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Stress-driven diffusion in a drying liquid paint layer

B. W. VAN DE FLIERT and R. VAN DER HOUT

Mathematical Institute, Leiden University,
PO Box 9512, 2300 RA Leiden, The Netherlands

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A model is presented for the diffusion-driven drying of a polymeric solution such as liquid paint. Included is a stress build-up and relaxation in the polymer network of the viscoelastic material, which influences the diffusion process. The behaviour of the (one-dimensional) model is analysed by means of the maximum principle and illustrated with numerical calculations.

1 Introduction

Many liquid paints consist mainly of resin, pigment and volatile solvent. Due to solvent evaporation there will be compositional changes during the drying. This can, for instance, result in surface tension gradients (Marangoni effect), as was first stressed by Overdiep [1]. The resin consists of monomers or polymers which form a network during the drying process. The gel-like material which is formed creates stresses in the paint layer and 'squeezes out' the solvent, a phenomenon called stress-driven diffusion.

In the literature dealing with this type of diffusion, one concentrates on penetration of liquids into polymer material, a slab made up of polymer [2]–[6]. The penetration of the solvent by diffusion is enhanced by the polymer relaxation, which sometimes results in a sharp diffusion front. In the polymer science literature this shock-like behaviour is referred to as case II diffusion or non-Fickian behaviour. An extension of Fick's law is used when modelling the penetration process, where in addition to Fick's diffusion, a stress term is taken into account representing viscoelastic effects.

In the problem considered here, the drying of liquid paints, the diffusive behaviour is similar to that in the wetting problem. If liquid paint with volatile solvent is deposited on a substrate, we can assume that initially the polymer is dissolved and unstressed. The solvent of the liquid paint will evaporate at the moving air/paint interface and the remaining resin will form a polymer network once the paint layer becomes sufficiently dry. The polymer will then resist further shape changes when more solvent leaves the material. Stresses build up, which in a way pull the solvent from the wet region towards the dryer region near the surface, causing the enhanced drying.

The mathematical model equations derived here for the drying of volatile paints are the same as those commonly used for polymer wetting, except for the conditions at the moving free boundary (see also Edwards & Cohen [7]). We concentrate on conditions dictated by the flux of material; our motivation is that we want to determine the behaviour

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of the moving boundary. We first discuss in § 2 the mathematical model of stress-driven diffusion, including the choice of the viscoelastic relation for the stress. In § 3 we consider the boundary and initial conditions. In this we have not considered the effect of surface tension.

After deriving the model, our main concern is whether the model will produce physically acceptable values for the thickness and the volume fraction for all time. We restrict the discussion in this paper to the one-dimensional case. With the use of volume fractions instead of concentrations, the thickness of the film $h(t)$ can be related directly to the volume fraction of solvent $\phi(x,t)$ at any specific time. The full system of equations for the volume fraction of solvent ϕ and the thickness h will be shown to be given by

$$\left.\begin{array}{ll} \phi_t = (D(\phi)\phi_x)_x + (\kappa(\phi)\sigma_x)_x & \text{for } 0 < x < h(t),\ t > 0, \\ \sigma_t = g_1(\phi) + g_2(\phi)\phi_t - \{\beta_1(\phi) + \beta_2(\phi)\phi_t\}\,\sigma & \text{for } 0 < x < h(t),\ t > 0, \\ D(\phi)\phi_x + \kappa(\phi)\sigma_x = 0 & \text{for } x = 0,\ t > 0, \\ D(\phi)\phi_x + \kappa(\phi)\sigma_x = -K\phi(1-\phi) & \text{for } x = h(t),\ t > 0, \\ h_t = -K\phi \quad \text{with} \quad h(0) = h_0 & \text{for } x = h(t),\ t > 0, \\ \phi = \phi_0(x) \quad \text{and} \quad \sigma = 0 & \text{for } 0 \leqslant x \leqslant h_0,\ t = 0. \end{array}\right\} \tag{1.1}$$

Here D denotes the diffusion coefficient, κ is related to the porosity, K is an evaporation constant and the functions g_1, g_2, β_1 and β_2 will be introduced to model the viscoelastic properties of the material.

In § 4 we briefly look at the pure diffusive case, without stress build-up (say if $g_1 = g_2 = 0$; see also [8])

$$\left.\begin{array}{ll} \phi_t = (D(\phi)\phi_x)_x & \text{for } 0 < x < h(t),\ t > 0, \\ D(\phi)\phi_x = 0 & \text{for } x = 0,\ t > 0, \\ D(\phi)\phi_x = -K\phi(1-\phi) & \text{for } x = h(t),\ t > 0, \\ h_t = -K\phi \quad \text{with} \quad h(0) = h_0 & \text{for } x = h(t),\ t > 0, \\ \phi = \phi_0(x) & \text{for } 0 \leqslant x \leqslant h_0,\ t = 0. \end{array}\right\} \tag{1.2}$$

Assuming that the equation for ϕ is uniformly parabolic, application of the maximum principle then shows the following:

Theorem 1 *Suppose* $0 \leqslant \phi_0(x) \leqslant 1$ *for* $0 \leqslant x \leqslant h_0$, *with* $\phi_0 \not\equiv 0,\ \phi_0 \not\equiv 1$ *and let* (ϕ, h) *be a (classical) solution of* (1.2) *with* $0 < D_0 \leqslant D \leqslant D_1$. *Then for* $0 < t \leqslant T$ *and* $0 \leqslant x \leqslant h(t)$ *we have* $0 < \phi(x,t) < 1$, $\phi_x(h(t),t) < 0$ *and* $0 < h_1 < h(t) < h_0$.

The constant h_1 in this theorem only depends on the initial data ϕ_0 and h_0 and it the will be defined in equation (4.3). For the full model of stress-driven diffusion a similar result is found in § 5:

Theorem 2 *Suppose* $\kappa(0) = 0$, $\kappa(1) = 0$ *and* $0 < D_0 \leqslant D \leqslant D_1$. *Suppose* $0 \leqslant \phi_0(x) \leqslant 1$ *for* $0 \leqslant x \leqslant h_0$, *with* $\phi_0 \not\equiv 0,\ \phi_0 \not\equiv 1$ *and let* (ϕ, σ, h) *be a (classical) solution of* (1.1). *Then for* $0 < t \leqslant T$ *and* $0 \leqslant x \leqslant h(t)$ *we have* $0 < \phi(x,t) < 1$, $\phi_x(h(t),t) < 0$ *and* $0 < h_1 < h(t) < h_0$.

These theorems show that the model produces physically acceptable behaviour; the reader who is not interested in the proof may skip § 5.1. There are still many questions

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that remain unanswered, such as on the large and small time asymptotic behaviour of the solution. Detailed numerical calculations need to be performed in later studies and we show here only a first illustration of the expected behaviour. The results also need to be related to physical data where available. We will come back to this in the conclusion to this article.

For the pure diffusion problem (1.2) many questions have been answered after a transformation to a fixed frame, see [8]. Using a type of Lagrange coordinates it is possible to uncouple the evolution of the free boundary from the stress-diffusion equations. This was used for instance in [8] to prove the existence and uniqueness of a classical solution, using known results on uniformly parabolic equations. Since the full stress-diffusion system is not parabolic (in the sense of Petrovskiĭ [9, 10]), but rather a system of a parabolic equation and an ordinary differential equation, the existence and uniqueness result is not easily generalized to this system and this problem will not be addressed here. We will end this paper with some remarks on the transformation to the fixed frame.

2 Non-Fickian diffusion and Maxwell's equation

2.1 Species diffusion

For simplicity it is assumed that the material is made up of two species only. Denote the concentration of solvent by c_s and that of resin or polymer by c_p (mole per unit volume). Fick's law gives the mole fluxes as

$$\mathbf{j}_s = -c\left(D_{ss}\nabla\frac{c_s}{c} + D_{sp}\nabla\frac{c_p}{c}\right), \quad \mathbf{j}_p = -c\left(D_{ps}\nabla\frac{c_s}{c} + D_{pp}\nabla\frac{c_p}{c}\right),$$

where $c = c_p + c_s$. The Fickian diffusion coefficients may be functions of c_p, c_s, but also of pressure and temperature; we neglect the latter effects. With molar volumes $V_{m,p}$, $V_{m,s}$ the volume fractions are $\phi_p = V_{m,p}c_p$, $\phi_s = V_{m,s}c_s$ and the volume fluxes are given by $\mathbf{J}_p = V_{m,p}\mathbf{j}_p$, $\mathbf{J}_s = V_{m,s}\mathbf{j}_s$. We assume that the volume of the mixture is equal to the sum of the volumes of the constituents (there is no volume contraction due to mixing or some chemical process). In view of the physical geometry of the paint layer, we therefore assume that the volume fluxes add up to zero, $\mathbf{J}_p + \mathbf{J}_s = 0$. Fick's law then states that

$$\mathbf{j}_s = -cD_s\nabla\frac{c_s}{c}, \quad \mathbf{j}_p = -\alpha cD_s\nabla\frac{c_p}{c},$$

where D_s, α are defined as

$$D_s = (D_{ss} - D_{sp}), \quad \alpha = V_{m,s}/V_{m,p},$$

so that $(D_{pp} - D_{ps}) = \alpha D_s$. The diffusion equations are therefore

$$\frac{\partial c_s}{\partial t} = \nabla\cdot\left(cD_s\nabla\frac{c_s}{c}\right), \quad \frac{\partial c_p}{\partial t} = \nabla\cdot\left(\alpha cD_s\nabla\frac{c_p}{c}\right),$$

which can be rewritten in terms of c and ϕ_s by

$$\frac{\partial\phi_s}{\partial t} = \nabla\cdot\left(cD_s\nabla\frac{\phi_s}{c}\right), \quad \frac{\partial c}{\partial t} = (1-\alpha)\nabla\cdot\left(cD_s\nabla\frac{\phi_s}{V_{m,s}c}\right).$$

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But, with $c = (1-\phi_s)/V_{m,p} + \phi_s/V_{m,s}$ we find a diffusion equation in terms of the volume fraction ϕ_s only:

$$\frac{\partial \phi_s}{\partial t} = \nabla \cdot (D(\phi_s)\nabla\phi_s), \tag{2.1}$$

where

$$D(\phi_s) = \frac{D_s(\phi_s)\alpha}{\phi_s + \alpha(1-\phi_s)}$$

is a non-negative diffusion coefficient.

If we parametrize the moving surface by $\Gamma = 0$, so that in the paint region (where the diffusion takes place) we have $\Gamma(\mathbf{x}, t) < 0$, then at $\Gamma = 0$ the normal flux of polymer is determined by the (normal) velocity of the surface; with $\mathbf{n} = \nabla\Gamma/|\nabla\Gamma|$ the outward normal to the surface:

$$\mathbf{j}_p \cdot \mathbf{n} = -\alpha c D_s \nabla \frac{c_p}{c} \cdot \mathbf{n} = -c_p u_n = -c_p \Gamma_t / |\nabla\Gamma|;$$

from this it follows that the mole flux satisfies

$$\mathbf{j}_s \cdot \nabla\Gamma = \frac{c - c_s}{\alpha}\Gamma_t,$$

which means that, in comparison with the polymer flux, there is a sink of solvent at the boundary which corresponds to the evaporation of the solvent. We find for the volume flux

$$\mathbf{J}_s \cdot \nabla\Gamma = (1-\phi_s)\Gamma_t,$$

which relates directly to the conservation of polymer, as will be shown in § 3.

2.2 Non-Fickian diffusion

In the paper by Cohen, White and Witelski [5], a clear description is given of the stress-diffusion model for diffusion in a viscoelastic material. We will assume for the sake of simplicity, that the diffusion coefficient tensor and the stress tensor are isotropic. As we saw above, the volume flux vector $\mathbf{J}_p$ of polymer is then assumed proportional to the gradient of the volume fraction ϕ_p:

$$\frac{\partial \phi_p}{\partial t} = -\nabla \cdot \mathbf{J}_p, \quad \mathbf{J}_p = -D(\phi_s)\nabla\phi_p.$$

Denoting by $\Pi(\phi_p)$ the osmotic pressure, Fick's law can alternatively be written as

$$\mathbf{J}_p = -\kappa(\phi_p)\nabla\Pi(\phi_p) = -\kappa(\phi_p)\Pi'(\phi_p)\nabla\phi_p. \tag{2.2}$$

Here $\kappa(\phi_p)$ can be viewed as a permeability of the material in which the diffusion takes place. The Fickian diffusion is extended to include a contribution from the viscoelastic stress [11, 12] in the following way:

$$\mathbf{J}_p = -\kappa(\phi_p)\nabla\{\Pi(\phi_p) - \sigma\},$$

with the motivation that the volume flux vector $\mathbf{J}_p$ vanishes in the equilibrium situation where the forces balance. We thus obtain in terms of ϕ_s (writing $\tilde{\kappa}(\phi_s) := \kappa(\phi_p)$ and immediately dropping the tilde again)

$$\frac{\partial \phi_s}{\partial t} = \nabla \cdot \{D(\phi_s)\nabla\phi_s + \kappa(\phi_s)\nabla\sigma\}.$$

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Reduced to the one-dimensional case, with $\phi = \phi_s$ and denoting partial differentiation by subscripts, this reads

$$\phi_t = \{D(\phi)\phi_x + \kappa(\phi)\sigma_x\}_x . \tag{2.3}$$

We assume $D(\phi_s)$ to be a strictly positive diffusion coefficient, while κ is non-negative.

2.3 Maxwell equation

The viscoelastic relation for σ can be given by a memory integral equation (Boltzmann or Maxwell equation) – see, for instance, Joseph [13] or Durning [2]. This means that σ is given by a hereditary integral:

$$\sigma(x,t) = \int_0^t \exp\left\{-\int_\tau^t \beta\left(\phi(x,s), d\phi(x,s)\right)\, ds\right\} g\left(\phi(x,\tau), d\phi(x,\tau)\right)\, d\tau. \tag{2.4}$$

Here it is assumed that $\sigma = 0$ at $t = 0$, starting initially with an unstressed state. The function $1/\beta$ is the so-called relaxation time τ_p of the polymer solution, while g represents the viscoelastic model that is used for the material. The functions β and g may also depend on derivatives of ϕ, symbolically denoted by $d\phi$ in (2.4); depending on the rheological nature of the material, one expects dependence on time-derivatives ϕ_t but we do not exclude x or mixed derivatives at this point. By differentiating with respect to time, we find the more familiar differential form

$$\frac{\partial \sigma}{\partial t} + \beta(\phi, d\phi)\sigma = g(\phi, d\phi). \tag{2.5}$$

One of the simplest forms of such a viscoelastic relation is given by a Maxwell model, with the viscoelasticity modelled as, in series, one spring with Young's modulus $E(\phi)$ and one dashpot with viscosity $\eta(\phi)$. This gives:

$$\beta(\phi, \phi_t) = \frac{E(\phi)}{\eta(\phi)} - \frac{E'(\phi)\phi_t}{E(\phi)}, \quad g(\phi, \phi_t) = E(\phi)\dot{\gamma}. \tag{2.6}$$

This is the equation considered by Cohen & White [12, 14]. The strain rate $\dot{\gamma}$ in (2.6) is assumed to represent the rate of polymer swelling

$$\dot{\gamma} = -\frac{1}{\phi_p}\frac{\partial \phi_p}{\partial t} = \frac{\phi_t}{1-\phi}.$$

Immediately we find when both E and η are constant, that $g(\phi) = E\dot{\gamma}$ and $1/\beta = \eta/E$ represents the usual relaxation time. Limit cases for $E \to \infty$ or $\eta \to \infty$ correspond in the Maxwell model to a purely viscous and a purely elastic material respectively. Alternatively, other viscoelastic models can be used like the Jeffrey-element, Voigt-Kelvin or the Oldroyd-B model, consisting of different systems of springs and dashpots [13] (but the function g can become unduly more complicated). Instead of starting with the spring-dashpot system, one could start from the memory integral (2.4) or its differential form, and assume a functional form for β and g. For instance, Cohen *et al.* [12, 5] propose $\beta(\phi)$ only and $g(\phi) = \mu\phi$, with μ =const. Durning [2] uses $\beta(\phi)$ and g linear in ϕ_t, while Cox [4] considers $\beta(\phi)$ and $g(\phi)$. More generally we will assume here the following viscoelastic relation, which is just linear in ϕ_t:

$$\sigma_t = g_1(\phi) + g_2(\phi)\phi_t - \{\beta_1(\phi) + \beta_2(\phi)\phi_t\}\,\sigma. \tag{2.7}$$

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The functions $g_1, g_2, \beta_1, \beta_2$ are non-negative and depend only on ϕ. (Remark: without experimental data on the material properties it is not possible to conclude on the functional behaviour of the coefficients, and the choice of the Maxwell spring-dashpot system with $E(\phi)$ and $\eta(\phi)$ is then as arbitrary as a choice for $g_1, g_2, \beta_1, \beta_2$.) The enhanced diffusion is in fact immediately seen by taking a purely elastic model, without relaxation, $\sigma = E(\phi)\gamma$, which in terms of the relation (2.7) means taking $g_2(\phi)$ as the only non-zero function. The diffusion equation then reads:

$$\phi_t = \{D(\phi)\phi_x\}_x + \{\kappa(\phi)g_2(\phi)\phi_x\}_x.$$

2.4 Coefficients

If we rewrite the two equations (2.3) and (2.7) as a system of first-order equations, it is found that this system is parabolic, unless $D = 0$, $g_2 = 0$ and $\beta_2 = 0$, in which case it is hyperbolic. The hyperbolic system is exactly the case which Cox [4] considers as the leading-order system, which has then two non-trivial characteristic speeds given by

$$\tfrac{1}{2}(-\kappa' u \pm \sqrt{(\kappa' u)^2 + 4\kappa(g_1' - \beta_1'\sigma)}),$$

in our notation and with $u = \sigma_x$. Looking at (2.3) and (2.7) as a system of second order equations, we find that it is not parabolic in the sense of Petrovskiĭ [9, 10], as one eigenvalue vanishes, corresponding to the ordinary differential equation.

If we assume that $\beta_1 > 0$, and that one of the boundary conditions is a no-flux condition, then the only possible steady state is given by $\phi = 0, \sigma = g_1(0)/\beta_1(0)$ and $h = h_1$ (to be defined in equation (4.3)). There is one possible exception to this, namely when the functions D, κ, g_1, β_1 (all functions of ϕ only) satisfy the following algebraic relation:

$$D + \kappa\left(\frac{g_1}{\beta_1}\right)' = 0. \tag{2.8}$$

This is a very special case for which any set of functions $(\phi^*(x), \sigma^*(x), h^*)$ satisfying the conditions $\phi^* = 0$ at $x = h^*$, $\sigma^* = g_1(\phi^*)/\beta_1(\phi^*)$ and h^* constant, yields a steady state solution. The question whether such a steady state, $(\phi^*, \sigma^*, h^*) \neq (0, g_1(0)/\beta_1(0), h_1)$, can ever be reached from an (initially) unstressed state is still open; a positive answer to this question means the trapping of solvent in the paint layer for all time.

We note that $\kappa(0) = \kappa(1) = 0$ must be satisfied for a well-defined diffusion process, i.e. the flux should vanish when the volume fraction of either species vanishes. We will show later that the condition $\kappa(0) = \kappa(1) = 0$ implies that $0 \leqslant \phi \leqslant 1$. Of course, as ϕ is a volume fraction it should satisfy $0 \leqslant \phi \leqslant 1$ physically, and we show that this remains true for all time mathematically.

In most of the analysis it is assumed that $D(\phi)$ is strictly positive. In the derivation of the model, using the extended Fick's law (2.2) with the diffusion coefficient satisfying $D(\phi) = \kappa(\phi)\Pi'(\phi)$, the diffusion will be degenerate since $\kappa(0) = \kappa(1) = 0$ (if Π' is finite). In this paper, we do not want to emphasize the difficulties that may occur when the diffusion degenerates. Degenerate diffusion problems are often studied as a limit of non-degenerate problems and the non-degenerate problem therefore needs to be understood first. The uniform parabolicity means in this case, respecting the necessary vanishing of κ, that the

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osmotic pressure is assumed to behave such that $\lim \kappa(\phi)\Pi'(\phi)$ is bounded and strictly positive as ϕ approaches 0 or 1.

Perhaps we should also note that D cannot be strictly positive and satisfy the algebraic relation (2.8) at the same time.

We would like to conclude this section with some remarks on the choice of the coefficients in the model (1.1). Scaling laws have been derived for different stages in the polymer dissolution process by De Gennes [15, 16, 11]. We can assume that different scaling laws can be incorporated by choosing the functional relation of the coefficients $g_1, g_2, \beta_1, \beta_2, D$ and κ properly. A good example of choosing functions so as to model the material properties suitably is the choice of the diffusion coefficient in Witelski [6], which models the transition from a glass state to a rubber phase. This, however, does not account for a complete change in material properties, such as may occur when cross-linking takes place after oxidation.

A relation between the osmotic pressure and the solvent concentration can for instance be given by the ideal gas law $\Pi(\phi) = RT\phi_p$, where $\phi_p = 1 - \phi$. A conventional law for polymer systems is given by $\Pi(\phi) = RT\phi_p(1 + C\phi_p)^2$, where C may be a large constant. Brochard & De Gennes [11] find a scaling law for semi-dilute systems:

$$\Pi(\phi) \cong \frac{kT}{\xi^3(\phi)} \cong (1-\phi)^{9/4},$$

where k is Boltzmann's constant, T temperature, $\xi = ((1-\phi)/a)^{-3/4}$ the correlation length and a the monomer size. They obtain also that $E \cong \Pi$, where E is Young's modulus.

In § 5.2 we shall numerically solve the problem to give an illustration of the behaviour. In these calculations the following coefficients have been taken:

$$D(\phi) = mD_0E_0(1-\phi)^{m-1}\kappa(\phi), \quad \kappa(\phi) = \phi,$$

and the Maxwell model (2.6):

$$g_1 = 0, \quad g_2 = \frac{E(\phi)}{1-\phi} = E_0(1-\phi)^{m-1},$$

$$\beta_1 = \frac{E(\phi)}{\eta(\phi)} = \frac{E_0}{\eta_0}\phi(1-\phi)^m, \quad \beta_2 = -\frac{E'(\phi)}{E(\phi)} = \frac{m}{(1-\phi)}.$$

The case where g_1 is a given function and $g_2 \equiv 0$ gives the more interesting dynamics – see Figure 1b for the case in which $g_1(\phi) = \phi$. We have no well-founded physical motivation for this choice of parameters; in the Maxwell model this case is obtained if the strain rate is a function of ϕ only, such that $g_1(\phi) = E(\phi)\dot{\gamma}(\phi)$.

3 Boundary conditions

We will assume that the configuration is a thin layer of liquid paint, with on one side an impermeable substrate and with the upper surface free, and moving due to the evaporation of solvent into air.

A flux condition has been derived in § 2.1 for the Fickian diffusion model. This is readily generalized to the stress-diffusion model. We observe that this boundary condition follows from a conservation law. In the one-dimensional model the thickness of the film is $h(t)$

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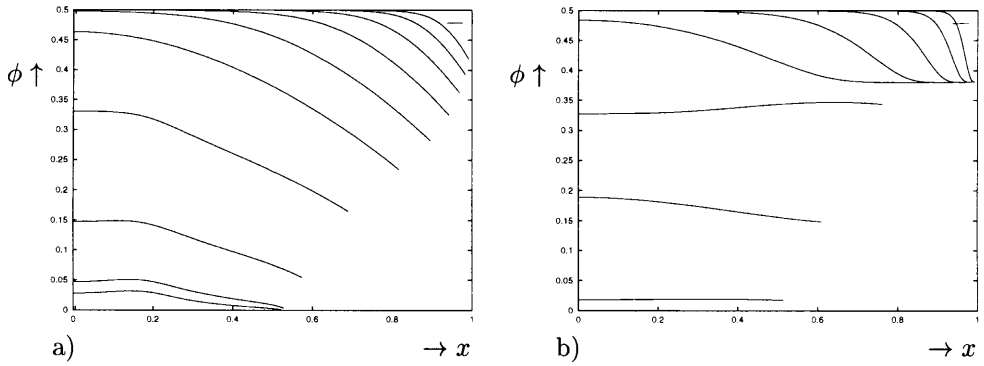


FIGURE 1. The two figures show the volume fraction of solvent ϕ as a function of x, the position in the layer. Different lines depict different times ($t = 0.01 \cdot 2^n, n = 0 \ldots 10$) where $\phi_0 \equiv 1/2$ and ϕ decreases in time. See text for the choice of the Maxwell model. Numerical values: $D_0 = 0.01, E_0 = 1, \eta_0 = 10, m = 3$. a) $g_1 = 0,\ g_2 = E_0(1-\phi)^{m-1}$, b) $g_1 = \phi,\ g_2 = 0$.

and from mass conservation of polymer we find

$$h_t = \frac{d}{dt}\int_0^{h(t)} \phi(x,t)\,dx = h_t\,\phi(h(t),t) - J(h(t),t) + J(0,t).$$

The solvent flux $J = -D(\phi)\phi_x - \kappa(\phi)\sigma_x$ satisfies $J(0,t) = 0$ at the fixed boundary and we find that

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

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

$$h_t = -K\,\phi(h(t),t), \quad \text{and so} \quad J(h(t),t) = K\,\phi(h(t),t)\left\{1 - \phi(h(t),t)\right\}.$$

Alternatively, the condition could read:

$$h_t = -Kf(\phi), \quad \text{with } f(0) = 0,\ f' > 0.$$

We assume that the layer is unstressed initially and that the volume fraction distribution is given.

Concluding, we have the following (1D) system of equations with initial and boundary conditions for ϕ, σ and h:

$$\left.\begin{array}{ll}
\phi_t = (D(\phi)\phi_x)_x + (\kappa(\phi)\sigma_x)_x & \text{for } 0 < x < h(t),\ t > 0,\\
\sigma_t = g_1(\phi) + g_2(\phi)\phi_t - \{\beta_1(\phi) + \beta_2(\phi)\phi_t\}\,\sigma & \text{for } 0 < x < h(t),\ t > 0,\\
D(\phi)\phi_x + \kappa(\phi)\sigma_x = 0 & \text{for } x = 0,\ t > 0,\\
D(\phi)\phi_x + \kappa(\phi)\sigma_x = -K\,\phi(1-\phi) & \text{for } x = h(t),\ t > 0,\\
h_t = -K\phi \ \text{ with } \ h(0) = h_0 & \text{for } x = h(t),\ t > 0,\\
\phi = \phi_0(x) \ \text{ and } \ \sigma = 0 & \text{for } 0 \leqslant x \leqslant h_0,\ t = 0.
\end{array}\right\} \tag{3.1}$$

Conditions on the initial data are

$$0 \leqslant \phi_0 \leqslant 1, \quad \text{and} \quad h_0 > 0.$$

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Writing $\varepsilon = 1/K$, the free-boundary condition resembles the kinetic condition (see [17] and references therein), apart from the factor $(1-\phi)$.

In the fast evaporation limit $K \to \infty$, the boundary conditions at $x = h(t)$ reduce formally to

$$\phi = 0, \quad \text{and} \quad h_t = -J = D(\phi)\phi_x + \kappa(\phi)\sigma_x. \tag{3.2}$$

These so-called Stefan conditions (also used, for instance, in Edwards & Cohen [7]) correspond to a negative latent heat. It has been proved [8] that the superheated Stefan problem is indeed the limit process for fast evaporation in the pure diffusion case without stress build-up.

4 Nonlinear diffusion with a free boundary

The pure diffusion case was studied separately in [8]. We will present a brief summary here. Assume that both $g_1 \equiv 0$ and $g_2 \equiv 0$, such that the initial condition for σ results in the trivial solution $\sigma \equiv 0$. Alternatively, take $\kappa \equiv 0$, which uncouples the equations and boundary conditions. For ϕ and h we now have the model of nonlinear diffusion with free boundary:

$$\left.\begin{array}{ll} \phi_t = (D(\phi)\phi_x)_x & \text{for } 0 < x < h(t),\ t > 0, \\ D(\phi)\phi_x = 0 & \text{for } x = 0,\ t > 0, \\ D(\phi)\phi_x = -K\phi(1-\phi) & \text{for } x = h(t),\ t > 0, \\ h_t = -K\phi & \text{for } x = h(t),\ t > 0,\ h(0) = h_0, \\ \phi = \phi_0(x) & \text{for } 0 \leqslant x \leqslant h_0,\ t = 0. \end{array}\right\} \tag{4.1}$$

The diffusion is non-degenerate if there exist constants D_0, D_1:

$$0 < D_0 \leqslant D(\phi) \leqslant D_1 < \infty. \tag{4.2}$$

We have shown [8] that a classical solution exists for all time if $0 \leqslant \phi_0 < 1$ and

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

From the fact that there is conservation of polymer, i.e.

$$\frac{d}{dt}\int_0^{h(t)} 1 - \phi(x,t)\,dx = 0,$$

we find an integral relation for h; denote by h_1 the volume of polymer

$$h_1 = h_0 - \int_0^{h_0} \phi_0(x)\,dx, \tag{4.3}$$

then

$$h(t) = h_1 + \int_0^{h(t)} \phi(x,t)\,dx. \tag{4.4}$$

This relation can also be obtained by integrating the differential equation over the domain $0 < x < h(\tau), 0 < \tau < t$, using that h is strictly decreasing. The following theorems have been proved earlier [8].

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Theorem 3 *Suppose* $0 \leqslant \phi_0(x) \leqslant 1$ *for* $0 \leqslant x \leqslant h_0$, *with* $\phi_0 \not\equiv 0$, $\phi_0 \not\equiv 1$ *and let* (ϕ, h) *be a classical solution of* (4.1) *with D satisfying* (4.2). *Then for* $0 < t \leqslant T$ *and* $0 \leqslant x \leqslant h(t)$ *we have* $0 < \phi(x,t) < 1$ *and* $\phi_x(h(t),t) < 0$. *Also* $0 < h_1 < h(t) < h_0$ *and* $h'(t) < 0$ *for* $t > 0$.

Using the integral equation (4.4) and

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

we immediately find the following bounds on $h(t)$ for $t > 0$:

$$0 < h_1 < h(t) < h_0, \quad h(t) > \max(0, h_0 - Kt). \tag{4.5}$$

Theorem 4 *For a solution pair* (ϕ, h) *of* (4.1) *with* $0 \leqslant \phi_0 \leqslant 1$, $\phi_0 \not\equiv 1$ *and* $0 < D_0 \leqslant D \leqslant D_1$, *we have:*

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

For the linear diffusion equation (or heat equation) the solution ϕ can be obtained from an integral equation of Volterra type, using the fundamental solution and Green's identity [18]. Finite time blow-up as for the supercooled Stefan problem will not occur due to the conditions on ϕ_0 [19]. The existence of a (classical) solution for the nonlinear diffusion has been shown [8] by using a coordinate transformation to a fixed frame. Similar mass Lagrangian variables were used by Meirmanov [20] for the Stefan problem. We will come back to this transformation in the concluding remarks.

5 Stress-driven diffusion with a free boundary

For the system (3.1) including the build-up of stress, the conservation of polymer is still guaranteed and we find the same integral equation for the thickness $h(t)$:

$$h(t) = h_1 + \int_0^{h(t)} \phi(x,t)\, dx. \tag{5.1}$$

Recall that we have defined the volume of polymer by:

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

The following result is similar to Theorem 3.

Theorem 5 *Suppose* $\kappa(0) = 0$, $\kappa(1) = 0$ *and D satisfies* (4.2). *Suppose* $0 \leqslant \phi_0(x) \leqslant 1$ *for* $0 \leqslant x \leqslant h_0$, *with* $\phi_0 \not\equiv 0$, $\phi_0 \not\equiv 1$ *and let* (ϕ, σ, h) *be a classical solution of* (3.1). *Then for* $0 < t \leqslant T$ *and* $0 \leqslant x \leqslant h(t)$ *we have* $0 < \phi(x,t) < 1$ *and* $\phi_x(h(t),t) < 0$ *and* $0 < h_1 < h(t) < h_0$.

The proof of this theorem is given in § 5.1.

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We expect, similar to the result in Theorem 4, that a solution triple (ϕ, σ, h) of (3.1) with $\beta_1(0) \neq 0$ has the following asymptotic behaviour, $\lim_{t\to\infty} h(t) = h_1$ and

$$\lim_{t\to\infty} \phi(x,t) = 0, \quad \text{and} \quad \lim_{t\to\infty} \sigma(x,t) = g_1(0)/\beta_1(0), \quad \text{for all } x \in [0, h_1].$$

To prove this result, further analysis on the behaviour of the stress is required.

5.1 Proof of Theorem 5

We first fix the domain by specifying the shape of the boundary. With $H(t)$ a given function $H \in C^1[0,T]$ with $H(0) = h_0$, let $\Phi(x,t), \Theta(x,t)$ be a classical solution (assuming such a solution exists) of the boundary value problem

$$\left.\begin{array}{ll}
\Phi_t = (D(\Phi)\Phi_x)_x + (\kappa(\Phi)\Theta_x)_x & \text{for } 0 < x < H(t),\ 0 < t \leqslant T, \\
\Theta_t = g_1(\Phi) + g_2(\Phi)\Phi_t - \{\beta_1(\Phi) + \beta_2(\Phi)\Phi_t\}\Theta & \text{for } 0 < x < H(t),\ 0 < t \leqslant T, \\
D(\Phi)\Phi_x + \kappa(\Phi)\Theta_x = 0 & \text{for } x = 0,\ 0 < t \leqslant T, \\
D(\Phi)\Phi_x + \kappa(\Phi)\Theta_x = -K\Phi(1-\Phi) & \text{for } x = H(t),\ 0 < t \leqslant T, \\
\Phi = \phi_0(x),\ \Theta = 0 & \text{for } 0 \leqslant x \leqslant h_0,\ t = 0.
\end{array}\right\} \tag{5.2}$$

Define the Kirchhoff transform

$$u(x,t) = \int_0^{\Phi(x,t)} D(s)\,ds, \quad \text{and set } \bar{u} = \int_0^1 D(s)\,ds.$$

Next, introduce the differential operator

$$Nu = \hat{D}(u)u_{xx} + \hat{D}(u)\,(\hat{\kappa}(u)\Theta_x)_x - u_t,$$

where we have replaced $D(\Phi)$ and $\kappa(\Phi)$ by the corresponding functions $\hat{D}(u)$ and $\hat{\kappa}(u)$, so that $\hat{\kappa}(0) = \hat{\kappa}(\bar{u}) = 0$.

We show only that $\Phi(x,t) < 1$; the result $\Phi(x,t) > 0$ is proved similarly. We can follow the proof of the maximum principle by Protter & Weinberger [21]. We use the following lemmas.

Lemma 1 *Let a function w satisfy $Nw > 0$ in a bounded region $E \subset \mathbb{R}^2$. If $w(x,t) < \bar{u}$ for $0 \leqslant t < t_0$ then w cannot attain the value $\bar{u}$ at a point (x_0, t_0) when x_0 is interior in $E \cap \{t = t_0\}$.*

Proof Suppose the maximum $\bar{u}$ was attained at (x_0, t_0); then at this point

$$w = \bar{u}, \quad \hat{\kappa}(w) = \hat{\kappa}(\bar{u}) = 0, \quad w_t \geqslant 0, \quad w_{xx} \leqslant 0, \quad w_x = 0$$

and the contradiction follows directly from

$$Nw = \hat{D}(w)w_{xx} + \hat{D}(w)\left(\hat{\kappa}(w)\Theta_{xx} + \hat{\kappa}'(w)w_x\Theta_x\right) - w_t \leqslant 0 \quad \text{at } (x_0, t_0). \qquad \square$$

Lemma 2 *Let E be a domain in $\mathbb{R}^2$ in which the equality $Nu = 0$ is satisfied, and let $E_{t_1} = \{(x,t) \in E : t \leqslant t_1\}$. If $u \leqslant \bar{u}$ in E_{t_1} and $u(x_1, t_1) = \bar{u}$, then $u = \bar{u}$ at every point (x,t) in E_{t_1} which can be connected with (x_1, t_1) by a horizontal or vertical line segment lying in E_{t_1}.*

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The proof is similar to the proof of Protter & Weinberger ([21], ch. 3, Theor. 2). We define the function $v = \exp -\alpha[(x-x_1)^2 + (t-t_1)^2] - \exp\left(-\alpha R^2\right)$ on a disk S with centre (x_1, t_1) and the radius R so that the disk and its boundary are contained in E.

If we take $w = u + \alpha^2 v$ for $\alpha > 0$, and use the mean value theorem several times (for example, $\hat{D}(w) = \hat{D}(u) + \varepsilon v \hat{D}'(\varphi)$ for a $\varphi \in (u, u + \alpha^2 v)$), then we find after some straightforward calculations that Nw satisfies

$$Nw = Nu + \exp -\alpha[(x-x_1)^2 + (t-t_1)^2] + \mathcal{O}(\alpha).$$

Therefore, if we choose α sufficiently small it follows that $Nw > 0$.

Now following the proof of Protter and Weinberger, if we can construct an interior point where w becomes equal to $\bar{u}$, Lemma 1 supplies a contradiction. This is left to the reader.

Lemma 3 *Let E be a domain in $\mathbb{R}^2$ in which the equality $Nu = 0$ is satisfied, and let $E_{t_0} = \{(x,t) \in E : t \leqslant t_0\}$. Suppose that u is continuously differentiable at the boundary point $P = (x_0, t_0)$, that $u(P) = \bar{u}$, $u(x,t) < \bar{u}$ for $(x,t) \in E_{t_0}$, that P lies on the boundary of a disk S tangent to ∂E, centred at (x_1, t_1) with $x_1 \neq x_0$ and that S_{t_0}, the portion of S below $t = t_0$, lies in E_{t_0}. Let $\partial/\partial v$ denote an outward directional derivative from E_{t_0} at P then*

$$\frac{\partial u}{\partial v} > 0 \quad \textit{at } P.$$

Proof By defining w as in the proof of Lemma 2 and by using Lemma 1, the proof is given by following the lines of the proof of the boundary point lemma in ([21], Ch. 3, Theor. 3).

Lemma 2 and its equivalent for the lower bound, show that $0 < \Phi < 1$ at the interior points. The boundary point Lemma 3 yields that at a boundary point P with either $\Phi(P) = 0$ or $\Phi(P) = 1$, the normal derivative satisfies $\partial\Phi/\partial v \neq 0$. When $\kappa(0) = \kappa(1) = 0$, this contradicts the given boundary conditions at $x = H(t)$ in equation (5.2).

If we now assume that a solution (ϕ, σ, h) of equation (3.1) exists, then from the same arguments as for Φ, we find that $0 < \phi < 1$ for $t > 0$ and $0 \leqslant x \leqslant h(t)$. With, in particular, $\phi(h(t), t) < 0$, we find that $h(t)$ is a strictly decreasing function. Using the integral equation (5.1) and

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

we find the same bounds on $h(t)$ as in equation (4.5), for $t > 0$:

$$0 < h_1 < h(t) < h_0, \quad h(t) > \max(0, h_0 - Kt). \tag{5.3}$$

□

5.2 Numerical behaviour

A simple transformation to a fixed frame allows us to compute the solution of the problem numerically with a standard procedure. The unknown function $h(t)$ now appears explicitly

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in the evolution equations. Letting $z = x/h(t), \tau = t$, then the transformed system reads:

$$\left.\begin{aligned}
&\phi_\tau = \frac{z}{h}h_\tau\phi_z + \frac{1}{h^2}(D(\phi)\phi_z)_z + \frac{1}{h^2}(\kappa(\phi)\sigma_z)_z && \text{for } 0 < z < 1,\ t > 0,\\
&\sigma_\tau = \frac{z}{h}h_\tau\{\sigma_z - g_2(\phi)\phi_z + \beta_2(\phi)\sigma\phi_z\} + \\
&\qquad + g_1(\phi) + g_2(\phi)\phi_\tau - \{\beta_1(\phi) + \beta_2(\phi)\phi_\tau\}\sigma && \text{for } 0 < z < 1,\ t > 0,\\
&D(\phi)\phi_z + \kappa(\phi)\sigma_z = 0 && \text{for } z = 0,\ t > 0,\\
&D(\phi)\phi_z + \kappa(\phi)\sigma_z = -Kh\phi(1-\phi) && \text{for } z = 1,\ t > 0,\\
&h_\tau = -K\phi && \text{for } z = 1,\ t > 0,\ h(0) = h_0,\\
&\phi = \phi_0(z),\quad \sigma = 0 && \text{for } 0 \leqslant z \leqslant 1,\ t = 0.
\end{aligned}\right\} \tag{5.4}$$

The calculations shown in Figure 1 have been done with the NAG Fortran Library procedure D03PPF, which integrates a system of nonlinear parabolic (elliptic) partial differential equations in one space variable, with coupled ordinary differential equations. The numerical routine applies automatic adaptive spatial remeshing, and is based on finite differences, the method of lines and a backward differentiation formula or, optionally, a theta method.

We will not discuss the numerical procedure here, nor will these very preliminary numerical results be compared with any experimental evidence. The numerical investigation needs much more emphasis than can be given here and we postpone it therefore to later studies. The figure below is an illustration of the possible behaviour for different diffusion and stress profiles, i.e. materials with different rheological properties.

6 Concluding remarks

This paper presents a model to be used as a framework for experiments on the drying of polymer solutions such as paint. There is hardly any data available for these systems of drying paint layers. The rheological properties of the material are usually measured dynamically (e.g. flow measurements of polymer systems) and it is not clear whether these data apply to the time-dependent but steady system of a drying paint. There are, apart from the extensive data on the chemical properties and drying time-scales, only some measurements available on the global, maximum stress. When performing new experiments to find the required diffusion and stress profiles, our model can suggest what are the most important experimental questions.

There are several unanswered questions, among which most importantly the diffusion profiles and the other coefficients in the model. Cox [4] studies the phenomenon of sharp fronts by assuming that the process is principally driven by the stress; Cohen *et al.* [5, 7, 6] use a step-like diffusion coefficient to generate the phenomenon. For these systems some asymptotic properties have been shown, but it cannot be expected that the phenomenon of a sharp diffusion front will be noticeable in a paint layer. We expect asymptotically that $\phi \to 0, h \to h_1, \sigma \to g_1/\beta_1$ at an exponential rate, as is the case for the pure diffusion model, but work needs to be done here.

We end this paper with some remarks on a transformation to a fixed frame, other than the one used in the numerics. The reason for using these Lagrangian coordinates is that the transformation uncouples the evolution of the free boundary from the stress-diffusion equations. The choice of the new coordinates is based on the fact that the mass of polymer

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is constant:

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

and we find a coordinate transformation to a fixed frame by introducing new space and time coordinates:

$$y = \int_x^{h(t)} \{1 - \phi(x,t)\}\, dx, \quad \tau = t. \tag{6.1}$$

For the pure diffusive case, without stress build-up, this transformation has been used to prove the following (see [8]): the existence and uniqueness of a classical solution, using known results on uniformly parabolic equations; the rate of convergence to the trivial state as $t \to \infty$; and the convergence of the model to the superheated Stefan problem, in the fast evaporation limit $K \to \infty$.

All these items are still open questions for the model including the stress build-up and relaxation. The conservation of polymer for this model allows us to use the same Lagrangian coordinates; writing

$$u(y,\tau) = \int_0^{\phi(x,t)} D(s)\, ds, \quad p(y,\tau) = \sigma(x,t), \quad \hat{D}(u) = D(\phi), \quad \text{etc.},$$

then u, p satisfy the boundary value problem:

$$\left.\begin{array}{ll}
u_\tau = (1-u)^2(\hat{D}(u)u_y + \hat{\kappa}(u)p_y)_y & 0 < y < h_1,\ \tau > 0, \\
p_\tau = \hat{g}_1(u) - \hat{\beta}_1(u)p + (\hat{g}_2(u) - \hat{\beta}_2(u)p)u_\tau + & \\
\quad (p_y - \hat{g}_2(u)u_y + \hat{\beta}_2(u)pu_y)(1-u)\left(\hat{D}(u)u_y + \hat{\kappa}(u)p_y\right) & 0 < y < h_1,\ \tau > 0, \\
\hat{D}(u)u_y + \hat{\kappa}(u)p_y = Ku & y = 0,\ \tau > 0, \\
\hat{D}(u)u_y + \hat{\kappa}(u)p_y = 0 & y = h_1,\ \tau > 0, \\
u(y,0) = \phi_0(x), \quad p = 0 & 0 \leqslant y \leqslant h_1,\ \tau = 0.
\end{array}\right\}$$

The equation for the thickness h is uncoupled and reads:

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

This system may be a good starting point for the analysis of the drying of liquid paint.

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