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The effect of a changing diffusion coefficient in super-Case II polymer-penetrant systems

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In certain polymer-penetrant systems, nonlinear viscoelastic effects dominate those of Fickian diffusion. By introducing a dependence of the chemical potential on concentration history, this behaviour can be modelled by a memory integral. The mathematical framework presented is a moving boundary-value problem where the boundary separates the polymer into two distinct states: glassy and rubbery. In each region, a different operator holds at leading order. The problem which results is not solvable by similarity solutions, but can be solved by perturbation and integral equation techniques. By introducing a new model where the diffusion coefficient changes with phase, asymptotic solutions are obtained where sharp fronts initially move like $t^{\frac{3}{2}}$. This 'super-Case II' behaviour is found in various non-Fickian polymer-penetrant systems.

1. Introduction

Recently, engineers and scientists have found many uses for polymers and other synthetic materials, revolutionizing entire industries and creating new ones. This sudden explosion in the development of these materials has thrust materials science to the forefront of mathematical research, especially since modelling of the dynamics of synthetic materials is a relatively new field. Though there are uncertainties among chemical engineers and materials scientists as to the exact physical mechanisms involved, all agree that the standard Fickian flux $\tilde{J} = -D(\tilde{C})\nabla\tilde{C}$, where $\tilde{C}$ is the concentration and $D(\tilde{C})$ is the second-order diffusion tensor, is not general enough to model the desired behaviour accurately. It is also a growing consensus that some sort of viscoelastic effect is as important as molecular diffusion in the dynamics of many of these materials.

These new materials hold astounding promise. Microlithographic patterning using polymer substrates has emerged as a major technology (Thompson *et al.*, 1983). New types of adhesives will adhere more while weighing less (Martuscelli & Marchetta, 1987; Shimabukuro, 1991). 'Smart' polymer gels and synthetic polymers will forever change how doctors administer medicine, as they allow internal or external on-site administrations (Tarche, 1991; Roseman & Mansdorf, 1983; Langer, 1990; Paul & Harris, 1976). Polymer films have great value in protective clothing, equipment, and sealants (Vrentas *et al.*, 1975).

Polymer-penetrant systems are particularly interesting since much of the observed behaviour is inconsistent with a purely Fickian diffusion model. For instance, unless pathological conditions are met, moving Fickian fronts always proceed with speed proportional to $\tilde{t}^{-\frac{1}{2}}$. However, in so-called super-Case II diffusion in polymers, concentration fronts propagate with speed proportional to $\tilde{t}^{\frac{1}{2}}$ (Crank, 1976; Vieth, 1991; Jacques *et al.*, 1974). It is the special behaviour of these super-Case II fronts that we wish to model. These fronts are usually sharp, and often the concentration flux into the phase change boundary is *less* than the concentration flux out! Though the concentration fronts are sharp, there is no discontinuity in $\tilde{C}$ as has been observed in other, more standard chemical systems (Crank, 1984).

The polymers we wish to study can occupy one of two phases: *glassy* or *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. Thus, in any effective model there will be a hereditary integral term associated with the 'memory' of the polymer with respect to its material history. In the rubbery state, the polymer swells, making the relaxation time almost instantaneous. Hence, such memory effects are much smaller in the rubbery state.

In order to incorporate this more complicated behaviour into the model, Edwards & Cohen (1995a) have proposed the following much more general model for the flux:

$$\tilde{\boldsymbol{J}} = -\sum_{n=1}^{\infty} D_n(\tilde{C})\nabla\int_{\Omega}\int_{-\infty}^{\tilde{t}} \mathcal{F}_n[\tilde{C}(\tilde{\boldsymbol{x}}',\tilde{t}')]\mathcal{G}_n[\tilde{\boldsymbol{x}}-\tilde{\boldsymbol{x}}',\tilde{t}-\tilde{t}',\tilde{C}(\tilde{\boldsymbol{x}}',\tilde{t}')]\,\mathrm{d}\tilde{t}\,\mathrm{d}\tilde{\boldsymbol{x}}', \quad (1.1)$$

where the D_n are second-order tensors, the $\mathcal{F}_n$ are general differential operators on $\tilde{C}$ which model the dependency of $\tilde{\boldsymbol{J}}$ on different dynamical processes, and the $\mathcal{G}_n$ are general nonlinear hereditary kernels. Each term in the expansion represents a flux contribution from a different source, such as molecular diffusion or viscoelastic effects. Therefore, (1.1) is general enough to model accurately many types of anomalous diffusive behaviour. Furthermore, note that if we let $\mathcal{F}_n = \delta_{1n}\tilde{C}(\tilde{\boldsymbol{x}}',\tilde{t}')$ and $\mathcal{G}_n = \delta_{1n}\delta(\tilde{\boldsymbol{x}}-\tilde{\boldsymbol{x}}',\tilde{t}-\tilde{t}')$ we obtain the Fickian diffusion flux.

Experimentalists note several important properties in the polymer-penetrant systems which we wish to study. The polymer is affected by past values of the concentration and its time derivative (Thomas & Windle, 1978, 1982; Durning, 1985), which indicates that both terms should be in our functionals $\mathcal{F}_n$. By substituting proper functional forms into (1.1), Edwards & Cohen (1995a) derive the following system of partial differential equations:

$$\tilde{C}_{\tilde{t}} = \nabla\cdot[D(\tilde{C})\nabla\tilde{C} + E(\tilde{C})\nabla\tilde{\sigma}], \quad (1.2a)$$

$$\tilde{\sigma}_{\tilde{t}} + \beta(\tilde{C})\tilde{\sigma} = f(\tilde{C}, \tilde{C}_{\tilde{t}}). \quad (1.2b)$$

In equations (1.2), $\tilde{\sigma}$ is simply a mathematical artifice introduced to simplify what would be a highly nonlinear partial integrodifferential equation into two coupled partial differential equations. However, note that equation (1.2b) is in the form of an evolution equation for viscoelastic stress. In addition, the additional 'forces' on the system that are caused by a term of the form of $\tilde{\sigma}$ can be thought of as analogous to those caused by the trace of an actual mechanical stress tensor. Therefore, for purposes of analogy and heuristic physical interpretation *only,* we will refer to $\tilde{\sigma}$ as a 'stress'.

Simplified forms of (1.2) have been studied in the past by Cohen and his colleagues, though none attempted a moving boundary problem. In addition, the contribution in this paper reflects the first time that an asymptotic analysis has been done on a moving boundary problem where the diffusion coefficient has been allowed to vary nonlinearly with concentration.

Cohen & White (1989, 1991) eliminate the dependence of f on $\tilde{C}_{\tilde{t}}$. They perform steady-state analyses on a finite domain and trace the position and stability of a moving front. Cox (1988) and Cox & Cohen (1989) perform asymptotic analyses and numerical simulations of equations (1.2) on a finite domain holding some of the variable parameters fixed, obtaining long-time Fickian profiles. In addition, they add convective terms to (1.2a) and use phase plane analysis to find travelling wave solutions. Hayes (1990) and Hayes & Cohen (1992) add a bimolecular reaction term to (1.2a). In addition to solving for travelling wave solutions, they solve (1.2) on a finite domain numerically and using perturbation methods. In some of these solutions they find shocks in the solution profiles. Cohen *et al.* (1995) extend the work of Cohen & White to multiple dimensions. A multivalued solution which satisfies an ordinary differential equation formulation is presented; in addition, a rule is stated which allows one to determine the position of a shock in the multivalued solution.

Edwards & Cohen (1995a,b) and Edwards (1994, 1995) have studied this model in the context of a moving boundary-value problem. However, in that previous work only $\beta(\tilde{C})$ was allowed to vary across the front. Though this allowed modelling which incorporated some features of non-Fickian transport, the authors were unable to replicate super-Case II behaviour. In contrast, in this paper we shall allow $\beta(\tilde{C})$ *and* $D(\tilde{C})$ to vary discontinuously across the front, indicating distinct values in the glassy and rubbery regions. By allowing the diffusion coefficient to vary in this manner, we will be able to obtain new super-Case II results where the front moves proportional to $\tilde{t}^{\frac{3}{2}}$.

The moving boundary-value problem which ensues is not solvable by similarity solutions. In addition, it does not involve matching two different parameter values; rather, it involves matching solutions resulting from two different operators. Hence, we rely upon an integral method developed by Boley (1961) which gives solutions which are not in closed form. In order to use such a method, we simplify our model, using experimental data as a guide, to determine the dominant physical processes in the system we wish to study. By using a perturbation expansion in a suitable small parameter, we obtain asymptotic estimates for the motion of the front and the functional form of our solution profiles.

When the diffusion coefficient is allowed to vary with concentration, the resulting solutions replicate several additional features of polymer-penetrant systems. The singular perturbation problem which results leads to sharp fronts moving initially with speed $\tilde{t}^{\frac{1}{2}}$, which we have come to associate with polymer-penetrant systems. In addition, the stress has its maximum exactly at the phase transition—something not seen in previous analyses of (1.2) when the diffusion coefficient was not allowed to vary (Edwards, 1995; Edwards & Cohen, 1995a).

2. Governing equations

For analytical tractability, we consider a one-dimensional problem on a semi-infinite domain. By choosing a semi-infinite interval, we have eliminated complications that occur due to the swelling of the polymer entanglement network in the rubbery region. We now denote the glassy region (the region ahead of the front) with sub- and superscripts g and the rubbery region (the region behind the front) with sub- and superscripts r. By making suitable substitutions for f in (1.2), we obtain

$$\tilde{C}_{\tilde{t}} = [D(\tilde{C})\tilde{C}_{\tilde{x}} + E\tilde{\sigma}_{\tilde{x}}]_{\tilde{x}}, \tag{2.1}$$

$$\tilde{\sigma}_{\tilde{t}} + \beta(\tilde{C})\tilde{\sigma} = \eta\tilde{C} + \nu\tilde{C}_{\tilde{t}}, \tag{2.2}$$

where E, η, and ν are constants. A discussion of various physically appropriate forms for $D(\tilde{C})$, $E(\tilde{C})$, and $f(\tilde{C}, \tilde{C}_{\tilde{t}})$ can be found in Cohen & White (1991).

The term $\beta(\tilde{C})$ is worthy of special attention. It is the inverse of the *relaxation time*, so its dependence on $\tilde{C}$ will be important and nonnegligible. However, experiments have shown that variations in the relaxation time *within* phases seem to contribute little to the overall behaviour. Therefore, we average the relaxation time in each phase and use it as the overall value there. Thus we have

$$\beta(\tilde{C}) = \begin{cases} \beta_g & \text{if } 0 \leqslant \tilde{C} \leqslant \tilde{C}_*, \\ \beta_r & \text{if } \tilde{C} > \tilde{C}_*, \end{cases} \tag{2.3}$$

where $\tilde{C}_*$ is the value of the concentration at which the phase transition takes place. 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. Therefore, we see that $\beta_g \ll \beta_r$.

We wish to model the penetration of solute into an initially 'dry' semi-infinite unstressed polymer where the concentration at the boundary is a given function $\tilde{C}_b(\tilde{t})$. Therefore, we have

$$\tilde{C}(\tilde{x}, 0) = 0, \qquad \tilde{\sigma}(\tilde{x}, 0) = 0, \tag{2.4}$$

$$\tilde{C}(0, \tilde{t}) = \tilde{C}_b(\tilde{t}), \quad \tilde{C}_b'(\tilde{t}) \geqslant 0, \quad \tilde{C}_b(\tilde{t}) > \tilde{C}_* \qquad \text{for all } \tilde{t} > 0. \tag{2.5}$$

The conditions in (2.5) guarantee that the boundary is always in the rubbery region. This phase discontinuity between boundary and polymer at time $\tilde{t} = 0$ implies that our phase transition front $\tilde{s}(\tilde{t})$ must initially be at the boundary:

$$\tilde{s}(0) = 0. \tag{2.6}$$

At the front $\tilde{s}(\tilde{t})$, the stress and the concentration are continuous (Knauss & Kenner, 1980):

$$\tilde{C}(\tilde{s}(\tilde{t}),\tilde{t}) = \tilde{C}_*, \qquad \tilde{\sigma}^{r}(\tilde{s}(\tilde{t}),\tilde{t}) = \tilde{\sigma}^{g}(\tilde{s}(\tilde{t}),\tilde{t}). \tag{2.7}$$

Here we are assuming that there is a fundamental change that takes place in the polymer as we go from the glassy to the rubbery state; this change can be described as a 'phase transition' in the polymer. Experimentally, this has been shown to be related to a stretching of the polymer entanglement network. The flux used up by the polymer in this stretching is directly analogous to the energy used up in melting in a standard two-phase heat conduction problem. The last conduction at the front comes from considering the moving boundary-value problem as a Stefan problem:

$$[(D(\tilde{C}_*) + \nu E)\tilde{C}_{\tilde{x}}]_{\tilde{s}} + \frac{E(\beta_g - \beta_r)\tilde{\sigma}(\tilde{s}(\tilde{t}),\tilde{t})}{\tilde{s}'(\tilde{t})} = a\tilde{C}_c\tilde{s}'(\tilde{t}), \tag{2.8}$$

where $\tilde{C}_c$ is the maximum of $\tilde{C}_b(\tilde{t})$, and hence corresponds to the saturation level of the polymer. Note that, since $\beta_r > \beta_g$, we have a negative contribution to the left-hand side of (2.8) from the stress. Note also that the classical technique of seeking similarity solutions will not in general solve an equation of the form of (2.8).

Here a is the *phase change parameter.* Equation (2.8) states that the difference between the flux into and out of the front is used up in the phase transition. In a standard problem, the constant a is related to the latent heat of melting of the substance. Note also that we have a negative contribution to the left-hand side, so we cannot be assured that a is positive, as was always true in the latent heat formulation. In fact, in some non-Fickian systems, a decrease in the concentration gradient will *slow* the front. This is also consistent with taking $a < 0$. Like the latent heat in a Stefan problem, a must be known in order to solve the problem. However, there are experiments which can be performed to determine a, just as there are experiments which can be performed to determine the latent heat of a substance. One such experiment is outlined in Edwards & Cohen (1995b).

More interesting is the appearance of $\tilde{s}'$ in the denominator of some of our flux terms. This condition is highly unusual and leads to nonstandard front motion, especially when one considers the fact that $\tilde{s}'$ may also appear in the expressions for the concentration and the flux. In general, the behaviour is highly complicated and cannot be solved by the method of similarity variables.

In order to make the problem analytically tractable, we make one more simplifying assumption. As stated before, the diffusion coefficient often, though not always, increases dramatically as the polymer goes from the glassy to rubbery state. However, as with $\beta(\tilde{C})$, changes *within* phases are less important. Hence, we perform the same averaging as we did with the relaxation time to obtain the following form for $D(\tilde{C})$:

$$D(\tilde{C}) = \begin{cases} D_g & \text{if } 0 \leq \tilde{C} \leq \tilde{C}_*, \\ D_r & \text{if } \tilde{C} > \tilde{C}_*. \end{cases} \tag{2.9}$$

Since we have chosen this simplistic form, equation (2.1) may be written

$$\tilde{C}_{\tilde{t}} = D(\tilde{C})\tilde{C}_{\tilde{x}\tilde{x}} + E\tilde{\sigma}_{\tilde{x}\tilde{x}}. \tag{2.10}$$

We introduce dimensionless variables as follows. We use the relaxation time in the glassy region, which is of the order of seconds, as our characteristic time rather than the much shorter relaxation time in the rubbery region. We normalize length by a mixture of the two scales. Summarizing, we have the following:

$$x = \tilde{x}\left(\frac{\beta_g}{D_r}\right)^{\frac{1}{2}}, \quad t = \tilde{t}\beta_g, \quad s(t) = \tilde{s}(t)\left(\frac{\beta_g}{D_r}\right)^{\frac{1}{2}}, \quad C(x, t) = \frac{\tilde{C}(\tilde{x}, \tilde{t})}{\tilde{C}_c}, \tag{2.11a}$$

$$\sigma(x, t) = \frac{\tilde{\sigma}(\tilde{x}, \tilde{t})}{\nu\tilde{C}_c}, \quad C_b(t) = \frac{\tilde{C}_b(\tilde{t})}{\tilde{C}_c}, \quad C_* = \frac{\tilde{C}_*}{\tilde{C}_c}. \tag{2.11b}$$

Then equations (2.10), (2.2), (2.8), (2.5), (2.4), (2.7), and (2.6) reduce to

$$C_t = \frac{D(C)}{D_r} C_{xx} + \frac{\nu E}{D_r} \sigma_{xx}, \tag{2.12a}$$

$$\sigma_t + \frac{\beta(C)}{\beta_g} \sigma = \frac{\eta}{\nu\beta_g} C + C_t, \tag{2.12b}$$

$$[(D(C_*) + \nu E)C_x]_s + \frac{\nu E(\beta_g - \beta_r)}{\beta_g} \frac{\sigma(s(t), t)}{\dot{s}} = aD_r\dot{s}, \tag{2.13}$$

$$C(0, t) = C_b(t), \qquad C(x, 0) = 0, \qquad \sigma(x, 0) = 0, \tag{2.14}$$

$$C(s(t), t) = C_*, \qquad \sigma^r(s(t), t) = \sigma^g(s(t), t), \tag{2.15}$$

$$s(0) = 0, \tag{2.16}$$

where the dot now indicates differentiation with respect to t.

Since $\beta(C)$ and $D(C)$ are constant on either side of the threshold level $C = C_*$, we may combine equations (2.12) to yield

$$C_{tt} = \frac{D(C) + \nu E}{D_r} C_{xxt} - \frac{\beta(C)}{\beta_g} C_t + \frac{\beta(C)D(C) + \eta E}{D_r\beta_g} C_{xx}. \tag{2.17}$$

It can be shown that the operator in (2.17) holds for σ as well. We now wish to solve these equations by using perturbation expansions in a small parameter ϵ to show that these equations lead to front speed proportional to $t^{\frac{1}{2}}$, sharp fronts, a stress maximum at the front, and other behaviour characteristic of non-Fickian polymer-penetrant systems.

3. The perturbation approach

In the previous section we noted that $\beta_g \ll \beta_r$. Therefore, we denote β_g/β_r by ϵ, where $0 < \epsilon \ll 1$. This is a very convenient parameter with which to perform an asymptotic analysis. In certain polymer-penetrant systems, the diffusion coefficient in the rubbery region is much greater than that of the glassy region. This motivates the choice $D_r = D_0\epsilon^{-1}$. We expect the effects of stress to be important, so we let $\eta = \eta_0\epsilon^{-1}$ in order to yield the richest balance of terms

(Edwards, 1994). It will be shown that these choices for the relative magnitudes of our parameters will lead to solutions which replicate the desired behaviour.

Making these substitutions in (2.17) and (2.12b), we see that for $C \leqslant C_*$ we have the following equations:

$$C^g_{tt} = \epsilon\alpha_g C^g_{xxt} - C^g_t + \left(\frac{\epsilon D_g}{D_0} + \kappa^2\right) C^g_{xx}, \tag{3.1a}$$

$$\sigma^g_t + \sigma^g = \frac{\kappa^2}{\gamma\epsilon} C^g + C^g_t, \tag{3.1b}$$

where $\kappa^2 = \eta_0 E/\beta_g D_0$, $\gamma = vE/D_0$, and $\alpha_g = D_g/D_0 + \gamma$. Similarly, we see that in the rubbery region we have

$$C^r_{tt} = (1 + \epsilon\gamma) C^r_{xxt} - \epsilon^{-1} C^r_t + (\epsilon^{-1} + \kappa^2) C^r_{xx}, \tag{3.2a}$$

$$\epsilon\sigma^r_t + \sigma^r = \frac{\kappa^2}{\gamma} C^r + \epsilon C^r_t. \tag{3.2b}$$

In addition, equation (2.13) becomes

$$\alpha_g \epsilon C^g_x(s(t), t) - C^r_x(s(t), t) - \frac{\gamma\sigma(s(t), t)}{\dot{s}} = a\dot{s}. \tag{3.3}$$

Note that the change in $D(C)$ makes the concentration flux contribution from the rubbery region swamp that from the glassy region.

Upon examination of equations (3.1b) and (3.2b), we postulate the following expansions for C and σ in ϵ:

$$C = C^0 + o(1), \qquad \sigma^r = \sigma^{1r} + o(1), \qquad \sigma^g = \sigma^{0g}\epsilon^{-1} + o(\epsilon^{-1}).$$

We note immediately from the above that either $\sigma^{0g}(s(t), t) = 0$ or we have a maximum in the stress at the front. Inserting our expansions into (3.1a), (3.2a), and (3.3), and retaining terms to leading order, we have the following:

$$C^{0g}_{tt} = -C^{0g}_t + \kappa^2 C^{0g}_{xx}, \tag{3.4}$$

$$C^{0r}_t = C^{0r}_{xx}, \tag{3.5}$$

$$\alpha_g \epsilon C^{0g}_x(s(t), t) - C^{0r}_x(s(t), t) - \frac{\gamma\sigma^{0g}(s(t), t)}{\epsilon\dot{s}} = a\dot{s}. \tag{3.6}$$

From equation (3.4) we see that there are three separate cases to consider: $\dot{s} = \kappa$, $\dot{s} < \kappa$, and $\dot{s} > \kappa$. We restrict ourselves to the case where $\dot{s} \leqslant \kappa$. In order to consider such cases, we need to introduce boundary layer variables as follows:

$$\zeta = \frac{x - s(\tau)}{\epsilon^m}, \qquad \tau = t, \qquad \frac{\partial}{\partial x} = \epsilon^{-m}\frac{\partial}{\partial \zeta}, \tag{3.7a}$$

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial \tau} - \dot{s}\epsilon^{-m}\frac{\partial}{\partial \zeta}, \qquad C^g(x, t) \sim C^{0+}(\zeta, \tau) + o(1). \tag{3.7b}$$

Substituting equations (3.7) in equations (3.1a), we have the following (to leading orders):

$$-2\dot{s}\epsilon^{-m}C^{0+}_{\zeta\tau} + \epsilon^{-2m}\dot{s}^2C^{0+}_{\zeta\zeta} = -\epsilon^{1-3m}\alpha_g\dot{s}C^{0+}_{\zeta\zeta\zeta} + \epsilon^{-m}\dot{s}C^{0+}_{\zeta} + \epsilon^{-2m}\kappa^2C^{0+}_{\zeta\zeta}. \quad (3.8)$$

If $\dot{s} = \kappa$, then it can be shown that the stress cannot be matched across the moving front. Therefore, we conclude that $\dot{s} < \kappa$. In this case, $m = 1$ and (3.8) becomes

$$\alpha_g\dot{s}C^{0+}_{\zeta\zeta\zeta} + (\dot{s}^2 - \kappa^2)C^{0+}_{\zeta\zeta} = 0.$$

However, we see that for $s < \kappa t$ there is no bounded solution as $\zeta \rightarrow \infty$, which is the matching region for the glassy polymer. Thus, there is no layer in the concentration in the glassy region. Since (3.1a) also holds for σ^g, we see that there is no layer in the stress, either. So, in order to match $\sigma^r = O(1)$ to $\sigma^g = O(\epsilon^{-1})$, we need a boundary layer in the rubbery region around $x = s(t)$. Introducing the scalings in (3.7) with $\sigma^r(x, t) \sim \epsilon^{-1}\sigma^{0-}(\zeta, \tau)$ and $m = 1$ into (3.2b), we have (to leading order)

$$-\epsilon^{-1}\dot{s}\sigma^{0-}_{\zeta} + \epsilon^{-1}\sigma^{0-} = \frac{\kappa^2}{\gamma}C^r - \dot{s}C^r_{\zeta}.$$

Using the fact that $\sigma^r = O(1)$, we note that $\sigma^{0-}(-\infty, \tau) = 0$. Therefore, the solution becomes

$$\sigma^{0-}(\zeta, \tau) = \sigma^{0g}(s(\tau), \tau)e^{\zeta/\dot{s}}, \quad (3.9)$$

which decays as $\zeta \rightarrow -\infty$, as required.

Substituting our scalings (3.7) in (3.2a) in order to find the boundary-layer equation for $C^r(x, t) \sim C^{0-}(\zeta, \tau)$, we have

$$0 = -\dot{s}C^{0-}_{\zeta\zeta\zeta} + C^{0-}_{\zeta\zeta},$$

the solution of which is, subject to our boundary condition (2.15),

$$C^{0-}(\zeta, \tau) = C^{0r}(s(\tau), \tau) + [C_* - C^{0r}(s(\tau), \tau)]e^{\zeta/\dot{s}}. \quad (3.10)$$

Note that in this case (3.6) becomes, to leading order,

$$\frac{C^{0r}(s(t), t) - C_*}{\dot{s}} - \frac{\gamma\sigma^{0g}(s(t), t)}{\dot{s}} = 0, \quad (3.11)$$

which does not explicitly involve a. Therefore, in this case, we see that the feature which controls the dynamics is a balance between the two contributions to the flux.

4. The integral method

For reasons that will become clear later, we consider the case where

$$C_*(1 + \kappa^2) < 1. \quad (4.1)$$

Though we have constructed solutions using various boundary conditions for our model (Edwards, 1995; Edwards & Cohen, 1995a,b), in this case we use a linear profile which ramps the concentration up to 1:

$$C_{\mathrm{b}}(t)=\begin{cases} C_* + (1-C_*)t/r & \text{if } 0<t<r \\ 1 & \text{if } t>r \end{cases}, \quad \text{with } 0<r<\frac{1-C_*}{C_*\kappa^2}. \tag{4.2}$$

The restrictions on r will also become clear later.

To solve our very complicated system, we use the integral method adopted by Boley (1961). In his paper, he extended the equations which held on either side of the front separating the two phases so that they held on the entire domain under consideration. Then by introducing *fictitious* boundary conditions which 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 equations (3.1a) and (3.2a) to the full semi-infinite region. Doing so, equations (3.5), (4.2), (3.4), (2.14), (2.15), (3.11), and (2.16) become

$$T^{\mathrm{r}}_t = T^{\mathrm{r}}_{xx} \quad (0<x<\infty), \qquad T^{\mathrm{r}} \equiv C^{0\mathrm{r}} \quad (0<x<s(t)), \tag{4.3}$$

$$T^{\mathrm{r}}(x,0)=f_{\mathrm{i}}(x), \qquad T^{\mathrm{r}}(0,t)=\begin{cases} C_* + (1-C_*)t/r & \text{if } 0<t<r, \\ 1 & \text{if } t>r, \end{cases} \tag{4.4}$$

$$T^{\mathrm{g}}_{tt} = \kappa^2 T^{\mathrm{g}}_{xx} - T^{\mathrm{g}}_t \quad (0<x<\infty), \qquad T^{\mathrm{g}} \equiv C^{0\mathrm{g}} \quad (s(t)<x<\infty), \tag{4.5}$$

$$T^{\mathrm{g}}(0,t)=f_{\mathrm{b}}(t), \qquad T^{\mathrm{g}}(x,0)=0, \qquad T^{\mathrm{g}}_t(x,0)=0, \tag{4.6}$$

$$T^{\mathrm{g}}\big(s(t),t\big)=C_*, \tag{4.7}$$

$$T^{\mathrm{r}}\big(s(t),t\big)-\gamma\sigma^{0\mathrm{g}}\big(s(t),t\big)=C_*, \tag{4.8}$$

$$s(0)=0. \tag{4.9}$$

However, since (3.10) does not provide a front condition to solve in the rubbery region, we note that we have too many unknowns if we introduce a fictitious initial condition $f_{\mathrm{i}}(x)$. Fortunately, we note that the boundary layer in this problem can play the role of 'adjusting' the rubbery concentration—exactly the role of the fictitious initial condition in Boley's method. Therefore, we set $f_{\mathrm{i}}(x)$ equal to the actual initial condition for the problem, so

$$T^{\mathrm{r}}(x,0)\equiv 0. \tag{4.10}$$

Note that in some sense the two approaches are equivalent. If we were not using a perturbation method and were tackling the full equations directly, some fictitious initial condition $C^{0\mathrm{r}}(x,0)$ could be constructed which would replicate the boundary-layer behaviour of our problem.

Using Green's functions, we determine that the solution of equations (4.3), (4.4), and (4.10) is given by

$$T^{\mathrm{r}}(x,t)=\frac{x}{2(\pi\gamma)^{\frac{1}{2}}}\int_0^t \frac{T^{\mathrm{r}}(0,z)}{(t-z)^{\frac{3}{2}}}\exp\left(-\frac{x^2}{4\gamma(t-z)}\right)\mathrm{d}z. \tag{4.11}$$

We begin by substituting our expression for $T^r(0, t)$ in the case where $t < r$:

$$T^r(x, t) = \left(\frac{(2t + x^2)(1 - C_*)}{2r} + C_*\right) \operatorname{erfc}\left(\frac{x}{2t^{\frac{1}{2}}}\right) - \frac{(1 - C_*)x}{r}\left(\frac{t}{\pi}\right)^{\frac{1}{2}} \exp\left(-\frac{x^2}{4t}\right). \tag{4.12}$$

We may solve similarly for the case where $t > r$:

$$\begin{aligned} T^r(x, t) = \operatorname{erfc}\left(\frac{x}{2t^{\frac{1}{2}}}\right) + (1 - C_*)\left(1 - \frac{x^2 + 2t}{2r}\right)\left[\operatorname{erf}\left(\frac{x}{2t^{\frac{1}{2}}}\right) - \operatorname{erf}\left(\frac{x}{(t - r)^{\frac{1}{2}}}\right)\right] \\ - \frac{(1 - C_*)x}{r\pi^{\frac{1}{2}}}\left[t^{\frac{1}{2}} \exp\left(-\frac{x^2}{4t}\right) - (t - r)^{\frac{1}{2}} \exp\left(-\frac{x^2}{4(t - r)}\right)\right]. \end{aligned} \tag{4.13}$$

Again using Green's functions, we determine that the solution of (4.5, 4.6) is given by

$$\begin{aligned} T^g(x, t) &= \mathrm{H}(\kappa t - x) \\ &\times \left(\frac{x}{2}\int_{x/\kappa}^{t} \mathrm{e}^{-z/2} f_b(t - z) \frac{\mathrm{I}_1\left((\kappa^2 z^2 - x^2)^{\frac{1}{2}}/2\kappa\right)}{(\kappa^2 z^2 - x^2)^{\frac{1}{2}}}\,\mathrm{d}z + f_b(t - x/\kappa)\mathrm{e}^{-x/2\kappa}\right), \end{aligned} \tag{4.14}$$

where I_1 is the first modified Bessel function and H is the Heaviside step function.

From the form of equation (4.8) we see that in order to solve our problem we will need to calculate σ^{0g}. An easy way to solve for σ^{0g} is to note that equation (4.5) also holds for σ^{0g}. Our initial conditions are the same, so $\sigma^{0g}(0, t)$ may be calculated from (3.1b):

$$\sigma^{0g}(0, t) = \frac{\kappa^2 \mathrm{e}^{-t}}{\gamma}\int_0^t f_b(z)\mathrm{e}^z\,\mathrm{d}z. \tag{4.15}$$

Now we may immediately solve for σ^{0g}, which is also valid only for $x < \kappa t$:

$$\sigma^{0g}(x, t) = \frac{x}{2}\int_{x/\kappa}^{t} \mathrm{e}^{-z/2}\sigma^{0g}(0, t - z)\frac{\mathrm{I}_1\left((\kappa^2 z^2 - x^2)^{\frac{1}{2}}/2\kappa\right)}{(\kappa^2 z^2 - x^2)^{\frac{1}{2}}}\,\mathrm{d}z + \sigma^{0g}(0, t - x/\kappa)\mathrm{e}^{-x/2\kappa}. \tag{4.16}$$

Since our region of interest for solving for our unknown functions is where $s < \kappa t$, we may omit the Heaviside function and equation (4.7) becomes

$$\frac{s}{2}\int_{s/\kappa}^{t} \mathrm{e}^{-z/2} f_b(t - z)\frac{\mathrm{I}_1\left((\kappa^2 z^2 - s^2)^{\frac{1}{2}}/2\kappa\right)}{(\kappa^2 z^2 - s^2)^{\frac{1}{2}}}\,\mathrm{d}z + f_b(t - s/\kappa)\mathrm{e}^{-s/2\kappa} = C_*. \tag{4.17}$$

However, note from (4.14) that there is a discontinuity around $x = \kappa t$ which our full equation (3.1a) cannot propagate. Therefore, we then let $\dot{s} = \kappa$ and $m = \frac{1}{2}$ in (3.8), which then becomes, to leading order,

$$-2\kappa C^{0+}_{\zeta\tau} = -\alpha_g \kappa C^{0+}_{\zeta\zeta\zeta} + \kappa C^{0+}_{\zeta}.$$

Letting $C^{0+} = \mathrm{e}^{-\tau/2}T^+$ and integrating once with respect to ζ, we have

$$-2T^+_{\tau} = -\alpha_g T^+_{\zeta\zeta}. \tag{4.18}$$

Our initial condition is found from (4.17) to be

$$T^{+}(\zeta, 0) = f_{\mathrm{b}}(0)\mathrm{H}(-\zeta). \tag{4.19}$$

Solving (4.18) subject to (4.19) yields

$$C^{0+}(\zeta, \tau) = \frac{f_{\mathrm{b}}(0)\mathrm{e}^{-\tau/2}}{2}\operatorname{erfc}\left(\frac{\zeta}{(2\alpha_{\mathrm{g}}\tau)^{\frac{1}{2}}}\right). \tag{4.20}$$

Now we will perform asymptotics in time in order to complete the solution of our problem.

5. Asymptotic results

5.1 *Small-time asymptotics*

We begin by performing small-time asymptotics. We postulate the following expansions of our unknown functions:

$$f_{\mathrm{b}}(t) \sim f_0, \qquad s(t) \sim s_0 t^n \quad (n \geqslant 1), \tag{5.1}$$

where our restriction on n comes from the fact that we wish to study super-Case II behaviour. Substituting (5.1) into (4.17), we have

$$\frac{f_0 s_0 t^n}{2}\int_{s/\kappa}^{t} \mathrm{e}^{-z/2}\frac{\mathrm{I}_1\left((\kappa^2 z^2 - s^2)^{\frac{1}{2}}/2\kappa\right)}{(\kappa^2 z^2 - s^2)^{\frac{1}{2}}}\,\mathrm{d}z + f_0\left(1 - \frac{s_0 t^n}{2\kappa}\right) \sim C_*.$$

We see immediately from the leading-order balance that

$$f_0 = C_*. \tag{5.2}$$

Using (5.2) and (4.15) in (4.16), we have

$$\sigma^{0\mathrm{g}}(s(t), t) \sim \frac{\kappa^2 C_*}{\gamma}\left(t - \frac{s_0 t^n}{\kappa}\right). \tag{5.3}$$

Using (5.3) and the leading orders of (4.12) in (4.8), we have

$$C_* - \frac{C_* s_0 t^{n-\frac{1}{2}}}{\pi^{\frac{1}{2}}} + \frac{t(1 - C_*)}{r} - \gamma\left(\frac{\kappa^2 C_*}{\gamma}\right)\left(t - \frac{s_0 t^n}{\kappa}\right) = C_*. \tag{5.4}$$

Matching the leading order of (5.4) gives

$$-\frac{C_* s_0 t^{n-\frac{1}{2}}}{\pi^{\frac{1}{2}}} + \frac{t(1 - C_*)}{r} - \kappa^2 C_* t + \kappa C_* s_0 t^n = 0. \tag{5.5}$$

Upon examination of (5.5), we see that the dominant balance is $n = \frac{3}{2}$, which yields

$$s_0 = \left(\frac{1 - C_*}{C_* r} - \kappa^2\right)\pi^{\frac{1}{2}}. \tag{5.6}$$

Since $n = \frac{3}{2}$, we have automatically that $s(t) < \kappa t$. Note from equation (5.6) that in order to have $s_0 > 0$ as required, the compatibility condition in (4.2) must be true.

Summarizing our results, we have the following, where we recall (3.9) and (3.10):

$$C^{0\mathrm{r}}(x, t) \sim T^{\mathrm{r}}(x, t) + \left[C_* - T^{\mathrm{r}}(s(t), t)\right] \exp\left(\frac{x - s(t)}{\epsilon\dot{s}}\right), \tag{5.7a}$$

$$T^{\mathrm{r}}(x, t) = \begin{cases} \left(\dfrac{2t + x^2}{2r} + C_*\right) \operatorname{erfc}\left(\dfrac{x}{2t^{\frac{1}{2}}}\right) - \dfrac{(1 - C_*)x}{r}\left(\dfrac{t}{\pi}\right)^{\frac{1}{2}} \exp\left(-\dfrac{x^2}{4t}\right) & \text{if } t < r, \\ \operatorname{erfc}\left(\dfrac{x}{2t^{\frac{1}{2}}}\right) + (1 - C_*)\left(1 - \dfrac{x^2 + 2t}{2r}\right)\left[\operatorname{erf}\left(\dfrac{x}{2t^{\frac{1}{2}}}\right) - \operatorname{erf}\left(\dfrac{x}{2(t - r)^{\frac{1}{2}}}\right)\right] & \\ \quad - \dfrac{(1 - C_*)x}{r\pi^{\frac{1}{2}}}\left[t^{\frac{1}{2}} \exp\left(-\dfrac{x^2}{4t}\right) - (t - r)^{\frac{1}{2}} \exp\left(-\dfrac{x^2}{4(t - r)}\right)\right] & \text{if } t > r, \end{cases} \tag{5.7b}$$

$$\sigma^{0-}(x, t) = \sigma^{0\mathrm{g}}(s(t), t) \exp\left(\frac{x - s(t)}{\dot{s}}\right). \tag{5.7c}$$

Note that the expressions in (5.7) are good for all time.

We also have

$$t \longrightarrow 0$$

$$s(t) \sim \left(\frac{1 - C_*}{C_* r} - \kappa^2\right) t^{\frac{3}{2}} \pi^{\frac{1}{2}}, \tag{5.8}$$

$$x < \kappa t$$

$$C^{0\mathrm{g}}(x, t) \sim$$
$$C_*\left(\frac{x}{2}\int_{x/\kappa}^{t} \mathrm{e}^{-z/2} \frac{\mathrm{I}_1\left((\kappa^2 z^2 - x^2)^{\frac{1}{2}}/2\kappa\right)}{(\kappa^2 z^2 - x^2)^{\frac{1}{2}}}\,\mathrm{d}z + \mathrm{e}^{-x/2\kappa}\right) - \frac{C_* \mathrm{e}^{-t/2}}{2} \operatorname{erfc}\left(\frac{\kappa t - x}{(2\alpha_{\mathrm{g}}\epsilon t)^{\frac{1}{2}}}\right), \tag{5.9a}$$

$$\sigma^{0\mathrm{g}}(x, t) \sim$$
$$\frac{C_* \kappa^2}{\gamma}\left(\frac{x}{2}\int_{x/\kappa}^{t} \mathrm{e}^{-z/2}\left(1 - \mathrm{e}^{-(t - z)}\right) \frac{\mathrm{I}_1\left((\kappa^2 z^2 - x^2)^{\frac{1}{2}}/2\kappa\right)}{(\kappa^2 z^2 - x^2)^{\frac{1}{2}}}\,\mathrm{d}z + \left(1 - \mathrm{e}^{-(t - x/\kappa)}\right)\mathrm{e}^{-x/2\kappa}\right), \tag{5.9b}$$

$$x > \kappa t$$

$$C^{0\mathrm{g}}(x, t) \sim \frac{C_* \mathrm{e}^{-t/2}}{2} \operatorname{erfc}\left(\frac{x - \kappa t}{(2\alpha_{\mathrm{g}}\epsilon t)^{\frac{1}{2}}}\right). \tag{5.10}$$

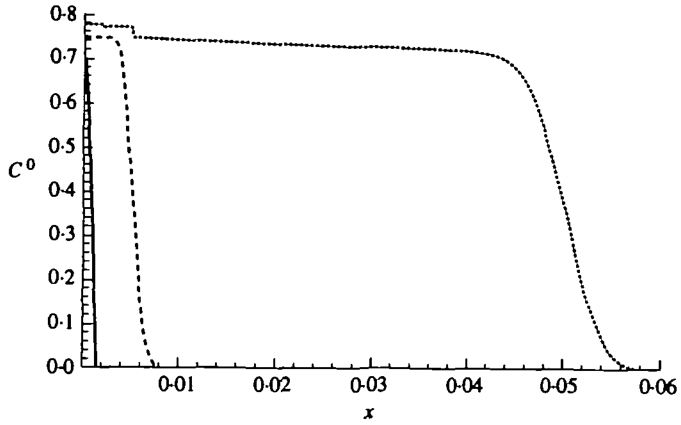

FIG. 1. Concentration profiles: $C_* = 0{\cdot}75$, $r = 1$, $\gamma = 0{\cdot}5$, $\alpha_g = 1$, $\epsilon = 0{\cdot}0001$, $\kappa = 0{\cdot}5$. In decreasing order of darkness: $t = 0{\cdot}001, 0{\cdot}01, 0{\cdot}1$.

Figure 1 shows graphs of our concentration field expansions for small times (though they are large enough that $\epsilon = o(t)$) and for parameters which satisfy (4.1) and (4.2). Note that we see a three-stage profile. The concentration starts at 0, then rises through the boundary layer around $x = \kappa t$. The boundary layer doesn't seem that sharp since our x scale is so small. Then there is a relatively flat region in the glassy polymer until the second boundary layer brings the concentration from the transition value C_* to the rubbery region described by (5.7b).

Figure 2 shows graphs of our stress field for the same parameters and times as before. The case where $t = 0{\cdot}001$ appears only as an extra pixel near $(0, 0)$. Note that we have a maximum at $x = s(t)$ as hypothesized earlier. Therefore, the stress which builds up in the polymer as the penetrant builds up in the glassy region is

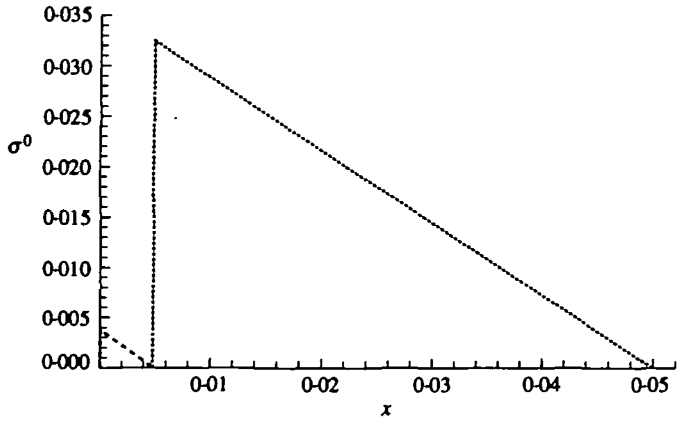

FIG. 2. Stress profiles: $C_* = 0{\cdot}75$, $r = 1$, $\gamma = 0{\cdot}5$, $\alpha_g = 1$, $\epsilon = 0{\cdot}0001$, $\kappa = 0{\cdot}5$. In decreasing order of darkness: $t = 0{\cdot}001, 0{\cdot}01, 0{\cdot}1$.

nearly totally released when the polymer enters the rubbery state. Note also that there is no discontinuity at $x = \kappa t$ since $\sigma^{0g}(0, 0) = 0$.

5.2 *Large-time asymptotics*

Next we perform large-time asymptotics. We begin by noting that, for long time, equation (4.5) behaves like

$$\kappa^2 T^g_{xx} = T^g_t + o(1), \tag{5.11}$$

and equation (3.2b) behaves like

$$\sigma^{0g} = \frac{\kappa^2}{\gamma} C^{0g}. \tag{5.12}$$

Hence, using equation (5.12) evaluated at the front, equation (4.8) becomes

$$T^r\big(s(t), t\big) = C_*(1 + \kappa^2). \tag{5.13}$$

From our condition that $C \leqslant 1$, we see that (4.1) must hold. Then, using equation (4.13) in (5.13), we see that

$$\operatorname{erfc}\left(\frac{s}{2t^{\frac{1}{2}}}\right) + (1 - C_*)\left(1 - \frac{s^2 + 2t}{2r}\right)\left[\operatorname{erf}\left(\frac{s}{2t^{\frac{1}{2}}}\right) - \operatorname{erf}\left(\frac{s}{(t - r)^{\frac{1}{2}}}\right)\right]$$
$$- \frac{(1 - C_*)s}{r\pi^{\frac{1}{2}}}\left[t^{\frac{1}{2}} \exp\left(-\frac{s^2}{4t}\right) - (t - r)^{\frac{1}{2}} \exp\left(-\frac{s^2}{4(t - r)}\right)\right] = C_*(1 + \kappa^2).$$

The only way to get an $O(1)$ balance is if $s(t) \sim 2s_\infty t^{\frac{1}{2}}$. In this case, when we asymptotically expand for large time, only the first term contributes to leading order, so we have

$$\operatorname{erfc} s_\infty = C_*(1 + \kappa^2). \tag{5.14}$$

Now we wish to expand our glassy solution. From the form of (5.11), we see that the operator in (4.11) is now a long-time asymptotic solution in the *glassy* region, so we have

$$T^r(x, t) = \frac{x}{2(\pi\gamma)^{\frac{1}{2}}} \int_0^t \frac{f_b(z)}{(t - z)^{\frac{3}{2}}} \exp\left(-\frac{x^2}{4\gamma(t - z)}\right) dz. \tag{5.15}$$

We see that the dominant contribution to (5.15) for $x \propto t^{\frac{1}{2}}$ and t large is from the neighbourhood of $z = t$. Therefore, we postulate the following expansion:

$$f_b(t) \sim f_\infty + o(1) \quad \text{as } t \to \infty.$$

Substituting our expression into (5.8), we immediately see that

$$T^g \sim f_\infty \operatorname{erfc}\left(\frac{x}{2\kappa t^{\frac{1}{2}}}\right). \tag{5.16}$$

Using (5.16) in (4.8), we have

$$f_\infty = \frac{C_*}{\operatorname{erfc}(s_\infty/\kappa)}. \tag{5.17}$$

Summarizing our results, we have the following:

$$t \to \infty$$

$$s(t) \sim 2s_\infty t^{\frac{1}{2}}, \qquad \operatorname{erfc} s_\infty = C_*(1+\kappa^2), \tag{5.18}$$

$$x < \kappa t$$

$$C^{0g}(x,t) \sim \frac{C_*}{\operatorname{erfc}(s_\infty/\kappa)}\left(\frac{x}{2}\int_{x/\kappa}^{t} e^{-z/2}\frac{I_1\left((\kappa^2z^2-x^2)^{\frac{1}{2}}/2\kappa\right)}{(\kappa^2z^2-x^2)^{\frac{1}{2}}}\,dz + e^{-x/2\kappa}\right) - \frac{C_* e^{-t/2}}{2\operatorname{erfc}(s_\infty/\kappa)}\operatorname{erfc}\left(\frac{\kappa t - x}{(2\alpha_g\epsilon t)^{\frac{1}{2}}}\right), \quad 7 \tag{5.19a}$$

$$\sigma^{0g}(x,t) \sim \frac{C_*\kappa^2}{\gamma\operatorname{erfc}(s_\infty/\kappa)}\left(\frac{x}{2}\int_{x/\kappa}^{t} e^{-z/2}\frac{I_1\left((\kappa^2z^2-x^2)^{\frac{1}{2}}/2\kappa\right)}{(\kappa^2z^2-x^2)^{\frac{1}{2}}}\,dz + e^{-x/2\kappa}\right), \tag{5.19b}$$

$$x > \kappa t$$

$$C^{0g}(x,t) \sim \frac{C_* e^{-t/2}}{2\operatorname{erfc}(s_\infty/\kappa)}\operatorname{erfc}\left(\frac{\kappa t - x}{(2\alpha_g\epsilon t)^{\frac{1}{2}}}\right). \tag{5.20}$$

Figure 3 shows graphs of our long-time concentration field expansions for the same parameters as before. The three-stage behaviour is not as pronounced in this model since $C^{0g}(\kappa t, t)$ is exponentially decaying. The clearest picture of the sharp front at $x = \kappa t$ is shown for $t = 6$. The glassy region has a nearly Fickian profile, as does the rubbery region, but they are still separated by the sharp boundary layer at $x = s(t)$.

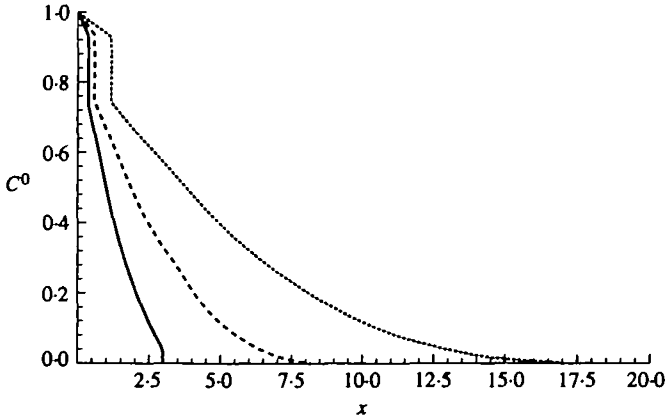

FIG. 3. Concentration profiles: $C_* = 0{\cdot}75$, $r = 1$, $\gamma = 0{\cdot}5$, $\alpha_g = 1$, $\epsilon = 0{\cdot}0001$, $\kappa = 0{\cdot}5$. In decreasing order of darkness: $t = 6, 24, 96$.

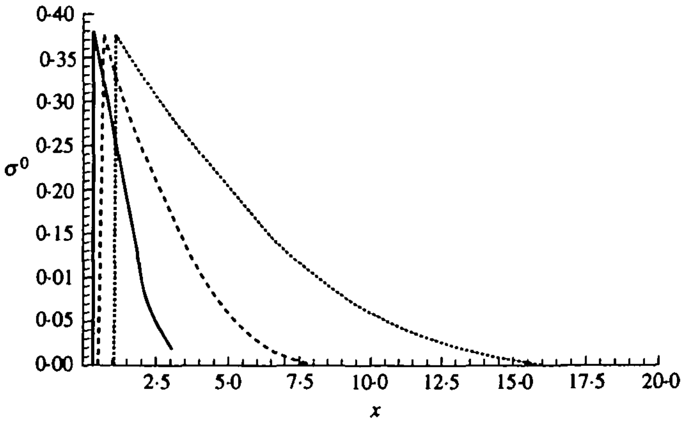

FIG. 4. Stress profiles: $C_* = 0{\cdot}75$, $r = 1$, $\gamma = 0{\cdot}5$, $\alpha_g = 1$, $\epsilon = 0{\cdot}0001$, $\kappa = 0{\cdot}5$. In decreasing order of darkness: $t = 6, 24, 96$.

Figure 4 shows graphs of our long-time stress field expansions for the same parameters as before. Note the gap that arises for $t = 6$. This is due to the fact that Fig. 4 is a graph of (5.19b), which is not uniformly valid up to the front $x = \kappa t$. However, the error behaves like $e^{-t/2}$, and thus becomes negligible for the larger values of t. Once again note the slow Fickian rise of the stress, which reaches its maximum at $x = s(t)$ before plunging quickly down to 0.

6. Conclusions

When discussions about non-Fickian polymer-penetrant systems take place, the subject of the molecular diffusion coefficient naturally arises. It is known that in some systems the diffusion coefficient greatly increases as the polymer changes from the glassy to the rubbery state. What is only surmised is the degree to which such a change influences the qualitative structure of the solution. The results in this paper shed new light upon this subject.

The moving boundary condition which resulted from our model was highly unusual, due to the presence of terms like $\dot{s}$ in the denominator of one of our terms. Therefore, it was not solvable by similarity variables, and Boley's method had to be used. The moving boundary condition involved matching two different operators at the front, rather than the same operator with different coefficients. The solution for the concentration exhibited two fronts: a leading subcharacteristic front $x = \kappa t$, as well as our true front $x = s(t)$.

Since $D(C)$ had vastly different values on either side of the front, this caused a large difference in the size of the flux from the glassy and rubbery regions. This discrepancy manifested itself by making the stress in the glassy region an order of magitude larger than the stress in the rubbery region. The parameter a did not play a role here to leading order; hence the flux used up in the phase transition is not a dominant effect. The dominant balance is between the concentration and stress contributions to the flux. This produced a situation where the stress had its maximum *exactly* at the secondary front. However, this behaviour is directly dependent on our choice of $D(C)$ as having a discontinuity at the phase transition. Therefore, this is where our assumption of a phase-transition model played a pivotal role. If $D(C)$ were made to depend smoothly on C throughout all phases of the polymer, the flux contributions would be of roughly the same size at the moving front. Regardless, other models which do not incorporate a phase transition, but do have a rapidly increasing diffusion coefficient, still have steep fronts (Fu & Durning, 1993).

We note that, even after making several simplifying assumptions, our resulting equations (2.12–2.16) are extremely versatile, for many other types of non-Fickian behaviour have been modelled using the same equations (Edwards, 1994).

In this paper, we chose to use analytical and asymptotic methods rather than numerical ones. Obviously no choice is without disadvantages. We sacrificed computed profiles for all x and t and avoided the challenges which a numerical implementation of our problem would entail. In addition, attacking the problem analytically necessitated making many simplifying assumptions. However, the analytical problem is certainly not without challenges, and by remaining true to the analytics, we now have solutions with explicit dependence on various physical and state parameters. Having these dependences explicitly derived can provide guidance to chemical engineers who may wish to check our results in the laboratory or extend our work to more complicated geometries and systems.

Acknowledgements

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