

# Transient Instability in Case II Diffusion

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**ABSTRACT:** A well-known model of one-dimensional Case II diffusion is reformulated in two dimensions. This 2-D model is used to study the stability of 1-D planar Case II diffusion to small spatial perturbations. An asymptotic solution based on the assumption of small perturbations and a small driving force is developed. This analysis reveals that while 1-D planar diffusion is indeed asymptotically stable to small spatial perturbations, it may exhibit a transient instability. That is, although any small perturbation is damped out over sufficiently long times, the amplitude of any perturbation initially grows with time. © 1998 John Wiley & Sons, Inc. *J Polym Sci B: Polym Phys* 36: 2941–2947, 1998  
**Keywords:** Case II diffusion; stability; multidimensional Stefan-like Problem; asymptotic analysis

## INTRODUCTION

In the last few decades several models have been proposed to describe the diffusion of solutes in glassy polymers. Thus far, the great diversity of polymers and their properties has precluded the formulation of a general model applicable to the study of diffusion in any given polymer. Rather classes of polymers have been recognized that share common properties. The phenomenon known as Case II diffusion characterizes one of these classes; it is defined by the presence of a sharp discontinuity within the polymer which separates a glassy region with negligible solute concentration from a swollen rubbery region with high solute content. Further, Case II diffusion is said to occur when this front moves with near constant speed.

Alfrey et al.,<sup>1</sup> were among the first researchers to consider the mathematical modelling of swelling polymers subjected to this anomalous diffusion. They noted that, for certain polymers the swelling behavior, and the stresses thereby created were of primary interest. Later researchers, such as Cohen and Erneux,<sup>2</sup> or Edwards and Co-

hen,<sup>3</sup> have continued this line of inquiry, studying the coupling of stress and diffusion in polymer penetrant systems.

A second approach to the mathematical modelling of Case II diffusion was proposed by Astarita and Sarti.<sup>4</sup> They captured the phenomena of non-Fickian diffusion by incorporating a phenomenological law into a one-dimensional Stefan-like formulation of a moving boundary problem describing solute penetration. Detailed mathematical analysis of models incorporating the phenomenological power law formulation of Astarita and Sarti were carried out.<sup>5–7</sup> In the first of these reports, Fasano et al. proved well-posedness and derived qualitative properties of the solution. In the second, Cohen and Erneux<sup>6</sup> derived asymptotic approximations to the solutions for a general class of models, while Guidotti<sup>7</sup> proved the validity of these approximations.

Nonetheless, research to date has been directed toward understanding the behavior of solutions to one-dimensional models, while of course, real polymers are three dimensional! The question of the stability of one-dimensional planar diffusion to two-dimensional spatial perturbations is of interest. In fact, in many applications, such as in controlled release pharmaceuticals, the polymers utilized are very thin, suggesting that two-dimensional effects

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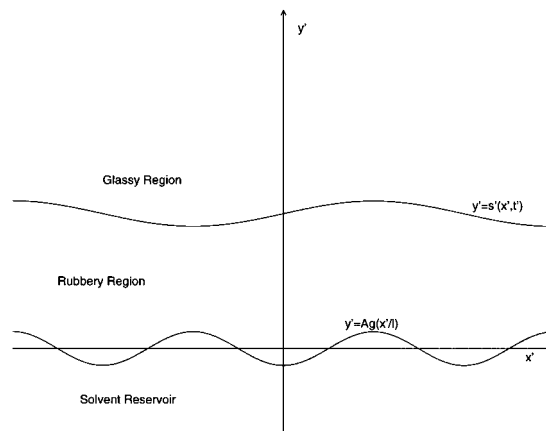
may be relevant. We begin to investigate these questions. First, we formulate a model, again based on the Astarita and Sarti phenomenological law, for two-dimensional diffusion of a solute in a glassy polymer. In particular, we study the stability of one-dimensional planar diffusion by imposing infinitesimal spatial perturbations on both the topography of the polymer film and on the concentration of the solute to which it is exposed. We utilize the small nature of the perturbations in the development of an asymptotic theory. We show that the one-dimensional front is asymptotically stable to an arbitrary infinitesimal perturbation, but that such perturbations may greatly affect the temporal evolution of these fronts. In fact, we show that if the perturbation is resolved into Fourier modes, each modal disturbance initially grows in time. Further, we find that higher order modes decay faster than lower order modes. Consequently, when observed at finite time, the moving front may exhibit a characteristic long wavelength disturbance. This type of behavior has been observed in the study of solidification of pure metals.<sup>8</sup> There, this behavior, which may be termed “practical instability,” may have serious consequences for the manufacturing process. We consider this possibility in the polymer case and discuss a method for mitigating this effect.

## FORMULATION OF THE MODEL

In this section, we reformulate the one-dimensional model of sorption of solutes in glassy polymers proposed by Astarita and Sarti<sup>4</sup> to allow for two-dimensional effects. We begin by assuming that a polymer half-space is exposed to a reservoir of solute comprised of a small molecule capable of diffusing into the polymer. The polymer is assumed to fill the region above the curve  $y' = Ag(x'/l)$  and to be separated by a sharp interface in two parts (see Fig. 1). The first part, a swollen rubbery portion, occupies the region  $Ag(x'/l) < y' < s'(x', t')$  and we assume that solute is free to diffuse through this area. Accordingly, we assume that, in this region, solute concentration satisfies the diffusion equation

$$\frac{\partial C}{\partial t'} = D\Delta' C \quad \text{in } Ag(x'/l) < y' < s'(x', t) \quad (1)$$

where  $C$  denotes solute concentration,  $D$  is the diffusivity of the rubbery region, and  $\Delta'$  is the two-dimensional Laplacian operator. Next, we



**Figure 1.** Sketch of the model geometry.

impose boundary conditions on each side of the rubbery portion. Along the outer polymer boundary, i.e., where the polymer is exposed to solute, we impose the constant concentration condition

$$C(x', Ag(x'/l), t') = C_0 + C_1 f(x'/l). \quad (2)$$

Note that this condition embodies two distinct two dimensional effects. First, the surface of the polymer is assumed to have a topography defined by  $g(x'/l)$ , and second, the solute concentration is allowed to vary in the  $x'$  direction as defined by  $f(x'/l)$ . Then, at the moving front we impose the following conditions

$$C \frac{\partial s'}{\partial t'} = -D \frac{\partial C}{\partial y'} + D \frac{\partial s'}{\partial x'} \frac{\partial C}{\partial x'} \quad \text{at } y' = s' \quad (3)$$

$$\frac{\partial s'}{\partial t'} = \left( 1 + \left( \frac{\partial s'}{\partial x'} \right)^2 \right)^{1/2} k(C - C^*)^m \quad \text{at } y' = s'. \quad (4)$$

Note that eq. (3) is simply a mass balance applied across the moving front, while (4) is a generalization of the phenomenological law proposed by Astarita and Sarti<sup>4</sup> to two dimensions. In particular, following Astarita and Sarti, we assume that front velocity is proportional to the excess concentration over some equilibrium value  $C^*$ . In contrast to the one-dimensional case, the phenomenological law is applied in the direction of the normal velocity, hence the presence of the square root term. We note that both  $k$  and  $m$  are phenomenological quantities. Finally, we impose the initial condition

$$s'(x', 0) = Ag(x'/l). \quad (5)$$

Next, we introduce scaled variables and re-write our governing equations in dimensionless form. First, we choose a characteristic length,  $l$ , and define

$$x = \frac{x'}{l}, \quad y = \frac{y'}{l}, \quad s = \frac{s'}{l}.$$

We note that this length scale  $l$ , is assumed to be defined by the functions  $f$  and  $g$  and represents some characteristic length of the disturbance in the  $x$  direction at the outer polymer boundary. Then, we define a dimensionless concentration

$$u = \frac{C - C^*}{C_0 - C^*}$$

and a dimensionless time

$$t = \frac{D(C_0 - C^*)}{l^2 C^*} t'.$$

Introducing these scalings into eqs. (1)–(5) we obtain

$$\delta \frac{\partial u}{\partial t} = \Delta u \quad \gamma g(x) < y < s(x, t) \quad (6)$$

$$(1 + \delta u) \frac{\partial s}{\partial t} = - \frac{\partial u}{\partial y} + \frac{\partial s}{\partial x} \frac{\partial u}{\partial x} \quad \text{at } y = s(x, t) \quad (7)$$

$$\frac{\partial s}{\partial t} = \left( 1 + \left( \frac{\partial s}{\partial x} \right)^2 \right)^{1/2} \kappa u^m \quad \text{at } y = s(x, t) \quad (8)$$

$$u = 1 + \epsilon f(x) \quad \text{at } y = \gamma g(x) \quad (9)$$

$$s(x, 0) = \gamma g(x) \quad (10)$$

where here

$$\epsilon = \frac{C_1}{C_0 - C^*}, \quad \gamma = \frac{A}{l},$$

$$\delta = \frac{C_0 - C^*}{C^*}, \quad \kappa = \frac{\kappa l C^*}{D} (C_0 - C^*)^m.$$

The parameter  $\epsilon$  is a measure of the amplitude of the spatial perturbation to the solute concentration at the boundary. Similarly,  $\gamma$  is the aspect ratio of the disturbance to the polymer topography and measures its amplitude. The parameter

$\delta$ , which also arises in the study of the one-dimensional problem<sup>2,6</sup> is a measure of the driving force applied to the polymer. That is, it is a measure of the excess concentration over the equilibrium value. Finally, the parameter  $\kappa$  is a measure of the relative effects of the front kinetics to diffusion through the polymer and may be interpreted as a nondimensional front speed.

### AN ASYMPTOTIC THEORY

We note that eqs. (6)–(10) are inherently nonlinear and that an exact solution is beyond our grasp. In this section, we develop an asymptotic theory which allows us to study the stability of one-dimensional planar Case II diffusion to small spatial perturbations. We begin by assuming that the amplitude of the spatial perturbation to the concentration at the boundary is small, i.e., we assume  $\epsilon \ll 1$ . In addition, we require that the aspect ratio of the polymer's surface topography is also small and of the same order as  $\epsilon$ . Hence, we let  $\gamma = \epsilon \beta$  where  $\beta = O(1)$ . Next, we assume an expansion in powers of  $\epsilon$  for  $u$  and  $s$

$$u(x, y, t) \sim u_0(x, y, t) + \epsilon u_1(x, y, t) + \dots \quad (11)$$

$$s(x, t) \sim s_0(x, t) + \epsilon s_1(x, t) + \dots \quad (12)$$

and insert these expansions into our governing eqs. (6)–(10). Equating to zero the coefficients of powers of  $\epsilon$  yields systems of equations for the  $u_n$ 's and the  $s_n$ 's. The leading order system is

$$\delta \frac{\partial u_0}{\partial t} = \Delta u_0 \quad (13)$$

$$(1 + \delta u_0) \frac{\partial s_0}{\partial t} = - \frac{\partial u_0}{\partial y} + \frac{\partial s_0}{\partial x} \frac{\partial u_0}{\partial x} \quad \text{at } y = s_0 \quad (14)$$

$$\frac{\partial s_0}{\partial t} = \left( 1 + \left( \frac{\partial s_0}{\partial x} \right)^2 \right)^{1/2} \kappa u_0^m \quad \text{at } y = s_0(x, t) \quad (15)$$

$$u_0 = 1 \quad \text{at } y = 0 \quad (16)$$

$$s_0(x, 0) = 0. \quad (17)$$

We note immediately that, to leading order the  $x$ -dependent perturbations do not play any role. Hence, we may take  $u_0 = u_0(y, t)$  and  $s_0$

=  $s_0(t)$ , which allows us to simplify our leading order system to

$$\delta \frac{\partial u_0}{\partial t} = \frac{\partial^2 u_0}{\partial y^2} \tag{18}$$

$$(1 + \delta u_0) \frac{\partial s_0}{\partial t} = - \frac{\partial u_0}{\partial y} \text{ at } y = s_0 \tag{19}$$

$$\frac{\partial s_0}{\partial t} = \kappa u_0^m \text{ at } y = s_0(x, t) \tag{20}$$

$$u_0 = 1 \text{ at } y = 0 \tag{21}$$

$$s_0(0) = 0. \tag{22}$$

This reduced system, i.e., eqs. (18)–(22), is essentially the one-dimensional model studied by Cohen and Erneux,<sup>2,6</sup> for short times, long times, and in the limit  $\delta \rightarrow 0$ . We shall rely upon their results. Now, using the fact that  $u_0$  and  $s_0$  are independent of  $x$  and Taylor expanding our boundary conditions about  $\epsilon = 0$  where necessary, we arrive at the following system of equations for  $u_1$  and  $s_1$

$$\delta \frac{\partial u_1}{\partial t} = \Delta u_1 \tag{23}$$

$$\delta \left( u_1 + s_1 \frac{\partial u_0}{\partial y} \right) \frac{\partial s_0}{\partial t} + (1 + \delta u_0) \frac{\partial s_1}{\partial t} = - \frac{\partial u_1}{\partial y} - s_1 \frac{\partial^2 u_0}{\partial y^2} \text{ at } y = s_0 \tag{24}$$

$$\frac{\partial s_1}{\partial t} = \kappa u_0^{m-1} \left( u_1 + s_1 \frac{\partial u_0}{\partial y} \right) \text{ at } y = s_0 \tag{25}$$

$$u_1 = f(x) - \beta g(x) \frac{\partial u_0}{\partial y} \text{ at } y = 0 \tag{26}$$

Next, we study the  $O(1)$  and  $O(\epsilon)$  equations (18)–(26), in the small  $\delta$  limit; our aim is to derive amplitude equations for the  $x$ -dependent perturbations to the moving front. To represent the solution  $u_0, s_0$  in the small  $\delta$  limit, we note from Cohen and Erneux,<sup>2,6</sup> that we may write

$$u_0(y, t) = 1 - \dot{s}_0 y + O(\delta) \tag{27}$$

$$\dot{s}_0(t) = \kappa(1 - s_0 \dot{s}_0)^m \tag{28}$$

where the dot denotes differentiation with respect to time. Now, letting  $\delta \gg \epsilon$  tend to zero in eqs. (23)–(26) and using the leading order solution we obtain

$$\Delta u_1 = 0 \tag{29}$$

$$\frac{\partial s_1}{\partial t} = - \frac{\partial u_1}{\partial y} \tag{30}$$

$$\frac{\partial s_1}{\partial t} = \kappa(1 - \dot{s}_0 s_0)^{m-1} (u_1 - s_1 \dot{s}_0) \text{ at } y = s_0 \tag{31}$$

$$u_1 = f(x) + \beta g(x) \dot{s}_0 \text{ at } y=0 \tag{32}$$

$$s_1(x, 0) = \beta g(x) \tag{33}$$

Noting that any real polymer is finite in the  $x$  direction, we assume that  $f$  and  $g$  are periodic functions and may be expanded in a Fourier sine series

$$f(x) + \beta g(x) \dot{s}_0 = \sum_{n=1}^{\infty} p_n(t) \sin(n\pi x). \tag{34}$$

We note that any constant term could have been included in the leading order solution hence this representation is sufficiently general to include any arbitrary periodic  $f$  and  $g$ . Then, we seek solutions  $u_1$  and  $s_1$  in the form

$$u_1(x, y, t) = \sum_{n=1}^{\infty} \psi_n(y, t) \sin(n\pi x) \tag{35}$$

$$s_1(x, t) = \sum_{n=1}^{\infty} \sigma_n(t) \sin(n\pi x). \tag{36}$$

Substituting these expansions into eqs. (29)–(33) and using orthogonality, we find that the  $\psi_n$  and  $\sigma_n$  must satisfy

$$\frac{\partial^2 \psi_n}{\partial y^2} - n^2 \pi^2 \psi_n = 0 \tag{37}$$

$$\dot{\sigma}_n = - \frac{\partial \psi_n}{\partial y} \text{ at } y = s_0 \tag{38}$$

$$\dot{\sigma}_n = \kappa(1 - \dot{s}_0 s_0)^{m-1} (\psi_n - \sigma_n \dot{s}_0) \text{ at } y = s_0 \tag{39}$$

$$\psi_n(0, \cdot) = p_n \tag{40}$$

$$\sigma_n(0) = \beta g_n \tag{41}$$

where the  $g_n$ 's are the Fourier sin series coefficients of  $g(x)$ . Eq. (37) is easily solved for  $\psi_n$  and the result can be used to eliminate in favor of  $\sigma_n$  throughout the remainder of the system. After some manipulation, we arrive at the following ordinary differential equation for the time evolution of each spatial modal disturbance to the planar front, i.e., for each  $\sigma_n$

$$\begin{aligned} \dot{\sigma}_n + \frac{\kappa \dot{s}_0 (1 - \dot{s}_0 s_0)^{m-1} n\pi \cos h(n\pi s_0)}{n\pi \cos h(n\pi s_0) + \sin h(n\pi s_0)} \sigma_n \\ = \frac{\kappa (1 - \dot{s}_0 s_0)^{m-1} n\pi p_n}{n\pi \cos h(n\pi s_0) + \sin h(n\pi s_0)}. \end{aligned} \tag{42}$$

For the convenience of the reader, we collect the equations defining the behavior of the moving front. We have

$$\begin{aligned} s(x, t) \sim s_0(t) \\ + \epsilon \sum_{n=1}^{\infty} \sigma_n(t) \sin(n\pi x) + O(\epsilon^2, \delta) \end{aligned} \tag{43}$$

$$\dot{s}_0 = \kappa (1 - s_0 \dot{s}_0)^m \tag{44}$$

$$\begin{aligned} \dot{\sigma}_n + \frac{\kappa \dot{s}_0 (1 - \dot{s}_0 s_0)^{m-1} n\pi \cos h(n\pi s_0)}{n\pi \cos h(n\pi s_0) + \sin h(n\pi s_0)} \sigma_n \\ = \frac{\kappa (1 - \dot{s}_0 s_0)^{m-1} n\pi p_n}{n\pi \cos h(n\pi s_0) + \sin h(n\pi s_0)} \end{aligned} \tag{45}$$

$$s_0(0) = 0 \tag{46}$$

$$\sigma_n(0) = \beta g_n \tag{47}$$

$$p_n(t) = 2 \int_0^1 (f(x) + \beta g(x) \dot{s}_0) \sin(n\pi x) dx. \tag{48}$$

**DISCUSSION**

In the previous section, we developed an asymptotic theory for the behavior of the moving front in a 2-D model of a polymer penetrant system. In particular, we considered the stability of a 1-D planar front by imposing small spatial perturba-

tions on the polymer surface topography and on the driving solute concentration. Our asymptotic theory yielded a system of equations describing the temporal evolution of the moving front [(43)–(48)]. In this section, we study these equations to gain an understanding of how the perturbation evolves. First, we show that in general, i.e., for real positive  $m$ , the planar front is asymptotically stable. To see this, we begin by noting that for such  $m$ , the inequality  $s_0 \dot{s}_0 \leq 1$  is valid for all time. This follows from the fact that it is true at  $t = 0$  and that a contradiction is obtained using eq. (44) if  $s_0 \dot{s}_0$  is assumed equal to one at any later time. From this fact and eq. (44) we conclude that  $s_0$  is a monotonically increasing function of time. Now, if we assume that  $s_0$  is bounded, then  $\dot{s}_0$  must converge to zero as time tends to infinity, but again, this is precluded by eq. (44). Hence,  $s_0$  must be unbounded. Combining this fact with the inequality above, we conclude that

$$s_0 \dot{s}_0 \rightarrow 1 \text{ as } t \rightarrow \infty.$$

In particular, this implies that  $s_0$  behaves like  $t^{1/2}$  for large  $t$ . Next, we note that, for any  $n$ , eq. (45) has the form

$$\dot{\sigma} + M(t)\sigma(t) = N(t).$$

In view of the properties of  $s_0$  we see that

$$M(t) \sim \dot{s}_0^{\frac{2m-1}{m}} \sim t^{\frac{1-2m}{2m}} \text{ for } t \gg 1,$$

which readily implies that  $M$  is not integrable. On the other hand, using the asymptotic behavior of  $s_0$  and eq. (48), we find that  $N$  is integrable. Now, the equation for  $\sigma$  is linear and first order and can be integrated to yield:

$$\sigma(t) = e^{-\int_0^t M(r) dr} \sigma_0 + \int_0^t e^{-\int_\tau^t M(r) dr} N(\tau) d\tau. \tag{49}$$

Combining this representation with our observations about  $M$  and  $N$ , it is easily seen that  $\sigma \rightarrow 0$  as  $t \rightarrow \infty$ . In fact it is obvious that the first term on the right-hand side of (49) converges to zero. For any given  $\epsilon > 0$  we can split the integral term into

$$\begin{aligned} & \left| \int_0^{T_\varepsilon} e^{-\int_\tau^t M(r) dr} N(\tau) d\tau + \int_{T_\varepsilon}^\infty e^{-\int_\tau^t M(r) dr} N(\tau) d\tau \right| \\ & \leq e^{-\int_{T_\varepsilon}^t M(r) dr} \int_0^\infty |N(\tau)| d\tau + \int_{T_\varepsilon}^\infty |N(\tau)| d\tau \leq \varepsilon, \end{aligned}$$

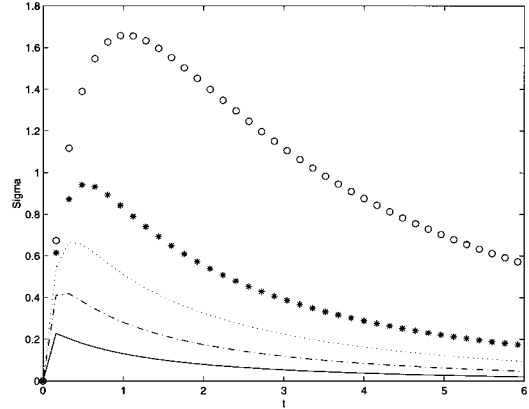
in such a way that the inequality holds for  $t$  large enough. Hence, we conclude that the planar front is asymptotically stable. Now, even though we have shown that the planar front is asymptotically stable, numerical solutions of eq. (45) show that initially the perturbation to the front is growing. Noting this fact, we now examine several special cases to illustrate the spectrum of possible behaviors. For simplicity, throughout the remainder of this discussion, we restrict our attention to the linear phenomenological law, i.e., we set  $m = 1$  in eqs. (43)–(48). With this assumption, we may solve explicitly for the leading order behavior of the moving front. We find

$$s_0(t) = -\frac{1}{\kappa} + \sqrt{2t + \frac{1}{\kappa^2}}. \tag{50}$$

We note that for short times  $s_0(t) \sim \kappa t + O(t^2)$ , that is, we have Case II diffusion. For a full discussion of the behavior of the planar front the reader is referred to ref. [6]. First, we consider the case of a flat polymer. That is, in equations (43)–(48) we set  $\beta = 0$ . Hence the only disturbance to planar diffusion is caused by perturbations in solute concentration, i.e., through  $f(x)$ . We note that this assumption implies that the  $p_n$ 's are time independent. In fact, they are simply the Fourier sine coefficients of  $f(x)$ . Further, eq. (45) simplifies to

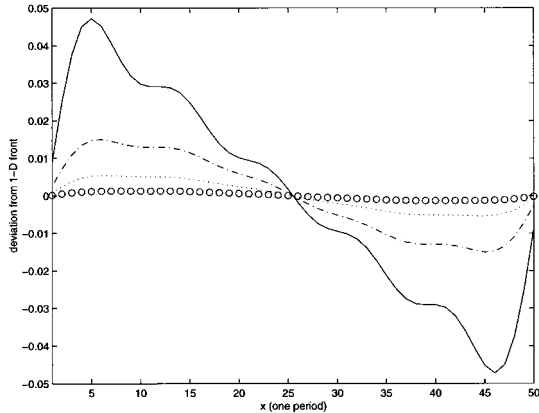
$$\begin{aligned} \dot{\sigma}_n + \frac{\dot{s}_0 \kappa n \pi \cos h(n\pi s_0)}{n\pi \cos h(n\pi s_0) + \sin h(n\pi s_0)} \sigma_n \\ = \frac{\kappa n \pi p_n}{n\pi \cos h(n\pi s_0) + \sin h(n\pi s_0)}. \end{aligned} \tag{51}$$

We may easily solve this equation numerically for various  $n$ 's; that is we may examine the modal behavior of the disturbance to the moving front. In Figure 2, we plot  $|\sigma_n|$  versus time for various  $n$ 's. So that we may reasonably compare the behavior of various modes, we fix the  $p_n$ 's and  $\kappa$ . Examining Figure 2, we are led to several conclusions. First, we observe that initially the amplitude of each mode is



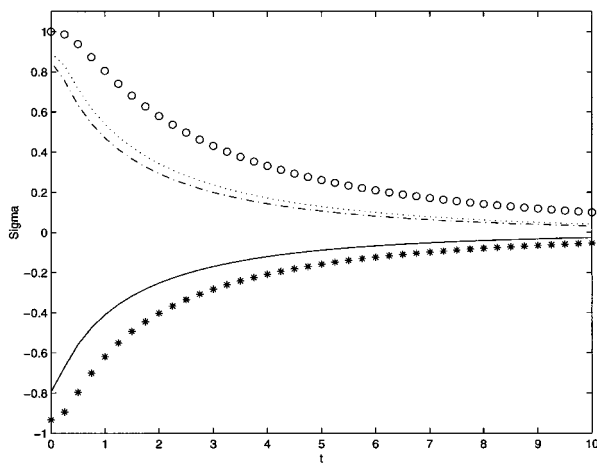
**Figure 2.** Modal disturbance to the planar front for flat a polymer film.

growing; however, for sufficiently long times, all  $\sigma_n$ 's eventually decay to zero in agreement with our above results. Since numerical evidence suggests that no mode ever becomes truly large, i.e.,  $O(1/\varepsilon)$ , the assumptions of our asymptotic theory are not violated, and we again note that the 1-D planar solution is indeed stable to this type of 2-D perturbations. On the other hand the initial growth of each mode implies that if the front is observed at a finite time, it may exhibit a 2-D or  $x$  dependent structure. We term this transient behavior “practical instability” since for all practical purposes the planar front may indeed be disturbed if in a given application the time of interest is sufficiently short. Further, we note that higher order modes peak more quickly and at a lower value than lower order modes. Given this, we may ask what the front looks like when observed at various finite times. From Figure 2, it is clear that for any finite time, the structure of the front will be dominated by the lower order or long wavelength modes. In Figure 3, we plot  $s_1(x, t)$  versus  $x$  for various times using randomly chosen Fourier coefficients for  $f(x)$ . We see that the predicted long wavelength structure becomes rapidly apparent. We note that the curves shown in Figure 3 are for times longer than the initial growing phase. Next, we consider the case of a uniform solute and a polymer with a given surface topography. That is, in eqs. (43)–(48) we set  $f(x) = 0$  and do not choose  $\beta = 0$ . Here, the  $p_n$ 's become time dependent but are simply given by  $g_n \beta \dot{s}_0(t)$ . The amplitude equation for each mode is again given by (51), but now with non-zero initial conditions, (47). In Figure 4 we again plot  $|\sigma_n|$  versus time for various  $n$ 's. We again observe that for sufficiently long times the amplitude of each mode decays to zero. Further, we note that in this case, all

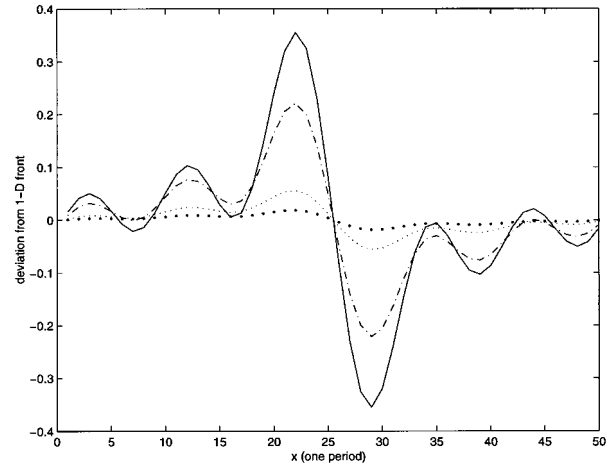


**Figure 3.** Structure of front disturbance for various times, flat polymer film.

modes are monotonically decreasing. That is, there is no initial growth in time. However, as above, at fixed finite times, the front structure is dominated by low order modes (see Fig. 5). Finally, we note that similar behavior has been observed in models of solidification of pure metals.<sup>8</sup> There, a long wavelength structure to a moving front may have undesirable consequences for the casting process. It has been suggested that controlling mold surface topographies might alleviate this effect. Here, in our polymer-penetrant system, we may ask a similar question. That is, can we choose a polymer surface topography in such a way as to mitigate the effect of



**Figure 4.** Modal disturbance to the planar front for a given film topography.



**Figure 5.** Structure of front disturbance for various times, given film topography.

solute concentration perturbations? From our analysis we see that the answer is indeed yes. In particular, examining eqs. (34), (42), and (43) we see that we can select a polymer surface topography to cause rapid decay of any given mode. We suggest that in certain applications where fine control over solute penetration is important, such a strategy may prove useful.

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