MODELING, SIMULATIONS, AND PARAMETRIC STUDIES OF THE DIP COATING PROCESS WITH THE EFFECT OF SOLVENT EVAPORATION RATE AND BULK REACTION RATE

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MODELING, SIMULATIONS, AND PARAMETRIC STUDIES OF THE DIP COATING PROCESS WITH THE EFFECT OF SOLVENT EVAPORATION RATE AND BULK REACTION RATE

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ABSTRACT

In this paper we study the dip coating problem. We present a thin film model based on the lubrication approximation that includes an evaporation effect of the solvent and the bulk reaction effect of erbium oxide to determine the thickness of the coatings. We solve the problem numerically with the modified two-step Lax-Wendroff scheme [1]. While the two main mechanisms influencing the final film thickness are the solvent evaporation rate and the erbium oxide reaction, we also study how the dynamic viscosity, the angle of the inclined substrate, the characteristic depth of the solution thickness, the initial profile of the solution thickness, and the length of substrate affect the coating thickness. The developed model can be used in many coating industries to predict the coating thickness and approximate drying time.
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CHAPTER I

INTRODUCTION

One of the most simple and important techniques used to coat fluid onto a surface is dip coating. Dip coating is generally used in many industrial processes to deposit a thin film of solution consisting of solute and solvent onto substrates for such purposes as protection, magnetization, controlling refractive index, and lubrication. It is a very economical and simple process and the films prepared by this process have excellent electrical and optical properties [2, 3, 4]. The process involves immersing a substrate into a reservoir of solution for some time, thereby ensuring that the substrate is completely wetted, and then withdrawing the substrate from the solution bath (see Figure 2.1). The shape of the substrates can be a plate, cylinder, or irregular-shaped object. The fact that the geometry of the substrates can vary widely is one of the distinguishing features of the dip coating technique. From the literature reviewed, the film thickness depends on many factors; for example, withdrawal speed, gravitational acceleration, solvent evaporation, surface tension, numbers of cycling, physical properties of the fluid, etc [2, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19].
An early dip coating analysis was first presented by Landau and Levich [20]. The model considered the case of an infinite, low velocity moving plate and a relatively large liquid container (which results in a problem with no edge effects). The model derivation was based on Newtonian fluid flow and ignored solvent evaporation and Marangoni effects (the effects from surface tension). An expression for the deposited liquid film thickness, $h$, on a flat and homogeneous substrate withdrawn at the velocity $U$ from a bath of liquid with density $\rho$, dynamic viscosity $\mu$, and surface tension $\sigma$, is

$$h = 0.946 \sqrt{\frac{\sigma}{\rho g}} C a^{2/3}. \quad (1.1)$$

Here $g$ is the gravitational constant and $Ca = \frac{\mu U}{\sigma}$ is the capillary number. This approximate solution is valid for small capillary numbers. The withdrawal speed $U$ is the most common parameter used to control the film thickness. The faster the substrate is withdrawn, the thicker will be the film deposited. This is because the viscous drag of the moving substrate is proportional to the withdrawal speed. At higher withdrawal speed, a large force results in a greater amount of the liquid moving upwards with the substrate, and hence a thicker film. There have been a large number of researchers studying the film thickness dependency on the withdrawal speed, for example [4, 9, 10, 18]. However, we do not include the effect of the withdrawal speed in our mathematical model because the experimental system that we simulate is based solely on gravity-driven drainage of the solvent.

Since then various authors have attempted to improve the accuracy of equation (1.1) by retaining some of the neglected terms and by introducing new small
terms. In this connection, we cite the work of [21, 22, 23]. Wilson [21] used a more formal analysis based on matched asymptotic expansions to derive an $O(Ca)$ correction term. He showed that the Landau-Levich result is an asymptotic solution valid as the capillary number tends to zero, which is a fact not properly appreciated hitherto. Moreover, he presented how the results may be applied to the coating of a horizontal roller. Krechetnikov and Homsy [22] analyzed generic nontrivial deviations from the Landau-Levich law in the presence of an extra body force originating from an interaction between a coating liquid and a substrate. In [23], White and Tallmadge proposed a gravity corrected theory.

Including the effect of solvent evaporation into the dip coating analysis is crucial for correct prediction of film thickness. We assume that the evaporation rate is constant as in [5, 6, 24]. There are numbers of researchers who consider the effect of solvent evaporation in the coating process [5, 6, 7, 9, 13, 24]. Yimsiri and Mackley [9] showed that spin and dip coating of light-emitting polymer solutions is particularly sensitive to the evaporation rate of the solvents. Cregan and O’Brien [7] derived a simple model of spin-coating with small evaporation effects by using a formal asymptotic approach. Meyerhofer’s work [24] was credited as being the first attempt to model the effects of solvent evaporation and the associated viscosity rise on the thickness of dried films during spin coating. Using a one-dimensional model for film thickness and solvent evaporation, he proposed that film thinning occurs in two distinct stages. At first, the effect of evaporation is negligible and the film thins mainly by centrifugally-driven flow toward the edge of the substrate. During the sec-
ond stage, solvent evaporation becomes the dominant mechanism for film thinning as the viscosity rise due to solvent evaporation reduces the radial outflow significantly. Thus, it is a common practice in the coating community to separate the dip coating process into two stages for modeling [3, 5, 6, 7, 24]. At the start of the process there exists a very short time when the fluid thickness decreases very rapidly due to gravity while solvent evaporation has relatively little effect. We do not attempt to model this short transient stage of the process because the details of the flow during this phase have a small effect on the long time solutions and the final film thickness [5, 6]. After this stage the film is relatively thin and the rate of thinning due to gravity and evaporation rate are of the same order. Thereafter, there is little flow due to gravity while the solvent evaporation is the main contributor to the rate of thinning. After all the solvent has evaporated, a thin layer of solute remains on the substrate. Later, Meyerhofer’s model was extended into a two-dimensional analysis [5, 6, 13] using a two-component system as the mathematical model.

Lee et al. [17] presented a thin film model based on the lubrication approximation with an evaporation effect. They focused on dip coating of an ethanol based silica-surfactant solution onto a polished Si wafer substrate and assumed that the surfactant surface concentration does not change with respect to position on the surface and hence the surface tension is a constant at the leading order so that the surface tension gradient is zero, i.e. there are no Marangoni effects. In [5, 6] the effect of surface tension gradients (Marangoni effects) were neglected. In particular, surface tension generally decreases with increasing temperature [8]. In the present paper,
we assume that the system is isothermal and hence the temperature gradient is zero. Further, we do not include a surfactant. Thus, we do not include surface tension gradient effects. In contrast, Qu et al. [18] developed a method for measuring the film thickness by combining the effect of evaporation and Marangoni flow.

This work is motivated by dip coating experiments being conducted at The University of Akron. In these experiments, the solution was made by dissolving the erbium acetate in an acidic solvent. The erbium acetate exists as a salt in the solution. Upon dipping the fibers, the erbium salt solution coats the fiber’s surface. Heating the fibers in a furnace has two effects. First, the solvent evaporates, leaving only the erbium salts. Second, the salts are driven off, leaving a coating. Based on the temperature of calcination, this coating is believed to be erbium oxide. The results show that the average height of the coating thickness is observed to be between 1 and 2 µm and the drying time is about 3 hours [25]. Based on this motivation, we develop the dip coating model including the erbium oxide reaction with the ultimate goal of having a coating thickness of 1 µm in about 3 hours.

It is very important to point out how this paper is different from others. The dip coating model used here is different from the usual dip coating models in the literature because we include a bulk reaction that produces the solute concentration. Other approaches have solute to begin with, while in this work it is created by this reaction. Hayes and O’Brien [5, 6] used a lubrication approximation to exploit the thinness of the liquid film in simplifying the Navier-Stokes equations. They emphasized obtaining approximate analytic solutions rather than numerically solving the
governing partial differential equations. The emphasis in this work is on the numerical computation of the leading order of the evolution equations using a two-step Lax-Wendroff scheme with source terms [1].

We assume that the viscosity of the solution is constant. The assumption of constant viscosity is a reasonable approximation in many practical situations [5, 6]. The thickness of the deposited film depends on the viscosity in theory [10, 24]. Moreover, we use the mathematical model from [5, 6] to predict the evolving coating thickness. The model not only includes the effect of solvent evaporation under the influence of gravity but also the effect of a bulk reaction to form erbium oxide. In addition, we also observe how other parameters such as the dynamic viscosity, the angle of the inclined substrate, the characteristic depth of the solution thickness, the initial profile of the solution thickness, and the length of the substrate affect the final coating thickness.

The objectives of our work and the outline of the paper are as follows. In Chapter II, we formulate the problem mathematically, presenting hydrodynamic and solute concentration models. In Chapter III, we simplify the problem via non-dimensionalization and the lubrication approximation, and obtain the solutions for the solvent and coating free-surface by asymptotic expansions. The numerical solution procedure for the full problem is presented in Chapter IV, and the results and discussion are presented in Chapter V. Finally, we make some closing remarks, outline limitations of the model, and define future work in Chapter VI.
CHAPTER II

THE MATHEMATICAL MODEL

In this chapter, we will generally write equations in terms of dimensional variables indicated by a hat (\(^\wedge\)) notation.

Figure 2.1: Schematic Diagram of Dip Coating Process: (a) immersion, (b) wetting, and (c) withdrawal.
Figure 2.2: A Thin Fluid Layer Flowing Down an Incline Plane.

Figure 2.3: Schematic of Dip Coating Process for $\theta = \frac{\pi}{2}$
2.1 Problem Description

The dip coating process involves immersing a substrate into a reservoir of solution for some time to ensure that the substrate is completely wetted, and then withdrawing the substrate from the solution bath under the influence of gravity (see Figure 2.1). As the solvent evaporates, a solid film is deposited upon the surface of the substrate as a function of position and time. To quantify the thickness of the solution on the substrate, we assume that it equals the sum of the solvent and the solute thicknesses \([5, 6, 24]\). This leads to the expression

\[
\hat{\lambda}(\hat{x}, \hat{t}) = \hat{h}(\hat{x}, \hat{t}) + \hat{s}(\hat{x}, \hat{t}),
\]  

(2.1)

where \(\hat{\lambda}\) is the solution thickness, \(\hat{h}\) is the solvent thickness, and \(\hat{s}\) is the solute thickness. In contrast, real solutions do not follow this assumption, but the difference is small and does not affect the final film results. Mathematically, the final coating results when \(\hat{\lambda} = \hat{s}\) or \(\hat{h} = 0\). The relationship between the solute concentration (volume fraction) and the solution thickness is represented by

\[
\hat{s}(\hat{x}, \hat{t}) = \hat{c}(\hat{x}, \hat{t}) \hat{\lambda}(\hat{x}, \hat{t}) = \hat{c}(\hat{x}, \hat{t}) \left( \hat{h}(\hat{x}, \hat{t}) + \hat{s}(\hat{x}, \hat{t}) \right),
\]  

(2.2)

where \(\hat{c}\) is the solute concentration (volume fraction) \([5, 6, 24]\). The value of solute concentration (volume fraction) is between 0 and 1. If \(\hat{c} = 0\), there is no solute present in the solution and if \(\hat{c} = 1\), we have the thickness of the solute coating when all the solvent is evaporated.
2.2 Hydrodynamic Model

Typically, the coating is a thin layer of a liquid applied dynamically to a solid substrate. We start forming the mathematical model by considering the flow of a thin layer of viscous fluid on an inclined plane as shown in Figure 2.2 and introducing a system of coordinates \((\hat{x}, \hat{z})\) where the \(\hat{x}\)-axis coincides with the plane bed inclined at the angle \(\theta\) with respect to the horizon and the \(\hat{z}\)-axis is normal to the plane bed. Let \(\hat{U}\) and \(\hat{W}\) be the two velocity components in the \(\hat{x}\) and \(\hat{z}\) directions. Typically, the velocity in the \(\hat{z}\) direction, perpendicular to the substrate, is much smaller than the velocity along the substrate, in the \(\hat{x}\) direction. In the following, we will present the basic model for the simulation of an incompressible Newtonian fluid. The continuity or incompressibility equation describing the conservation of mass is given by

\[
\hat{U}_\hat{x} + \hat{W}_\hat{z} = 0, \tag{2.3}
\]

along with the two Navier-Stokes equations describing the conservation of linear momentum. The momentum equation in the \(\hat{x}\) direction is

\[
\hat{U}_t + \hat{U}\hat{U}_\hat{x} + \hat{W}\hat{U}_\hat{z} = -\frac{1}{\rho}\hat{P}_\hat{x} + \nu \left(\hat{U}_{\hat{x}\hat{x}} + \hat{U}_{\hat{z}\hat{z}}\right) + g \sin \theta, \tag{2.4}
\]

and the momentum equation in the \(\hat{z}\) direction is

\[
\hat{W}_t + \hat{U}\hat{W}_\hat{x} + \hat{W}\hat{W}_\hat{z} = -\frac{1}{\rho}\hat{P}_\hat{z} + \nu \left(\hat{W}_{\hat{x}\hat{x}} + \hat{W}_{\hat{z}\hat{z}}\right) - g \cos \theta, \tag{2.5}
\]

where \(\nu\) is the kinematic viscosity, \(\rho\) is the density of water, \(\mu = \nu \rho\) is the dynamic viscosity, \(g\) is the gravity, and \(\hat{P}\) is the pressure. The left-hand sides of the momentum
equations denote inertial forces, which are balanced on the right hand sides by the pressure gradient, viscous forces, and gravity. In the schematic of the dip coating process, the substrate is usually lifted vertically (see Figure 2.1(c)). Therefore, we take $\theta = \frac{\pi}{2}$ and the schematic diagram of the fluid flow is shown in Figure 2.3. Hence, equations (2.4) and (2.5) can be simplified to

$$\hat{U}_t + \hat{U} \hat{U}_x + \hat{W} \hat{U}_z = -\frac{1}{\rho} \hat{P}_x + \nu \left( \hat{U}_xx + \hat{U}_xz \right) + g,$$  
(2.6)

$$\hat{W}_t + \hat{U} \hat{W}_x + \hat{W} \hat{W}_z = -\frac{1}{\rho} \hat{P}_z + \nu \left( \hat{W}_xx + \hat{W}_xz \right).$$  
(2.7)

There is no slip between the liquid and the plate, hence, the boundary condition at $\hat{z} = 0$ is

$$\hat{U} = \hat{W} = 0 \quad \text{on} \quad \hat{z} = 0. \quad (2.8)$$

This condition is posed for all time which means the model assumes $\dot{s} \ll \dot{\lambda}$. On the other hand, the top of the surface is a free boundary and it is necessary to specify a kinematic boundary condition for the motion, and two dynamic boundary conditions for the stresses acting on it. Since the top is a material surface, it must be always composed of the same fluid particles. The fluid velocity must be tangential to the moving surface at all times. We describe the top surface by

$$F(\hat{x}, \hat{z}, \hat{t}) \equiv \hat{z} - \hat{\lambda}(\hat{x}, \hat{t}) = 0.$$  
(2.9)
The unit normal to the surface ($\vec{n}$) and the unit tangent to the interface ($\vec{t}$) are given by

$$\vec{n} = \frac{\nabla F(\hat{x}, \hat{z}, \hat{t})}{|\nabla F(\hat{x}, \hat{z}, \hat{t})|} = \frac{\langle -\hat{\lambda} \hat{x}, 1 \rangle}{\sqrt{1 + (\hat{\lambda})^2}},$$

$$\vec{t} = \frac{\langle 1, \hat{\lambda} \hat{x} \rangle}{\sqrt{1 + (\hat{\lambda})^2}}. \quad (2.10)$$

After taking the derivative of equation (2.9) with respect to time, it follows that

$$\hat{\lambda}_t = \hat{W} - \hat{\lambda} \hat{x} \hat{U}. \quad (2.11)$$

This is the kinematic boundary condition on the top fluid surface without the effect of evaporation. Let $E_v$ be the evaporation rate, which has the units of length/time. After including evaporation into the model, the kinematic boundary condition is given by

$$\hat{\lambda}_t = \hat{W} - \hat{\lambda} \hat{x} \hat{U} - E_v \quad \text{on} \quad \hat{z} = \hat{\lambda}(\hat{x}, \hat{t}). \quad (2.12)$$

Next, we define $\mathbf{T}$ to be the stress tensor, which has units of force/area and is denoted by

$$\mathbf{T} = \left( \begin{array}{cc} \hat{\sigma}_{\hat{x}\hat{x}} & \hat{\sigma}_{\hat{x}\hat{z}} \\ \hat{\sigma}_{\hat{z}\hat{x}} & \hat{\sigma}_{\hat{z}\hat{z}} \end{array} \right) = \left( \begin{array}{cc} -\hat{P} + \mu \hat{U}_z & \frac{\mu}{2} \{\hat{U}_z + \hat{W}_\hat{z}\} \\ \frac{\mu}{2} \{\hat{U}_z + \hat{W}_\hat{z}\} & -\hat{P} + \mu \hat{W}_\hat{z} \end{array} \right). \quad (2.13)$$

For the normal stress balance at a free surface, the stress is balanced by the local curvature of the interface (units of 1/length) and the surface tension (units of
force/length) which is represented by the following expression:

\[ \vec{n} \cdot \mathbf{T} \cdot \vec{n} = \hat{\sigma} \hat{\kappa}, \tag{2.14} \]

where \( \hat{\sigma} \) is the surface tension and

\[ \hat{\kappa} = \frac{\hat{\lambda}_{x\hat{x}}}{\left(1 + (\hat{\lambda}_{\hat{z}})^2\right)^{3/2}}, \tag{2.15} \]

is the local curvature. Equation (2.14) leads us to the following normal stress balance condition

\[ -\hat{P} + \mu \left[ \hat{U}_{\hat{z}} (\hat{\lambda}_{\hat{z}})^2 - \hat{\lambda}_{x} (\hat{U}_{\hat{z}} + \hat{W}_{\hat{z}}) + \hat{W}_{\hat{z}} \right] \frac{1}{1 + (\hat{\lambda}_{\hat{z}})^2} = \hat{\sigma} \hat{\lambda}_{x\hat{x}} \left(1 + (\hat{\lambda}_{\hat{z}})^2\right)^{3/2}. \tag{2.16} \]

The shear stress balance at the top surface is balanced by the local surface tension gradients and so the shear stress balance condition equation is given by

\[ \vec{t} \cdot \mathbf{T} \cdot \vec{n} = -\nabla \hat{\sigma} = -\frac{\partial \hat{\sigma}}{\partial T} \frac{\partial T}{\partial S}, \tag{2.17} \]

where \( T \) is the temperature and \( S \) is the arc length along the free surface. Simplifying equation (2.17), we have

\[ \frac{\mu \hat{\lambda}_{\hat{z}} (\hat{W}_{\hat{z}} - \hat{U}_{\hat{z}}) + \frac{\mu}{2} \left(1 - (\hat{\lambda}_{\hat{z}})^2\right) (\hat{U}_{\hat{z}} + \hat{W}_{\hat{z}})}{1 + (\hat{\lambda}_{\hat{z}})^2} = -\frac{\partial \hat{\sigma}}{\partial T} \frac{\partial T}{\partial S}. \tag{2.18} \]

In addition, we assume that the system is isothermal so the temperature gradient is zero, with no shear in the system. Hence, equation (2.18) reduces to

\[ \hat{\lambda}_{x} (\hat{W}_{\hat{z}} - \hat{U}_{\hat{z}}) + \frac{1}{2} \left(1 - (\hat{\lambda}_{\hat{z}})^2\right) (\hat{U}_{\hat{z}} + \hat{W}_{\hat{z}}) = 0. \tag{2.19} \]
2.3 Solute Concentration Model

In order to complete the formulation of the mathematical problem we need the governing equation of the solute concentration ($\hat{c}$), expressed by

$$\hat{c}_t + \hat{U}\hat{c}_x + \hat{W}\hat{c}_z = \frac{E_v\hat{c}}{\lambda} + \frac{(1 - \hat{c})K}{\rho_{er}} + \hat{D}(\hat{c}_{xx} + \hat{c}_{zz}),$$

subject to the conditions

$$\hat{c}_z = 0 \text{ on } \hat{z} = 0, \quad (2.21)$$

$$\nabla \hat{c} \cdot \vec{n} = 0 \text{ on } \hat{z} = \hat{\lambda}. \quad (2.22)$$

Here $\hat{D}$ is the solute diffusivity which has units of length$^2$/time, $\rho_{er}$ is the density of erbium, and $K$ is a constant parameter defined by mass of erbium oxide created per volume of the liquid per time. The left-hand side of the governing equation presents the convective transport terms

$$\hat{c}_t + \vec{V} \nabla \hat{c} = \hat{c}_t + \hat{U}\hat{c}_x + \hat{W}\hat{c}_z,$$

where $\vec{V} = <\hat{U}, \hat{W}>$ is the local fluid velocity, and the right hand side has the diffusive transport term $\hat{D}(\hat{c}_{xx} + \hat{c}_{zz})$ [26]. In addition, the term

$$\frac{E_v\hat{c}}{\lambda},$$

illustrates the change in $\hat{c}$ due to the evaporation. Moreover, we include a bulk reaction rate of the erbium oxide

$$\frac{(1 - \hat{c})K}{\rho_{er}},$$
into our model which makes the present paper different from others. Note that the following expression

\[ 1 - \hat{c} = 1 - \frac{\hat{s}}{\hat{\lambda}} = \frac{\hat{\lambda} - \hat{s}}{\hat{\lambda}} = \frac{\hat{h}}{\hat{\lambda}}, \]

represents the volume fraction of liquid so that the reaction rate \( K \) is proportional to the amount of solvent \( \hat{h} \). The solvent contains the erbium that reacts with oxygen to form the erbia (erbium oxide).
CHAPTER III
SOLUTION PROCEDURE

This chapter outlines the solution of the dimensional equations in Chapter 2. A solution will be formulated first for the dynamics of the fluid flow and then the solute concentration solution will be developed with the use of equation (2.2). The mathematical tools used here include non-dimensionalization, the lubrication approximation, and asymptotic expansion.

3.1 Scaling

An essential first step of any analytical approximation is the art of scaling. First, we introduce the small aspect ratio \( \epsilon = d/L \ll 1 \), where \( d \) is the characteristic depth of the solution thickness and \( L \) is the characteristic length of the substrate in the \( z \) and \( x \) directions respectively. Typically, the thickness, \( d \), is much smaller than the characteristic length scale, \( L \), and the typical velocity in the \( z \) direction is much smaller than that in the \( x \) direction, so \( W = \epsilon U \). Table 3.1 summarizes the non-dimensional variables employed. Here, \( U_0 \) and \( T_0 \) are the characteristic velocity and
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temperature respectively. Moreover, we choose the following dimensionless groups:

\[ Re = \frac{dU_0}{\nu} = \text{Reynolds number}, \quad (3.1) \]

\[ Pe = \frac{dU_0}{D} = \text{Peclet number}, \quad (3.2) \]

\[ Bo = \frac{\rho gd^2}{\sigma} = \text{Bond number}. \quad (3.3) \]

The Reynolds’ number is the ratio of inertia and viscous terms, the Peclet number measures the relative importance of convection and diffusion, and the Bond number is a measure of surface tension compared to gravity forces. Sometimes a Bond number can also be interpreted as a Capillary number \((Ca)\), \(Ca = \frac{\mu U_0}{\sigma} = \frac{\rho gd^2}{\sigma} = Bo\). The Capillary number represents the relative effect of viscous forces versus surface tension.

Next, we apply the non-dimensionalization technique to the dimensional governing equations in Chapter 2 and find,

\[ U_x + W_z = 0, \quad (3.4) \]

for the mass conservation equation (2.3), and

\[ \epsilon Re (U_t + UU_x + WU_z) = -P_x + \epsilon^2 U_{xx} + U_{zz} + 1, \quad (3.5) \]

and

\[ \epsilon^3 Re (W_t + UW_x + WW_z) = -P_z + \epsilon^2 \left( \epsilon^2 W_{xx} + W_{zz} \right), \quad (3.6) \]

for the Navier Stokes equations (2.6) and (2.7) in the \(x\) and \(z\)-directions respectively.

At the bottom, the boundary condition equation (2.8) becomes

\[ U = W = 0 \quad \text{on} \ z = 0. \quad (3.7) \]
At the top of the surface, \( z = \lambda(x,t) \), the normal stress balance condition equation (2.16) becomes

\[
-P + \epsilon^2 \left[ \epsilon^2 U_x(\lambda_x)^2 - \lambda_x(U_z + \epsilon^2 W_x) + W_z \right] = \frac{\epsilon^3 \lambda_{xx}}{Bo (1 + (\epsilon \lambda_x)^2)^{3/2}}. \tag{3.8}
\]

Here \( Bo \) is very small for most materials and for mathematical convenience we approximate \( Bo \approx \bar{B}\epsilon^2 \) where \( \bar{B} \) is an order \( O(1) \) constant. Hence, equation (3.8) changes to

\[
-P + \epsilon^2 \left[ \epsilon^2 U_x(\lambda_x)^2 - \lambda_x(U_z + \epsilon^2 W_x) + W_z \right] = \frac{\epsilon \lambda_{xx}}{\bar{B} (1 + (\epsilon \lambda_x)^2)^{3/2}}, \tag{3.9}
\]

and the non-dimensionalized tangential component of the stress (2.19) is

\[
2\epsilon^2 \lambda_x (W_z - U_z) + (1 - (\epsilon \lambda_x)^2) (U_z + \epsilon^2 W_x) = 0. \tag{3.10}
\]

We introduce another dimensionless parameter \( E \) for the rate of evaporation where

\[
E = \frac{E_vL}{dU_0} = \frac{E_v}{\epsilon U_0}, \tag{3.11}
\]

for use in the kinematic condition equation (2.12). Moreover, the equation (3.11) implies \( E_v \) is small. Finally, the non-dimensionalized kinematic condition equation is given by

\[
\lambda_t = W - U\lambda_x - E \quad \text{on} \quad z = \lambda. \tag{3.12}
\]

For the solute concentration equation (2.20), we have

\[
\epsilon Pe \left( c_t + Uc_x + Wc_z \right) = \frac{dE_v c}{D\lambda} + \frac{d^2 K(1 - c)}{D\rho_{er}} + \epsilon^2 c_{xx} + c_{zz}. \tag{3.13}
\]

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In the equation (3.13), we define

\[
\frac{dE_v}{D} = \bar{E}\epsilon, \quad (3.14)
\]
\[
\frac{d^2K}{D\rho_{er}} = \bar{R}\epsilon, \quad (3.15)
\]

where \(\bar{E}\) and \(\bar{R}\) are order \(O(1)\) constant and have no units. For mathematical convenience, these orders of magnitude were chosen to balance the effects of the erbium oxide reaction and evaporation with the left-hand side of equation (3.13) so that solute transport is diffusion-dominated. Hence, the non-dimensionalized solute concentration equation is

\[
\epsilon Pe (c_t + U c_x + W c_z) = \frac{\epsilon \epsilon \bar{E}}{\lambda} + \epsilon \bar{R} (1 - c) + \epsilon^2 c_{xx} + c_{zz}, \quad (3.16)
\]

subject to the boundary conditions

\[
c_z = 0 \quad \text{on} \quad z = 0, \quad (3.17)
\]
\[
-\epsilon^2 c_x \lambda_x + c_z = 0 \quad \text{on} \quad z = \lambda. \quad (3.18)
\]

3.2 Hydrodynamics Solution Procedure

Equations (3.4), (3.5), (3.6), (3.7), (3.9), and (3.10) are used to define the solutions for the pressure \(P\) and the velocities \(U\) and \(W\). We assume the following asymptotic expansions for small \(\epsilon\):

\[
U(x,t) = U_0(x,t) + \epsilon U_1(x,t) + \epsilon^2 U_2(x,t) + \ldots, \quad (3.19)
\]
\[
W(x,t) = W_0(x,t) + \epsilon W_1(x,t) + \epsilon^2 W_2(x,t) + \ldots, \quad (3.19)
\]
\[
P(x,t) = P_0(x,t) + \epsilon P_1(x,t) + \epsilon^2 P_2(x,t) + \ldots. \quad (3.19)
\]
Plugging these expansions into the system (3.4), (3.5), and (3.6), one finds the leading order \(O(1)\) problem is given by

**Order \(O(1)\):**

\[
U_{0x} + W_{0z} = 0, \quad 0 = -P_{0x} + U_{0zz} + 1, \quad 0 = -P_{0z},
\]

subject to the conditions

\[
U_0 = W_0 = 0 \quad \text{on} \quad z = 0, \quad \text{(3.21)}
\]

and

\[
-P_0 = 0, \quad U_{0z} = 0 \quad \text{on} \quad z = \lambda. \quad \text{(3.22)}
\]

The solutions to this system are

\[
U_0 = -\frac{z^2}{2} + \lambda z, \quad \text{(3.23)}
\]

and

\[
W_0 = -\frac{\lambda_x z^2}{2}. \quad \text{(3.24)}
\]

The kinematic condition on \(z = \lambda\) at leading order is

\[
\lambda_t = W_0 - U_0 \lambda_x - E. \quad \text{(3.25)}
\]

Substituting the equations (3.23) and (3.24) into (3.25), we obtain the evolution equation at the leading order

\[
\lambda_t + \left(\frac{\lambda^3}{3}\right)_x + E = 0. \quad \text{(3.26)}
\]
One can show that the system for the first correction ($O(\epsilon)$) is given by

**Order $O(\epsilon)$:**

\[
U_{1x} + W_{1x} = 0,
\]
\[
Re(U_{0t} + U_0U_{0x} + W_0U_{0x}) = -P_{1x} + U_{1zz},
\]
\[
0 = -P_{1z},
\]  
(3.27)

subject to the conditions

\[
U_1 = W_1 = 0 \quad \text{on } z = 0,
\]  
(3.28)

and

\[
-P_1 = \frac{\lambda_{xx}}{B}, \quad U_{1z} = 0 \quad \text{on } z = \lambda.
\]  
(3.29)

The solutions to this system are

\[
U_1 = Re \left( \frac{z^3 \lambda_t}{6} + \frac{z^4 \lambda \lambda_x}{24} \right) - \frac{z^2 \lambda_{xxx}}{2B} + Az,
\]  
(3.30)

and

\[
W_1 = -\frac{Re}{120} \left( 5z^4 \lambda_{tx} + z^5(\lambda \lambda_{xx} + (\lambda_x)^2) \right) + \frac{z^3 \lambda_{xxxx}}{6B} + \frac{z^2 A_x}{2},
\]  
(3.31)

where

\[
A = A(x,t) = -Re \left( \frac{\lambda^2 \lambda_t}{2} + \frac{\lambda^4 \lambda_x}{2} \right) + \frac{\lambda \lambda_{xxx}}{B}.
\]  
(3.32)

The kinematic condition on $z = \lambda$ at this order is

\[
\lambda_t = (W_0 + \epsilon W_1) - (U_0 + \epsilon U_1) \lambda_x.
\]  
(3.33)

Substituting equations (3.23), (3.24), (3.30), and (3.31) into (3.33), we obtain

\[
\lambda_t + \left( \frac{\lambda^3}{3} \right)_x + E + \epsilon Re \left( -\frac{5\lambda^4 \lambda_t}{24} - \frac{3\lambda^6 \lambda_x}{40} \right)_x + \epsilon \frac{\lambda \lambda_{xxx}}{3} x = 0.
\]  
(3.34)
The leading order term in the evolution equation

\[ \lambda_t + \left( \frac{\lambda^3}{3} \right)_x + E, \]

includes the effect of fluid drainage and solvent evaporation and is in agreement with the models in [5] and [6]. The difference in this paper is that we include the correction term in the evolution equation where the term

\[ \epsilon Re \left( -\frac{5\lambda^4 \lambda_t}{24} - \frac{3\lambda^6 \lambda_x}{40} \right)_x, \]

represents the correction of flow effect and the last term

\[ \frac{\epsilon}{B} \left( \frac{\lambda^3 \lambda_{xxx}}{3} \right)_x, \]

represents the correction of the curvature and surface tension effect.

3.3 Solute Concentration Solution Procedure

We use a similar approach as illustrated in the previous section by assuming the following asymptotic expansion for small \( \epsilon \):

\[ c(x, z, t) = c_0(x, z, t) + \epsilon c_1(x, z, t) + \epsilon^2 c_2(x, z, t) + \ldots \quad (3.35) \]

Notice that the concentration depends on \( x, z, \) and \( t \). Substituting the above expansion into equations (3.16), (3.17), and (3.18), one can confirm that the system at leading order is
Order $O(1)$:

\begin{equation}
\frac{\partial}{\partial z^2} c_0 = 0, \tag{3.36}\end{equation}

subject to the conditions

\begin{equation}
c_0 = 0 \text{ on both } z = 0 \text{ and } z = \lambda. \tag{3.37}\end{equation}

Integrating equation (3.36) twice and using the boundary conditions in equation (3.37), we find that the solution at the leading order is

\begin{equation}c_0 = C(x, t), \tag{3.38}\end{equation}

where $C(x, t)$ is an unknown function which depends on $x$ and $t$. Notice that the solution at leading order is independent of $z$.

The system of the first correction is also derived and given by

Order $O(\epsilon)$:

\begin{equation}Pe \left( \frac{\partial c_0}{\partial t} + U_0 \frac{\partial c_0}{\partial x} + W_0 \frac{\partial c_0}{\partial z} \right) = \frac{\bar{E} c_0}{\lambda} + \bar{R} (1 - c_0) + c_{1zz}, \tag{3.39}\end{equation}

subject to the boundary conditions

\begin{equation}c_1 = 0 \text{ on both } z = 0 \text{ and } z = \lambda. \tag{3.40}\end{equation}

In order to obtain the evolution equation for the coating thickness ($s$), we integrate the equation (3.39) and define another dimensionless parameter

\begin{equation}R_p = \frac{\bar{R}}{Pe} = \frac{KL}{\rho_c U}. \tag{3.41}\end{equation}

After integrating and using the boundary condition at $z = 0$, we have

\begin{equation}c_1 = Pe \left[ C_1 z + C_x \left( \frac{-z^3}{6} + \frac{\lambda z^2}{2} \right) \right] + \left[ C \left( \frac{\bar{R} - \bar{E}}{\lambda} \right) - \bar{R} \right] z. \tag{3.42}\end{equation}
Next, we use the boundary condition at \( z = \lambda \) then the above expression becomes

\[
0 = Pe \left[ \lambda C_t + \frac{\lambda^3}{3} C_x \right] + (C - 1) R\lambda - C \tilde{E},
\]

\[
\frac{C \tilde{E}}{Pe} = \lambda C_t + \frac{\lambda^3}{3} C_x + \frac{R\lambda}{Pe} (C - 1),
\]

\[
CE = (\lambda C)_t - C \lambda_t + \frac{\lambda^3}{3} C_x + R_p \lambda (C - 1),
\]

\[
0 = (\lambda C)_t - C (E + \lambda_t) + \frac{\lambda^3}{3} C_x + R_p \lambda (C - 1). \tag{3.43}
\]

From equation (3.34), we find the expression

\[
E + \lambda_t = - \left( \frac{\lambda^3}{3} \right)_x + \epsilon \left[ Re \left( \frac{5 \lambda^4 \lambda_t}{24} + \frac{3 \lambda^6 \lambda_x}{40} \right)_x - \frac{1}{B} \left( \frac{\lambda^3 \lambda_{xxx}}{3} \right)_x \right]. \tag{3.44}
\]

Substituting equation (3.44) into equation (3.43), we have

\[
0 = (\lambda C)_t + \left( \frac{C \lambda^3}{3} \right)_x + R_p \lambda (C - 1) + cC \left[ Re \left( - \frac{5 \lambda^4 \lambda_t}{24} - \frac{3 \lambda^6 \lambda_x}{40} \right)_x + \frac{1}{B} \left( \frac{\lambda^3 \lambda_{xxx}}{3} \right)_x \right]. \tag{3.45}
\]

Further, we use the relationship \( s = c \lambda \approx C \lambda \). Therefore, the evolution equation of

the coating thickness \( s \) on \( z = \lambda \) is expressed by

\[
s_t + \left( \frac{s \lambda^2}{3} \right)_x + R_p (s - \lambda) + \frac{sc}{\lambda} \left[ Re \left( - \frac{5 \lambda^4 \lambda_t}{24} - \frac{3 \lambda^6 \lambda_x}{40} \right)_x + \frac{1}{B} \left( \frac{\lambda^3 \lambda_{xxx}}{3} \right)_x \right] = 0. \tag{3.46}
\]

Here, we obtain a modification of the models in [5] and [6] by adding the term

\[
R_p (s - \lambda),
\]

into our model at leading orders. Physically this term states the rate of change of the

coating thickness is proportional to \( (\lambda - s) \) which is the thickness of the liquid layer.

This is consistent with the model that assumes the coating material comes from bulk
reactions occurring in the liquid. The correction term

\[
\frac{s\epsilon}{\lambda} \left[ Re \left( -\frac{5\lambda^4\lambda_t}{24} - \frac{3\lambda^6\lambda_x}{40} \right)_x + \frac{1}{B} \left( \frac{\lambda^3\lambda_{xxx}}{3} \right)_x \right],
\]

illustrates how the liquid free surface influences the coating profile.

Finally, the non-dimensionalized model for dip coating is completely derived. For simplicity, we solve the model at the leading order. Hence, the system reduces to

\[
\begin{align*}
\lambda_t + \left( \frac{\lambda^3}{3} \right)_x &= -E, \\
s_t + \left( \frac{s\lambda^2}{3} \right)_x &= R_p(\lambda - s).
\end{align*}
\] (3.47)

The details of the numerical computation are presented in Chapter IV.
CHAPTER IV
NUMERICAL SOLUTION PROCEDURE

Suppose that the solution domain is divided into finite cells along the $x$-axis with equal length $dx$. Denote $x_i$ as a grid point on the $x$ location at $i$ where $1 \leq i \leq N_{\text{max}}$ and denote $W^n_i = W(x_i, t^n)$ as the value in the cell center $x_i$ at the time $t_n$. Let $dt$ be the incremental interval of time such that $t_{n+1} = t_n + dt$. Next, we re-write the system of governing equations (3.47) in matrix form:

$$
\begin{bmatrix}
\lambda \\
s
\end{bmatrix}_t = \begin{bmatrix}
-\frac{\lambda^3}{3} \\
-\frac{s\lambda^2}{3}
\end{bmatrix} + \begin{bmatrix}
-E \\
R_p(\lambda - s)
\end{bmatrix}.
$$

(4.1)

In equation (4.1), if we let $W = \begin{bmatrix} \lambda \\ s \end{bmatrix}$, $F = \begin{bmatrix} -\frac{\lambda^3}{3} \\ -\frac{s\lambda^2}{3} \end{bmatrix}$, and $S = \begin{bmatrix} -E \\ R_p(\lambda - s) \end{bmatrix}$ the equation is exactly matched with the partial differential equation in [1] where $S$ is called the source array. In addition, one can see that the source array could be written as

$$
\begin{bmatrix}
-E \\
R_p(\lambda - s)
\end{bmatrix} = \begin{bmatrix}
0 & 0 \\
R_p & -R_p
\end{bmatrix} \begin{bmatrix}
\lambda \\
s
\end{bmatrix} + \begin{bmatrix}
-E \\
0
\end{bmatrix},
$$

(4.2)

or

$$
S = CW + \bar{S},
$$

(4.3)
where \( C = \begin{bmatrix} 0 & 0 \\ R_p & -R_p \end{bmatrix} \), and \( \bar{S} = \begin{bmatrix} -E \\ 0 \end{bmatrix} \). Hence, the alternative form of equation (4.1) is

\[
W_t = F_x + CW + \bar{S}.
\] (4.4)

Since the partial differential equations (4.1) and (4.4) have the same form as the partial differential equations in [1], we use their two-step Lax-Wendroff scheme with source terms to solve this system. In this case, the following condition is required to obtain a stable solution:

\[
|A| > 0,
\] (4.5)

where \( A = I - \frac{dt}{2} C \), and \( I \) is the identity matrix. The details of deriving the two-step Lax-Wendroff scheme can be found in [1]. The scheme is of second-order accuracy in both space and time.

4.1 Two-step Lax-Wendroff Scheme with Source Terms

In [1], Zhang and Tabarrok showed that the two-step Lax-Wendroff scheme with source terms preserves the wave profile correctly while the standard Lax-Wendroff scheme [27] leads to oscillations at discontinuous wavefronts. However, for problems without a source term the standard Lax-Wendroff scheme can also preserve the wave profile correctly. The two-step Lax-Wendroff scheme with source term is expressed
by the following

\[
\begin{align*}
W_{i+1/2}^{n+1/2} &= \frac{1}{2} (W_i^n + W_{i+1}^n) + \frac{dt}{2dx} (F_{i+1}^n - F_i^n) + \frac{dt}{4} (S_i^n + S_{i+1}^n), \\
W_i^{n+1} &= A^{-1} \left( W_i^n + \frac{dt}{dx} (F_{i+1/2}^{n+1/2} - F_{i-1/2}^{n+1/2}) + \frac{dt}{2} (S_i^n + \bar{S}_{i+1}^{n+1}) \right),
\end{align*}
\]

where \( A^{-1} = \begin{bmatrix} 1 & 0 \\ s_1 & s_2 \end{bmatrix} \) is the inverse of \( A \) in which \( s_1 = \frac{dtR_p}{2+dtR_p} \) and \( s_2 = \frac{2}{2+dtR_p} \).

The first step of the scheme, equation (4.6), calculates the value at grid point \( i + 1/2 \) and the half time level \( n + 1/2 \) using the known values at time level \( n \). Then the output of the first step \( W_{i+1/2}^{n+1/2} \) is used as an input at the second step of the scheme in order to obtain the term \( F_{i+1/2}^{n+1/2} \) at grid point \( i \) and the term \( F_{i-1/2}^{n+1/2} \) at grid point \( i-1 \). The second step updates the values at the cell center at time level \( n + 1 \) via equation (4.7).

Next, we define

\[
\begin{align*}
G_i &= \lambda_i^{n+1/2}, \quad \text{and} \\
J_i &= s_i^{n+1/2},
\end{align*}
\]

for grid points \( 1 \leq i \leq N_{\text{max}} - 1 \) and the following constant parameters

\[
\begin{align*}
r_1 &= \frac{dt}{6dx}, \quad r_2 = -dtE, \quad r_3 = \frac{r_2}{2}, \quad r_4 = 2r_1, \quad r_5 = \frac{dtR_p}{4}, \quad \text{and} \quad r_6 = 2r_5,
\end{align*}
\]
for mathematical convenience. Now, we simplify equations (4.6) and (4.7) with the use of equations (4.8) and (4.9). Hence, the results are

\[
G_i = \frac{1}{2} (\lambda_i^n + \lambda_{i+1}^n) + r_1 ((\lambda^3)_i^n - (\lambda^3)_{i+1}^n) + r_3, \tag{4.10}
\]

\[
J_i = \left( \frac{1}{2} - r_5 \right) (s_i^n + s_{i+1}^n) + r_1 ((s\lambda^2)_i^n - (s\lambda^2)_{i+1}^n) + r_5 (\lambda_i^n + \lambda_{i+1}^n), \tag{4.11}
\]

\[
\lambda_i^{n+1} = \lambda_i^n + r_4 ((G^3)_{i-1} - (G^3)_i) + r_2, \tag{4.12}
\]

\[
s_i^{n+1} = s_1 r_2 + \lambda_i^n (s_1 + s_2 r_6) + s_2 (1 - r_6) s_i^n
+ r_4 \left[ s_1 ((G^3)_{i-1} - (G^3)_i) + s_2 \left( J_{i-1}(G^2)_{i-1} - J_i(G^2)_i \right) \right]. \tag{4.13}
\]

Finally, we can predict the solution thickness \( \lambda \) and the coating thickness \( s \) numerically via equations (4.12) and (4.13) respectively. The next issue we need to consider for every numerical problem is the boundary and the initial conditions.

### 4.2 Boundary and Initial Conditions

The initial solute thickness \( (s) \) at time \( t = 0 \) must be zero so that we use a plausible initial condition of the solute thickness of the form

\[
s(x, 0) = 0, \tag{4.14}
\]

and we assume that the initial depth of the solution takes the form

\[
\lambda(x, 0) = f(x), \tag{4.15}
\]

where \( f(x) \) is a known function. In this paper, we suggest three possible forms of this function based on the fluid profile (see Appendix A).
At the first grid point \( x_{(1)} = 0 \), left boundary, it is clear that there are no effects of evaporation or bulk reaction from a numerical point of view. On the other hand, at the end of the substrate \( x_{(N_{\text{max}})} = L \), right boundary, we assume the boundary conditions take the form

\[
\lambda(L, t)_{xx} = 0, \quad (4.16)
\]
\[
s(L, t)_{xx} = 0, \quad (4.17)
\]

for the solution and coating thickness respectively. These conditions allow any propagating waves to pass through the boundary without any artificial reflections. The conditions are discretized using backward differences with second order accuracy:

\[
\lambda^{n+1}_{N_{\text{max}}} = \frac{1}{2} \left( 5\lambda^{n+1}_{N_{\text{max}}-1} - 4\lambda^{n+1}_{N_{\text{max}}-2} + \lambda^{n+1}_{N_{\text{max}}-3} \right), \quad (4.18)
\]
\[
s^{n+1}_{N_{\text{max}}} = \frac{1}{2} \left( 5s^{n+1}_{N_{\text{max}}-1} - 4s^{n+1}_{N_{\text{max}}-2} + s^{n+1}_{N_{\text{max}}-3} \right). \quad (4.19)
\]
CHAPTER V

RESULTS AND DISCUSSION

It is important to explain how we define the values of variables in the coding program, especially the values of evaporation $E_v$ and bulk reaction rate $K$. We use a trial and error method in simulation until we obtained an approximate coating thickness of 1 $\mu m$ in about 3 hours, consistent with the actual data in the experiment. The simulation can be done by adjusting the non-dimensional values of $E$ and $R_p$ related to $E_v$ and $K$ respectively. With this idea we find that the appropriate values of $E$ and $R_p$ are $3.5 \times 10^{-6}$ and $3.5 \times 10^{-4}$ respectively. Then we can calculate the values of $E_v$ and $K$ from equations (3.11) and (3.41),

$$E_v = \frac{dEU}{L} = \frac{dE\rho gd^2}{L\mu},$$

$$K = \frac{R_p\rho_{er}U}{L} = \frac{R_p\rho_{er}\rho gd^2}{\mu L}.$$  \hspace{1cm} (5.1)

Substituting all the relevant parameters from Table 5.1 into the above expressions, we find that the constant solvent evaporation rate is $E_v = 9.80665 \times 10^{-11}$ m/s and the erbium oxide reaction rate is $K = 8.89070889 \times 10^{-4}$ g/cm$^3$/s.
Table 5.1: Relevant parameters and their typical magnitudes for calculating solvent evaporation rate and erbium oxide reaction rate

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristic layer thickness</td>
<td>$d$</td>
<td>0.01</td>
<td>cm</td>
</tr>
<tr>
<td>Characteristic horizontal length</td>
<td>$L$</td>
<td>7</td>
<td>cm</td>
</tr>
<tr>
<td>Gravity</td>
<td>$g$</td>
<td>980.665</td>
<td>cm/s²</td>
</tr>
<tr>
<td>Density of water</td>
<td>$\rho$</td>
<td>1</td>
<td>g/cm³</td>
</tr>
<tr>
<td>Density of erbium</td>
<td>$\rho_{er}$</td>
<td>9.066</td>
<td>g/cm³</td>
</tr>
<tr>
<td>Dynamic viscosity</td>
<td>$\mu$</td>
<td>5</td>
<td>g/ms</td>
</tr>
</tbody>
</table>

5.1 Results

Since we want to study what parameters affect the coating thickness, we first establish the set of parameters based on the final film thickness of 1 $\mu$m in about 3 hours then we vary one parameter while others are fixed. Those parameters include solvent evaporation rate, erbium oxide reaction rate, dynamic viscosity, the angle of the inclined substrate, the characteristic depth of the solution thickness, the initial profile of the solution thickness, and the length of the substrate.

5.1.1 Base parameter set

The base parameter set illustrates the plots of coating thickness, solvent thickness, and solution thickness as a function of time. Figure 5.1 (a) shows the plot of the
coating thickness at three different times: 30 minute, 1 hour, and 2 hours. It shows that the coating thickness increases as time increases. Figure 5.1 (b) is a zoomed detail of Figure 5.1 (a) from $x = 0$ to $x = 1$ cm and it tells us that at the leading edge of the substrate, the coating thickness ($s$) does not show any significant variation on the long time solution while it is getting thicker after $x = 1$ cm. Figure 5.1 (c) and (d) show that the solvent thickness ($h$) decreases as time increases. This is because, in the dip coating process, more of the solvent has evaporated and drained off as time is increasing. Hence, we have less solvent left, and therefore the solvent thickness is decreasing. You also see that the three traces have different starting points. This is due to the fact that the solvent has completely evaporated in the region before the starting point. Figure 5.1 (e) and (f) present plots of the solution thickness ($s + h$). Similar to the solvent thickness, the solution thickness is decreasing as time increases. The most important feature here is the point where it changes the slope of the curvature (see dashed line, $T = 2$ hours). Comparing with the dashed line in Figure 5.1 (c), we notice that the $x$ location where the point starts changing the slope of the curvature is the same $x$ location where the dashed line starts. This location denotes the drying line of the solvent. Figure 5.2 shows a plot of the drying line. The drying line is defined by $h(x, t) = 0$ or $\lambda(x, t) = s(x, t)$. It is a curve which effectively bounds the relevant part of $x, t$ space corresponding to the point where the solution has completely dried or the solvent is all evaporated. Here, the estimated drying time is about 12,420 seconds and the coating thickness is about 1.048 $\mu$m (which is also equal to the solution thickness).
5.1.2 The effect of the solvent evaporation

We fix all parameter values in the base set while we vary the solvent evaporation rate. The results are shown in Figure 5.3. This figure shows that increasing the evaporation rate decreases the coating thickness (see Figure 5.3 (a)). With the higher evaporation rate the solvent evaporates faster, hence, faster drying times (see Figure 5.3 (d)). In Figure 5.3 (d), the actual drying times at $E_v = 9.80665 \times 10^{-10}$, $9.80665 \times 10^{-11}$, and $9.80665 \times 10^{-12}$ m/s are 3996, 12420, and 27447 seconds respectively.

5.1.3 The effect of the erbium oxide reaction

In Figure 5.4 (a), notice that increasing the erbium oxide reaction rate also increases the coating thickness. The analysis of the governing equation of solution thickness, $\lambda_t + \frac{(\lambda^3)x}{3} = -E$, tells us that the solution thickness does not depend on the reaction rate. This can be confirmed by the plots of solution thickness in Figure 5.4 (c). In Figure 5.4 (c) we see that the solid line and dashed line lie on each other. We know that the solution thickness is equal to the sum of the solvent and the solute (coating) thickness. It is clear that if the solution thickness does not change then the coating thickness is high when the solvent thickness is low and vice versa. Figure 5.4 (b) shows that at the higher reaction rate the solvent thickness is thinner but the coating thickness is thicker. The drying times are represented in Figure 5.4 (d) and are 3673, 12420, and 20326 seconds with respect to the reaction rate $K = 8.89070889 \times 10^{-3}$, $8.89070889 \times 10^{-4}$, and $8.89070889 \times 10^{-5}$ g/cm$^3$/s respectively. Our results show that increasing the reaction rate reduces the drying time.
5.1.4 The effect of the dynamic viscosity

The dynamic viscosity of solutions is a function of the concentration of polyvinylpyrrolidone (PVP) in g per 100 cc solution [25] and it affects the velocity of the fluid drainage. The higher the dynamic viscosity the slower liquid moves downward, and hence the larger the coating thickness will be. Not only does the coating thickness get larger, but the solvent and the solution thicknesses are also larger as the dynamic viscosity is increased. Increasing the dynamic viscosity also increases drying times because the fluid moves slower down the substrate, and hence the drying time increases. These results are displayed in Figure 5.5.

5.1.5 The effect of the angle of an inclined substrate

Another factor that could possibly affect the coating thickness is the angle between the substrate and the horizontal direction. In Figures 5.6 (a) and 5.6 (b), we compare the coating thickness at angles $\theta = 10^0$ and $90^0$. It is noticeable that the coating thickness is larger at upstream locations when the size of the angle is smaller, while the thickness is smaller at downstream locations. This is also shown in Figures 5.6 (c) and 5.6 (d), which are plots of the coating thickness at angles of $\theta = 10^0$ and $60^0$. In addition, the drying time increases with decreasing angle (see Figure 5.6 (e)). The reason is that the closer $\theta$ is to $\frac{\pi}{2}$ the faster fluid flow is moving due to the effect of gravity.
5.1.6 The effect of the characteristic depth of the solution thickness

The next parameter which affects the coating thickness is the original depth of the solution. After withdrawing the substrate from the solution bath, if we have more solution to begin with, the larger will be the coating thickness, and the longer the drying time will be (see results in Figure 5.7).

5.1.7 The effect of the initial profile of the solution thickness

We present three different initial profiles of the solution thickness in Appendix A. At long times, the initial profile does not significantly affect the coating thickness or the drying time (see Figure 5.8 (c) and (d)). However, each initial profile results in a different coating and a solution thickness at short times (see Figure 5.8 (a) and (b)).

And the last parameter that we observe is the length of the substrate. We find that it does not affect the coating thickness.
Figure 5.1: (a) Plots of the coating thickness ($s$) at time $T = 30$ minutes (solid), $T = 1$ hour (dotted), and $T = 2$ hours (dashed), (b) Zoom-in of Figure (a) on the $x$-axis between 0 and 1 cm, (c) Plots of the solvent thickness ($h$), (d) Zoom-in of Figure (c), (e) Plots of the solution thickness ($s + h$), and (f) Zoom-in of Figure (e).
Figure 5.2: Plot of the drying line. $E_v = 9.80665 \times 10^{-11}$ m/s. $K = 8.89070889 \times 10^{-4}$ g/cm$^3$/s.
Figure 5.3: Plots of the effect of the solvent evaporation. The dotted, solid, and dashed lines illustrate $E_v = 9.80665 \times 10^{-10}$, $9.80665 \times 10^{-11}$, and $9.80665 \times 10^{-12}$ m/s respectively. Figures (a)-(c) show the comparison among these evaporation rates at fixed time $T = 1$ hour. (a) Plots of the coating thickness, (b) Plots of the solvent thickness, (c) Plots of the solution thickness, and (d) Plots of the drying line.
Figure 5.4: Plots of the effect of the erbium oxide reaction. The dotted, solid, and dashed lines illustrate $K = 8.89070889 \times 10^{-3}$, $8.89070889 \times 10^{-4}$, and $8.89070889 \times 10^{-5}$ g/cm$^3$/s respectively. Figure (a)-(c) show the plots at fixed time $T = 1$ hour. (a) Plots of the coating thickness, (b) Plots of the solvent thickness, (c) Plots of the solution thickness, and (d) Plots of the drying line.
Figure 5.5: Plots of the effect of the dynamic viscosity $\mu$. The dot-dash-dot, dash-dot-dash, solid, dotted, and dashed lines illustrate $\mu = 1, 2, 5, 10,$ and $15 \text{ g/m/s}$ respectively. Figure (a)-(c) show the plots at fixed time $T = 1$ hour. (a) Plots of the coating thickness, (b) Plots of the solvent thickness, (c) Plots of the solution thickness, and (d) Plots of the drying line.
Figure 5.6: Plots of the effect of the angle of an inclined substrate $\theta$. Figure (a) and (b) are plots of the coating thickness at fixed time $T = 2$ hours between $\theta = 10^\circ$ and $90^\circ$. Figure (c) and (d) are plots of coating thickness at fixed time $T = 2$ hours between $\theta = 10^\circ$ and $60^\circ$. Figure (e) is plots of the drying line.
Figure 5.7: Plots of the effect of the characteristic depth of the solution thickness $d$. The dotted, dashed, and solid lines demonstrate the initial depth of the solution thickness at 25, 50, and 100 $\mu$m respectively. (a) Plots of the coating thickness at $T = 10$ minutes. (b) Plots of the drying lines.
Figure 5.8: Plots of the effect of the initial profile of the solution thickness. The solid, dotted, and dashed lines represent the initial profile 1, 2, and 3 respectively. (a) Plots of the coating thickness at $T = 1$ and 2 seconds. (b) Plots of the solution thickness at $T = 0, 1,$ and 2 seconds. (c) Plots of the coating thickness at $T = 100$ seconds. (d) Plots of the drying line.
CHAPTER VI
CLOSING REMARKS AND FUTURE WORK

We have developed a comprehensive model for predicting the coating thickness resulting from a dip coating process under the influence of gravity and solvent evaporation. The intent of the comprehensive model is to include a bulk reaction rate for the creation of erbium oxide which will produce the solute concentration (rather than to assume the presence of solute in the initial solution). The solution procedure is critical to realizing this intent. Hence, we have made many simplifying assumptions to reduce the complex model to a simpler (but still relevant) model. These assumptions are

- solvent evaporation and erbium oxide reaction rates are constant and small,
- dynamic viscosity of the solution is constant,
- the effect of a surface tension gradient is neglected,
- the depth scale $d$ is much smaller than the length scale $L$.

After non-dimensionalization, we use the lubrication approximation and asymptotic analysis to solve the comprehensive models and obtain evolution equations for the solution and coating thicknesses. For the numerical simulations of these evolving equations, we use the two-step Lax-Wendroff scheme with second-order accuracy.
The main difficulty of solving the comprehensive model is the fourth order partial differential equations. To keep the numerical simulations at a manageable level, we solved the model only to leading order. The numerical results show that the solvent evaporation and a bulk reaction are important phenomena that influence the coating thickness. The effect of increasing evaporation is to decrease the coating thickness. The effect of increasing the bulk reaction is to increase the coating thickness.

In this paper, the interrelationships between processing factors are also investigated. These factors include the dynamic viscosity of the solution, the angle of an inclined substrate, the characteristic depth of the solution thickness, the initial profile of the solution thickness, and the length of the substrate. Parametric studies of these factors reveal general trends that a thicker coating thickness develops on the substrate with the higher viscosity, and in systems with higher levels of original depth of solution thickness. Each initial profile used here gives virtually the same results for long times, but slightly different results for short times. At smaller angles between the substrate and the horizontal line, there is a larger thickness on the upstream, and a smaller on the downstream. The length of the substrate has no effect on the coating thickness.

The model we have developed provides reasonable trends for the coating thickness. However, to become more useful to the application engineer, we must benchmark the model against experimental data as the processing parameters are varied. Moreover, we need to detail the actual bulk reaction in order to accurately model the creation of erbium oxide. Furthermore, we plan to solve an evolution equa-
tion with both leading order and correction terms in our future work. Once all of
these are included, a more valid model will be achieved and we can then predict the
coating thickness and drying times more accurately. This predictive capability will
be quite useful in the formulation of new products and processes.


APPENDIX A

INITIAL PROFILE OF SOLUTION THICKNESS

Note that the following three functions are presented in non-dimensional form. The first profile assumes that the initial solution thickness acts as a square root function until the flow reaches a specific point on the substrate and after this point the solution thickness becomes uniform. Hence, the function is given by

\[ f_1(x) = \begin{cases} \sqrt{xL} & \text{for } 0 < x < \frac{1}{L}, \\ 1 & \text{for } \frac{1}{L} \leq x \leq 1. \end{cases} \]  

(A.1)

The second profile is a hyperbolic function over the entire substrate:

\[ f_2(x) = \frac{x}{x + \frac{0.01}{L}} \text{ for } 0 \leq x \leq 1. \]  

(A.2)

The last profile is similar to the first. The difference is that it is a quarter circle instead of a square root function before the solution thickness becomes uniform. The function is represented by

\[ f_3(x) = \begin{cases} \sqrt{1 - \left(\frac{xL}{d} - 1\right)^2} & \text{for } 0 < x < \frac{4}{L}, \\ 1 & \text{for } \frac{4}{L} \leq x \leq 1. \end{cases} \]  

(A.3)

All three functions are shown in Figure A.1.
Figure A.1: Plots of $f_1(x)$, $f_2(x)$, and $f_3(x)$ for $0 \leq x \leq 1$. 
program code

implicit none

integer ip,i,k,tmax,nmax,np,b
integer front(10000001)
double precision dx,dt,d,l,tol,r1,r2,r3,r4,r5,r6,s1,s2,E,rp
double precision x(100001),lam(100001,2),iop,rhoe,tk,pi,theta,sit
double precision s(100001,2),g(100001),j(100001)
double precision Tscale,xscale,zscale,vis,rhowa,grav,Ev,bigk
double precision Uscale,Wscale,Pscale,Epsil
character*1 iflag
character*13 flname
character*3 chan3

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theta=pi/2.d0
sit=sin(theta)
write(6,*) 'Enter id (1 character)'
read(5,77) iflag

77 format(a1)

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open(8, file='input'/iflag)

    write(8,*) 'initial option',ip,' & tol =', tol
write(8,*) 'print int values for every',np,' time steps'
write(8,*) 'viscosity',vis,'g/(m*s)'
write(8,*) 'rhowater and rhoerbium are',rhowa,rhoe,'g/(cm)^3  respectivly'
write(8,*) 'gravity',grav,' cm/s^2'

Epsil=d/l
write(6,*) 'The epsilon value is',Epsil
write(8,*) 'The epsilon value is',Epsil

Uscale=(rhowa*grav*d**2)/vis
write(6,*) 'Uscale is (unit of m/s)',Uscale
write(8,*) 'Uscale is (unit of m/s)',Uscale

Wscole=Uscale*Epsil
write(6,*) 'Wscole is (unit of m/s)',Wscole
write(8,*) 'Wscole is (unit of m/s)',Wscole

Pscole=rhowa*grav*l
write(6,*) 'Pscole is (unit of g/cm/s^-2)',Pscole
write(8,*) 'Pscole is (unit of g/cm/s^-2)',Pscole


\[
E = \frac{E_v}{(\varepsilon \ast \text{Uscale})}
\]

write(6,*) 'The solvent evaporation rate is (unit of m/s)', Ev, ' and E =', E
write(8,*) 'The solvent evaporation rate is (unit of m/s)', Ev, ' and E =', E

\[
\text{rp} = \frac{\text{bigk} \ast l}{(\rho_e \ast \text{Uscale} \ast 1.d2)}
\]

write(6,*) 'Bigk is (unit of g/cm^3/s)', bigk, ' and Rp =', rp
write(8,*) 'Bigk is (unit of g/cm^3/s)', bigk, ' and Rp =', rp

\[
\text{Tscale} = l / (\text{Uscale} \ast 1.d2)
\]

xscale = l

zscale = d

write(6,*) 'Tscale (s)=', Tscale
write(6,*) 'xscale (cm)=', l, ' zscale (cm)=', zscale
write(8,*) 'Tscale (s)=', Tscale
write(8,*) 'xscale (cm)=', l, ' zscale (cm)=', zscale

c  Setting the spatial grids
c  Changing the value of dx also need to change the value of nmax

dx = 1.d3+1

nmax = 1.d3+1
c time grid

dt=1d-3

write(8,*) 'dt =',dt,' dx =',dx

tmax = 10**9

c we dont know how long the process will stop so we set a big value of tmax

write(6,*) 'Nmax =',nmax,' Tmax =',tmax

c define Front and other parameters

c Front uses for stopping the process.

c The process stops when Front moves to the end the substrate.

front(1)=1

r1=dt/(dx*6.d0)

r2=-dt*E

r3=r2*.5d0

r4=2.d0*r1

r5=dt*rp*.25d0

r6=2.d0*r5

s1=dt*rp/(dt*rp+2.d0)

s2=2.d0/(dt*rp+2.d0)

c initial condition
k = 0

call ooutfn('lamb',chan3(k),iflag,1)
call ooutfn('film',chan3(k),iflag,2)

do i=1,nmax
   x(i)=dfloat(i-1)*dx
   lam(i,1) = IOP(ip,x(i),l,zscale)
   s(i,1) = 0.d0
   c Y axis will be unit in (um) by mul. 10000
   write(1,*) x(i)*l,lam(i,1)*zscale*1.d4
   write(2,*) x(i)*l,s(i,1)*zscale*1.d4
end do

close(1)
close(2)

c main time loop

do k=1,tmax-1

   i=1
   g(i)=.5d0*(lam(i,1)+lam(i+1,1))+
   sit*r1*(lam(i,1)**3-lam(i+1,1)**3)+r3
   j(i)=(.5d0-r5)*(s(i,1)+s(i+1,1))+r1*((lam(i,1)**2)*s(i,1)
   -(lam(i+1,1)**2)*s(i+1,1))+r5*(lam(i,1)+lam(i+1,1))
c Below if front(k) < 2, The do-loop will skip

    do i=2,front(k)
        lam(i,2)=lam(i,1)
        s(i,2)=s(i,1)
    enddo

    do i=front(k)+1,nmax-1
        g(i)=.5d0*(lam(i,1)+lam(i+1,1)) +
        sit*r1*(lam(i,1)**3-lam(i+1,1)**3)+r3
        j(i)=.5d0-r5*(s(i,1)+s(i+1,1))+r1*((lam(i,1)**2)*s(i,1) -
        (lam(i+1,1)**2)*s(i+1,1)) +r5*(lam(i,1)+lam(i+1,1))
        lam(i,2)=lam(i,1)+sit*r4*(g(i-1)**3-g(i)**3)+r2
        s(i,2)=s1*r2+(s1+s2*r6)*lam(i,1)+(1.d0-r6)*s2*s(i,1) +
        r4*(sit*s1*(g(i-1)**3-g(i)**3) +
        s2*(j(i-1)*g(i-1)**2-j(i)*g(i)**2))
    enddo

i=nmax

    lam(i,2)=.5d0*(5.d0*lam(i-1,2)-4.d0*lam(i-2,2)+lam(i-3,2))
    s(i,2)=.5d0*(5.d0*s(i-1,2)-4.d0*s(i-2,2)+s(i-3,2))

c checking condition
i=front(k)

do while ( ((lam(i,2)-s(i,2)).lt.tol) .and. i.lt.nmax )
   i=i+1
enddo

front(k+1)=i-1

c write(6,*) k+1,front(k+1)

if (front(k+1) .ge. nmax-1) then
   tk=(k+1)*Tscale*dt
   write(6,*) 'Calculation Complete at Real Time (s)=',tk
   write(6,*) 'The solute thickness is (um)',s(nmax-1,2)*zscale*1.d4
   write(8,*) 'Calculation Complete at Real Time (s)=',tk
   write(8,*) 'at time step ', k+1
   write(8,*) 'The solute thickness is (um)',s(nmax-1,2)*zscale*1.d4
   close(8)

c exit
   goto 1
endif

c printing intermediate values at every np time steps

if (np*((k+1)/np) .eq. k+1) then
   call ooutfn('lamb',chan3((k+1)/np),iflag,1)

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call ooutfn('film', chan3((k+1)/np), iflag, 2)
call ooutfn('solv', chan3((k+1)/np), iflag, 3)
write(6,*) 'output file', chan3((k+1)/np), k+1, front(k+1)
do i=1, nmax
  write(1,*) x(i)*l, lam(i,2)*zscale*1.d4
  write(2,*) x(i)*l, s(i,2)*zscale*1.d4
  write(3,*) x(i)*l, (lam(i,2)-s(i,2))*zscale*1.d4
end do
close(1)
close(2)
close(3)
end if

c update the values for the next time step

do i=1, nmax
  lam(i,1)=lam(i,2)
  s(i,1)=s(i,2)
enddo
enddo
1 continue
c output when lam=s

open(1, file='lam'/iflag)
open(2, file='s'/iflag)
do i=1,nmax
    write(1,*), x(i)*l, lam(i,2)*zscale*1.d4
    write(2,*), x(i)*l, s(i,2)*zscale*1.d4
endo
close(1)
close(2)
c output of drying line

open(1, file='Front'/iflag)
open(2, file='Dry'/iflag)
do i=1,k+1
    write(1,*), dfloat(i)*dt*Tscale, front(i)*dx*l
    write(2,*), front(i)*dx*l, dfloat(i)*dt*Tscale
endo
close(1)
close(2)
stop
end

c c c c c c c c c c c c c c c c c c c c c c c c c c c c c c c c c c c c c
c initial condition of lambda=f(x)
c x here in the input is nondimensional (Xdim=1*Xnondim)

function iop(ip,x,l,zscale)
implicit none
integer ip
double precision x,iop,l,zscale
if (ip .eq. 1) then
  if (x .le. 1.d0/l) then
    iop=sqrt(l*x)
  else
    iop=1.d0
  end if
elseif (ip .eq. 2) then
  iop=x/(x+1d-2/l)
elseif (ip .eq. 3) then
  if (x .le. zscale/l) then
iop=sqrt(1.d0-(1*x/zscale-1.d0)**2)

else

   iop=1.d0

end if

end if

return

end

subroutine ooutfn(fprr,fid,cflag,lun)

  c usage
  c type *,’ Enter file id’
  c accept (2a), id
  c call ooutfn(id,’i’,1) creates output file i’id’.dat
  c taken from Nazanin Imani

  character*3 fid
  character*1 cflag
  character*4 fprr

  integer lun
  character*20 flname

  flname = fprr // cflag // fid

  open(unit=lun,file=flname,err=150)

return
write(6,*),'*** ERROR IN OPENING FILE ***'
return
end

function chan3(M)
  c Stephen Cardarelli, Oct 2003
  c provides time step files 000 to 999
  implicit none
  character*3 chan3
  integer i,j,k,M,countout
  countout = M
  i = countout/100
  countout = countout - (i*100)
  j = countout/10
  k = countout - (j*10)
  chan3 = char(i+48)//char(j+48)//char(k+48)
return
end