QUARTERLY OF APPLIED MATHEMATICS
VOLUME LI, NUMBER 3
SEPTEMBER 1993, PAGES 405–423

ANALYSIS AND APPLICATION OF A CONTINUATION METHOD FOR A SELF-SIMILAR COUPLED STEFAN SYSTEM

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Abstract. This work deals with a continuation method for computing solutions to a self-similar two-component Stefan system in which the diffusion coefficients depend on the concentrations. The procedure computes a one-parameter homotopy connecting the known solution of a simplified problem (when the parameter is zero) to the solution of the problem at hand (when the parameter is one). Local convergence of the method and local existence and uniqueness of solutions for the original system are proven. Also, several examples coming from precipitant-driven protein crystal growth are discussed. The most interesting of these is a Stefan problem containing a porous media equation that corresponds to the liquid phase being in a meta-stable state near the spinodal region. The bifurcation code AUTO is used in the computations.

1. Introduction. For many years, computational methods have been developed to handle moving boundary problems. The various methods (including finite difference, finite element, enthalpy, lines, etc.) have been reviewed by Crank [6]. In this paper, a rather different method is discussed: a continuation method for computing similarity solutions for a self-similar Stefan system. The system under consideration, (2.1), is a one-phase, one-dimensional, two-component system coming from protein crystal growth. Here the first component is a protein concentration, while the second is the concentration of a precipitating agent, often a salt. The system is nontrivial in that each diffusivity is allowed to depend on the concentration of both constituents. When both diffusivities do depend on both concentrations, this approach is more easily formulated than the enthalpy method [8, p. 943]. While the presentation given here is only with respect to (2.1), the method can in principle be used for other related self-similar problems. For example, single component problems, systems with cross-diffusion terms (where the flux of one component depends on the gradient of the other), or "waiting time" problems such as those studied by Kath and Cohen [19] could also be considered. Finally, although direct application of this method is limited to a narrow class of problems, the results obtained have broader implications since, as in the classical case, the solutions of many problems that are not themselves

Received January 30, 1991.
1991 *Mathematics Subject Classification.* Primary 35R35.

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self-similar (e.g., when the initial conditions are not constant) would be expected to tend asymptotically to similarity solutions [28, §II.2.3 and §II.2.6].

Briefly, the approach is to consider a nontrivial self-similar semi-infinite or infinite moving boundary problem, insert a continuation parameter (or perhaps several parameters), make an appropriate restriction of the problem to a finite interval, and finally compute a homotopy of solutions leading from a known solution when the continuation parameter is zero to the desired solution when the continuation parameter is, say, one. The restriction of the problem to a finite interval is accomplished by adapting the work of Friedman and Doedel [16]. The analysis gives an existence and uniqueness proof (local in the continuation parameter) for the system, as well as a convergence proof for the numerical method. Similar truncation issues have been addressed previously by, among others, de Hoog and Weiss [17] and Lentini and Keller [21]. The homotopy of solutions is computed using the numerical package AUTO, Doedel [10], Doedel and Kernévez [12].

The protein-precipitant system (2.1) is quite similar mathematically to a one-phase alloy solidification problem (cf. [6, §1.3.7 and §6.2.7(ii)]. Similarity solutions for the alloy solidification problem with constant diffusion coefficients have been discussed by Rubinšteĭn [28, I.2.3]. It is well known that such similarity solutions are often unstable in the sense that a nonplanar (possibly dendritic) interface with an associated mushy region may form when the liquid phase is supersaturated near the interface (cf., e.g., [23, 29, 1]). Since protein crystals are grown from supersaturated solutions, one should also be concerned about such issues here. Indeed the physics of organic crystal growth is very complicated, depends strongly on which organic substance is being prepared, and is not well understood (cf. Rosenberger [27] for a general discussion and a review of the folklore). In practice, nonplanar interfaces sometimes occur, though they are almost always undesirable. Flat interfaces can be achieved, however, from supersaturated protein-precipitant solutions when the crystals are grown carefully, and such growth processes are generally described by one-dimensional models [26, 27]. When the growth process is slow (protein crystals grow at rates of roughly a millimeter per day), when the process is governed by diffusion rather than convection (e.g., in a microgravity environment), and when the interface kinetics are instantaneous (i.e., the interface concentrations are at their equilibrium values), system (2.1) is a fairly accurate, if simplistic, lowest-order model of the growth process [14].

As mentioned above, the one complication considered here is the dependence of the diffusivities on concentration. Such dependencies for organic compounds and precipitants (salts) have been measured, e.g., by Myerson and Senol [24] and Chang and Myerson [4]. Of particular interest is the physically observed rapid decrease in diffusivity as a concentration approaches its spinodal value. This decrease is consistent with thermodynamical considerations [13]: For a concentration u, let $D(u)$ be the diffusivity of u and let $\psi(u)$ be the Gibb's free energy. Then

$$D(u) = M\psi''(u), \tag{1.1}$$

where the constant M is the mobility. The region where $\psi'' < 0$ is, by definition, the spinodal interval. The region where the liquid phase is supersaturated but $\psi'' > 0$ is often referred to as "meta-stable" (e.g., Fife [15]). It should be emphasized that here

"stability" is in the sense of phase separation and coarsening rather than interface stability and dendrite formation. A meta-stable liquid is stable in the sense that it does not undergo the phase separation that occurs for concentrations lying in the spinodal interval.

The second example of §5 deals with this sort of situation. There the protein concentration is governed by a porous media equation, which becomes singular for concentrations near the far-field value. This corresponds to growing a protein crystal from a liquid phase whose initial concentrations lie in the meta-stable region near the spinodal interval. Asymptotic methods lead to a description of the protein concentration profile as the problem becomes singular (cf. Theorems 2, 3).

This paper is divided into four main parts: The first gives an overview of the protein-precipitant system, and the second describes the continuation method. In the third, existence, uniqueness, and convergence are proven locally for the homotopy, i.e., when the continuation parameter is small. Finally the last section presents several examples, including the meta-stable solution example mentioned above. The last two sections can be read independently of each other.

2. Overview of the system. Consider the following system, which is a simple model for precipitant-assisted protein crystal growth [14]:

$$
\begin{aligned}
&\text{(a)} \quad p_t = [D_p p_x]_x + v p_x, && x \in (0, \infty), \ t > 0,\\
&\text{(b)} \quad n_t = [D_n n_x]_x + v n_x, && x \in (0, \infty), \ t > 0,\\
&\text{(c)} \quad v(p_s - p) = D_p p_x, && x = 0, \ t > 0,\\
&\text{(d)} \quad v(n_s - n) = D_n n_x, && x = 0, \ t > 0,\\
&\text{(e)} \quad f(p, n) = 0, && x = 0, \ t > 0;\\
&\text{(f)} \quad p = p_\infty, && x \in (0, \infty), \ t = 0,\\
&\text{(g)} \quad n = n_\infty, && x \in (0, \infty), \ t = 0.
\end{aligned}
\tag{2.1}
$$

The notation is as follows: x measures the distance from the solid-liquid interface, p is the protein concentration, n is the precipitant (*der Niederschlagende*) concentration, p_s and n_s are the constant, uniform concentrations in the solid, p_∞ and n_∞ are uniform initial concentrations, and v is the interface velocity (cf. Fig. 1 on p. 408). The triple $(p(x, t), n(x, t), v(t))$ is called a solution if it satisfies system (2.1).

Throughout this discussion, variables as subscripts denote partial derivatives *except* for the diffusivities D_p and D_n. The diffusivities are assumed to depend on the concentrations, viz. $D_p \equiv D_p(p, n)$ and $D_n \equiv D_n(p, n)$, and to be sufficiently smooth and positive (though possibly small) for all values of the concentrations considered. Equations (2.1a, b) are then just diffusion equations in moving reference frame, while (2.1c, d) are classical Stefan conditions representing mass conservation at the interface. The third interface condition, $f = 0$, is a solubility relation, which guarantees that the two liquid-phase constituents are in equilibrium at the interface. It is this last condition that drives the motion of the interface. For $v > 0$, one needs that the liquid phase be supersaturated. The specific requirements that supersaturation places on p_s, n_s, p_∞, n_∞, and $f(p, n)$ will be discussed in more detail below.

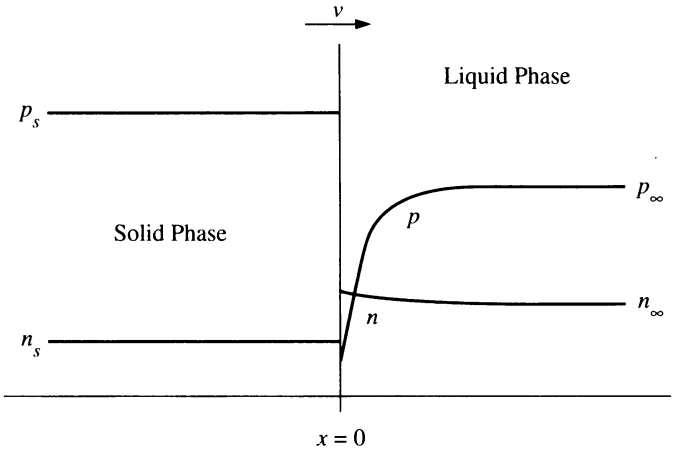

FIG. 1. Schematic diagram of the protein crystal growth configuration. The relative sizes of p and n are not to scale.

Note that system (2.1) is invariant under the well-known similarity transformation $(x, t) \to (\beta x, \beta^2 t)$. Hence define $\xi \equiv x/(2\sqrt{t})$. In terms of ξ, system (2.1) becomes

$$\begin{aligned}
&\text{(a)} \quad 0 = (D_p p_\xi)_\xi + 2(\lambda + \xi)p_\xi, \\
&\text{(b)} \quad 0 = (D_n n_\xi)_\xi + 2(\lambda + \xi)n_\xi; \\
&\text{(c)} \quad 2\lambda(p_s - p) = D_p p_\xi, \qquad \xi = 0, \\
&\text{(d)} \quad 2\lambda(n_s - n) = D_n n_\xi, \qquad \xi = 0, \\
&\text{(e)} \quad f(p, n) = 0, \quad \xi = 0; \\
&\text{(f)} \quad p = p_\infty, \qquad \xi = \infty, \\
&\text{(g)} \quad n = n_\infty, \qquad \xi = \infty,
\end{aligned} \tag{2.2}$$

where $\lambda \equiv v\sqrt{t}$ is constant.

When the diffusivities are constant, the p and n components of the solution of (2.2a, b, f, g) can be given explicitly in terms of error functions. Finding a complete solution of system (2.2) in the constant diffusivity case is then reduced to solving the interface conditions at $\xi = 0$. Specifically, one must find a triple (p_0, n_0, λ) that satisfies

$$\begin{aligned}
&\text{(a)} \quad \operatorname{xerfc}\left(\lambda \Big/ \sqrt{D_p^0}\right) = \frac{p_\infty - p_0}{p_s - p_0}, \\
&\text{(b)} \quad \operatorname{xerfc}\left(\lambda \Big/ \sqrt{D_n^0}\right) = \frac{n_\infty - n_0}{n_s - n_0}, \\
&\text{(c)} \quad f(p_0, n_0) = 0,
\end{aligned} \tag{2.3}$$

where $\operatorname{xerfc}(x) \equiv \sqrt{\pi} x e^{x^2} \operatorname{erfc}(x)$.

LEMMA 1. Suppose that $p_\infty < p_s$ and that $n_s < n_\infty$. Also suppose that f is continuous in both its arguments and that $f(p_\infty, n_\infty)$ and

$$f\left(0, \frac{n_\infty - n_s \operatorname{xerfc}(\sqrt{D_p/D_n}\,\operatorname{xerfc}^{-1}(p_\infty/p_s))}{1 - \operatorname{xerfc}(\sqrt{D_p/D_n}\,\operatorname{xerfc}^{-1}(p_\infty/p_s))}\right)$$

have opposite signs. Then there exists at least one solution (p_0, n_0, λ) of (2.3) with $\lambda > 0$ and $p_0 \in (0, p_\infty)$.

Proof. First recall several basic facts about the function $\operatorname{xerfc}(x)$:

(a) $\operatorname{xerfc}(0) = 0$,
(b) $\operatorname{xerfc}'(0) = \sqrt{\pi}$,
(c) $\operatorname{xerfc}(x)$ is monotonically increasing,
(d) $\lim_{x\to\infty} \operatorname{xerfc}(x) = 1$.

So there exists $\operatorname{xerfc}^{-1}: [0, 1) \to [0, \infty)$. Since $p_\infty < p_s$ and $n_s < n_\infty$, one can combine (2.3a) and (2.3b) to eliminate λ and thereby define a function $P(\cdot)$ such that $n_0 = P(p_0)$. Note that the domain of $P(\cdot)$ includes $[0, p_\infty]$. By assumption $f(0, P(0))$ and $f(p_\infty, P(p_\infty))$ have opposite signs. Hence there is a $p_0 \in (0, p_\infty)$ and a $\lambda > 0$ such that $n_0 = P(p_0)$ and (p_n, n_0, λ) is a solution of (2.3). □

REMARKS. (1) Obviously the sign of $f(\cdot, \cdot)$ is arbitrary. For definiteness, assume that the liquid is supersaturated when $f(p_\infty, n_\infty) > 0$. Physically not a lot is known about the solubility relations for proteins; but the assumption that $f(\cdot, \cdot)$ is continuous is reasonable, and typically the equilibrium concentration of protein decreases as the precipitant concentration increases [18]. Given more information on f, one could hope to show that the above triple is the unique solution.

(2) A similar argument for the existence of a solution to a different Stefan problem is given in an appendix by Pego [25].

3. The continuation method. To set up the continuation procedure, a continuation parameter α is inserted in each of the diffusion coefficients, viz., $D_p \equiv D_p(\alpha p, \alpha n)$ and $D_n \equiv D_n(\alpha p, \alpha n)$. For $\alpha = 0$ at least one error-function solution is given by Lemma 1, provided that $D_p = D_p^0$ and $D_n = D_n^0$ are both positive and that p_s, n_s, p_∞, n_∞, and $f(p, n)$ satisfy the assumptions of that lemma. We then wish to compute to $\alpha = 1$, which is of course the original problem.

Local justification of the continuation procedure depends on the asymptotic behavior of a solution of system (2.2) for large ξ. This behavior is established in the following lemma.

LEMMA 2. Suppose that $u(\xi)$ satisfies

$$\begin{aligned} (D(u)u')' + 2(\lambda + \xi)u' &= 0, \\ u \to u_\infty \quad &\text{as } \xi \to \infty, \end{aligned} \tag{3.1}$$

where $D(u) > 0\ \forall u$ and $D(\cdot) \in C^2$ on some neighborhood of $u = u_\infty$ with $D_\infty \equiv D(u_\infty) \neq 0$. Then as $\xi \to \infty$,

$$u' = O(e^{-(\xi+\lambda)^2/D_\infty})$$

and hence also

$$|u - u_\infty| = O(e^{-(\xi+\lambda)^2/D_\infty}).$$

Proof. Write Eq. (3.1) as $(Du')' + [2(\lambda+\xi)/D](Du') = 0$. Direct integration then yields for some constant A_0 that

$$D(u)u' = A_0 e^{-\int_{\xi_0}^{\xi} 2(\eta+\lambda)/D(u)\,d\eta}$$

where ξ_0 may be chosen to be as large as desired. Since $D(\cdot) \in C^2$, consider its Taylor expansion about u_∞. For some constant A_1, it follows that

$$D(u)u' = A_1 e^{-(\xi+\lambda)^2/D_\infty} \exp\left(-\int_{\xi_0}^{\xi} \frac{2D'(u^{**})}{D_\infty^2}(u^* - u_\infty)(\eta+\lambda)\,d\eta\right),$$

where either $u \le u^* \le u^{**} \le u_\infty$ or $u_\infty \le u^{**} \le u^* \le u$. The proof is then complete provided that for some $\varepsilon > 0$, $|u - u_\infty| = O(\xi^{-2-\varepsilon})$; but since $D(u)u'$ and its derivative always have opposite sign, both terms in (3.1) must approach zero. Hence $D(u)u' = o(\xi^{-1})$. Repeated differentiation of (3.1) (to the extent possible) then yields that derivatives of $D(u)u'$ are also $o(\xi^{-1})$. Upon substituting back into (3.1), one finds that $|u - u_\infty| = o(\xi^{-3})$, and the proof is complete. □

Written as a first-order system with the continuation parameter, system (2.2) is

$$\begin{aligned}
&\text{(a)}\quad u_1' = u_3,\\
&\text{(b)}\quad u_2' = u_4,\\
&\text{(c)}\quad u_3' = -\frac{2(\xi+\lambda)u_3 + \alpha\nabla D_p\cdot(u_3,u_4)u_3}{D_p(\alpha u_1,\alpha u_2)},\\
&\text{(d)}\quad u_4' = -\frac{2(\xi+\lambda)u_4 + \alpha\nabla D_n\cdot(u_3,u_4)u_4}{D_n(\alpha u_1,\alpha u_2)},\\
&\text{(e)}\quad 2\lambda(p_s - u_1) = D_p(\alpha u_1,\alpha u_2)u_3, \qquad \xi = 0,\\
&\text{(f)}\quad 2\lambda(n_s - u_2) = D_n(\alpha u_1,\alpha u_2)u_4, \qquad \xi = 0,\\
&\text{(g)}\quad f(u_1,u_2) = 0, \qquad \xi = 0,\\
&\text{(h)}\quad u(\infty) = u_\infty \equiv (p_\infty, n_\infty, 0, 0),
\end{aligned} \tag{3.2}$$

where $u \equiv (p, n, p_\xi, n_\xi)$. Let ξ_R be the right computational endpoint. We now follow the approach used to compute heteroclinic orbits for autonomous systems by Doedel and Friedman [11]: we require that $u(\xi_R)$ lie tangent to the stable manifold of the fixed point u_∞ of system (3.2). (Lemma 2 assures that u_∞ is indeed a fixed point.) The major differences between the problem considered by Doedel and Friedman and the present problem are that this system has an explicit continuation parameter, α, and that it is nonautonomous. This latter difference means that the integral "phase condition" required by Doedel and Friedman is no longer needed because this problem is not translation invariant, but that the eigenvalue problem for the stable manifold is more complicated. The "standard" linearization for an autonomous system near a fixed point would have the form $u' = Au$ for some

matrix A, but the asymptotic behavior of Eq. (3.1) leads one in this case to consider $u' = \xi Au$.

Specifically, system (3.2) is of the form

$$u' = F(\xi, u, \lambda, \alpha) \equiv F_0(u, \alpha) + (\xi + \lambda)F_1(u, \alpha).$$

Lemma 2 implies that $F(u, \lambda, \alpha, \xi) \sim (\xi + \lambda)F_1(u, \alpha)$ as $\xi \to \infty$, and by direct computation one finds that the matrix $F_{1u}(u_\infty, \alpha)$ is diagonal with eigenvalues

$$(\mu_1, \mu_2, \mu_3, \mu_4) = \left(\frac{-2}{D_p(\alpha p_\infty, \alpha n_\infty)}, \frac{-2}{D_n(\alpha p_\infty, \alpha n_\infty)}, 0, 0\right) \tag{3.3}$$

and, hence, that the stable manifold at $\xi = \infty$ is two dimensional [stable manifold theorem using $\zeta \equiv (\xi+\lambda)^2/2$]. Therefore to restrict to a finite interval, replace (3.2h) by the equations

$$\begin{aligned} &\text{(a)} \quad F_{1u}(u_\infty, \alpha)v_i = \mu_i v_i, \qquad i \in \{1, 2\}, \\ &\text{(b)} \quad u(\xi_R) = u_\infty + c_1 v_1 + c_2 v_2, \end{aligned} \tag{3.4}$$

where v_1 and v_2 are the corresponding eigenvectors and c_1 and c_2 are constants. Equation (3.4b) is then back-substituted into system (3.2) and Eq. (3.4a) to eliminate u_∞. This leaves four equations with seven side conditions. At least formally then, one would expect three scalar parameters, which are to be computed in the continuation process, viz. λ, c_1, c_2. The computational right endpoint ξ_R is fixed throughout the continuation.

The actual computations are performed using the bifurcation tracking code AUTO, moving from the error function solution at $\alpha = 0$ to a similarity solution of system (2.1) at $\alpha = 1$. AUTO computes the homotopy using a polynomial approximation (collocation method). At each step in the continuation process, a discretized version of the system is solved using Newton or Newton-Chord iterations. The computational details of this method are given by Doedel and Kernévez [12]. AUTO is much more powerful than is demonstrated here. It handles many types of bifurcation problems and computes solutions using a pseudo-arclength continuation, which makes the designation of an explicit continuation parameter unnecessary.

4. Existence, uniqueness, and convergence. The justification for the above process parallels that presented by Friedman and Doedel [16] for heteroclinic orbits. The goal is to show that an appropriate operator is Fredholm, and a simplified version of the implicit function theorem of Descloux and Rappaz can be applied to establish existence, uniqueness, and error estimates for the approximate problem. The collection of lemmas that follows establishes the hypotheses needed to apply this implicit function theorem. Throughout what follows, let C denote generic positive constants.

Define the standard norms

$$\|u\|_0 \equiv \left(\sum_{i=1}^{4} \|\mu_i\|_{L^2}^2\right)^{1/2}$$

and

$$\|u\|_j^2 \equiv \|u\|_0^2 + \|du/dt\|_0^2 + \cdots + \|d^j u/dt^j\|_0^2, \qquad j \geq 0.$$

Finally let H_j be the Hilbert space of vector-valued functions on $\{0 < \xi < \infty\}$ with finite $\|\cdot\|_j$ norm. By Lemma 2, we are led to look for solutions of system (3.2) of the form $u(\xi) = w(\xi) + u_\infty$ where $w \in H_1$. In this regard, consider the operator $\Phi\colon H_1 \times \mathbb{R}^2 \to H_0$ defined by

$$\Phi(\cdot, w, \lambda, \alpha) \equiv w' - F(\cdot, w + u_\infty, \lambda, \alpha). \tag{4.1}$$

Let $(w_0, \lambda^0, 0) \in H_1 \times \mathbb{R}^2$ be a solution of $\Phi = 0$, and define the linearized operator $\Phi_w^0\colon H_1 \to H_0$ by

$$\Phi_w^0 \equiv \Phi_w(\cdot, w_0, \lambda^0, 0) = \frac{d}{d\xi} - A(\cdot),$$

where

$$A(\cdot) \equiv F_u(\cdot, w_0(\cdot) + u_\infty, \lambda^0, 0).$$

LEMMA 3. The operator $\Phi_w^0\colon H_1 \to H_0$ is a Fredholm operator with

$$\dim \mathcal{N}(\Phi_w^0) = 2 \text{ and } \operatorname{codim} \mathcal{R}(\Phi_w^0) = 0.$$

Proof. Recalling the results of Lemma 2, define the matrix $A \equiv \lim_{\xi\to\infty} \frac{1}{\xi} A(\xi) = F_{1u}(u_\infty, 0)$, and consider the system

$$(\Phi_w^0 w)(\xi) = w'(\xi) - A(\xi)w(\xi) = 0. \tag{4.2}$$

By the definitions of $A(\xi)$ and A, and noting that $|F_{uu}|$ is bounded for ξ sufficiently large, one finds

$$|A(\xi) - (\xi + \lambda)A| < C|w_0(\xi)|,$$

which implies that

$$\int_0^\infty |A(\xi) - (\xi + \lambda)A|\, d\xi < \infty$$

since $|w_0(\xi)|$ decays super exponentially as $|\xi| \to \infty$. By [5, Theorem 1, p. 88] [again using $\zeta \equiv (\xi+\lambda)^2/2$], this last inequality assures that system (4.2) has a fundamental system of solutions $v_i(\xi)$ satisfying

$$v_i(\xi) \sim e^{\mu_i(\xi+\lambda)^2/2} v_i \quad \text{as } \xi \to \infty, \qquad i = 1, 2, 3, 4,$$

where v_i corresponds to A. Hence $\mathcal{N}(\Phi_W^0) = \operatorname{span}\{v_i(\xi),\ i = 1, 2\}$ (the other two are not in H_1).

Now consider $\mathcal{R}(\Phi_w^0)$. Let H_{-j} denote the dual space of H_j, with norm

$$\|v\|_{-j} = \sup_{\|u\|_j = 1} |(u, v)_{L^2}|.$$

Also let $\langle u, v\rangle$ denote the duality pairing between these spaces, and let $e^* \in H_0$ be in $\mathcal{R}(\Phi_w^0)^\perp$. Then

$$\langle \Phi_w^0 w, e^*\rangle = 0 \quad \forall w \in C_0^\infty(\mathbb{R}^n),$$

which implies that $(\Phi_w^0)^* e^* = 0$ in the sense of distributions where $(\Phi_w^0)^*$ is the adjoint of Φ_w^0. Since system (3.2) is a system of ordinary differential equations, e^* can be identified with a smooth function ψ satisfying

$$(\Phi_w^0)^* \psi \equiv \psi' + A^{\mathrm{T}}(\xi)\psi = 0.$$

Noting that the eigenvalues of $-A(\xi)$ are nonnegative and that $\psi \in H_0 \Leftrightarrow \psi \in (L^2)^4$, one finds that $\mathscr{R}(\Phi_w^0) = H_0$. Therefore $\mathscr{R}(\Phi_w^0)^{\perp}$ is trivial, and

$$\operatorname{codim} \mathscr{R}(\Phi_w^0) = 0.$$

Hence Φ_w^0 is Fredholm and this completes the proof of Lemma 3. □

For there to be a unique solution, the interface conditions (2.1c–e) must be included. Define the operator $\Psi\colon H_1 \times \mathbb{R}^2 \to H_0 \times \mathbb{R}^3$ as

$$\Psi(\cdot, w, \lambda, \alpha) \equiv (\Phi(\cdot, w, \lambda, \alpha), I(w, \lambda, \alpha)),$$

where

$$I(w, \lambda, \alpha) \equiv \begin{cases} 2\lambda(p_s - u_1) - D_p(\alpha u_1, \alpha u_2)u_3, \\ 2\lambda(n_s - u_1) - D_n(\alpha u_1, \alpha u_2)u_4, \\ f(u_1, u_2). \end{cases} \tag{4.3}$$

The following lemma extends the results of Lemma 3 to the operator Ψ.

LEMMA 4. Define the operator $\Psi'(\cdot, w_0, \lambda^0, 0)\colon H_1 \times \mathbb{R} \to H_0 \times \mathbb{R}^3$ as

$$\Psi'(\cdot, w_0, \lambda^0, 0) \equiv \begin{bmatrix} \Phi_w^0 & \Phi_\lambda^0 \\ I_w^0 & I_\lambda^0 \end{bmatrix}.$$

This operator is Fredholm with index 1 and with $\mathscr{R}(\Psi') = H_0 \times \mathbb{R}^3$.

Proof. First note that $\Phi_\lambda^0\colon \mathbb{R} \to H_0$, $I_w^0\colon H_1 \to \mathbb{R}^3$, and $I_\lambda^0\colon \mathbb{R} \to \mathbb{R}^3$ are computed from (4.1) and (4.3). The Bordering Lemma then gives the desired result.

LEMMA 5 (Bordering Lemma). Let X, Y be Banach spaces, and consider the operator

$$S = \begin{pmatrix} A & B \\ C & D \end{pmatrix} : X \times \mathbb{R}^p \to Y \times \mathbb{R}^q,$$

with bounded linear operators $A\colon X \to Y$, $B\colon \mathbb{R}^p \to Y$, $C\colon X \to \mathbb{R}^q$, $D\colon \mathbb{R}^p \to \mathbb{R}^q$. If A is Fredholm of index N, then S is Fredholm of index $N + p - q$.

Proof of Lemma 5. Write S as the sum of diagonal and off-diagonal matrices. Then S is seen to be the sum of a compact operator and a block diagonal operator having the indicated index (cf. [3, Lemma 2.5, Appendix A2; 20, IV, Theorem 5.26]). □

Since with regard to the Banach spaces of this lemma, $\operatorname{index}(\Phi_w^0) = 2$, the Bordering Lemma implies that $\operatorname{index}(\Psi') = 1$. The statement regarding the range follows from Lemma 3 and the linear independence of the interface conditions. This concludes the proof of Lemma 4. □

Now define an approximate (truncated) operator Ψ_{T} with the appropriate asymptotic behavior as $\xi \to \infty$:

$$\Psi_{\mathrm{T}}(\cdot, w, \lambda, \alpha) \equiv (\Phi_{\mathrm{T}}(\cdot, w, \lambda, \alpha), I(w, \lambda, \alpha)),$$

where

$$\Phi_T(\xi, w, \lambda, \alpha) \equiv \begin{cases} \Phi(\xi, w, \lambda, \alpha), & \xi \le \xi_R, \\ w' - (\xi + \lambda)F_{1u}(u_\infty, \alpha)w, & \xi > \xi_R. \end{cases}$$

The next lemma establishes a pointwise convergence condition for Ψ and Ψ_T and a convergence condition on the derivatives at the initial solution.

LEMMA 6. For the operators defined above,

$$\|\Psi(\cdot, w, \lambda, \alpha) - \Psi_T(\cdot, w, \lambda, \alpha)\| \le Ce^{\mu\xi_R^2/2} \to 0 \quad \text{as } \xi_R \to \infty,$$
$$\|\Psi'(\cdot, w_0, \lambda^0, 0) - \Psi_T'(\cdot, w_0, \lambda^0, 0)\| \le Ce^{\mu\xi_R^2/2} \to 0 \quad \text{as } \xi_R \to \infty,$$

where $\mu < 0$ is an upper bound on the negative eigenvalues of Eq. (3.3), and C does not depend on ξ_R.

Proof. From the definitions of Φ and Φ_T,

$$\|\Psi(\cdot, w, \lambda, \alpha) - \Psi_T(\cdot, w, \lambda, \alpha)\| = \|F(\xi, w + u_\infty, \lambda, \alpha) - (\xi + \lambda)F_{1u}(u_\infty, \alpha)w\|_{H_0[\xi_R, \infty)}.$$

Now recall the result from Lemma 1 that $w = u - u_\infty$ exhibits super exponential decay as $\xi \to \infty$. By the definitions of $\|\cdot\|_0$ and again noting that $|F_{uu}|$ is bounded, one finds

$$\|\Psi(\cdot, w, \lambda, \alpha) - \Psi_T(\cdot, w, \lambda, \alpha)\| \le C\|w\|^2_{H_0[\xi_R, \infty)} \le Ce^{\mu\xi_R^2/2}.$$

Similarly, recalling that $|F_{\lambda uu}|$ is also bounded, one finds

$$\begin{aligned} &\|(\Phi_w(\cdot, w_0, \lambda^0) - D_w\Phi_T(\cdot, w_0, \lambda^0, 0))v\|_0 \\ &\quad \le C\|[F_u^i(\xi, w_0 + u_\infty, \lambda^0, 0) - (\xi + \lambda^0)F_{1u}^i(u_\infty, \lambda^0, 0)]v\|_{H_0[\xi_R, \infty)} \\ &\quad \le Ce^{\mu\xi_R^2/2}\|v\|_1 \quad \forall v \in H_1 \end{aligned}$$

and

$$\begin{aligned} &\|\Phi_\lambda(\cdot, w_0, \lambda^0, 0) - D_\lambda\Phi_T(\cdot, w_0, \lambda^0, 0)\|_0 \\ &\quad \le C\|F_\lambda^i(\xi, w_0 + u_\infty, \lambda^0, 0) - (\xi + \lambda^0)F_{1\lambda}^i(u_\infty, \lambda^0, 0)w_0\|_{H_0[\xi_R, \infty)} \\ &\quad \le C\|w_0\|^2_{H_0[\xi_R, \infty)} \le Ce^{\mu\xi_R^2/2}. \end{aligned}$$

Combining the above inequalities yields the second of the desired bounds. □

The above lemmas are sufficient to establish the hypotheses of a simplified version of the implicit function theorem [9, Theorem 3.1, p. 326] (cf. also [16, Theorem 1]). The main result of this section follows from that theorem. Note that since the

present continuation is with respect to an explicit parameter, the linear functional needed for that theorem is trivially defined.

THEOREM 1. Suppose (w_0, λ^0) satisfies $\Psi(\cdot, w_0, \lambda^0, 0) = 0$. Then there exist positive constants ξ_R^0, α_0, ε, C and two unique C^1 maps $(w(\alpha), \lambda(\alpha))$ and $(w_T(\alpha), \lambda_T(\alpha))$ satisfying for $|\alpha| < \alpha_0$ and $\xi_R > \xi_R^0$ the following conditions:

$$\Psi(\cdot, w(\alpha), \lambda(\alpha), \alpha) = 0, \qquad \|(w(\alpha), \lambda(\alpha)) - (w_0, \lambda_0)\|_{H_1 \times \mathbb{R}} < \varepsilon,$$

$$\Psi_T(\cdot, w_T(\alpha), \lambda_T(\alpha), \alpha) = 0, \qquad \|(w_T(\alpha), \lambda_T(\alpha)) - (w_0, \lambda_0)\|_{H_1 \times \mathbb{R}} < \varepsilon,$$

and

$$|\lambda(\alpha) - \lambda_T(\alpha)| + \|w(\alpha) - w_T(\alpha)\|_1 \le C\|w(\alpha)\|_1 e^{\mu \xi_R^2/2}.$$

5. Examples: Degenerate diffusion. Now let us consider several specific examples: the first is an easy test case where both diffusivities are taken to be constant; in the second, one of the diffusivities has a linear singularity; and the third is a more elaborate case where both of the diffusivities depend on both constituent concentrations. Mathematically, the second example corresponds to a Stefan problem with the heat equation replaced by the porous media equation. In each case, at least one of the diffusion processes is degenerate at $\alpha = 1$.

For each of the examples, let $p_\infty = 1.6 \times 10^{-3}$, $n_\infty = 2.0 \times 10^{-2}$, $p_s = 3.2 \times 10^{-3}$, $n_s = 1.0 \times 10^{-2}$ (all in mole fractions). Also let $f(p, n) = 1000p + 10n - 1$. These parameter values along with this linear solubility relation are taken from [14, 18]. They are typical for protein-precipitant systems, and they satisfy the assumptions of Lemma 1 and the first remark following that lemma. In particular $f(p_\infty, n_\infty) > 0$, while in the first two examples $f(0, P(0)) \simeq -0.8 < 0$ and in the third $f(0, P(0)) = -0.7 < 0$. The very small values of the mole-fraction concentrations, particularly of the protein in the crystal, are indicative of the size of the protein molecules (they are huge) and of the amount of water that is trapped in the crystal (as much as 50% by weight [22]).

EXAMPLE 1. Let $D_p = D_p^0(1 - \alpha)$ and $D_n = D_n^0$ (constant) with $D_p^0 = 1.0 \times 10^{-7}$, $D_n^0 = 1.0 \times 10^{-5}$ (cm^2/sec). These values for D_p^0 and D_n^0 are also typical. Since neither diffusivity depends on either constituent concentration, both concentration profiles are error functions, and since $D_p^0 < D_n^0$, a scaling analysis shows that the precipitant profile satisfies

$$|n(\xi) - n_\infty| = O\left(\sqrt{D_p^0/D_n^0}\right) \tag{5.1}$$

[14]. Since D_p is proportional to $1 - \alpha$, a scaling argument shows that λ is proportional to $\sqrt{1 - \alpha}$. This proportionality is displayed in the continuation computation of λ in Fig. 2 on p. 416.

EXAMPLE 2. Meta-Stable liquid phase. Let $D_p = D_p^0(1 - \alpha p/p_\infty)$ and $D_n = D_n^0$, again with $D_p^0 = 1.0 \times 10^{-7}$, $D_n^0 = 1.0 \times 10^{-5}$ (cm^2/sec). Then as $\alpha \to 1$, the problem becomes singular for protein concentrations near p_∞. Physically this does not correspond to a particular protein. Rather it is what one might expect if one

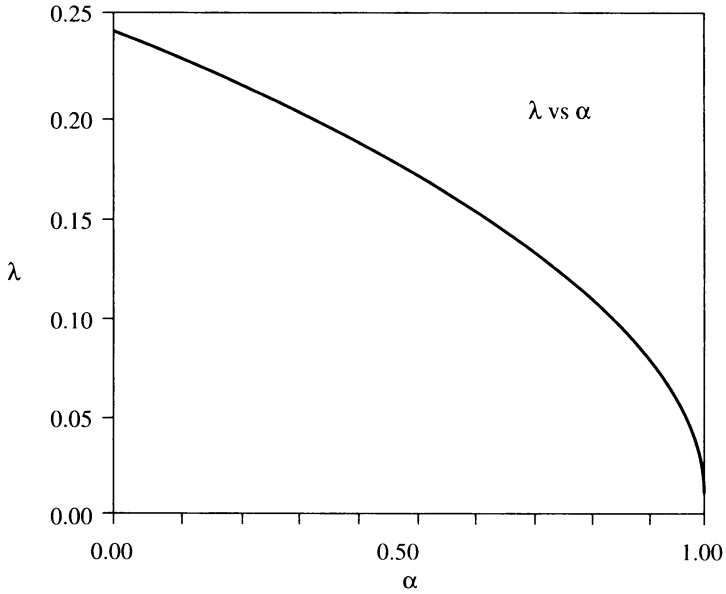

FIG. 2. Growth parameter for $D_p = D_p^0(1-\alpha)$ and $D_n = D_n^0$. The variable λ is dimensionless, i.e., here $\lambda \equiv v\sqrt{t/D_p^0}$. At the right end, $\alpha \simeq 0.999$.

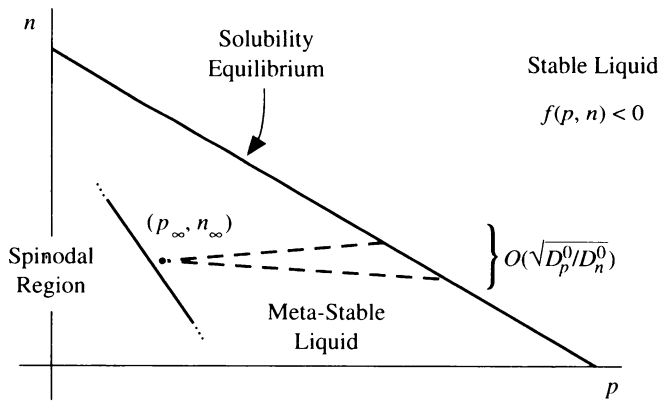

FIG. 3. Schematic of the solubility relation. For the solubility equilibrium curve (line), $f(p, n) = 0$. For the meta-stable liquid, $f(p, n) > 0$ while $D_p(p) > 0$. For the spinodal region, $D_p(p) < 0$.

were to run an experiment with a typical protein and if the experiment were set up so that the initial and far-field concentrations (p_∞, n_∞) are near the spinodal region [recall Eq. (1.1)]. This arrangement is depicted in Fig. 3. The precipitant profile is again relatively flat since Eq. (5.1) still must be satisfied. Diffusivities that decrease sharply as concentrations approach spinodal values have been described by Myerson and Senol [24] and Chang and Myerson [4]. Here α is proportional to $-\partial D_p/\partial p$.

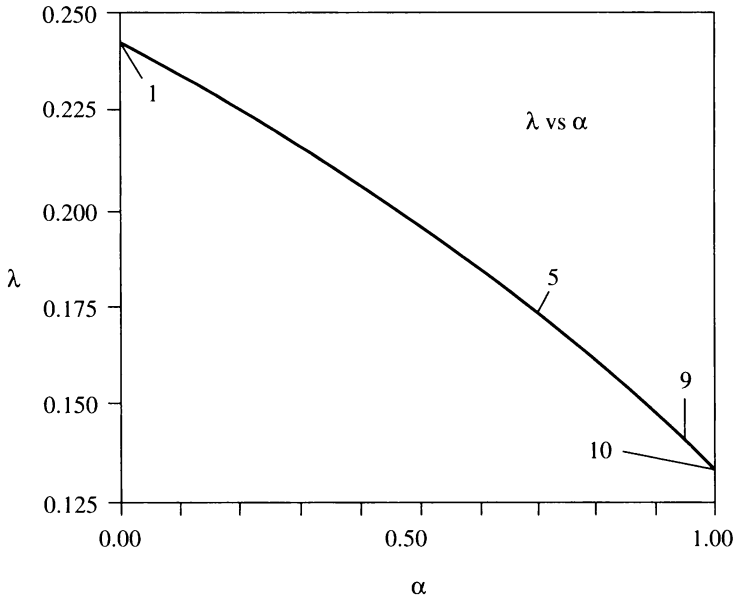

FIG. 4. Growth parameter for $D_p = D_p^0(1 - \alpha p/p_\infty)$ and $D_n = D_n^0$. Again λ is dimensionless: $\lambda \equiv v\sqrt{t/D_p^0}$. At label 10, $\alpha \simeq 0.994$.

The continuation computation for this system is presented in Figs. 4 and 5. Figure 4 is a plot of the growth parameter λ versus α. Figure 5 on p. 418 shows the profiles of p and p_ξ for various labeled points on the λ-α curve. As α increases, the profile of p_ξ becomes linear for small ξ with a rapid change at $p = p_\infty$. Note that the behavior of λ is different from Fig. 2, where D_p is independent of concentration: here $\lambda \nrightarrow 0$ as $\alpha \to 1$.

The accuracy of the computations for α near 1 is supported by the following results. The first deals with the case $\alpha = 1$, while the second considers the asymptotic limit as $\alpha \to 1$. The second is based on the standard definitions in, say, Bender and Orszag [2].

THEOREM 2. Let $D_p = D_p^0(1 - p/p_\infty)$, i.e., take $\alpha = 1$. Then for each value of $p(0) < p_\infty$, there exists a unique weak solution of (2.2a) and (2.2f). Furthermore, there is a ξ_∞ such that $p(\xi) = p_\infty$ for $\xi \geq \xi_\infty$ and $p(\xi) < p_\infty$ for $\xi < \xi_\infty$. Finally

$$\lim_{\xi \to \xi_\infty^-} p_\xi(\xi) = \frac{2(\lambda + \xi_\infty)p_\infty}{\sqrt{D_p^0}}. \tag{5.2}$$

Proof. Set $\phi \equiv 1 - p/p_\infty$ and $\eta \equiv (\lambda + \xi)/\sqrt{D_p^0}$. Equation (2.2a) is then

$$(\phi\phi')' + 2\eta\phi' = 0. \tag{5.3}$$

The existence and uniqueness of the weak solution, the boundedness of ϕ', and the existence of ξ_∞ all follow from a shooting argument of Craven and Peletier [7]. The limiting value of p_ξ as $\xi \to \xi_\infty$ can be computed following the argument for

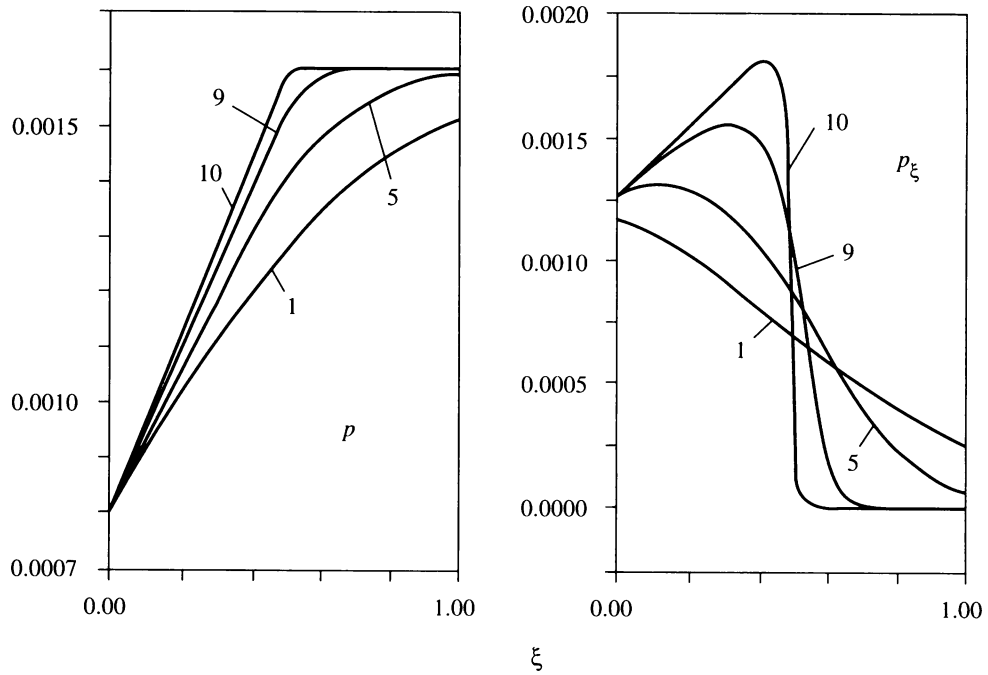

FIG. 5. Protein concentration (in mole fractions) and similarity gradient for several α values. Labels match those in Fig. 4. Note how rapidly p_ξ changes as $\alpha \to 1$. Again ξ is dimensionless: here $\xi \equiv x \Big/ 2\sqrt{tD_p^0}$.

Theorem 3 of [7, p. 80]. Integration of Eq. (5.3) yields

$$\phi\phi' + 2\eta\phi = (\phi\phi')(0) + 2\int_0^\eta \phi = -2\int_\eta^{\eta_\infty} \phi,$$

where $\eta_\infty \equiv (\lambda + \xi_\infty) \Big/ \sqrt{D_p^0}$. Dividing by ϕ and noting that since ϕ is decreasing

$$0 \le \frac{2}{\phi(\eta)} \int_\eta^{\eta_\infty} \phi \le 2(\eta_\infty - \eta),$$

one finds that

$$\lim_{\eta \to \eta_\infty^-} \phi' = -2\eta_\infty. \quad \square$$

THEOREM 3. Let $D_p(\alpha p) = D_p^0(1 - \alpha p/p_\infty)$, let ξ_∞ be the position of the corner shock discussed in Theorem 2, and let $p(\xi)$ satisfy (2.2a), (2.2c), and (2.2f) with $p(0) = p_0$. Then as $\alpha \to 1^-$, the outer solution of (2.2a) for $\xi < \xi_\infty$ is

$$p_{\text{out}}(\xi) = \frac{D_p^0 p_\infty (p_s - p_0)}{3\alpha p_s - 2\alpha p_0 - p_\infty}\xi^2 + \frac{2\lambda p_\infty (p_s - p_0)}{D_p^0(p_\infty - \alpha p_0)}\xi + p_0 + O(\xi^3),$$

with

$$\lambda = \sqrt{\frac{D_p^0(p_\infty - \alpha p_0)^3}{2p_\infty(\alpha p_s - p_\infty)(3\alpha p_s - 2\alpha p_0 - p_\infty)}}.$$

Moreover, let the inner scaling as $\alpha \to 1^-$ be

$$X \equiv \frac{\xi - \xi_\infty}{(1-\alpha)\sqrt{D_p^0}}.$$

Then for $1 - \alpha \ll 1$, the lowest-order inner solution p_{in}^0 satisfies

$$p_{\text{in}}^0(X) \sim p_\infty \left(1 + 2\frac{1-\alpha}{\alpha}\frac{(\xi_\infty + \lambda)}{\sqrt{D_p^0}}X\right) \quad \text{as } X \to -\infty \tag{5.4}$$

and

$$p_{\text{in}}^0(X) \sim p_\infty \left(1 - \frac{1-\alpha}{\alpha}e^{-2(\xi_\infty+\lambda)X/\sqrt{D_p^0}}\right) \quad \text{as } X \to +\infty. \tag{5.5}$$

Finally as $\alpha \to 1^-$, $p(\xi)$ converges to the singular solution discussed in Theorem 2.

Proof. Write the derivative of p in the form $p_\xi(\xi) = m\xi + b + O(\xi^2)$. Then b is given by (2.2c), m by evaluating (2.2a) at $\xi = 0$, and λ by requiring that (2.2a) be satisfied to second order in ξ.

To understand the inner asymptotics, let

$$P(X) \equiv \frac{\alpha}{1-\alpha}\left(1 - \frac{p(\xi)}{p_\infty}\right).$$

Then (2.2a) becomes

$$0 = ((1+P)P')' + 2(\eta_\infty + (1-\alpha)X)P',$$

where again $\eta_\infty \equiv (\lambda + \xi_\infty)/\sqrt{D_p^0}$. Dropping the higher-order $(1-\alpha)$-term and integrating twice, one finds that

$$\ln(P_0) + P_0 = -2\eta_\infty X + \ln(P_0(0)) + P_0(0).$$

Let $p_{\text{in}}(X) \equiv p(\xi)$. The claim then follows by considering $|X|$ large and writing the result in terms of p_{in}.

Finally, for the convergence result, let $\phi_\alpha \equiv \alpha(1 - p/p_\infty)$, and again let $\eta \equiv (\lambda + \xi)/\sqrt{D_p^0}$. Then (2.2a) becomes

$$((1 - \alpha + \phi_\alpha)\phi_\alpha')' + 2\eta\phi_\alpha' = 0. \tag{5.6}$$

Writing (5.3) and (5.6) as first-order systems, one sees that for $\phi > 0$ by a regular perturbation argument using Gronwall's inequality, $\phi_\alpha \to \phi$ pointwise as $\alpha \to 1$; but from the proof of Lemma 2, we know that ϕ_α is monotonically decreasing to 0. Since $\phi \equiv 0$ for $\eta \geq n_\infty$, it follows that $\phi_\alpha \to \phi$ uniformly. □

REMARKS. (1) Written in terms of ξ, p_{in} also converges to the singular solution. Compare (5.4) with (5.2), and (5.5) with $p \equiv p_\infty$.

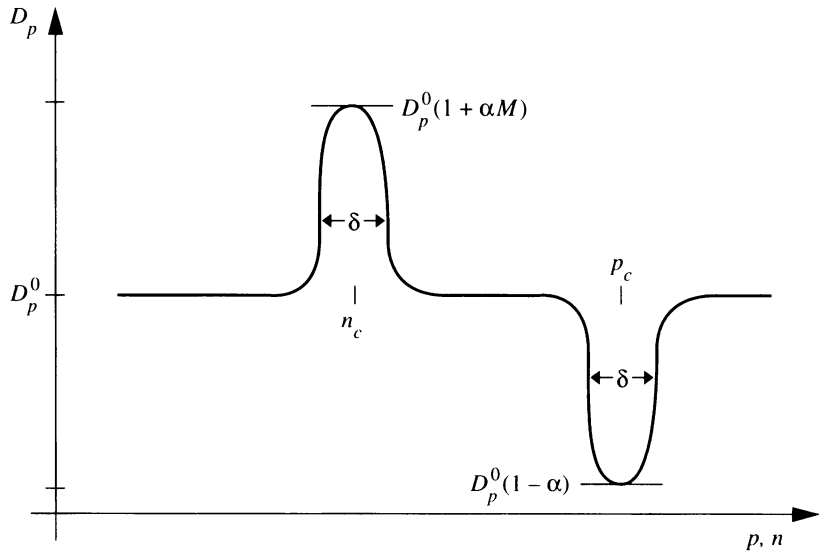

FIG. 6. Schematic diagram of $D_p(\alpha p, \alpha n)$ for Example 3.

(2) One is tempted to try the following argument: To find an outer solution away from the discontinuity in p_ξ, assume that $p_{\xi\xi}$ is bounded and that $D_p(p_\infty) \to 0$. These assumptions imply that p_ξ is a line, but the y-intercept for this line is inconsistent with (2.2c), and both the slope and y-intercept fail to match the computed values. The problem is that the assumptions are inconsistent: $p_{\xi\xi}$ becomes unbounded in the region where $D_p(p)$ is small. There is also an exact quadratic solution of (2.2a) that fails to satisfy the boundary conditions.

(3) The position of the corner shock is given to $O(\xi^3)$ and lowest order in α by solving $p_{\text{out}}(\xi_\infty) = p_\infty$. So in terms of the original variables, $x_\infty(t) = 2\xi_\infty\sqrt{t}$. Thus for α near 1, the corner shock position is a second moving boundary for the problem.

(4) Obviously the presence of the precipitant is not important for the last two theorems. The same results also hold for one-component systems.

EXAMPLE 3. For this final example, let

$$D_p = D_p^0(1 - \alpha e^{-((p-p_c)/\delta)^2})(1 + M\alpha e^{-((n-n_c)/\delta)^2})$$

and

$$D_n = D_n^0(1 - \alpha e^{-((n-n_c)/\delta)^2})(1 + M\alpha e^{-((p-p_c)/\delta)^2}).$$

These diffusivities are mirror images, with narrow ridges and troughs at critical concentrations p_c and n_c. Near n_c and away from p_c, the p-concentration increases from D_p^0 to $D_p^0(1+\alpha M)$, while near p_c and away from n_c, it decreases to $D_p^0(1-\alpha)$ (cf. Fig. 6). The diffusivities do not correspond to typical protein-precipitant systems.

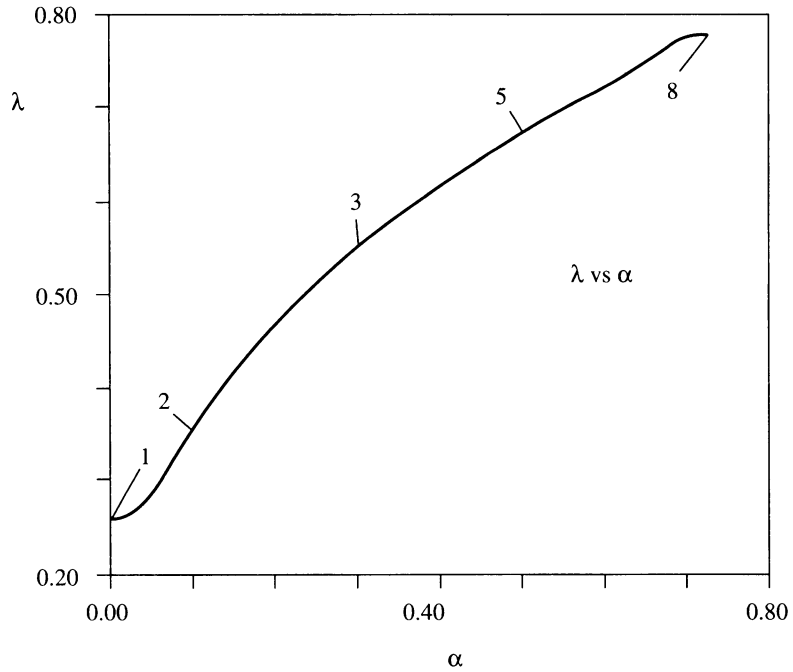

FIG. 7. Growth parameter for Example 3. At label 8, $\alpha \simeq 0.725$. $D_p = D_p^0(1 - \alpha e^{-((p-p_c)/\delta)^2})(1 + M\alpha e^{-((n-n_c)/\delta)^2})$, and $D_n = D_n^0(1 - \alpha e^{-((n-n_c)/\delta)^2})(1 + M\alpha e^{-((p-p_c)/\delta)^2})$.

They are, however, indicative of the complicated profiles that would be expected when, for example, something like hydrogen bonding occurs at critical concentrations. This effect would cause molecules of one constituent to form chains or lattices, inhibiting their movement while creating additional interstitial space for the other constituent. Note that the relative positions of α and the concentrations in this example differ from what they were in the analysis and the first two examples. This requires a minor change in the code but does not present a serious difficulty.

Computations for this system are presented in Figs. 7, 8 (see p. 422). Again the first figure is a plot of the growth parameter, but this time the second displays p and n. In these computations, the critical concentrations are $p_c = 0.001$ and $n_c = 0.021$, while $M = 1000$ and $\delta^2 = 10^{-7}$. Also for this example, $D_p^0 = D_n^0 = 1$. These parameter values lead to singular diffusivities in the middle of the concentration ranges. There are two main observations in these figures: First, plateaux form in each concentration at the ξ-value corresponding to the critical value of the other concentration. This results in an internal layer in the protein concentration, which moves deeper into the liquid phase as $\alpha \to 1$. The second observation is the "kink" in the growth parameter for large values of α. As α increases, the diffusivities become increasingly singular, and the growth parameter in particular becomes more difficult to compute accurately.

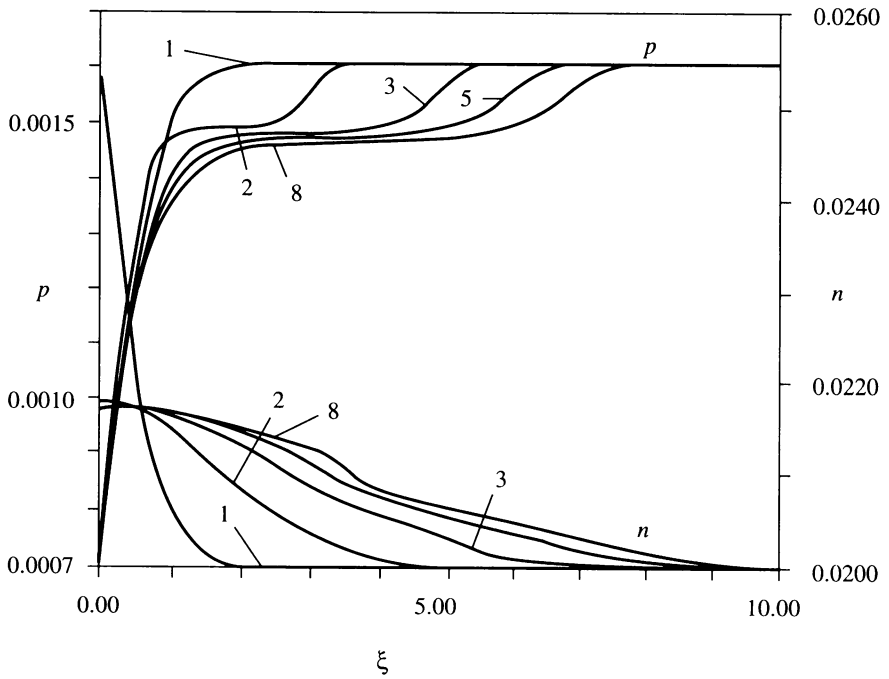

FIG. 8. p and n-values for Example 3 for several α values. Labels match those in Fig. 7.

Acknowledgments. The author wishes to thank Mark Friedman, Arunan Nadarajah, and Bert Peletier for a number of helpful discussions.

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