expression is

$$\sigma^{0r}(x,t) \sim \frac{(1-C_*)e^{-t}}{\operatorname{erf} s_0}\left[x\sqrt{\frac{t}{\gamma\pi}}\exp\left(-\frac{x^2}{4\gamma t}\right) - \frac{x^2}{2\gamma}\operatorname{erfc}\left(\frac{x}{2\sqrt{\gamma t}}\right) + (t-1)\operatorname{erf}\left(\frac{x}{2\sqrt{\gamma t}}\right)\right] + e^{-t}, \quad x \to 0. \tag{5.14}$$

Note that in (5.10)–(5.12) and (5.14) the asymptotic variable for the expansion is the independent variable for the fictitious boundary condition. Hence, in (5.12) and (5.14), since $f^i(x)$ does not depend on t, this is a small x asymptotic expansion good for all t. This statement is true, provided that the dominant contribution to (4.23) for small x comes from z small. This occurs as long as $f^i(z)e^{-z^2}$, which is the general behavior of the integrand in (4.23) for small x, remains bounded for large z.

Figure 2 shows graphs of our concentration results (5.10) and (5.12) for a certain set of parameters (which satisfies (4.1)) and different time values. The jump in the graphs of the different equations occurs at $s(t)$ and is due to the fact that the expansions used are valid only to leading order in t in each region.

Figure 3 shows graphs of our stress results (5.11) and (5.14) for the same parameters and times. One thing to note is that the stress at the boundary is beginning to decay. This trend will become more pronounced as the experiment progresses.

6. Large-time asymptotics. Next we look at the solution for $t \to \infty$. We begin by examining the last two terms of (4.25). For any $s(t)$ not proportional to t, one of these terms will be growing for large t. We expect our concentrations and their derivatives to be bounded for large t, so this large term would have nothing to balance it. Therefore, we conclude that $s(t) \sim 2s_\infty t\sqrt{\gamma}$ for large t.

This means that for large t our error functions from the previous section, which we derived by assuming that f^i and f^b were constant, will die exponentially. In addition, we see that for $s(t) \propto t$ the dominant contribution to the integrals in (4.23)–(4.25) comes from the values of f^i and f^b for large values of x and t. Hence, a naïve assumption that f^b behaves like a constant for large t will be incorrect since it will once again lead to decaying error functions. Therefore, we see that f^i and f^b must become *unbounded* for large values of t and x.

Since the error functions die exponentially, if we assume that f^i and f^b diverge as polynomial functions of their respective variables, the exponential decay will swamp

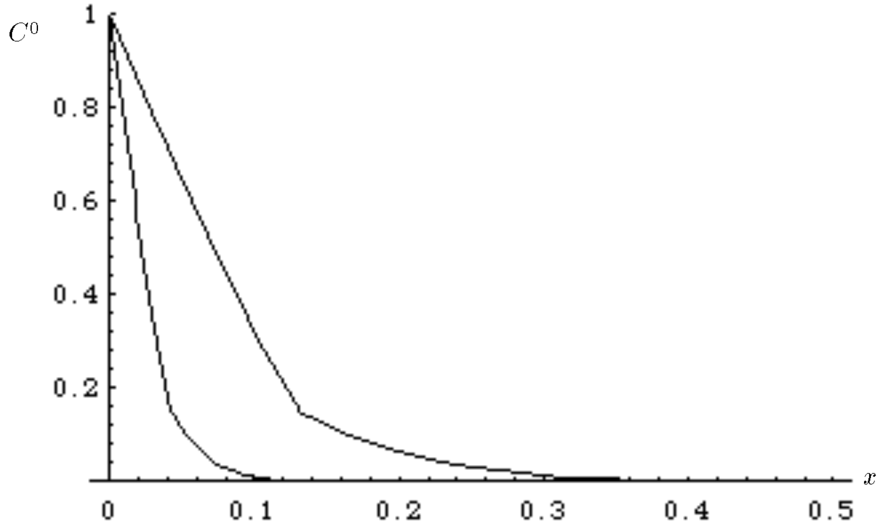

FIG. 2. *Concentration profiles:* $a = 0.5$, $C_* = 0.15$, $\gamma = 1$. *In decreasing order of darkness:* $t = 0.001, 0.01, 0.1$.

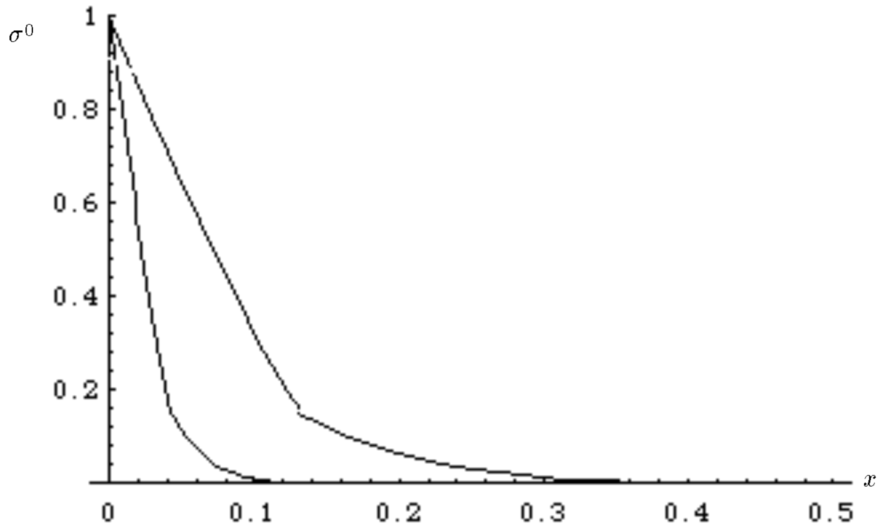

FIG. 3. *Stress profiles:* $a = 0.5$, $C_* = 0.15$, $\gamma = 1$. *In decreasing order of darkness:* $t = 0.001$, 0.01, 0.1.

that divergence. Therefore, we need a *growing* exponential term in f^i and f^b. Thus, we assume the following form for f^b:

$$f^b(t) \sim f^b_\infty e^{A_b^2 t}, \qquad t \to \infty. \tag{6.1}$$

The form of (6.1) was chosen because it is the most tractable analytically. However, other forms that would yield different representations for our functions are possible. Therefore, once we have chosen this form for $f^b(t)$ and an analogous form for $f^i(x)$, our analysis of the problem at hand is essentially over and the remainder of the work is pure asymptotics.

Using (6.1) in (4.22), we have

$$\begin{aligned} T^g(x,t) \sim \frac{f^b_\infty}{2} e^{A_b^2 t} \Bigg[&\exp\left(\frac{A_b x}{\sqrt{\gamma}}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{\gamma t}} + A_b\sqrt{t}\right) \\ &+ \exp\left(-\frac{A_b x}{\sqrt{\gamma}}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{\gamma t}} - A_b\sqrt{t}\right)\Bigg]. \end{aligned} \tag{6.2}$$

Now, asymptotically expanding (6.2) for large t (using our assumption for $s(t)$) and substituting the result in (4.24), we have

$$\frac{f^b_\infty}{2}\left\{\frac{1}{(s_\infty + A_b)\sqrt{\pi t}} \exp(-s_\infty^2 t) + \exp[(A_b^2 - 2A_b s_\infty)t] \operatorname{erfc}\left[(s_\infty - A_b)\sqrt{t}\,\right]\right\} = C_*,$$

from which we have

$$f^b_\infty = C_*, \qquad A_b = 2s_\infty. \tag{6.3}$$

Special care must also be taken with T^r. Once again, our error functions from the previous section will decay as $t \to \infty$. Therefore, we expect $f^i(x)$ to be exponentially large as $x \to \infty$:

$$f^i(x) \sim f^i_\infty e^{A_i x}, \quad x \to \infty; \qquad A_i > 0,$$

and (4.20) becomes the following:

$$\begin{aligned}&T^r(x,t) \sim 1 - \frac{f^i_\infty}{2}\exp[(A_i^2\gamma - 1)t]\times\\ \text{(6.4)}\qquad &\left[e^{A_i x}\operatorname{erfc}\left(-\frac{x}{2\sqrt{\gamma t}} - A_i\sqrt{\gamma t}\right) - e^{-A_i x}\operatorname{erfc}\left(\frac{x}{2\sqrt{\gamma t}} - A_i\sqrt{\gamma t}\right)\right].\end{aligned}$$

Upon substitution of (6.4) and our expression for $s(t)$, the leading orders of (4.23) become

$$\begin{aligned}&\frac{f^i_\infty}{2}\exp[(A_i^2\gamma - 1)t]\left\{e^{2A_i s_\infty t\sqrt{\gamma}}\operatorname{erfc}[-(s_\infty + A_i\sqrt{\gamma})\sqrt{t}]\right.\\ &\qquad\qquad\left.-e^{-2A_i s_\infty t\sqrt{\gamma}}\operatorname{erfc}[(s_\infty - A_i\sqrt{\gamma})\sqrt{t}]\right\} = 1 - C_*,\end{aligned}$$

from which we have

$$\text{(6.5)}\qquad A_i = \frac{-s_\infty + \sqrt{s_\infty^2 + 1}}{\sqrt{\gamma}}, \qquad f^i_\infty = 1 - C_*.$$

Now we must solve for s_∞ by substituting our new results into (4.25). Before proceeding, we see that the only terms in the derivatives of (6.2) and (6.4) that are not exponentially decaying for $s(t) \propto t$ are the derivatives of the exponentials $e^{-A_b x}$ and $e^{A_i x}$. Keeping that argument in mind, we have the following for (4.25):

$$\begin{aligned}&-\frac{C_* A_b}{2\sqrt{\gamma}}\exp\left(A_b^2 t - \frac{A_b s}{\sqrt{\gamma}}\right)\operatorname{erfc}\left(\frac{s}{2\sqrt{\gamma t}} - A_b\sqrt{t}\right)\\ \text{(6.6)}\qquad &+\frac{A_i(1-C_*)}{2}\exp\left[(A_i^2\gamma - 1)t + A_i s\right]\operatorname{erfc}\left(-\frac{s}{2\sqrt{\gamma t}} - A_i\sqrt{\gamma t}\right) = \frac{a\dot{s}}{\gamma} + \frac{C_*}{\dot{s}}.\end{aligned}$$

Substituting our expressions for A_i, A_b, and $s(t)$ and expanding for large t, we have

$$\text{(6.7)}\qquad -\frac{2C_* s_\infty}{\sqrt{\gamma}} + \frac{(C_* - 1)(s_\infty - \sqrt{s_\infty^2 + 1})}{\sqrt{\gamma}} = \frac{2a s_\infty}{\sqrt{\gamma}} + \frac{C_*}{2 s_\infty\sqrt{\gamma}}.$$

Rearranging terms, we have that s_∞ is one of

$$\text{(6.8)}\qquad s_{\infty\pm} = \frac{1}{2}\left[\frac{1 - 2C_* a - 3C_* \pm (1 - C_*)\sqrt{1 - 4C_* - 4C_* a}}{2(1+a)(C_* + a)}\right]^{1/2}.$$

Since $a > 0$ by (4.1), the requirement that

$$\text{(6.9)}\qquad C_* \le \frac{1}{4(1+a)}$$

guarantees that $s_{\infty\pm}$ are real.

Next we check the stability of our solutions to see which of $s_{\infty\pm}$ corresponds to the stable front. Thus, we introduce an $o(1)$ perturbation $\delta(t) \gg \epsilon$ of $s(t)$ into (4.15), which yields (to leading order in δ)

$$T_x^g(s(t),t) - T_x^r(s(t),t) + \delta[T_{xx}^g(s(t),t) - T_{xx}^r(s(t),t)] = \frac{C_*}{\dot{s}} + \frac{a\dot{s}}{\gamma} + \frac{\dot{\delta}}{\dot{s}}\left(\frac{a\dot{s}}{\gamma} - \frac{C_*}{\dot{s}}\right).$$

Using (4.11), (4.15), (4.17), (4.21), and our expression for $s(t)$, we have

$$\frac{\delta}{\gamma}[T_t^g(s(t),t) - T_t^r(s(t),t) + 1 - C_*] = \frac{\dot{\delta}}{2\gamma s_\infty}\left(2as_\infty - \frac{C_*}{2s_\infty}\right).$$

Using the total derivative of (3.5) with respect to x, we have

$$\frac{\delta}{\gamma}(-\dot{s}[T_x(s(t),t)]_s + 1 - C_*) = \frac{\dot{\delta}(4as_\infty^2 - C_*)}{4s_\infty^2}.$$

Using (4.15) and our expression for $s(t)$, we have

$$\delta(1 - 2C_* - 4as_\infty^2) = \frac{\dot{\delta}(4as_\infty^2 - C_*)}{4s_\infty^2}. \tag{6.10}$$

Since the other quantities are always positive, the criterion for stability is that the ratio of the two parenthesized quantities is negative. This will make $\delta(t)$ decay exponentially as $t \to \infty$.

The parenthesized quantity on the left is zero when

$$a = \frac{1}{4C_*} - 1 - \frac{\lambda^2}{4C_*}, \text{ where } (C_* - 1)\lambda^2 + 2(1 - 3C_* + 2C_*^2)\lambda + 5C_* - 8C_*^2 - 1 = 0.$$

However, the discriminant of the quadratic is negative, so the parenthesized quantity on the left is always of the same sign (namely positive). The parenthesized quantity on the right is always negative for $s_{\infty-}$, and it is positive for $s_{\infty+}$ when

$$C_* \leq \frac{1 - (1 + 2a - 2\sqrt{a^2 + a})^2}{4(1 + a)}, \tag{6.11}$$

which for $a > 0$ is stronger than (6.9). Thus, we have our compatibility condition (4.1).

Figure 4 shows our two compatibility conditions as a function of a. Note that as $a \to \infty$, condition (6.11) approaches condition (6.9). We also note that as $a \to 0$ or $a \to \infty$, the range of validity for our solution is very thin. As $a \to \infty$, we see that the second term on the left-hand side of (4.8) becomes negligible. Therefore, we would be left with a standard Stefan condition where the front would move with speed proportional to $t^{-1/2}$. As $a \to 0$, we see that (4.8) would allow solutions with fronts where $\dot{s}$ grows as $t \to \infty$.

We may now complete our representations for large t:

$$s(t) \sim 2s_\infty t\sqrt{\gamma}, \qquad t \to \infty, \tag{6.12a}$$

$$s_\infty = \frac{1}{2}\left[\frac{1 - 2C_*a - 3C_* - (1 - C_*)\sqrt{1 - 4C_* - 4C_*a}}{2(1 + a)(C_* + a)}\right]^{1/2}. \tag{6.12b}$$

Using (6.3) in (6.2), we immediately have

$$\begin{aligned} C^{0g}(x,t) \sim \frac{C_* e^{4s_\infty^2 t}}{2}&\left[\exp\left(\frac{2s_\infty x}{\sqrt{\gamma}}\right)\operatorname{erfc}\left(\frac{x}{2\sqrt{\gamma t}} + 2s_\infty\sqrt{t}\right)\right. \\ &\left. + \exp\left(-\frac{2s_\infty x}{\sqrt{\gamma}}\right)\operatorname{erfc}\left(\frac{x}{2\sqrt{\gamma t}} - 2s_\infty\sqrt{t}\right)\right], \quad t \to \infty, \end{aligned} \tag{6.13}$$

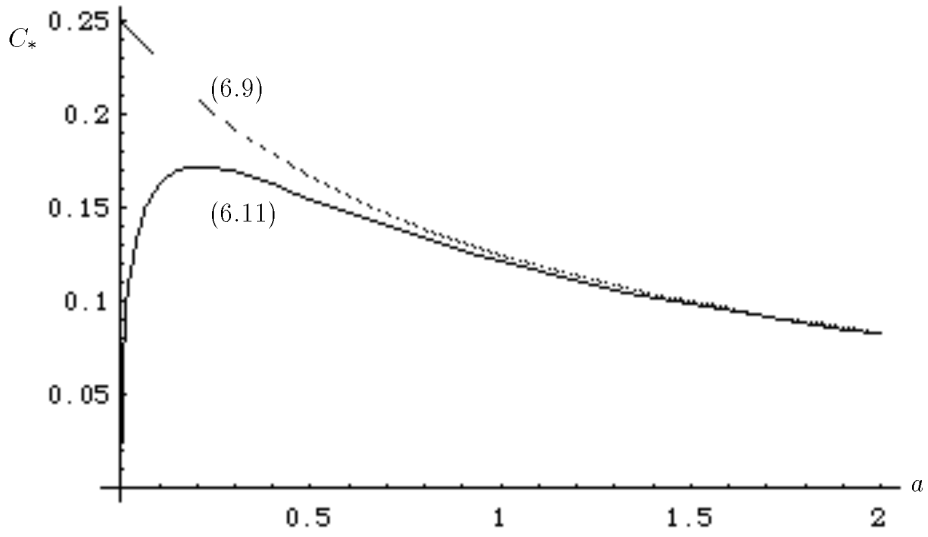

FIG. 4. *Graphs of equations* (6.9) *and* (6.11).

and from (4.7a) we have

$$\sigma^{0g}(x,t) \sim \frac{C_* e^{4s_\infty^2 t}}{2}\left[\exp\left(\frac{2s_\infty x}{\sqrt{\gamma}}\right)\operatorname{erfc}\left(\frac{x}{2\sqrt{\gamma t}}+2s_\infty\sqrt{t}\right)\right.$$

$$\left.+\exp\left(-\frac{2s_\infty x}{\sqrt{\gamma}}\right)\operatorname{erfc}\left(\frac{x}{2\sqrt{\gamma t}}-2s_\infty\sqrt{t}\right)\right], \quad t\to\infty. \tag{6.14}$$

Using (6.5) in (6.4), we have

$$A_i = \frac{-s_\infty+\sqrt{s_\infty^2+1}}{\sqrt{\gamma}}, \tag{6.15}$$

$$C^{0r}(x,t) \sim 1-\frac{1-C_*}{2}\exp\left[(A_i^2\gamma-1)t\right]\times$$

$$\left[e^{A_i x}\operatorname{erfc}\left(-\frac{x}{2\sqrt{\gamma t}}-A_i\sqrt{\gamma t}\right)-e^{-A_i x}\operatorname{erfc}\left(\frac{x}{2\sqrt{\gamma t}}-A_i\sqrt{\gamma t}\right)\right], \quad x\to\infty. \tag{6.16}$$

Now we continue by solving for σ^{0r} for large t. When taking the derivative of (6.16), we see that the dominant term is the following:

$$C_t^{0r} \sim -\frac{(1-C_*)(A_i^2\gamma-1)}{2}\exp[(A_i^2\gamma-1)t]e^{A_i x}\operatorname{erfc}\left(-\frac{x}{2\sqrt{\gamma t}}-A_i\sqrt{\gamma t}\right). \tag{6.17}$$

We may now take the error function to be approximately equal to 2 and substitute into (4.5b) to obtain the following:

$$\sigma^{0r}(x,t) \sim -\frac{2(1-C_*)s_\infty}{s_\infty-\sqrt{s_\infty^2+1}}\exp\left[-(s_\infty-\sqrt{s_\infty^2+1})\left(\frac{x}{\sqrt{\gamma}}-2s_\infty t\right)\right]+f(x)e^{-t}, \tag{6.18}$$

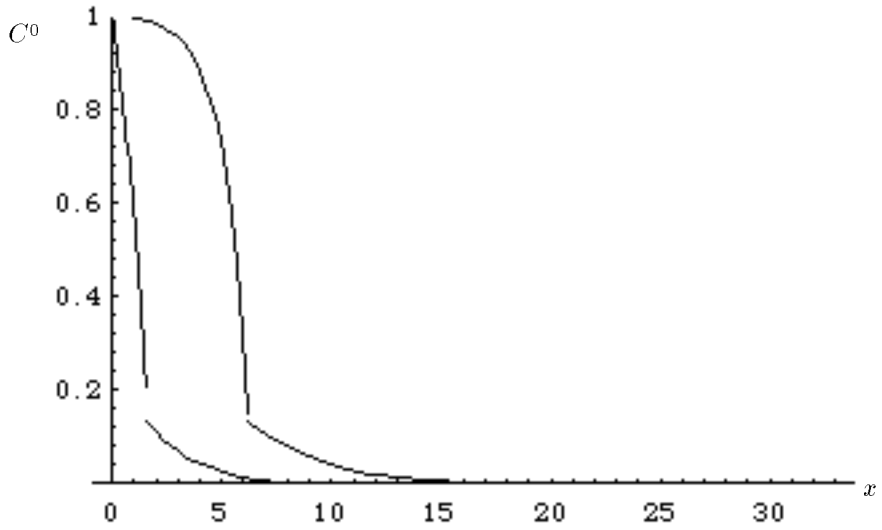

FIG. 5. *Concentration profiles:* $a = 0.5$, $C_* = 0.15$, $\gamma = 1$. *In decreasing order of darkness:* $t = 6, 24, 96$.

where $f(x)$ is once again chosen to satisfy our boundary condition (4.7b). This yields

$$\sigma^{0r}(x,t) \sim \frac{2(1-C_*)s_\infty}{\sqrt{s_\infty^2+1}-s_\infty} \exp\left[-(s_\infty - \sqrt{s_\infty^2+1})\left(\frac{x}{\sqrt{\gamma}} - 2s_\infty t\right)\right]$$

$$+\left[C_* - \frac{2(1-C_*)s_\infty}{\sqrt{s_\infty^2+1}-s_\infty}\right] \exp\left(\frac{x}{2s_\infty\sqrt{\gamma}} - t\right), \quad x \to \infty. \tag{6.19}$$

Figure 5 shows graphs of our concentration results (6.13) and (6.16) for the same set of parameters as before. Since (6.16) satisfies our boundary condition $C(0,t) = 1$, we have used it as the plot for the entire domain $0 < x < s(t)$. The only difference between (6.16) and the more reliable (5.12) to leading orders as $x \to 0$ and $t \to \infty$ is the coefficient of e^{-t}; hence for the purposes of graphical interpretation the two are indistinguishable. Note that as $t \to \infty$, the gap between our solutions narrows.

More important, although not as sharp as profiles generated by other forms of our model [10], [18], our front is still sharper than those found in systems modeled by a simple constant-coefficient Fickian model. A graph of such a profile is shown in Fig. 6. Our profile, where the concentration is almost identically 1 behind the front before plunging sharply downward at the front, has been seen experimentally in polymer-penetrant systems [7]. Therefore, our model replicates two important features of such systems: constant front speed and sharp interfaces.

Figure 7 shows graphs of our stress results (6.14) and (6.19) for the same parameters and times. An argument similar to the one outlined earlier can be made for plotting (6.19) for $x \to 0$ rather than (5.14). As expected, our stress now has a maximum slightly behind the front (the position of which can be ascertained from the gap). In addition, in the region where the concentration of the penetrant is nearly 1, the stress in the polymer is nearly 0; that is, the polymer is fully relaxed.

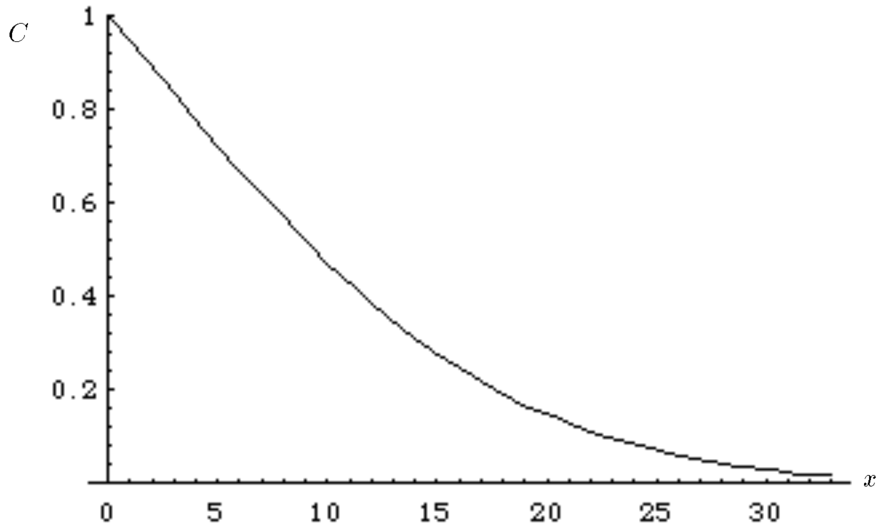

FIG. 6. *Constant-coefficient Fickian error-function profile.*

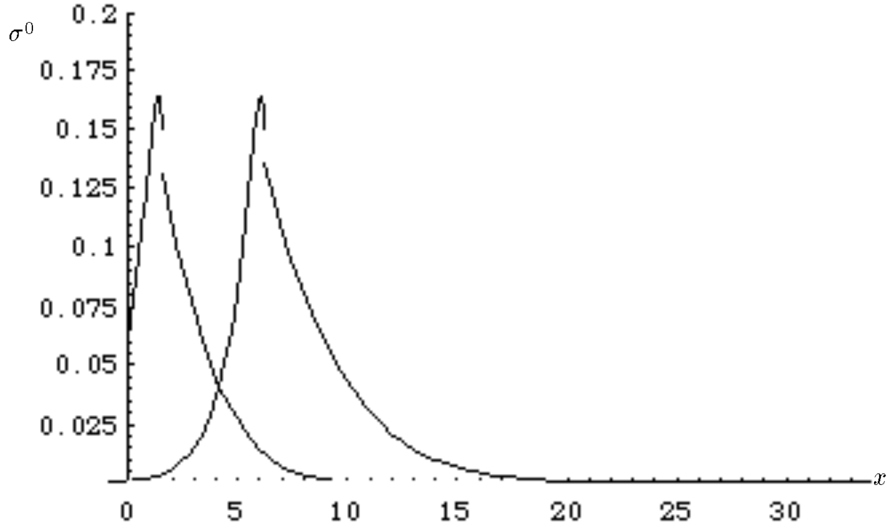

FIG. 7. *Stress profiles:* $a = 0.5$, $C_* = 0.15$, $\gamma = 1$. *In decreasing order of darkness:* $t = 6$, 24, 96.

7. Remarks. The results in this paper clearly demonstrate that non-Fickian behavior occurs in many polymer-penetrant systems. We have constructed asymptotic results where the diffusion coefficient is small, in which case the addition of a non-negligible viscoelastic stress term to the chemical potential introduces memory effects that greatly affect the character of the solution. In addition, the moving boundary-value problem becomes much more difficult mathematically, since it no longer yields to simplistic similarity-variable techniques. Therefore, more sophisticated methods, such as that of Boley, must be used.

The system of integrodifferential equations that results cannot be solved in closed form; thus, an asymptotic solution is expedient. For any $a > 0$, a solution that for small time moved with speed proportional to $t^{-1/2}$, as expected from a diffusive system, was found. This is indicative of the fact that as $t \to 0$, the effect of memory is not yet important, since our definition of the stress implies that the time history begins at $t = 0$.

However, as time progresses, the effects of memory become more and more important. This memory effect, which makes its presence felt in the second term on the left-hand side of (4.8), eventually forces the front to move with constant speed, a phenomenon not seen in Fickian systems with bounded initial and boundary conditions. In addition, as time grows ever larger, our equations lead to solutions where an increasing portion of the rubbery polymer is fully saturated, and the width of the decay to C_* is much narrower than in Fickian systems. This behavior successfully models some of the phenomena seen in polymer-penetrant systems [7].

Obviously, (4.1) is a restrictive class of parameters. However, this does not mean that solutions do not exist when C_* does not satisfy (6.11). What can we say about such systems when a is positive? Well, our discussion in the first paragraph of § 6 still holds; that is, the front must move with constant speed to satisfy the long-time asymptotics of (4.25). However, our solution (6.12) is based on the assumption that the next order in the asymptotic expansion of $s(t)$ as $t \to \infty$ is $O(1)$. If the next term is larger than $O(1)$, then our expansions for T^g and T^r would diverge. For instance, if $s(t) \sim s_\infty t + O(t^{1/2})$, then one of the bracketed terms in (6.13) would be exponentially growing.

Therefore, it is possible that when C_* does not satisfy (6.11), solutions still exist; however, two facets of our analysis must change. First, we must allow for the possibility that there is a correction to $s(t)$ that is greater than $O(1)$. To obtain such solutions, we must abandon such simplistic expressions as (6.1) for our fictitious boundary conditions and incorporate such functional forms as the product of polynomial and growing exponential terms. However, to leading order the front would still move with constant speed by our discussion in the beginning of § 6.

By properly postulating a flux (2.1a), using our physical and mathematical knowledge and intuition about polymer-penetrant systems, we were able to obtain results that replicate several salient features of such systems. By reducing the size of the diffusion coefficient, thereby emphasizing the effects of the nonlinear viscoelastic term, we have obtained fronts that move with constant speed. These fronts, which are sharper than those found in ordinary diffusive systems, have been found experimentally to be characteristic of certain polymer-penetrant systems.

8. Nomenclature.

8.1. Variables and parameters.

Units are listed in terms of length (L), mass (M), moles (N), or time (T). If the same letter appears both with and without tildes, the letter with a tilde has dimensions but the letter without a tilde is nondimensionalized. The equation number where a particular quantity first appears is listed, if applicable.

$\tilde{a}$: coefficient in flux-front speed relationship (3.3), units N/L^3.

A: constant, variously defined.

$\tilde{C}(\cdot, \tilde{t})$: concentration of penetrant or diluent at position $\cdot$ and time $\tilde{t}$, units N/L^3.

$D(\tilde{C})$: binary diffusion coefficient for system, units L^2/T.

$E(\tilde{C})$: coefficient preceding the stress term in the modified diffusion equation, units NT/M (2.1a).

$f(\cdot)$: arbitrary function, variously defined.

$\tilde{\mathbf{J}}(\cdot, \tilde{t})$: flux at position $\cdot$ and time $\tilde{t}$, units N/L^2T.

p: variable exponent for small-time asymptotics.

$\tilde{s}(\tilde{t})$: position of secondary front, defined as $\tilde{C}(\tilde{s}(\tilde{t}), \tilde{t}) = \tilde{C}_*$, units L (3.1).

$\tilde{t}$: time from imposition of external concentration, units T (2.1b).

T: imbedding of C from one region to the fully semi-infinite region (4.9a).

$\tilde{x}$: distance from boundary, units L (2.1a).

z: dummy integration variable.

$\mathcal{Z}$: the integers.

$\beta(\tilde{C})$: inverse of the relaxation time, units T^{-1} (2.1b).

γ: nondimensional parameter, value $\nu E/D_0$ (4.5a).

ϵ: perturbation expansion parameter, value β_g/β_r (4.2a).

η: coefficient of concentration in stress evolution equation, units ML^2/NT^3 (2.1b).

ν: coefficient of $\tilde{C}_{\tilde{t}}$ in stress evolution equation, units ML^2/NT^2 (2.1b).

$\tilde{\sigma}(\tilde{x}, \tilde{t})$: stress in polymer at position $\tilde{x}$ and time $\tilde{t}$, units M/LT^2 (2.1b).

8.2. Other notation.

b: as a subscript or superscript, used to indicate a quantity at $x = 0$ (4.13).

c: as a subscript, used to indicate the characteristic value of a quantity (2.5).

g: as a subscript or superscript, used to indicate the glassy state (2.3).

i: as a subscript or superscript, used to indicate a quantity at $t = 0$ (4.10).

$j \in \mathcal{Z}$: as a subscript or superscript, used to indicate a term in an expansion, in either t, x, or ϵ.

r: as a subscript or superscript, used to indicate the rubbery state (2.3).

$'$: used to indicate a dummy integration variable (2.1b).

$\dot{}$: used to indicate differentiation with respect to t (3.7).

$*$: as a subscript, used to indicate at the transition value between the glassy and rubbery states (2.3).

∞: as subscript, used to indicate a term in an expansion in t or x.

$[\cdot]_{\tilde{s}}$: jump across the front $\tilde{s}$, defined as $\cdot^g(\tilde{s}^+(\tilde{t}), \tilde{t}) - \cdot^r(\tilde{s}^-(\tilde{t}), \tilde{t})$ (3.3).

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