

---

Faculty of Mathematical Sciences

University of Twente

University for Technical and Social Sciences

---

---

P.O. Box 217

7500 AE Enschede

The Netherlands

Phone: +31-53-4893400

Fax: +31-53-4893114

Email: memo@math.utwente.nl

---

MEMORANDUM No. 1583

Drying a liquid paint layer

H. SUSANTO<sup>1</sup> AND B.W. VAN DE FLIERT

MAY 2001

ISSN 0169-2690

---

<sup>1</sup>Dept. of Mathematics, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Jl. Ganesa 10 Bandung, Indonesia

# Drying a Liquid Paint Layer

Hadi Susanto

Dept. of Mathematics,

Faculty of Mathematics and Natural Sciences,

Institut Teknologi Bandung, Jl. Ganesa 10 Bandung,

Indonesia

B.W. van de Fliert

Faculty of Mathematical Sciences,

University of Twente, P.O. Box 217, 7500 AE Enschede,

The Netherlands

## Abstract

Subject of this study is the free boundary problem of a liquid layer that is dried by evaporation. Using a Stefan type problem, we model the diffusion driven drying of a layer of liquid paint consisting of resin and solvent. The effect of a small perturbation of the flat boundary is considered. We include the discussion of evaporation constant as a free parameter. For both small and big wavenumber, the high speed of evaporation can lead to instability. We first recognize this instability in the linearized equation. Using numerical calculations, we show that the instability also happens in the full equation.

## Keywords

free boundary problem, liquid coating, evaporation, Stefan problem

## AMS subject classifications

35K20, 35K60, 35R35, 80A22

# 1 Introduction

Liquid paints consist mainly of resin, pigment and volatile solvent. Due to solvent evaporation, there will be compositional changes and surface moving during the drying. Then the model results in a Stefan type problem (see [2, 3, 11]), so a free boundary problem similar to models for phase transitions.

In this paper we consider a simple model where we assume that the drying process happens through diffusion and evaporation of the solvent. The model equation is a linear convection-diffusion equation and the boundary conditions are dictated by conservation of polymeric material and solvent. We are interested in the behaviour of the moving boundary. In the case of fast evaporation, the model reduces to the more familiar Stefan problem with undercooling.

We briefly derive the model equations in section 2 in which we use volume fraction instead of concentration. We restrict the analysis to the two-dimensional case only.

In section 3, we show the non-dimensionalisation of the equations. After non-dimensionalising, we consider the effect of a small perturbation of the flat boundary of the one-dimensional non-convective system. We observe in section 4 that there is an instability for certain conditions. We use numerical calculations in this paper to convince ourselves that the instability which has been found in the perturbed one-dimensional equations is not caused by mathematical effect of linearisation around a free and moving boundary. We postulate in section 5 that this instability can happen in this model if the speed of the evaporation is faster than the speed of the diffusion.

## 2 Derivation of the models equation

Let  $\phi(x, t)$  denote the solvent volume fraction with  $0 \leq \phi \leq 1$  and  $\mathbf{q}$  the fluid velocity. Then for the solvent, the *convective flux* is  $\mathbf{j}_c = \mathbf{q}\phi$  and the *diffusive* or *relative flux* is  $\mathbf{j}_d = -D\nabla\phi$ , where  $D$  is a diffusion coefficient.

Because the rate of change of particles is equal to the sum of the absolute flux  $\mathbf{j}$  across its surface, we get

$$\frac{\partial}{\partial t} \int_{\Omega(t)} \phi dV = - \int_{\Gamma(t)} \mathbf{j} \cdot \mathbf{n} dA = - \int_{\Omega(t)} (\nabla \cdot \mathbf{j}) dV.$$

The absolute flux itself consists of the convective term and the diffusive term. And by assuming that all the variables are continuous, the equation above gives

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot (\mathbf{q}\phi) + \nabla \cdot (D\nabla\phi). \quad (1)$$

By noting that the fluid flow satisfies the continuity equation and assuming that the fluid is incompressible, then equation (1) becomes

$$\frac{\partial \phi}{\partial t} + \mathbf{q} \cdot \nabla \phi = \nabla \cdot D\nabla\phi. \quad (2)$$

The layer of liquid paint  $\Omega(t)$  may have a fixed boundary at a substrate, which we will denote by  $\Gamma_0$ . There is no flux both of solvent and the total fluid at that

impermeable substrate, so that

$$\mathbf{q} \cdot \mathbf{n}_0 = 0, \quad \mathbf{j} \cdot \mathbf{n}_0 = 0, \quad (3)$$

where  $\mathbf{n}_0$  is normal vector of the substrate.

The free surface of the this problem can move. The necessary conditions in determining this movement are called *kinematic conditions*. At the upper surface denoted by  $\Gamma(t)$  which is free and moving due to the evaporation of solvent into air the kinematic conditions read

$$\mathbf{q} \cdot \mathbf{n} = V_n + E, \quad (4)$$

$$\mathbf{j} \cdot \mathbf{n} = (\phi \mathbf{q} - D\nabla\phi) \cdot \mathbf{n} = V_n \phi + E, \quad (5)$$

where  $V_n$  is the speed of the free surface in the direction of the outward normal  $\mathbf{n}$  and  $E$  is the evaporation term. If we assume that the free boundary  $\Gamma(t)$  can be described by the boundary of the support of a function  $\eta(\mathbf{x}, t) = y - h(x, t) = 0$ , then the speed of the free surface is given by  $V_n = -\eta_t/|\nabla\eta|$ .

In this paper we take the simple case of constant diffusion coefficient. Rewrite (5), using (4), to get

$$D\nabla\phi \cdot \mathbf{n} = -(1 - \phi)E. \quad (6)$$

Since  $E$  should satisfy  $E = 0$  for  $\phi = 0$ ,  $E > 0$  for  $0 < \phi \leq 1$  and it's likely that  $E$  is non-decreasing in  $\phi$ , we can take at the beginning the simplest form

$$E = K\phi, \quad (7)$$

with evaporation constant  $K$ .

Initially, there are solvent concentration and depth of layer

$$\phi(\mathbf{x}, 0) = \phi_0(\mathbf{x})$$

for  $\mathbf{x} \in \overline{\Omega(0)}$  where the initial domain  $\Omega(0)$  has boundaries  $\Gamma_0$  and  $\Gamma(0)$ .

### 3 Non-dimensionalising the Equations

When reduced to two dimensional equations and writing  $\mathbf{q} = (u, v)$ , (2), (3), (6) and (7) give

$$\left\{ \begin{array}{l} \phi_t + u\phi_x + v\phi_y = D(\phi_{xx} + \phi_{yy}), \\ \phi_y = 0, \\ D(-h_x\phi_x + \phi_y) \frac{1}{\sqrt{1+h_x^2}} = -E(1 - \phi), \\ v = h_t + uh_x + E\sqrt{1+h_x^2}, \\ h = h_0(x) > 0, \\ \phi = \phi_0(x, y) > 0, \end{array} \right. \quad \text{for} \quad \left\{ \begin{array}{l} 0 < y < h(x, t), \quad t > 0, \\ y=0, \quad t > 0, \\ y=h(x, t), \quad t > 0, \\ y=h(x, t), \quad t > 0, \\ t = 0, \\ 0 \leq y \leq h_0, \quad t = 0. \end{array} \right. \quad (8)$$

The differential equations needed to determine  $u$  and  $v$  are derived in 3.1 while the boundary conditions are discussed separately in 3.2.

### 3.1 Creeping Flow Equation

To determine  $u$  and  $v$ , we start with the Navier-Stokes equation for an incompressible flow, that is

$$\rho \frac{D\mathbf{q}}{Dt} = \mathbf{F} - \nabla p + \mu \nabla^2 \mathbf{q} \quad (9)$$

where  $\mathbf{F}$  is body force, i.e. gravity or electromagnetic field,  $p$  is the pressure and  $D/Dt$  is the material derivative. Here the density  $\rho$  and the coefficient of dynamic viscosity  $\mu$  are taken constant.

Next, we want to nondimensionalize (9). Suppose there are a typical speed  $U$  and one length scale  $L$  for which it will be clear later on what the typical choices are in the problem. Since there are also  $\rho$  and  $\mu$  involved, there is no unique way of nondimensionalising. Write :

$$\mathbf{x} = L\bar{\mathbf{x}}, \quad \mathbf{q} = U\bar{\mathbf{q}}, \quad t = \frac{L}{U}\bar{t}, \quad p = \rho U^2 \bar{p},$$

then (9), by dropping the bar and neglecting body forces, becomes

$$\frac{D\mathbf{q}}{Dt} = -\nabla p + \frac{1}{Re} \nabla^2 \mathbf{q} \quad (10)$$

where  $Re = \rho \frac{UL}{\mu}$  is the *Reynolds number*.

For the low Reynolds number case, rescale  $\bar{p} = \frac{1}{Re} \tilde{p}$ , so we get

$$\nabla p = \nabla^2 \mathbf{q} \quad (11)$$

which is known as the equation for *creeping flow*.

We also get the choice of the typical velocity, that is  $U = D/L$ , which will scale the diffusion coefficient to 1 and the choice of the length scale, that is the typical height which can be the average of the initial height. The evaporation constant  $K$  is non-dimensionalised with  $U$ . Again in order to avoid cumbersome notation, we are using the same symbol  $K$  for the dimensionless evaporation constant.

In the convection-diffusion problem, we write the expressions for the velocities using a stream function  $\psi(x, y, t)$  for which  $u = \psi_y$  and  $v = -\psi_x$ . This stream function is coming from the continuity equation with incompressibility assumption, i.e.  $\nabla \cdot \mathbf{q} = 0$ .

### 3.2 Boundary Conditions

At the stationary solid boundary ( $y = 0$ ), a viscous fluid satisfies a no-slip condition, or  $\mathbf{q} = \mathbf{0}$ . At the free boundary, the surface tension is important to be taken into account. The surface tension coefficient  $\gamma$  arises as an energy associated with interfacial surfaces.

The stress which consists of hydrodynamic pressure and shear strain exerted on the water at the interface in the normal (here upward) direction is  $\sigma \mathbf{n}$ . If every point at the surface  $y = h(x, t)$  is moved infinitesimally a distance  $\delta n$  in the normal direction to  $y = h(x, t)$  at that point, then the work done on a surface element of

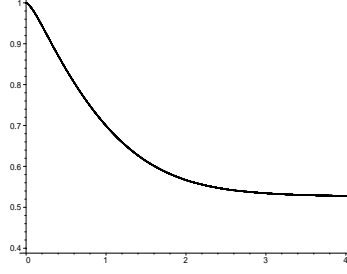


Figure 1: The thickness  $h(t)$  as a function of time for problem (14). Initial data  $\phi_0 = 1 - y$ ,  $K = 1$ .

length  $\delta S$  is  $\sigma \mathbf{n} \delta n \delta S$ , and this equals the change in surface energy  $\gamma \delta [\delta S] \mathbf{n}$  (see [8, 10]). Therefore, the appropriate boundary condition is

$$\sigma \mathbf{n} = 2\gamma \kappa \mathbf{n}, \quad (12)$$

where

$$\kappa = \frac{1}{2\delta S} \frac{\partial(\delta S)}{\partial n}$$

is the mean curvature of the surface. We can simply write twice the curvature of  $\eta(\mathbf{x}, t) = 0$  as  $2\kappa = \nabla \cdot \mathbf{n}$  where  $\mathbf{n} = \nabla \eta / |\nabla \eta|$  (see [12]).

As a consequence of nondimensionalising, we have the other boundary conditions

$$\begin{cases} (p - 2u_x)h_x + (u_y + v_x) = -Ch_{xx}h_x(1 + h_x^2)^{3/2}, & y=h(x, t), \quad t > 0, \\ -h_x(u_y + v_x) - p + 2v_y = Ch_{xx}(1 + h_x^2)^{3/2}, & \text{for } y=h(x, t), \quad t > 0, \\ \psi_x = \psi_y = 0, & y=0, \quad t > 0, \end{cases} \quad (13)$$

where  $C = \frac{\gamma}{\mu U}$ .

## 4 Stability of the Unsteady Flow

We consider a linear perturbation analysis of the solution of the one-dimensional non-convective Stefan problem

$$\begin{cases} \phi_t = \phi_{yy}, & 0 < y < h(t), \quad t > 0, \\ \phi_y = 0, & y=0, \quad t > 0, \\ \phi_y = -K\phi(1 - \phi), & \text{for } y=h(t), \quad t > 0, \\ h_t = -K\phi, & y=h(t), \quad t > 0, \\ h = 1, & t = 0, \\ \phi = \phi_0 > 0, & 0 \leq y \leq 1, \quad t = 0, \end{cases} \quad (14)$$

which has been discussed by [4, 5] for the full free boundary problem in the previous section. See figure 1 as the numerical result of (14). The numerical procedure will be explained later in the next section.

We start with assuming that the boundary is of the form

$$h(x, t) = H^0(t) + \delta (H^1(t) \cos kx + h^1(t)) + \mathcal{O}(\delta^2)$$

with initial conditions  $H^1(0) = 1$  and  $h^1(0) = 0$  for some small amplitude  $\delta$ . We would like now to define  $\phi = \Phi^0 + \delta (\Phi^1 \cos kx + \phi^1) + \mathcal{O}(\delta^2)$ , and similarly for  $\psi$ , but since naturally  $\phi$  is defined on  $Q_T(h) = \mathbb{R} \times (0, h(t)) \times (0, T]$ , while  $\Phi^i$  is defined on  $Q_T(H^0)$ , we write symbolically

$$\phi(x, y, t) \approx \Phi^0(y, t) + \delta (\Phi^1(y, t) \cos kx + \phi^1(y, t)) + \mathcal{O}(\delta^2),$$

and

$$\psi(x, y, t) \approx \delta (\Psi^1(y, t) \sin kx + \psi^1(y, t)) + \mathcal{O}(\delta^2).$$

Physically, the sinusoidal terms represent the levelling process while the ' $\cos 0x$ ' terms represent the evaporation. Because of the assumption of the form of the surface, we now have to use a Taylor expansion for  $\phi$  and  $\psi$  around  $H^0(t)$  to determine the volume fraction and the velocity at the surface which causes additional higher order terms in the free boundary conditions. We take  $\mathbf{q}$ , like  $\psi$ , of the order  $\mathcal{O}(\delta)$ , because we do a stability analysis for the special solution of the problem, i.e.  $(\phi, h, u, v, p) = (\Phi^0, H^0, 0, 0, 0)$ , where  $(\Phi^0, H^0)$  is the only solution of (14).

Since we have now a flow defined on a fixed domain, the  $\Psi^1$  and  $\psi^1$  in these equations, which are directly related to the vertical velocity, can be found independently of  $H^1$ ,  $h^1$ ,  $\Phi^1$  and  $\phi^1$ . After elimination of the pressure  $p$  from the creeping flow, we solve the bi-laplacian or biharmonic equation  $\nabla^4 (\Psi^1 \sin kx + \psi^1) = 0$  on the domain  $Q_T(H^0)$ , giving

$$\begin{aligned} \Psi^1 &= (P + Qy)e^{ky} + (R + Sy)e^{-ky}, \\ \psi^1 &= ay^3 + by^2 + cy + d. \end{aligned}$$

Then, by defining  $p \approx \delta p^1 + \mathcal{O}(\delta^2)$ , we can get the pressure (up to a constant):

$$p^1 = -2k \cos kx (Qe^{ky} + Se^{-ky}) + 6ax.$$

Next, we want to look for the constants. Satisfying the boundary conditions at  $y = 0$

$$\Psi^1 \sin kx + \psi^1 = \Psi_y^1 \sin kx + \psi_y^1 = 0,$$

and at  $y = H^0(t)$

$$(\Psi_{yy}^1 + k^2 \Psi^1) \sin kx + \psi_{yy}^1 = 0, \quad -p^1 - 2\Psi_y^1 k \cos kx = -CH^1 k^2 \cos kx,$$

we find

$$\begin{aligned} a &= b = c = d = 0, \\ P + R &= 0, \quad Pk - Rk + Q + S = 0, \\ (2Pk + 2Q + 2QkH^0)e^{kH^0} + (2Rk - 2S + 2SkH^0)e^{-kH^0} &= 0, \\ (-2Pk - 2QkH^0)e^{kH^0} + (2Rk + 2SkH^0)e^{-kH^0} &= -CkH^1. \end{aligned}$$

Solving these equations, we find that the stream function at  $y = H^0(t)$  satisfies

$$\psi(x, H^0, t) \approx \delta \xi H^1 \sin kx + \mathcal{O}(\delta^2), \quad (15)$$

where

$$\xi = -\frac{1}{2}C \frac{kH^0 - \sinh kH^0 \cosh kH^0}{(kH^0)^2 + \cosh^2 kH^0}. \quad (16)$$

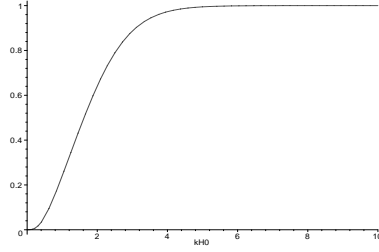


Figure 2:  $2\xi/C$  as a function of  $kH^0$  (see (16))

See figure 2 for a plot of  $\xi$ .

We have  $K$  as a free parameter here. This parameter represents the speed of the evaporation. There is a possibility to treat the evaporation process to be either slow or fast. Each case can give a different result. In the following subsection, we study three cases of  $K$ .

#### 4.1 Stability for Slow Evaporation

The first case is slow evaporation. We want to look at the behaviour of our solution if the evaporation constant is of  $\mathcal{O}(\delta)$ . The zeroth-order system gives

$$\Phi^0(y, t) = \frac{1}{H^0} \left( \int_0^{H^0} \phi_0(\zeta) d\zeta + \sum_{n=1}^{\infty} 2 \int_0^{H^0} \phi_0(\zeta) \cos\left(\frac{n\pi}{H^0}\zeta\right) d\zeta e^{-\frac{n\pi}{H^0}{}^2 t} \cos\left(\frac{n\pi}{H^0}y\right) \right)$$

and  $H^0 = 1$ .

The first order equations in  $\delta$  for the volume fraction are

$$\begin{cases} \Phi_t^1 - k\Phi_y^0\Psi^1 = \Phi_{yy}^1 - k^2\Phi^1, & \phi_t^1 = \phi_{yy}^1, & 0 < y < H^0, & t > 0, \\ \Phi_y^1 = -H^1\Phi_{yy}^0, & & y=H^0, & t > 0, \\ \phi_y^1 = -K\Phi^0(1 - \Phi^0) - h^1\Phi_{yy}^0, & \text{for } & y=H^0, & t > 0, \\ \Phi_y^1 = \phi_y^1 = 0, & & y=0, & t > 0, \\ \Phi^1 = \phi^1 = 0, & & 0 \leq y \leq 1, & t = 0. \end{cases} \quad (17)$$

The equations for the height read

$$\begin{aligned} H_t^1 &= -k\Psi^1, \\ h_t^1 &= -K\Phi^0, \end{aligned}$$

evaluated at  $y = H^0(t)$ .

With the given functions of  $\Phi^0$  and  $\Psi^1$ , we can get  $H^1$  and  $h^1$  explicitly, i.e.

$$H^1(t) = e^{-k\xi t}, \quad h^1(t) = \int_0^t -K\Phi^0(\tau) d\tau,$$

with  $\xi$  as in (16). From this solution for  $K = \mathcal{O}(\delta)$ , we see that the evaporation gives effect in the decreasing of the surface, not the levelling. The levelling process depends exponentially on the surface tension. With the known  $H^1$  and  $h^1$ , a similar equation and solution of (17) can be seen in [9] for a problem of heat conduction in a rod.



## 4.2 Stability for Evaporation Constant of $\mathcal{O}(1)$

With the assumption that  $K$  is  $\mathcal{O}(1)$ , the first order equations in  $\delta$  for the volume fraction are

$$\left\{ \begin{array}{ll} \Phi_t^1 - k\Phi_y^0\Psi^1 = \Phi_{yy}^1 - k^2\Phi^1, & \phi_t^1 = \phi_{yy}^1, & 0 < y < H^0, \quad t > 0, \\ \Phi_y^1 = -H^1\Phi_{yy}^0 - K(H^1\Phi_y^0 + \Phi^1)(1 - 2\Phi^0), & & y=H^0, \quad t > 0, \\ \phi_y^1 = -h^1\Phi_{yy}^0 - K(h^1\Phi_y^0 + \phi^1)(1 - 2\Phi^0), & \text{for} & y=H^0, \quad t > 0, \\ \Phi_y^1 = \phi_y^1 = 0, & & y=0, \quad t > 0, \\ \Phi^1 = \phi^1 = 0, & & 0 \leq y \leq 1, \quad t = 0. \end{array} \right. \quad (18)$$

The equations for the height read

$$\begin{aligned} H_t^1 &= -k\Psi^1 - K(H^1\Phi_y^0 + \Phi^1), \\ h_t^1 &= -K(h^1\Phi_y^0 + \phi^1), \end{aligned}$$

evaluated at  $y = H^0(t)$ .

We observe from figure 2 that for  $kH^0 > 5$ , the value of  $v$  is nearly independent of  $H^0(t)$ ,

$$v(x, H^0(t), t) \approx -\frac{1}{2}C\delta H^1 k \cos kx.$$

So, we find for  $H^1$

$$H_t^1 = -\frac{1}{2}kCH^1 - K(\Phi^1 + H^1\Phi_y^0).$$

Seeing this equation, we can conclude that for short time the disturbance may grow, since  $\Phi_y^0 < 0$  at  $y = H^0(t)$ . But this depends on the values of the wavenumber  $k$  and the scaled surface tension coefficient  $C$ .

When assuming that all quantities are uniformly bounded, we have that for large time the disturbance will always die out because  $\Phi^0 \rightarrow 0$  in time (see [5, 6]) which makes  $\Phi_y^0 \rightarrow 0$  and  $\Phi_{yy}^0 \rightarrow 0$  as well. This implies that the forcing term in (18) vanishes, which leaves approximately the following system for  $\Phi^1$

$$\left\{ \begin{array}{ll} \Phi_t^1 = \Phi_{yy}^1 - k^2\Phi^1, & 0 < y < H^0(t), \quad t > 0, \\ \Phi_y^1 = 0, & \text{for} \quad y=0, \quad t > 0, \\ \Phi_y^1 = -K\Phi^1, & y=H^0(t), \quad t > 0. \end{array} \right. \quad (19)$$

With the given function  $H^0(t)$  from (14), we argue that  $\Phi^1 \rightarrow 0$  for large time. This implies an exponential decay of  $H^1 \sim \exp(-Ckt/2)$  for short wavelength perturbations or a thick layer. Numerical results for some parameter values of (18) are given in figure 3. Those pictures show the instability of the problem, but this instability does disappear after a while. See the effect of taking different values of the surface tension coefficient to the stability of  $H^1$ .

For small  $kH^0$ , we have

$$v(x, H^0(t), t) \approx -\frac{1}{3}C\delta H^1 k^4 H^{03} \cos kx.$$

Now  $H^1$  satisfies

$$H_t^1 = -\frac{1}{3}Ck^4 H^{03} H^1 - K(\Phi_y^0 H^1 + \Phi^1).$$

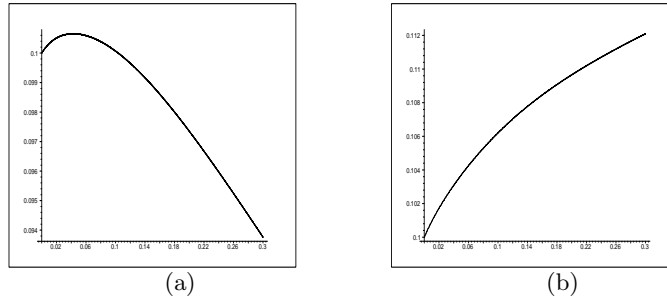


Figure 3:  $\delta H^1$  as a function of time with  $H_0^0 = 1$ ,  $\Phi_0^1 = 0$ ,  $\delta = 0.1$ ,  $H_0^1 = 1$ ,  $K = 1$ ,  $\phi_0 = 1 - y$ ,  $k = 6$ , (a)  $C = 0.1$  (b)  $C = 0$ . Multiplication of  $H^1$  with  $\delta$  has been done for comparison with the later result.

For small  $k$  and  $C$  the disturbance will indeed grow initially. But again with the assumption of boundedness of all quantities, we find  $H^1 \sim \exp(-Ck^4H^{0^3}t/3)$  for these long wavelengths or thin layers. Two numerical calculations again for  $H^1$  are given in figure 4 for the long wavelength case of (18). Compare picture 4.a to picture 3.a to get information that the smaller the wavenumber  $k$ , the bigger  $C$  is needed to stabilize the instability.

### 4.3 Stability for Fast Evaporation

We note that the boundary conditions in (13) generalize the Stefan problem with kinetic undercooling, i.e.  $\phi \neq 0$  at  $y = h$ . It is easily seen that the formal limit of this model in the case of fast evaporation, i.e. in the limit  $K \rightarrow \infty$ , is given by the Stefan problem with supercooling. In [5] it is shown that the sequence of solutions of (14) for increasing  $K$  indeed converges to the unique solution of the supercooled Stefan problem if  $0 \leq \phi_0 < 1$ , so that it is the proper limiting model for fast evaporation.

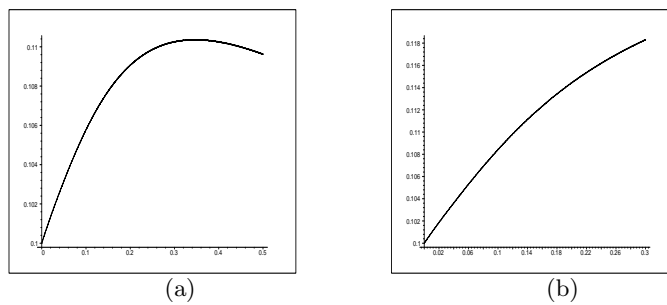


Figure 4:  $\delta H^1$  as a function of time with  $H_0^0 = 1$ ,  $\Phi_0^1 = 0$ ,  $\delta = 0.1$ ,  $H_0^1 = 1$ ,  $K = 1$ ,  $\phi_0 = 1 - y$ ,  $k = 2$ , (a)  $C = 0.4$  (b)  $C = 0$ .

Thus the problem becomes

$$\left\{ \begin{array}{l} \phi_t + \psi_y \phi_x - \psi_x \phi_y = \phi_{xx} + \phi_{yy}, \\ h_t + \psi_x + \psi_y h_x = \phi_y - h_x \phi_x, \\ \phi = 0, \\ \phi_y = 0, \\ \phi = \phi_0(x, y), \\ h = 1 + \delta \cos kx, \end{array} \right. \quad \text{for} \quad \begin{array}{l} 0 < y < h(x, t), \quad t > 0, \\ y = h(x, t), \quad t > 0, \\ y = h(x, t), \quad t > 0, \\ y = 0, \quad t > 0, \\ 0 \leq y \leq h_0(x), \quad t = 0, \\ t = 0. \end{array} \quad (20)$$

Substituting the linearizing form of the solution, we get equations in  $\mathcal{O}(\delta)$  :

$$\left\{ \begin{array}{l} \Phi_t^1 - k\Phi_y^0\Psi^1 = \Phi_{yy}^1 - k^2\Phi^1, \quad \phi_t^1 = \phi_{yy}^1, \\ \phi^1 = -h^1\Phi_y^0, \\ \Phi^1 = -H^1\Phi_y^0, \\ \Phi_y^1 = \phi_y^1 = 0, \\ \Phi^1 = \phi^1 = 0, \end{array} \right. \quad \text{for} \quad \begin{array}{l} 0 < y < H^0, \quad t > 0, \\ y = H^0, \quad t > 0, \\ y = H^0, \quad t > 0, \\ y = 0, \quad t > 0, \\ 0 \leq y \leq 1, \quad t = 0. \end{array} \quad (21)$$

Equations of the height in  $\mathcal{O}(\delta)$  read

$$\begin{aligned} H_t^1 &= \Phi_y^1 + H^1\Phi_{yy}^0 - k\Psi^1, \\ h_t^1 &= \phi_y^1 + h^1\Phi_{yy}^0. \end{aligned}$$

We expect, similar to the behaviour of the system for evaporation of  $\mathcal{O}(1)$ , that there is still an instability. Because at  $y = H^0(t)$ ,  $\Phi_{yy}^0 < 0$  and  $\Psi^1 > 0$ , to get information about the instability with this speed of evaporation, we have to identify the signum of  $\Phi_y^1$ . The analysis is given below.

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

$$\left\{ \begin{array}{l} \Phi_t^1 = \Phi_{yy}^1 - k^2\Phi^1, \\ \Phi^1 = -H^1\Phi_y^0 > 0, \\ \Phi_y^1 = 0, \\ \Phi^1 = \phi^1 = 0, \end{array} \right. \quad \text{for} \quad \begin{array}{l} 0 < y < H^0(t), \quad 0 < t < T, \\ y = H^0(t), \quad 0 < t < T, \\ y = 0, \quad 0 < t < T, \\ 0 \leq y \leq H^0(0), \quad t = 0. \end{array} \quad (22)$$

The existence of such a solution can be seen in [7]. One can get the solution using Laplace transform (see e.g. [9]). Next, introduce the differential operator

$$Nu = u_{yy} - u_t - k^2u.$$

Dissecting the problem (22) and using the theorems for the maximum principle related to the differential operator  $N$  given by Protter and Winberger ([13], ch. 2, section 3), we yield information that the positive maximum value of  $\Phi^1$  must be at  $y = 0$  or  $y = H^0(t)$ . But because the normal derivative of  $\Phi^1$  at  $y = 0$  disappears, the positive maximum value must not be at this point. Hence, the maximum value is attained at  $y = H^0(t)$  which means  $\Phi_y^1 > 0$  at this point, so there is a possibility for our system to behave unstable.

Numerical results given in figure 5 again show the instability for this fast evaporation, where the disturbance is growing faster than when the evaporation constant is of  $\mathcal{O}(1)$ . Even we can suppose that the growth of the disturbance at this speed of evaporation is the fastest growth that can exist in this model.

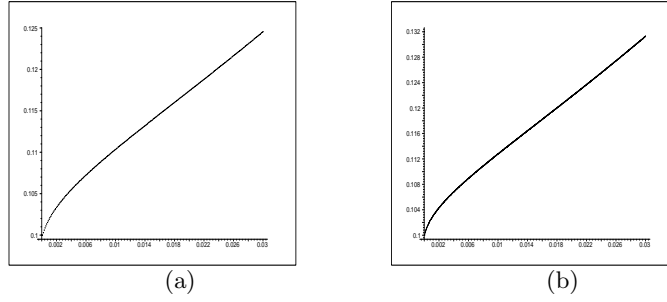


Figure 5:  $\delta H^1$  as a function of time for fast evaporation with  $H_0^0 = 1$ ,  $\Phi_0^1 = 0$ ,  $\delta = 0.1$ ,  $H_0^1 = 1$ ,  $\phi_0 = 1 - y$ ,  $k = 6$ , (a)  $C = 0.4$  (b)  $C = 0$ .

## 5 Instability Interpretation

We have seen that there is an instability in the linearized system, but we do not know yet whether this is caused by a mathematical effect of the linearisation around a moving boundary or indeed there is an instability in the problem for some conditions. Now we would like to see whether the instability which has been shown in the previous section exists in the full free boundary problem. If the answer is positive, the next question is: what is the mechanism so there is an instability in our free boundary problem. In this section, we only consider the non-convective problem, i.e.  $C = 0$ . As a consequence of this choice, the only flow that causes the mixing process within the layer is diffusion. The surface tension always causes the levelling for larger time, so the instability can be seen clearly if the surface tension is absent.

Now transform the moving boundary to a fixed boundary. Using  $z = y/h(x, t)$ ,  $\chi = x$ ,  $\tau = t$ , the differential operators become

$$\begin{aligned}\partial_t &= \partial_\tau - h_\tau \frac{z}{h} \partial_z, \\ \partial_y &= \frac{1}{h} \partial_z, \\ \partial_{yy} &= \frac{1}{h^2} \partial_{zz}, \\ \partial_x &= \partial_\chi - h_\chi \frac{z}{h} \partial_z, \\ \partial_{xx} &= \partial_{\chi\chi} - h_{\chi\chi} \frac{z}{h} \partial_z + h_\chi^2 \frac{z}{h^3} \partial_z - 2h_\chi \frac{z}{h} \partial_{\chi z} + 2h_\chi^2 \frac{z}{h^2} \partial_z + \left(\frac{zh_\chi}{h}\right)^2 \partial_{zz}.\end{aligned}$$

Numerical calculation of the free boundary problem (14) has been done by using this transformation. The transformation changes the physical domain to the numerical one as described in the pictures in figure 6. Then a numerical problem in the calculation of the full free boundary problem arises; that is, we need boundary conditions in  $x$ . But by matching  $l$ , the length of the computational domain along the  $x$ -axis of the problem with the period of the perturbation, we can solve the problem by choosing periodic boundary conditions.

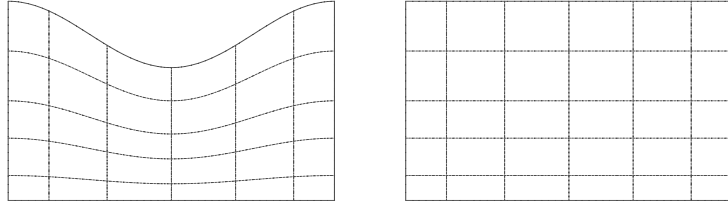


Figure 6: Physical and numerical domains.

### 5.1 Speed-difference-driven Instability

What we saw in figures 3, 4 and 5 which show the instability is that initially the amplitude of the perturbation grows, while globally the surface of the layer decreases. The initial form of the surface is  $1 + \delta \cos kx$ . We measure the amplitude of the perturbation in the full free boundary problem by the difference between the highest and the lowest points on the surface. To observe the behaviour in the full free boundary problem related to the initial conditions of figure 3, we get the amplitude of the perturbation as shown in figure 7.a. Hence we conclude that there is instability in the full problem. We can compare the two pictures, i.e. 3.a and 7.a, to verify that the numerical results of the linearized equation and the full problem have similar plots.

Because the speed of the decrease of the surface in the absence of surface tension only depends on the evaporation rate, while the evaporation itself is just a function of the concentration, then to analyze this phenomenon we plot the difference of the volume fraction at the lowest and at the highest points. Figure 7.b shows the difference of the volume fraction of the solvent (concentration at the highest point subtracted by concentration at the lowest one) for the instability shown in figure 7.a. To illustrate what is happening inside the layer, we plot the distribution of the solvent volume fraction within the layer which is shown in figure 8.

From figure 7.b, we see that the difference of the concentration is decreasing, but still the concentration at the lowest point is higher and therefore the evaporation is faster. Thus, the lowest point decreases faster than the highest ones. Special for this initial concentration case, at the beginning, the lowest point of the surface already has a bigger concentration compared to the other points, indeed the highest points

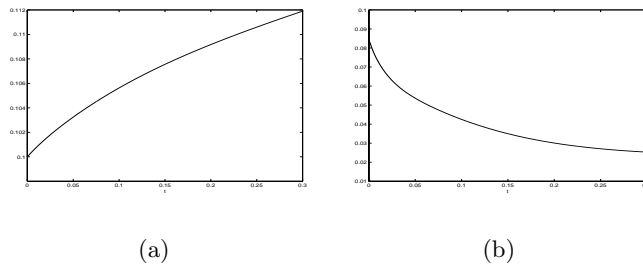


Figure 7: Amplitude of the perturbation (a) and difference of the concentration (b) as a function of time, initial data  $k = 6$ ,  $K = 1$ ,  $\delta = 0.1$ ,  $\phi_0 = 1 - y/(1 + \delta)$ .

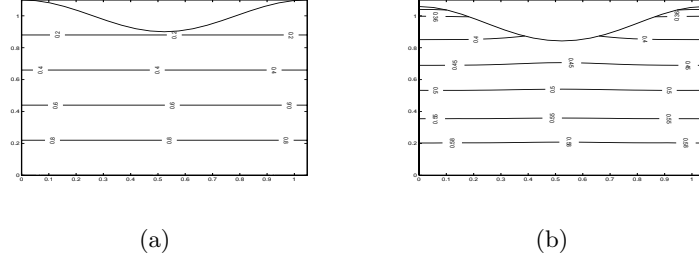


Figure 8: Distribution of the concentration initially (a) and at time 0.16 (b).

have the smallest concentration. So, it can be understood easily that this leads to instability, initially.

Then the question is what happens if we start with a condition where the lowest point has a lower concentration than the highest point. The solution of the problem with this initial condition is presented in figure 9.

For this initial condition, at the beginning, the amplitude decreases. After some time, the concentration of the lowest and the highest points are equal. Then, the instability comes out. In here we see the ‘peak’ of the concentration becoming the ‘valley’. See figure 10 for the distribution of the solvent inside the layer.

From that illustration, the amplitude of the perturbation decreases at the beginning because the concentration at the highest point is bigger than at the lowest one. As time evolves, the solvent diffuses to the region which has lower concentration. Simultaneously, the solvent at the surface evaporates. Then, after some time, when the concentration at both points are the same, again the lowest point is closer to the area with high solvent concentration which gives instability.

This behaviour of both initial concentrations can happen if the speed of the evaporation at the surface is bigger than the speed of the diffusion flow. It can be illustrated numerically that if the evaporation constant is of  $\mathcal{O}(\delta)$ , the instability will not exist anymore like what we saw in the linearized equations.

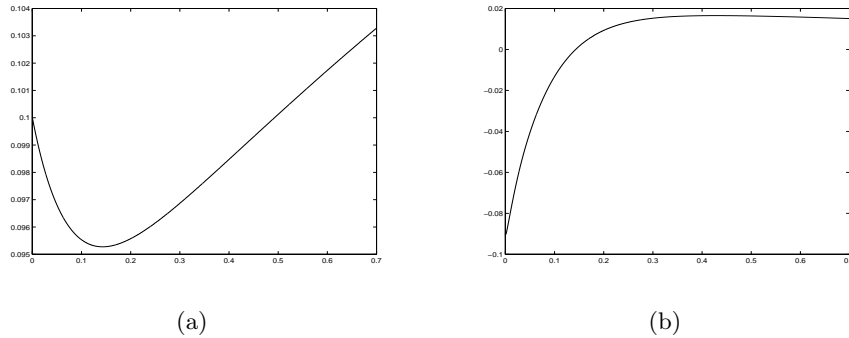


Figure 9: Amplitude of the perturbation (a) and the difference of the concentration (b) as a function of time with initial concentration  $\phi_0 = y/(1 + \delta)$  and the other initial parameter values as in figure 7.

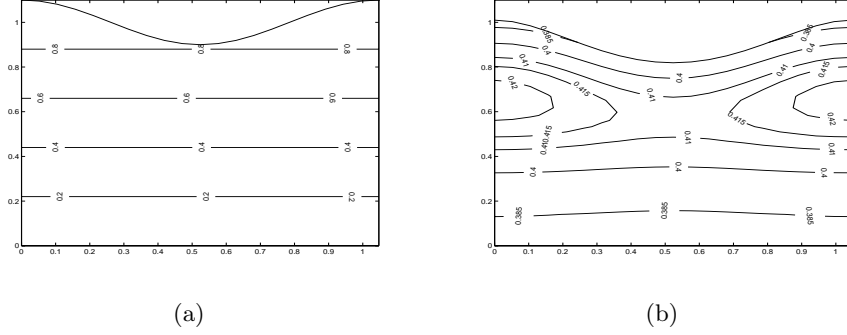


Figure 10: Distribution of the concentration initially (a) and at time 0.16 (b).

## 6 Variation on The Evaporation

We have done the calculations for the case of evaporation in the form as (7). We recognized the instability that is going to happen at first inspection from the linearisation equation which is shown by the  $K\Phi_y^0 H^1$ -term which comes from the Taylor expansion of the evaporation. Regarding to the previous section, indeed the instability is caused by the form of the evaporation.

Now we are looking at another form of the evaporation. Based on [14, 16], the surface area must be taken into account in the calculation of the rate of the evaporation. The information about the effect of the curvature to the evaporation is stated in [16] that the influence of the curvature on the evaporation is always very small if the surface area and the radius of the curvature remain constant. But if we consider a layer whose radius of curvature decreases as evaporation proceeds we have to take account of other factors in calculating the evaporation. We can suppose that one of the factors is surface tension.

In principle, surface tension makes a surface maintain the mechanical equilibrium between two fluids at different pressures.

Using the form which satisfies conditions that the phase on the concave side of the surface experiences a pressure greater than that on the convex side, the evaporation becomes zero if the curvature is negative infinite and the evaporation shall be constant if the curvature is positive infinite, we may have for instance the evaporation term

$$E = \frac{K}{A + Be^{Eh_{xx}}}\phi.$$

In here the  $h_{xx}$ -term represents the curvature. Solution of the problem is shown in figure 11. We see that another form of the evaporation term can stabilize the instability phenomenon. But as long as the evaporation term depends linearly on the volume fraction, the bigger initial concentration at the highest point compared to the lowest point, e.g.  $\phi_0 = 1 - y/(1 + \delta)$ , can lead to the instability initially.

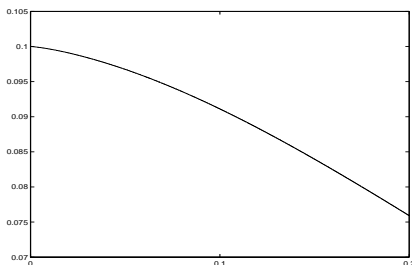


Figure 11: Amplitude of the perturbation as a function of time with  $K = A = B = D = 1$  and the same initial data as figure 7.

## 7 Conclusion

This work considers a simple linear diffusion problem which arises in studies of drying liquid paints. The model is similar to the free boundary problem of the phase change, the Stefan problem. We have restricted ourselves to the derivation of the model for the drying of a paint film in a specific process where we consider the process as dictated by diffusion and evaporation processes.

A small amplitude perturbation of the flat paint-air interface was discussed. The linearised equation given by this perturbed one-dimensional non-convective equations showed an instability. Numerical results have been used to convince ourselves that there is instability in the problem for some conditions. The difference of the speed of evaporation and diffusion is the cause of this instability. That is the reason why we call this instability a *speed-difference-driven instability*.

To stabilize this instability, surface tension is needed. Qualitatively, surface tension always causes levelling where the surface tension is assumed constant. Not only the surface tension  $\gamma$ , most of the coefficients involved in this study, e.g. the density  $\rho$ , the coefficient of viscosity  $\mu$  and the diffusion coefficient, are also taken constant. Non-constant diffusion coefficient  $D$  can be seen, for instance, in [17]. With a prediction that non-constant coefficient might influence the instability, study of coefficients depend on other variables will be addressed in future work.

## References

- [1] A.C. Fowler, *Mathematical Models in the Applied Sciences*, Cambridge University Press, 1997.
- [2] A. Friedman, Free Boundary Problems in Science and Technology, *Notice of AMS*. 47(8), 2000.
- [3] A. Friedman, *Partial Differential Equations of Parabolic Type*, Englewood Cliffs: Prentice-Hall, 1964.
- [4] B.W. van de Fliert, A Free Boundary Problem for Evaporating Layers, *Proceedings of the World Congress of Nonlinear Analysts*, Sicily, 2000. To appear in *Nonlinear Analysis*.



- [5] B.W. van de Fliert & R. van der Hout, A Generalized Stefan Problem in a Diffusion Model with Evaporation, *SIAM J. Appl. Math.* 60 (4), pp. 1128-1136, 2000.
- [6] B.W. van de Fliert & R. van der Hout, Stress-driven Diffusion in a Drying Liquid Paint Layer, *Eur. J. Appl. Math.* 9, pp. 447-461, 1998.
- [7] D.L. Bernstein, *Existence Theorems in Partial Differential Equations*, annals of math. study number 23, Princeton University Press, 1950.
- [8] H. Ockendon & J.R. Ockendon, *Viscous Flow*, Cambridge University Press, 1995.
- [9] H.S. Carslaw & J.C. Jaeger, *Conduction of Heat in Solids*, 2<sup>nd</sup> edition, Oxford University Press, 1959.
- [10] L.D. Landau & E.M. Lifshitz, *Fluid Mechanics*, 2<sup>nd</sup> edition, Oxford: Pergamon Press, 1987.
- [11] L.I. Rubenstein, *The Stefan Problem*, AMS, transl. math. monogr. vol. 27, 1971.
- [12] M.P. do Carmo, *Differential Geometry of Curves and Surfaces*, Englewood Cliffs: Prentice-Hall, 1976.
- [13] M.H. Protter & H.F. Weinberger, *Maximum Principles in Differential Equations*, Englewood Cliffs: Prentice-Hall, 1967.
- [14] N.A. Fuchs, *Evaporation and Droplet Growth in Gaseous Media*, London: Pergamon Press Ltd, 1959.
- [15] R.A. Cairncross, L.F. Francis, & L.E. Scriven, Predicting Drying in Coatings that React and Gel: Drying Regime Maps, *AIChE Journal* 42, No. 1, pp. 55-67, 1996.
- [16] R. Defay, I. Prigogine & A. Bellemans, *Surface Tension and Adsorption*, English edition, London: Longmans, Green & Co Ltd, 1966
- [17] T.P. Witelski, Traveling Wave Solutions for Case II Diffusion in Polymers, *J. of Polymer Science: Part B: Polymer Physica* 34, pp. 141- 150, 1996.