

A GENERALIZED STEFAN PROBLEM IN A DIFFUSION MODEL WITH EVAPORATION*

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Abstract. A model for species diffusion is presented, with evaporation at a moving free boundary. The resulting problem resembles a one-phase Stefan problem with superheating, but the usual Stefan condition at the moving boundary is replaced by a version which, in the classical setting, would violate conservation of energy. In the fast evaporation limit, however, the problem reduces to a classical nonlinear Stefan problem with negative latent heat.

Key words. species diffusion, Stefan problem

AMS subject classifications. 35K20, 35K60, 80A22

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1. Introduction. This work is motivated by studies of the drying of liquid paints. We are interested in describing the behavior of the moving interface due to the evaporation of solvent, this being an important driving force for the flow of the paint layer. Local differences in evaporation may give rise to Marangoni effects, which, in turn, influence the ultimate leveling of the surface. In this paper we do not consider those Marangoni effects, but our approach yields a simple model from which concentrations at the free boundary can be computed. When the model is used in a three-dimensional situation, Marangoni effects can be computed once relations between surface tension and concentrations are established. This, together with the traditional flow equations, would give a complete description of the behavior of the free boundary.

The liquid material is made up of different constituents, typically solvent, pigment, and resin, and the composition changes during the drying, which is a process of diffusion and evaporation. The model is then a diffusion equation with boundary conditions dictated by conservation of resin and pigment and loss of solvent. A more comprehensive version of this model has been described in [8], where we were interested in stress-driven diffusion rather than evaporation, and in [6].

We will briefly recall Fick's law and derive the boundary conditions in section 2. We will restrict our analysis to the one-dimensional situation. The system of equations for the volume fraction $\phi(x, t)$ and thickness $h(t)$ will be given by

$$\begin{aligned}
 (1.1) \quad & \phi_t = (D(\phi)\phi_x)_x, & 0 < x < h(t), \quad t > 0, \\
 & D(\phi)\phi_x = 0, & x = 0, \quad t > 0, \\
 & (1 - \phi)h_t = D(\phi)\phi_x, & x = h(t), \quad t > 0, \\
 & h_t = -K\phi, & x = h(t), \quad t > 0, \\
 & h = h_0, & t = 0, \\
 & \phi = \phi_0(x), & 0 \leq x \leq h_0, \quad t = 0.
 \end{aligned}$$

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Here K is a strictly positive constant and the diffusion coefficient D is assumed to be strictly positive and bounded. The first condition at $x = h(t)$ resembles the Stefan condition for phase transitions, but note that the additional factor of $(1 - \phi)$ would violate conservation of energy in this classical setting. The second condition is identical to the kinetic law as used in [15, 4, 16, 10].

Using the maximum principle, we first look at the properties of the solution in section 3.1. We discuss the existence and uniqueness of the solution of the problem in section 3.2. We shall prove that, if appropriate conditions on ϕ_0 and D are satisfied, there exists a unique classical solution (ϕ, h) of (1.1).

In the case of fast evaporation, the model reduces formally to the more familiar (nonlinear) Stefan problem with negative latent heat [9, 13]. We show in section 4 that this is indeed the fast evaporation limit, in the following sense: Let $(\phi^{(K)}, h^{(K)})$ be the solution of (1.1); then

$$\phi^{(K)} \rightarrow \phi^{(\infty)}, \quad h^{(K)} \rightarrow h^{(\infty)} \quad \text{as } K \rightarrow \infty,$$

in a sense to be defined later, where $(\phi^{(\infty)}, h^{(\infty)})$ is the unique classical solution of the nonlinear Stefan problem with negative latent heat (as defined in (4.1)).

2. Fick’s law and boundary conditions. It is assumed that the material is made up of two species only, for simplicity. Denote the volume fraction of solvent by ϕ_s and that of resin or polymer by ϕ_p , such that

$$\phi_s + \phi_p = 1 \quad \text{and} \quad \phi_s/V_s + \phi_p/V_p = c,$$

where V_p and V_s denote the molar volumes and c is the sum of the concentrations of solvent and resin (in mole per unit volume).

We assume that the volume fluxes add up to zero (related to mass conservation, assuming there are no voids or contractions), i.e., $\mathbf{J}_p + \mathbf{J}_s = 0$, and Fick’s law then gives the volume fluxes as

$$\mathbf{J}_s = -c\tilde{D}\nabla\frac{\phi_s}{c}, \quad \mathbf{J}_p = -\frac{V_s}{V_p}c\tilde{D}\nabla\frac{\phi_p}{c}.$$

The diffusion coefficient \tilde{D} may be a function of ϕ_p, ϕ_s (other dependencies such as those on pressure and temperature are neglected). Using the relations above for ϕ_s, ϕ_p , and c , or more specifically, $\phi_p = 1 - \phi_s$ and $c = c(\phi_s)$, the diffusion equation in terms of the volume fraction ϕ_s can be rewritten as

$$\frac{\partial\phi_s}{\partial t} = \nabla \cdot (D(\phi_s)\nabla\phi_s)$$

for a suitable function D , related to \tilde{D} . We assume this diffusion coefficient to be strictly positive and bounded.

Extensions of the Fickian diffusion may include a contribution due to viscoelastic stress [1, 2, 3, 5, 8].

We parametrize the moving surface by $\Gamma = 0$ so that in the paint region (where the diffusion takes place) we have $\Gamma(\mathbf{x}, t) < 0$. Assuming there exists a smooth boundary $\Gamma = 0$, the normal flux of polymer is determined by the (normal) velocity of this boundary. So the volume flux through the boundary, with $\mathbf{n} = \nabla\Gamma/|\nabla\Gamma|$ being the outward normal to the surface, is

$$\mathbf{J}_p \cdot \mathbf{n} |\nabla\Gamma| = -D(\phi_s)\nabla\phi_p \cdot \nabla\Gamma = -\phi_p \frac{\partial\Gamma}{\partial t} \quad \text{at } \Gamma = 0.$$

It follows from $\mathbf{J}_p + \mathbf{J}_s = 0$ that the flux of ϕ_s is given by

$$\mathbf{J}_s \cdot \nabla \Gamma = (1 - \phi_s) \frac{\partial \Gamma}{\partial t} \quad \text{at } \Gamma = 0,$$

which means that there is a (solvent) sink at the boundary of size $\partial \Gamma / \partial t$ which corresponds to the evaporation of the solvent.

A second condition at the free boundary is required. Note that due to the use of volume fractions it is really h_t that measures the flux of material. We assume that there exists a constant $K > 0$, comparable to Newton's law of cooling for the heat equation, such that

$$\frac{dh}{dt} = -K\phi_s(h(t), t) \quad \text{and} \quad J_s(h(t), t) = K\phi_s(h(t), t) \{1 - \phi_s(h(t), t)\}.$$

Apart from the factor $(1 - \phi_s)$, these conditions are the boundary conditions for the Stefan problem with negative latent heat and a kinetic law [15, 4, 16, 10].

The boundary conditions relate directly to the conservation of resin and pigment. This is most easily observed in the one-dimensional model, where the volume is really given by the thickness of the film $h(t)$. From mass conservation of polymer we find, with $\Gamma(x, t) = x - h(t)$,

$$\frac{dh}{dt} = \frac{d}{dt} \int_0^{h(t)} \phi_s(x, t) dx = \frac{dh}{dt} \phi_s(h(t), t) - J_s(h(t), t) + J_s(0, t).$$

The flux satisfies $J_s(0, t) = 0$ at the rigid boundary and we find that

$$J_s = -(1 - \phi_s) \frac{dh}{dt} \quad \text{at } x = h(t).$$

3. Nonlinear diffusion with a free boundary condition. We restrict ourselves in the following analysis to the one-dimensional case, write $\phi = \phi_s$, and denote partial differentiation by subscripts. We have the following system of equations for ϕ and h :

$$(3.1) \quad \begin{aligned} \phi_t &= (D(\phi)\phi_x)_x, & 0 < x < h(t), \quad t > 0, \\ D(\phi)\phi_x &= 0, & x = 0, \quad t > 0, \\ D(\phi)\phi_x &= -K\phi(1 - \phi), & x = h(t), \quad t > 0, \\ h_t &= -K\phi, & x = h(t), \quad t > 0, \\ h &= h_0, & t = 0, \\ \phi &= \phi_0(x), & 0 \leq x \leq h_0, \quad t = 0. \end{aligned}$$

We assume that there exist constants D_0, D_1 such that

$$(3.2) \quad D \in C^2[0, 1], \quad 0 < D_0 \leq D(\phi) \leq D_1 < \infty.$$

For the initial data we require that they satisfy the compatibility conditions

$$(3.3) \quad \phi_0 \in C^2[0, h_0], \quad \phi_{0,x}(0) = 0, \quad D(\phi_0(h_0))\phi_{0,x}(h_0) = -K\phi_0(h_0)(1 - \phi_0(h_0)),$$

and

$$(3.4) \quad 0 \leq \phi_0(x) \leq 1, \quad h_0 > 0.$$

A classical solution $(\phi(x, t), h(t))$ of this system is defined in the usual sense: For a function $h \in C^1[0, T)$, let

$$Q_T(h) = \{(x, t) : 0 < x < h(t), 0 < t \leq T\};$$

then a classical solution (ϕ, h) satisfies (1.1) with

- (i) $h \in C^1[0, T)$,
- (ii) $\phi \in C(\bar{Q}_T(h)) \cap C^{2,1}(Q_T(h))$,
- (iii) $\phi_x \in C(\bar{Q}_T(h))$.

As a special case we can take $\phi_0(x) \equiv 1$, i.e., the material consists of solvent only. One can easily write a solution,

$$\phi(x, t) = 1 \quad \text{for } 0 \leq x \leq h(t), \quad h(t) = h_0 - Kt,$$

which is valid only for $0 \leq t \leq h_0/K$ since at $t = h_0/K$ the complete layer has vanished.

In the fast evaporation limit $K \rightarrow \infty$, the boundary conditions at $x = h(t)$ reduce formally to what is known as the Stefan conditions, with negative latent heat,

$$(3.5) \quad \phi = 0 \quad \text{and} \quad h_t = D(\phi)\phi_x.$$

In this limit for $K \rightarrow \infty$, the initial condition $\phi_0(x) \equiv 1$ does not give a (classical) solution for positive time (see [7]). We exclude the pure solvent case and look for a classical solution for all time. In fact, we shall prove here only the existence of a unique classical solution if $\phi_0(x) \neq 1$ for all $x \in [0, h_0]$. We replace the condition (3.4) by

$$(3.6) \quad 0 \leq \phi_0(x) < 1, \quad h_0 > 0.$$

Many of the methods developed for the Stefan problem are applicable to the generalized system in (3.1), such as the transformation to integral equations in the linear case (D constant; see, for instance, Friedman [9]). Because of the combination of nonlinearity and negative latent heat, the proof of the existence of a solution was not found in the literature; most proofs of existence and uniqueness of solutions to similar problems use either the fundamental solution or a specific bound on the solution (which is related to the nondecreasing boundary in the classical Stefan problem). Schauder's theorem (see, for instance, Kyner [11]) could not be applied directly, due to the nonlinear mixed condition at the free boundary. The proofs given here depend primarily on the bounds on ϕ and the monotonicity of h .

3.1. Properties of the solution. We look first at some properties of the solution, assuming it exists. We have conservation of polymer and denote the mass (volume) of polymer by

$$(3.7) \quad h_1 = h_0 - \int_0^{h_0} \phi_0(x) dx.$$

We obtain an integral equation for the thickness $h(t)$:

$$(3.8) \quad h(t) = h_1 + \int_0^{h(t)} \phi(x, t) dx.$$

With the maximum principle we find the following.

LEMMA 3.1. *Let (ϕ, h) be a classical solution of (3.1) with conditions (3.2), (3.6), and $\phi_0 \neq 0$. Then for $(x, t) \in Q_T(h) \setminus \{t = 0\}$ we have $0 < \phi(x, t) < 1$, $\phi_x(h(t), t) < 0$ and $0 < h_1 < h(t) < h_0$.*

Proof. The domain of interest, $Q_T(h) = \{(x, t) : 0 < x < h(t), 0 < t \leq T\}$, is not yet known but must be found as part of the problem. In order to apply the maximum principle and the boundary point lemma [14], one can first fix the domain by specifying the shape of the boundary. Using the Kirchhoff transform

$$w(x, t) = \int_0^{\Phi(x,t)} D(s) ds =: g(\Phi)(x, t),$$

we find, in a standard way, that $0 < \phi(x, t) < 1$ for $t > 0$. In particular, $\phi(h(t), t) > 0$ for $t > 0$, and it thus follows that $h(t)$ is a strictly decreasing function.

We remark that with $h(t)$ strictly decreasing and sufficiently smooth, the integral relation (3.8) can also be obtained by integrating the differential equation over the domain $Q_T(h)$. Using this integral equation (3.8) and

$$h(t) = h_0 - K \int_0^t \phi(h(\tau), \tau) d\tau,$$

we immediately find the following bounds on $h(t)$,

$$(3.9) \quad 0 \leq h_1 \leq h(t) \leq h_0, \quad h(t) \geq \max(0, h_0 - Kt),$$

and strict inequalities apply for $t > 0$. □

Next we show the following asymptotic result.

LEMMA 3.2. *Suppose a solution pair (ϕ, h) of (3.1), conditions (3.2) and (3.6), exists for all positive time. Then we have*

$$\lim_{t \rightarrow \infty} h(t) = h_1 \quad \text{and} \quad \lim_{t \rightarrow \infty} \phi(x, t) = 0 \quad \text{for all } x \in [0, h_1].$$

Proof. We use a comparison of the Kirchhoff transform of ϕ ,

$$w(x, t) = g(\phi)(x, t) = \int_0^{\phi(x,t)} D(s) ds,$$

and the solution W of the linear boundary value problem

$$(3.10) \quad \begin{aligned} W_t &= D_0 W_{xx}, & 0 < x < h_0, \quad t > 0, \\ W_x &= 0, & x = 0, \quad t > 0, \\ W_x &= -\frac{K}{D_1}(1 - M)W, & x = h_0, \quad t > 0, \\ W &= W_0(x), & 0 \leq x \leq h_0, \quad t = 0, \end{aligned}$$

with the conditions $W_{0xx} \leq 0$, $W_0 \geq g(\phi_0)$ for all $0 \leq x \leq h_0$ and $W_{0x}(0) = 0$, $W_{0x}(h_0) = -K(1 - M)W_0(h_0)/D_1$. The constant M is defined as the maximum value of ϕ_0 , $M = \|\phi_0\|_\infty \leq 1$. Since the problem for W is linear, it is straightforward to show that $W \geq 0$ and that $W_t \leq 0$ and therefore $W_{xx} \leq 0$ for all $t > 0$.

We find that the function $v = w - W$ for $0 \leq x \leq h(t)$, $t \geq 0$, satisfies

$$\begin{aligned} v_x(h(t), t) &= -Kg^{-1}(w) \{1 - g^{-1}(w)\}_{|x=h(t)} - W_x|_{x=h(t)} \\ &\leq -\frac{K}{D_1}(1 - M)w|_{x=h(t)} + \frac{K}{D_1}(1 - M)W|_{x=h_0} \\ &\leq -\frac{K}{D_1}(1 - M)v|_{x=h(t)}. \end{aligned}$$

Then v satisfies

$$(3.11) \quad \begin{aligned} D(g^{-1}(w))v_{xx} - v_t &\geq 0, & 0 < x < h(t), \quad t > 0, \\ v_x &= 0, & x = 0, \quad t > 0, \\ v_x &\leq -\frac{K}{D_1}(1 - M)v, & x = h(t), \quad t > 0, \\ v &\leq 0, & 0 \leq x \leq h_0, \quad t = 0. \end{aligned}$$

Due to the sign in the condition at $x = h(t)$ it is not immediate that 0 is a supersolution. However, the maximum principle with the boundary point lemma still yields $v \leq 0$ for $0 \leq x \leq h(t)$, $t \geq 0$, and therefore $0 \leq w \leq W$. Since W tends to zero as $t \rightarrow \infty$ on $[0, h_0]$, it will also do so on $[0, h(t)]$. Thus $w(x, t) \rightarrow 0$ pointwise. After applying the transform g^{-1} we find that $\phi(x, t) \rightarrow 0$ as $t \rightarrow \infty$ and for each x in the spatial domain. With W attaining its maximum value in $x = 0$ for all t , the convergence is even uniform in x .

From (3.8) we conclude that $h(t) \rightarrow h_1$ as $t \rightarrow \infty$, with h_1 as defined in (3.7). \square

3.2. Existence and uniqueness. To prove the existence of a classical solution we use a coordinate transform to a fixed frame. The transform is based on the fact that the mass of polymer is constant at all times:

$$h_1 = \int_0^{h_0} \{1 - \phi_0(x)\} dx = \int_0^{h(t)} \{1 - \phi(x, t)\} dx.$$

The new coordinates are defined by

$$(3.12) \quad y = \int_x^{h(t)} \{1 - \phi(\bar{x}, t)\} d\bar{x}, \quad \tau = t,$$

and it is observed that in the fixed frame, for $0 \leq y \leq h_1$, the equation for the thickness h is uncoupled. Similar (mass) Lagrange variables were introduced by Meirmanov ([13, Chap. 5]), but due to the use of the Kirchhoff transform, his Lagrange coordinates do not automatically fix the domain and decouple the equations.

THEOREM 3.3. *There exists a unique classical solution of (3.1) when conditions (3.2), (3.3), and (3.6) are satisfied.*

Proof. Again define the Kirchhoff transform $g(\phi) = \int_0^\phi D(s)ds$; then with $D > 0$, the inverse g^{-1} is well defined. Let $a(v) = D(g^{-1}(v))(1 - g^{-1}(v))^2 \geq 0$.

We now consider the solution v of the boundary value problem:

$$(3.13) \quad \begin{aligned} v_\tau &= a(v)v_{yy}, & 0 < y < h_1, \quad \tau > 0, \\ a(v)v_y &= Ka(v)g^{-1}(v), & y = 0, \quad \tau > 0, \\ a(v)v_y &= 0, & y = h_1, \quad \tau > 0, \\ v &= v_0(y), & 0 \leq y \leq h_1, \quad \tau = 0, \end{aligned}$$

with the condition that $0 \leq g^{-1}(v_0) < 1$. Applying Theorem 7.4 of Ladyženskaja, Solonnikov, and Ural'ceva [12] with their inequalities (7.36) and using symmetry for the condition at $y = h_1$, we can conclude the existence of a unique classical solution $v(y, \tau)$. This solution satisfies

$$0 < g^{-1}(v)(y, \tau) < 1 \quad \text{for} \quad 0 \leq y \leq h_1, \quad \tau > 0.$$

Now define the function $h(\tau)$ as the solution of

$$h_\tau(\tau) = -v_y(0, \tau), \quad h(0) = h_0.$$

The function $h(\tau)$ is then strictly decreasing and $h(\tau) \in C^1[0, T)$.

We define the function

$$\phi(x, t) = g^{-1}(v)(y, \tau)$$

using the coordinate transform

$$(3.14) \quad x = \int_y^{h_1} \frac{1}{1 - g^{-1}(v)(\bar{y}, \tau)} d\bar{y}, \quad t = \tau.$$

We note that this transform is regular since $g^{-1}(v)$ is bounded away from one for all $\tau \geq 0$. It is the inverse of the transform given in (3.12).

We find that (ϕ, h) satisfies (3.1) if we take $v_0(y) = g(\phi_0)(x)$, and the existence of a classical solution of (3.1) is established.

For the uniqueness, we obtain with Lemma 3.1 that a solution (ϕ, h) of (3.1) satisfies $0 < \phi(x, t) < 1$ for $t > 0$ and that $h(t)$ is strictly decreasing. Applying the coordinate transform (3.12), and defining $v(y, \tau) = g(\phi)(x, t)$, we find that v satisfies (3.13) and the uniqueness is established. \square

4. The Stefan problem in the fast evaporation limit. We denote by $v^{(K)}$ the solution of (3.13) corresponding to the value K and similarly by $(\phi^{(K)}, h^{(K)})$ the solution of (3.1). We look at the fast evaporation limit, as $K \rightarrow \infty$.

THEOREM 4.1. *Let $(\phi^{(K)}, h^{(K)})$ be the solution of (3.1), with conditions (3.2), (3.3), and (3.6). Then*

$$\phi^{(K)} \rightarrow \phi^{(\infty)}, \quad h^{(K)} \rightarrow h^{(\infty)}, \quad \text{uniformly as } K \rightarrow \infty,$$

where $(\phi^{(\infty)}, h^{(\infty)})$ is the unique classical solution of the nonlinear Stefan problem with negative latent heat:

$$(4.1) \quad \begin{aligned} \phi_t &= (D(\phi)\phi_x)_x, & 0 < x < h(t), \quad t > 0, \\ D(\phi)\phi_x &= 0, & x = 0, \quad t > 0, \\ \phi &= 0, & x = h(t), \quad t > 0, \\ h_t &= D(\phi)\phi_x, & x = h(t), \quad t > 0, \\ h &= h_0, & t = 0, \\ \phi &= \phi_0(x), & 0 \leq x \leq h_0, \quad t = 0. \end{aligned}$$

Proof. Let $Q_T = (0, h_1) \times (0, T]$. Suppose $v^{(K_1)}$ and $v^{(K_2)}$ are the solutions of (3.13) with the same initial datum v_0 , but with $K_1 < K_2$. It is almost immediate to see that $v^{(K_1)}(y, \tau)$ is a supersolution for $v^{(K_2)}(y, \tau)$; i.e., $v^{(K_1)}(y, \tau) > v^{(K_2)}(y, \tau)$ for all $\tau > 0$ if $K_1 < K_2$. So for each $(y, \tau) \in Q_T$, the values $v^{(K)}(y, \tau)$ form a monotonically decreasing sequence for increasing K . Since this sequence is bounded from below, there exists a $v^{(\infty)}$ such that $v^{(K)}(y, \tau) \rightarrow v^{(\infty)}(y, \tau)$ pointwise as $K \rightarrow \infty$.

We note that $a(v)$ is bounded away from zero if initially $\phi_0 < 1$, as is required in condition (3.6). Define the Kirchoff transform of $1/a(v)$: $b(v) = \int_0^v 1/a(s) ds$. With both b and g^{-1} continuous in v , we find that also $b(v^{(K)}) \rightarrow b(v^{(\infty)})$ and $g^{-1}(v^{(K)}) \rightarrow g^{-1}(v^{(\infty)})$ as $K \rightarrow \infty$.

Now for any function $\psi \in C^{1,1}(\bar{Q}_T)$ we have

$$\begin{aligned} & \int_0^T \int_0^{h_1} \{b(v^{(K)})\psi_t + v^{(K)}\psi_{yy}\} dx dt \\ & - \int_0^{h_1} b(v^{(K)})\psi \Big|_{t=0}^{t=T} dx - \int_0^T K g^{-1}(v^{(K)})\psi \Big|_{y=0} dt - \int_0^T v\psi_y \Big|_{y=0}^{y=h_1} = 0. \end{aligned}$$

By the dominated convergence theorem we find that the limit function $v^{(\infty)}$ is a weak solution of

$$(4.2) \quad \begin{aligned} v_\tau &= a(v)v_{yy}, & 0 < y < h_1, \tau > 0, \\ v &= 0, & y = 0, \tau > 0, \\ v_y &= 0, & y = h_1, \tau > 0, \\ v &= v_0(y), & 0 \leq y \leq h_1, \tau = 0. \end{aligned}$$

Since this boundary value problem has a unique weak solution which is classical, it results that $v^{(\infty)}$ is the classical solution. With the sequence $\{v^{(K)}\}$ being monotonic, \bar{Q}_T compact, and the limit function continuous, the convergence is uniform.

Now also define $h^{(\infty)}$ in the limit for $K \rightarrow \infty$ by

$$h_\tau^{(\infty)}(\tau) = -v_y^{(\infty)}(0, \tau), \quad h^{(\infty)}(0) = h_0,$$

and let $\phi^{(\infty)}(x, t) = g^{-1}(v^{(\infty)})(y, \tau)$ with the coordinate transform (3.12). The pair of functions $(\phi^{(\infty)}, h^{(\infty)})$ so obtained satisfies the boundary value problem (4.1). Following the proof of Theorem 3.3 it is not difficult to show that there exists a unique classical solution to this problem (4.1).

We observe that

$$\sup |\phi^{(\infty)} - \phi^{(K)}| \leq \sup |g^{-1}(v^{(\infty)}) - g^{-1}(v^{(K)})| \rightarrow 0 \text{ as } K \rightarrow \infty,$$

where the first supremum is taken over $(x, t) \in \bar{Q}_T(h^{(\infty)}) \cap \bar{Q}_T(h^{(K)})$ and the second over $(y, \tau) \in \bar{Q}_T(h_1)$. This proves the result. \square

5. Concluding remarks. This work considers a nonlinear diffusion model which arises in studies of drying liquid paints. The model resembles the free boundary problem of the phase change of a supercooled liquid (or superheated solid), the Stefan problem with negative latent heat, although the Stefan condition is generalized to a flux condition, modeling the evaporation of solvent at the free boundary. Using (mass) Lagrangian coordinates the existence and uniqueness of a classical solution could be established here under some conditions of which the smoothness can probably be relaxed.

We conclude this paper with the following observations. As in Fasano and Primicerio [7] one finds relationships between h and ϕ by multiplying the diffusion equation by a polynomial in x and integrating over the domain, similar to (3.8). Defining, similar to $M_0 = h_1 = h_0 - \int_0^{h_0} \phi_0(x) dx$, the moments

$$M_1 = \frac{1}{2}h_0^2 - \int_0^{h_0} x\phi_0(x) dx, \quad M_2 = \frac{1}{3}h_0^3 - \int_0^{h_0} x^2\phi_0(x) dx,$$

(and so on) we find the relations (3.8) and

$$\begin{aligned} M_1 &= \frac{1}{2}h^2 - \int_0^{h(t)} x\phi(x) dx - \int_0^t \int_0^{h(\tau)} D(\phi)\phi_x dx d\tau, \\ M_2 &= \frac{1}{3}h^3 - \int_0^{h(t)} x^2\phi(x) dx - \int_0^t \int_0^{h(\tau)} 2xD(\phi)\phi_x dx d\tau. \end{aligned}$$

These relations hold in both cases $K < \infty$ and $K = \infty$. If $0 \leq \phi_0 \leq 1$, $\phi_0 \not\equiv 1$, and ϕ_0 sufficiently smooth, then $M_i > 0$. This results in the inequalities

$$\begin{aligned} \int_0^t \int_0^{h(\tau)} D(\phi)\phi_x dx d\tau &< \frac{1}{2}h^2 - \int_0^{h(t)} x\phi(x) dx, \\ \int_0^t \int_0^{h(\tau)} 2xD(\phi)\phi_x dx d\tau &< \frac{1}{3}h^3 - \int_0^{h(t)} x^2\phi(x) dx. \end{aligned}$$

In [7] the moments are used to show that no blow-up of the solution occurs whenever the initial datum satisfies $0 \leq \phi_0 \leq 1$. With the use of volume fractions, this condition is always satisfied in the present model. The fact that the boundary conditions are now given by a kinetic law and a generalized Stefan condition (not conserving energy) does not seem to affect the conservation of the moments.

Since the transformation to a fixed frame decouples the equation for the thickness, the transformed problem enables us to find the long time behavior by a straightforward linearization around the trivial solution. This results in an exponential decay of the thickness, as can be expected:

$$h(t) - h_1 \sim C \exp(-D(0)\alpha t)$$

with α the first positive zero of $D(0)\alpha \tan h_1\alpha = K$, which lies in the interval $(0, \pi/2h_1)$. In the limit for $K \rightarrow \infty$ this constant is $\alpha = \pi/2h_1$, which can also be found by linearizing the transformed Stefan problem in the fixed frame.

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