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Traveling Waves for Anomalous Diffusion in Polymers

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Abstract—Case II diffusion of a penetrant through a polymer matrix is characterized by constant front speed. Hence, a traveling-wave analysis is appropriate for the model equations. For the previously validated model analyzed here, conditions on the molecular and stress diffusion coefficients are obtained which guarantee the existence of a traveling wave. Conditions are derived under which an interior maximum in the stress develops. An exact solution for the concentration and stress fields is derived for a special case.

Keywords—Traveling-wave solutions, Polymer-penetrant systems, Case II diffusion.

1. INTRODUCTION

The designer properties of polymers have made them a preferred material in many industries. For instance, polymers are routinely used in conjunction with various penetrants in gaseous or liquid form. However, these systems routinely exhibit anomalous diffusion behavior, such as "Case II diffusion" [1,2], where a sharp concentration front moves with constant speed. Such behavior can be seen in the wetting of hydrogels [3].

There are several different models for this phenomenon [4–6]; the one we use arises from postulating [7] that the chemical potential μ is a function of both $\tilde{C}$, the penetrant concentration, and another variable $\tilde{\sigma}$. Using the facts that the flux $J = -\mu_x$ and $\tilde{C}_t = -J_x$, we obtain

$$\tilde{C}_t = \left[D\left(\tilde{C}\right) \tilde{C}_x + E\left(\tilde{C}\right) \tilde{\sigma}_x \right]_x . \tag{1.1a}$$

Here $D(\tilde{C})$ is the standard molecular diffusion coefficient and $E(\tilde{C})$ is the stress diffusion coefficient, which are nonnegative and nondecreasing.

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An important physical process in Case II diffusion is a viscoelastic stress in the polymer network [8], so we require that $\tilde{\sigma}$ (the stress) follows a viscoelastic evolution equation [7,9]:

$$\tilde{\sigma}_t + \beta(C)\tilde{\sigma} = \eta\tilde{C} + \nu\tilde{C}_t. \tag{1.1b}$$

In this way $\tilde{\sigma}$ can be thought of as an osmotically-induced viscoelastic "swelling pressure" [10], which is related to the trace of the stress tensor in the polymer network [7,9–11]. Here $\beta(\tilde{C}) > 0$ is the nondecreasing relaxation time for the polymer (treated as a viscoelastic solid).

2. THE TRAVELING-WAVE SYSTEM

Both numerical simulations [12] and experimental data (as discussed above) indicate that fronts moving with constant speed characterize Case II diffusion. Thus, following [5,11], we look for traveling-wave solutions of (1.1) corresponding to a front saturating a dry, unstressed polymer. If the saturation value is 1, the boundary conditions are given by

$$\tilde{C}(\infty,t) = 0, \qquad \tilde{\sigma}(\infty,t) = 0, \qquad \tilde{C}(-\infty,t) = 1. \tag{2.1}$$

Since equations (1.1) can be combined into a single third-order partial differential equation for $\tilde{C}$ [9], (2.1) is sufficient to make our problem well posed.

To find traveling-wave solutions, we let

$$\tilde{C}(x,t) = C(z), \quad \tilde{\sigma}(x,t) = \sigma(z), \quad z = x - Vt, \qquad V > 0. \tag{2.2}$$

All derivatives of C and σ vanish as $z \to \pm\infty$, so substituting (2.2) into (1.1b) and (2.1) yields

$$-V\sigma' + \beta(C)\sigma = \eta C - V\nu C', \tag{2.3}$$

$$(C,\sigma)(\infty) = (0,0), \qquad (C,\sigma)(-\infty) = \left(1, \frac{\eta}{\beta(1)}\right) \equiv (1,\sigma_*), \tag{2.4}$$

which yields the necessary value for the upstream stress.

Substituting (2.2) into (1.1a), we obtain the following:

$$-VC = D(C)C' + E(C)\sigma', \tag{2.5}$$

where we have used the downstream boundary conditions. If $D(0) = E(0) = 0$, then it may be the case that $C(z_*) = 0$ for some finite z_*, and, moreover, it is possible to obtain the physically unreasonable case where $C(z) < 0$ for some z. Therefore, we require that one of D or E be positive. In addition, in order for $(1,\sigma_*)$ to be a fixed point, one of $D(1)$ or $E(1)$ must diverge so that the corresponding product in (2.5) remains finite. This may seem like an unreasonable assumption, but in [13] the authors perform a similar analysis to obtain solutions of the type sought. If we take the more physically reasonable case where either $D(1)$ or $E(1) \gg 1$, we will obtain solutions which are nearly like traveling waves in character.

To analyze system (2.3),(2.5) more completely, we write it as a phase plane system:

$$C' = \frac{\left[-V^2 + \eta E(C)\right] C - \beta(C)E(C)\sigma}{V[D(C) + \nu E(C)]}, \tag{2.6a}$$

$$\sigma' = \frac{-\left[\eta D(C) + \nu V^2\right] C + \beta(C)D(C)\sigma}{V[D(C) + \nu E(C)]}. \tag{2.6b}$$

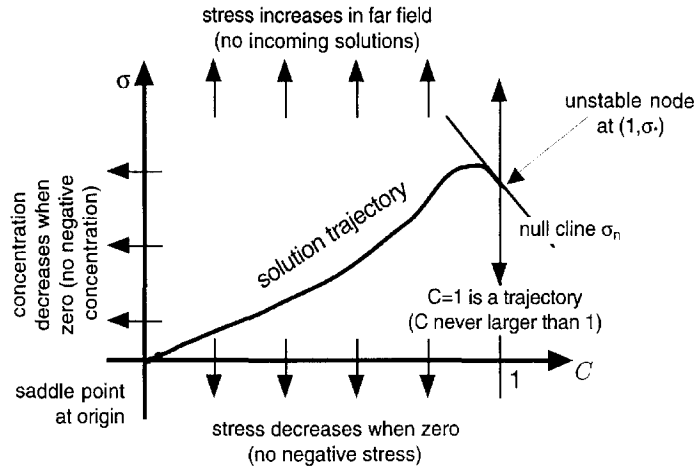

Figure 1. Schematic of phase plane.

Then our problem reduces to finding a heteroclinic orbit in the C-σ plane between the two points in (2.4) (see the schematic of the phase plane in Figure 1).

A linear analysis of (2.6) about the origin shows that the determinant of the Jacobian is given by $-\beta(0)/[D(0)+\nu E(0)] < 0$, so the origin is a saddle, and our traveling wave solution corresponds to one of the two stable trajectories. From (2.6b), we see that the null cline $\sigma_n(C)$ along which $\sigma' = 0$ is given by

$$\sigma_n(C) = \frac{\left[\eta D(C) + \nu V^2\right] C}{\beta(C) D(C)}. \tag{2.7a}$$

Since solutions with $\sigma < \sigma_n$ have $\sigma' < 0$, any solution with $\sigma < 0$ for $C > 0$ will not return to the origin, so our traveling-wave solution always has $\sigma > 0$. Note from (2.6a) that $C' < 0$ when

$$\beta(C)E(C)\sigma > \left[-V^2 + \eta E(C)\right] C. \tag{2.7b}$$

Thus, any solution with $C < 0$ for small enough σ will not return to the origin, and hence, our traveling-wave solution always has $C > 0$. Thus, the trajectory must approach the origin from the first quadrant (see Figure 1). If a heteroclinic orbit does not exist, the stable saddle point trajectory must originate from $\sigma = \infty$. But trajectories with large σ go to infinity since $\sigma > \sigma_n$ and $\sigma' > 0$. Thus, there must be a heteroclinic orbit as shown in Figure 1.

If we take $D(1) = E(1) = \infty$, $C = 1$ becomes a fixed line, inconsistent with our wish that $(1, \sigma_*)$ be the only upstream fixed point. If we take $E(1) = \infty$, then at $C = 1$ (2.6a) becomes $C' = [\eta - \beta(1)\sigma]/V\nu$, which is positive for $\sigma < \sigma_*$. This is the case of *sorption overshoot* [14], where the concentration can exceed the saturation value. We prefer to examine the standard case where $C < 1$ for all z, so we take $D(1) = \infty$ as in [13]. Since $C'(1) = 0$ for all σ, $C = 1$ is a trajectory in the phase plane, and our solution always has $C < 1$ for finite z. To summarize, in order to obtain physically realistic traveling waves, we take $D(0)E(0) \neq 0$, $D(1) = \infty$.

3. SPECIFIC CASES

To study the fixed point $(1, \sigma_*)$ in detail, we choose a specific functional form for $D(C)$:

$$D(C) = \frac{D_0}{1 - C}, \qquad D_0 > 0, \tag{3.1}$$

in which case (2.6) becomes

$$\begin{aligned} C' &= (1 - C)\frac{[-V^2 + \eta E(C)]C - \beta(C)E(C)\sigma}{V[D_0 + \nu(1 - C)E(C)]}, \\ \sigma' &= \frac{-[\eta D_0 + \nu V^2(1 - C)]C + \beta(C)D_0\sigma}{V[D_0 + \nu(1 - C)E(C)]}. \end{aligned} \tag{3.2}$$

A linear analysis of (3.2) about $(1, \sigma_*)$ shows that the determinant of the Jacobian is $\beta(1)/D_0 > 0$. Since $C = 1$ is a trajectory, $(1, \sigma_*)$ must be a node. The trace of the Jacobian is $[\beta(1)/V] + (V/D_0) > 0$, so $(1, \sigma_*)$ is an unstable node, as required.

To construct our plots, we choose the following functional forms and parameters:

$$E(C) = E_0 C, \qquad E_0 > 0, \tag{3.3a}$$

$$\beta(C) = 1 + \beta_0 C, \qquad \beta_0 > 0, \tag{3.3b}$$

$$D_0 = 1, \qquad E_0 = 1, \qquad \nu = 30, \qquad V = 1. \tag{3.4}$$

Figure 2 shows solution curves for varying η; note that an internal stress maximum forms for some η. Figure 1 shows that, if $\sigma_n'(1) > 0$, any trajectory with $\sigma > \sigma_*$ always has $\sigma' > 0$. Thus, for an internal maximum to occur, $\sigma_n'(1) < 0$, which for system (3.2) means that

$$\eta \left[1 - \frac{\beta'(1)}{\beta(1)}\right] < \frac{\nu V^2}{D_0}. \tag{3.5}$$

As η increases, the upstream stress value increases, so the stress buildup during transport will not create an internal maximum.

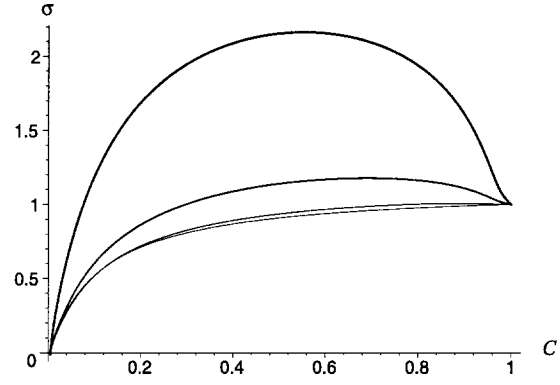

Figure 2. Phase plane trajectories for parameters in (3.4), $\beta_0 = 9$, and $\eta = 10$, 40, 160, 640 (in decreasing order of thickness).

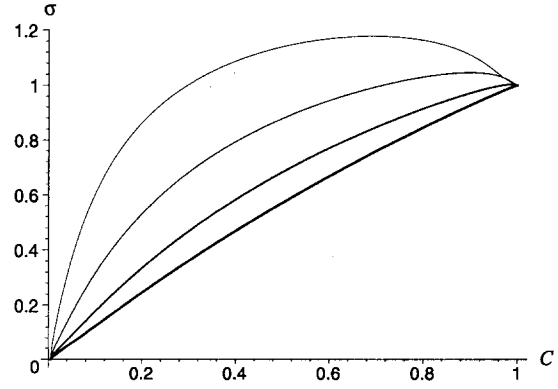

Figure 3. Phase plane trajectories for parameters in (3.4), $\eta = 40$, and $\beta_0 = 1/3$, 1, 3, 9 (in decreasing order of thickness).

Figure 3 shows solution curves for varying β_0. Increasing β_0 decreases the relaxation time, so imposed stresses will not have time to decay away. Thus, internal maxima will form consistent with (3.5), which shows that such maxima depend on the sensitivity of β to C at saturation.

To demonstrate our solution behavior more concretely, we specialize to the case where

$$\beta(C) = \frac{\eta}{\nu}. \tag{3.6}$$

Substituting (3.6) into (2.3), we obtain

$$-V\nu\sigma' + \eta\sigma = \nu\left(\eta C - V\nu C'\right) \implies \sigma = \nu C, \tag{3.7}$$

where we have used (2.4). Substituting (3.1), (3.3a), and (3.7) into (2.5), we obtain an equation which may be integrated. Choosing $C(0) = 1/2$ yields the implicit solution

$$\frac{C}{1-C} = \exp\left(-V_* z + \nu_*\left(C - \frac{1}{2}\right)\right), \qquad V_* = \frac{V}{D_0}, \quad \nu_* = \frac{\nu E_0}{D_0}. \tag{3.8}$$

Figure 4 shows a graph of the solution $C(z)$ in (3.8) for constant V_* and varying ν_*. This can occur when either ν or E_0 varies. If ν increases, the stress increases. If E_0 increases, the stress diffusion coefficient increases. In either case, the stress diffusion term is larger in (1.1a), and we would expect a less steep profile, as verified in the figure.

Figure 5 shows a graph of the solution $C(z)$ in (3.8) for constant ν_* and varying V_*. As the velocity of the traveling wave increases, the relative time for diffusion decreases, and we expect a steeper profile, as shown in the figure.

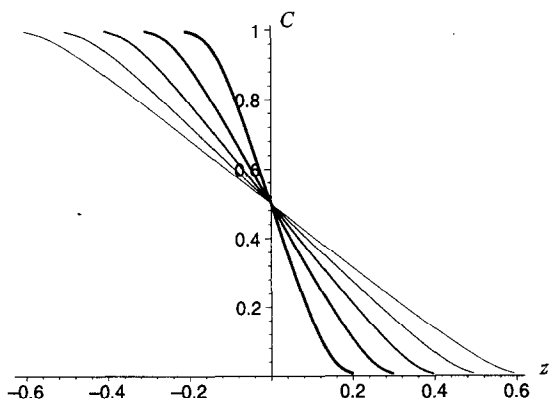

Figure 4. Graph of (3.8) with $V_* = 50$, $\nu_* = 10$, 20, 30, 40, 50 (in decreasing order of thickness).

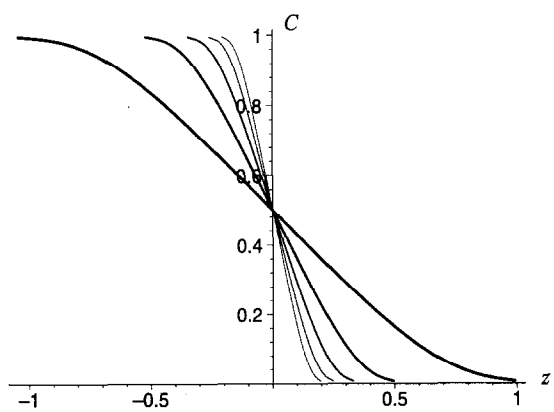

Figure 5. Graph of (3.8) with $\nu_* = 10$, $V_* = 10$, 20, 30, 40, 50 (in decreasing order of thickness).

4. CONCLUSIONS

Since concentration fronts move with constant speed in Case II diffusion, it is natural to look for traveling-wave solutions of the governing equations. By analyzing model (1.1), we showed that for a true traveling-wave solution to exist, one of the diffusion coefficients in (1.1a) must diverge as the polymer saturates. However, large diffusion coefficients will provide solutions that behave quite similarly to traveling waves.

Equation (3.5) shows that if the relaxation time is small, the stress will have an internal maximum, as illustrated in Figures 2 and 3. This occurs because stress accumulates inside the polymer faster than it can relax away. Though in general explicit solutions of (2.6) do not exist, we calculated an explicit solution for a specific case which exhibits the behavior described above.

REFERENCES

1. N. Thomas and A.H. Windle, Transport of methanol in poly-(methyl-methocrylate), *Polymer* **19**, 255–265, (1978).
2. N. Thomas and A.H. Windle, A theory of Case II diffusion, *Polymer* **23**, 529–542, (1982).
3. S.C. Ji and J.D. Ding, The wetting process of a dry polymeric hydrogel, *Polymer J.* **34**, 267–270, (2002).
4. G. Astarita and G.C. Sarti, Class of mathematical models for soprtion of swelling solvents in glassy polymers, *Polym. Eng. Sci.* **18**, 388–395, (1978).
5. C.J. Durning, D.A. Edwards and D.S. Cohen, Perturbation analysis of Thomas' and Windle's model of Case II transport, *AIChE J.* **42**, 2025–2035, (1996).
6. T. Qian and P.L. Taylor, From the Thomas-Windle model to a phenomenological description of Case-II diffusion in polymers, *Polymer* **4**, 7159–7163, (2000).
7. D.A. Edwards and D.S. Cohen, A mathematical model for a dissolving polymer, *AIChE J.* **18**, 2345–2355, (1995).
8. H.L. Frisch, Sorption and transport in glassy polymers—A review, *Polymer Engr. and Sci.* **20**, 2–13, (1980).
9. D.A. Edwards, Constant front speed in weakly diffusive non-Fickian systems, *SIAM J. Appl. Math.* **55**, 1039–1058, (1995).
10. J.C. Wu and N.A. Peppas, Modeling of penetrant diffusion in glassy polymers with an integral sorption Deborah number, *J. Polym. Sci. B* **31**, 1503–1518, (1993).
11. T.P. Witelski, Traveling wave solutions for case II diffusion in polymers, *J. Polym. Sci. B* **34**, 118–150, (1996).
12. T.Z. Fu and C.J. Durning, Numerical simulation of Case II transport, *AIChE J.* **39**, 1030–1044, (1993).
13. C.Y. Hui, K.C. Wu, R.C. Lasky and E.J. Kramer, Case II diffusion in polymers. II. Steady state front motion, *J. Appl. Phys.* **61**, 5137–5149, (1987).
14. N.S. Kalospiros, R. Ocone, G. Astarita and J.H. Meldon, Analysis of anomalous diffusion and relaxation in solid polymers, *Ind. Eng. Chem. Res.* **30**, 851–864, (1991).