MODELING AND SIMULATION OF DIFFUSION IN EVAPORATING POLYMER SOLUTIONS

A Thesis

Presented to

The Graduate Faculty at The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

Siamak Shams Es-haghi

May, 2015
Evaporation of solvent from a polymer solution has technological importance in technologies related to painting, coating, inkjet printing, manufacturing polymer films and production of electronic devices. Apart from the vast technological importance, it is one of the fundamental problems of soft condensed matter physics.

A mathematical model in the framework of nonequilibrium thermodynamics was developed to describe the evolution of concentration and temperature during evaporation of a solvent in a polymer solution. The governing equations derived from the fundamental equation of classical thermodynamics using the local equilibrium hypothesis, Prigogine’s theorem and Onsager’s reciprocity relations display more complex connection between heat and non-convective mass fluxes than what has been presented in the previous research works. The model developed herein describes evolution of concentration and temperature in an evaporating polymer solution in a thermodynamically consistent way and is able to capture the effect of thermal diffusion in polymer solutions. The derived governing equations which were formulated for a general 3D problem were solved numerically for a 1D solution casting problem using an explicit finite difference scheme. During the evaporation of solvent, the effect of thermal diffusion in polymer solutions manifests itself as an increase in local concentration of the
solvent on the warm side of a temperature gradient. The results of the model also can qualitatively capture some experimental observations regarding the Soret effect in polymer solutions.
DEDICATION

To my parents, my brother,

and my wife Sahar
ACKNOWLEDGEMENTS

I am very thankful for having the chance to take courses with professors that have professionally and kindly taught me some of their knowledge. It was very important, helpful and enjoyable for me to be your student.

I also would like to especially thank Professor Gerald Young and Professor Kevin Kreider for all their support, encouragement and great way of teaching. Your teaching methods were so inspiring that I will definitely use them if I have the chance to teach as a professor someday. And last but not least, I want to thank Professor Curtis Clemons and Professor Patrick Wilber for reading my thesis.
# TABLE OF CONTENTS

| LIST OF TABLES | ix |
| LIST OF FIGURES | x |

## CHAPTER

### I. INTRODUCTION

1.1 Background on Modeling Solution Casting Problem .......................... 1

1.2 A Brief Review of Nonequilibrium Thermodynamics .......................... 3

1.2.1 Local Equilibrium Hypothesis .......................................... 5

### II. MODEL FORMULATION

2.1 Governing Equations .................................................................. 7

2.2 Initial and Boundary Conditions for a 1-D Problem .......................... 14

### III. NUMERICAL SOLUTION PROCEDURE

3.1 Brief Review of the Problem ..................................................... 19

3.2 Nondimensionalization of Equations ............................................ 20

3.3 Front-fixing Approach to Deal with the Moving Boundary ............... 24

3.4 Discretization of Dimensionless Equations .................................. 27

### IV. SIMULATION RESULTS ......................................................... 33

### V. MODEL PREDICTIONS FOR POLYMER THERMAL DIFFUSION .......... 52

### VI. SUMMARY ................................................................. 57

### BIBLIOGRAPHY ........................................................... 60

### APPENDICES ............................................................. 63
APPENDIX A  CALCULATION OF EVAPORATING SOLVENT FLUX ............ 64
APPENDIX B  PHYSICAL PROPERTIES USED FOR SIMULATION............... 66
APPENDIX C  TIME DERIVATIVE OF FIELD VARIABLES AFTER
COORDINATE TRANSFORMATION ........................................... 67
APPENDIX D  CALCULATION OF CHEMICAL POTENTIAL ..................... 68
APPENDIX E  NOTATION .......................................................... 69
APPENDIX F  COMPUTER CODE .................................................. 72
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1: Variables and scales have been used for nondimensionalization.</td>
<td>21</td>
</tr>
<tr>
<td>3.2: Computation time for different levels of discretization.</td>
<td>32</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>1.1: Schematic representation of the solvent evaporation process.</td>
<td>15</td>
</tr>
<tr>
<td>3.1: Computational molecule for finite difference method.</td>
<td>27</td>
</tr>
<tr>
<td>4.1: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 298.15$ K, $V_\infty = 1.2$ m/s, $\phi$, $\theta$, $t^<em>$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^</em> = 0$.</td>
<td>34</td>
</tr>
<tr>
<td>4.2: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 318.15$ K, $V_\infty = 1.2$ m/s, $\phi$, $\theta$, $t^<em>$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^</em> = 0$.</td>
<td>35</td>
</tr>
<tr>
<td>4.3: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 338.15$ K, $V_\infty = 1.2$ m/s, $\phi$, $\theta$, $t^<em>$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^</em> = 0$.</td>
<td>36</td>
</tr>
<tr>
<td>4.4: Concentration profiles at the onset of evaporation of the solvent. a) $T_0$, $T_\infty = 298.15$ K, b) $T_0$, $T_\infty = 318.15$ K, c) $T_0$, $T_\infty = 338.15$ K, $V_\infty = 1.2$ m/s, $\phi$, $t^<em>$ and $\xi$ are volume fraction of the solvent, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^</em> = 0$.</td>
<td>38</td>
</tr>
<tr>
<td>4.5: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 298.15$ K, $V_\infty = 0.3$ m/s, $\phi$, $t^<em>$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^</em> = 0$.</td>
<td>40</td>
</tr>
</tbody>
</table>
4.6: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_{\infty} = 298.15$ K, $V_\infty = 0.6$ m/s, $\varphi$, $\theta$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. ...........................................

4.7: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_{\infty} = 318.15$ K, $V_\infty = 0.3$ m/s, $\varphi$, $\theta$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. ...........................................

4.8: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_{\infty} = 318.15$ K, $V_\infty = 0.6$ m/s, $\varphi$, $\theta$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. ...........................................

4.9: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_{\infty} = 338.15$ K, $V_\infty = 0.3$ m/s, $\varphi$, $\theta$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. ...........................................

4.10: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_{\infty} = 338.15$ K, $V_\infty = 0.6$ m/s, $\varphi$, $\theta$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. ...........................................

4.11: Concentration profiles at the onset of evaporation of the solvent. $T_0$, $T_{\infty} = 298.15$ K. (a) $V_\infty = 0.3$ m/s, (b) $V_\infty = 0.6$ m/s, $\varphi$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. ..........................................................................

4.12: Concentration profiles at the onset of evaporation of the solvent. $T_0$, $T_{\infty} = 318.15$ K. (a) $V_\infty = 0.3$ m/s, (b) $V_\infty = 0.6$ m/s, $\varphi$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. ..........................................................................

4.13: Concentration profiles at the onset of evaporation of the solvent. $T_0$, $T_{\infty} = 338.15$ K. (a) $V_\infty = 0.3$ m/s, (b) $V_\infty = 0.6$ m/s, $\varphi$, $t^*$ and $\xi$ are volume fraction of the solvent,
dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$.

4.14: Concentration profile for the whole evaporation process, $T_0 = 298.15$ K, $T_\infty = 338.15$ K, $V_\infty = 1.2$ m/s $\varphi$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$.

4.15: Two views of temperature profile for the whole evaporation process. $T_0 = 298.15$ K, $T_\infty = 338.15$ K, $V_\infty = 1.2$ m/s $\theta$, $t^*$ and $\xi$ are dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$.

4.16: Concentration profiles of solvent in a polymer solution during evaporation. Profiles are shown in 10-s increments starting at $t=0$ when the solvent concentration is uniform. Reproduced with permission from ref. [5].

F.1: Concentration profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 298.15$ K, $V_\infty = 1.2$ m/s $\varphi$. a) $\Delta\xi = 0.1$, b) $\Delta\xi = 0.01$, c) $\Delta\xi = 0.001$. $\varphi$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$.

F.2: Temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 298.15$ K, $V_\infty = 1.2$ m/s $\theta$. a) $\Delta\xi = 0.1$, b) $\Delta\xi = 0.01$, c) $\Delta\xi = 0.001$. $\theta$, $t^*$ and $\xi$ are dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 
CHAPTER I
INTRODUCTION

1.1 Background on Modeling Solution Casting Problem

Drying of polymer solutions, as an interesting example of a nonequilibrium phenomenon, is a crucial process which has significant importance in technologies related to painting, coating, manufacturing polymer films and production of electronic devices [1].

In order to develop a realistic model of this process, one should have a good understanding of the physics underlying the problem. Although modeling of this process has been addressed several times in [1-10] and references therein, the proposed governing equations are not theoretically sophisticated enough to describe the whole picture of evolution of the mentioned phenomenon governed by the processes of mass diffusion and heat conduction. In some of the literature cited above [1,2], the drying process of polymer solutions was considered as an isothermal process. Since the thermal conductivity of polymer solutions is very low and also because the evaporation of solvent results in a reduction in surface temperature of the film which has been confirmed experimentally [10], the isothermal assumption is not realistic.
In references mentioned above, the governing equations for describing drying of a polymer solution are formulated by simply considering the mass and heat balance equations in the system. In such a formulation the dimensionless governing equations for evolution of concentration of solvent \( \varphi \) and temperature \( \theta \) can be written in the form of

\[
\frac{\partial \varphi}{\partial t} = \frac{\partial}{\partial \xi} \left( \tilde{D} \frac{\partial \varphi}{\partial \xi} \right), \quad (1.1)
\]

\[
\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial \xi} \left( \tilde{K} \frac{\partial \theta}{\partial \xi} \right). \quad (1.2)
\]

In the general case, the mutual diffusion coefficient \( \tilde{D} \) and thermal conductivity \( \tilde{K} \) are functions of temperature and concentration, but there is no theoretical equation to show their functionality. Therefore, for simplification, constant values are often considered for these coefficients and in some cases empirical equations are used. In fact, the coupling between two equations originates from the temperature dependency of mutual thermal diffusion equation or concentration dependence of thermal conductivity.

In such a formulation given by Eqs. (1.1) and (1.2), there is no criterion to be sure that the model is thermodynamically consistent. Moreover, Eqs. (1.1) and (1.2) cannot capture the so-called thermal diffusion or Ludwig–Soret effect in polymer solutions in that polymer chains tend to migrate to a cold side of a temperature gradient. In effect, mass and heat diffusion are dissipative and irreversible phenomena and they contribute to entropy production in the system. Therefore, in order to develop a thermodynamically consistent model for heat and mass transfer in polymer solutions, the balance of entropy must be considered in the formulation of governing equations. Apart from the necessity of considering entropy balance the drying problem of a polymer solution is a
nonequilibrium problem and should be modeled in the framework of nonequilibrium thermodynamics.

1.2 A Brief Review of Nonequilibrium Thermodynamics

A thermodynamic system is part of the material universe that in general case can exchange energy and mass with the exterior. The energy can be exchanged by heat flow and work done by volume or surface forces. When there is no exchange of matter between the system and its exterior, the system is called closed. The thermodynamic state of a system is characterized by its state variables. State variables are macroscopic quantities which can be tensors of different orders [11].

A thermodynamic system is called to be in equilibrium when the state variables e.g., temperature, pressure, and chemical potential, are everywhere the same in the system [12]. Under external stimuli and perturbation, the thermodynamic state of the system will change and the system will be transferred to another state by a thermodynamic process. A thermodynamic process is called irreversible when the time symmetry is broken [13]. In effect, there is a privileged direction of time for evolution of irreversible thermodynamic processes. Fourier's law of heat conduction and Fick’s law of mass diffusion are examples of irreversible processes.

Nonequilibrium thermodynamics is a continuum theory for macroscopic description of irreversible processes. In the framework of nonequilibrium thermodynamics the balance equation for entropy plays a pivotal role. The balance equation for entropy is the local formulation of the second law of thermodynamics. The
balance of entropy in a thermodynamic system shows how the entropy in a volume element changes over time. The change in the entropy in a volume element originates from the flux of entropy into the system and also a source of entropy production due to dissipative phenomena that occur inside the volume element. The production of entropy due to irreversible phenomena is positive definite. For systems in equilibrium, however, the entropy production is zero. In fact a system is called to be in equilibrium when there is no source of entropy production. In the theory of nonequilibrium thermodynamics the main objective is to relate the rate of change of entropy production explicitly to the different irreversible processes that take place in the system. In order to do this, the differential form of conservation laws are needed which then can be related to the rate of entropy production using the Gibbs equation. In effect, using the Gibbs equation, the rate of change of entropy in a multi-component system is connected to the rate of change of energy and the rate of change of concentration of components. The rate of entropy production takes a simple form and will be presented as a sum of terms each of them is a product of a thermodynamic flux related to an irreversible phenomenon in the system and a thermodynamic force or affinity associated with that flux which reflects the non-uniformity in the system or deviations of some internal state variables from their equilibrium values. In such a formulation, the irreversible fluxes are unknown parameters and therefore we must consider an additional set of phenomenological equations, constitutive equations, to express the irreversible fluxes in terms of thermodynamic forces. According to experimental observations for a wide range of experimental conditions, the irreversible fluxes are linear functions of thermodynamic forces or affinities. Fick's law of diffusion, Fourier's law of heat conduction, and Ohm's law of
electric conduction are examples of this class of linear phenomenological laws. In these linear functions the cross-effects between different dissipative phenomena also can be considered. For example the thermal diffusion or Ludwig–Soret effect is a cross-effect in which both temperature and chemical potential gradients result in a mass diffusion flux [14]. Although, this linear regime of nonequilibrium thermodynamics, in which fluxes are presented as linear functions of thermodynamic forces, is mainly restricted to the study of near equilibrium phenomena, it can be used to describe a vast area related to transport phenomena.

Knowing the fact that Gibbs equation is valid for equilibrium conditions, a question arises as to how one can use the Gibbs equation to reach the expression for rate of entropy production in a system in which dissipative processes occur. The answer to this question is the local equilibrium hypothesis which will be explained as follows.

1.2.1 Local Equilibrium Hypothesis

Local equilibrium hypothesis is a fundamental assumption on which the theory of nonequilibrium thermodynamics has been constructed. According to this hypothesis, although the dissipative systems are not as a whole in equilibrium, when the deviation from equilibrium is not very high, at a given instant of time, equilibrium is achieved in each elemental volume in the system. By accepting this assumption, all the thermodynamic variables which are defined in equilibrium such as temperature, entropy, pressure and chemical potential become functions of space and time. Moreover, the Gibbs equation becomes valid for each volume element [13,14].
In Chapter II, governing equations for mass and heat transfer in an evaporating polymer solution will be derived in the framework of nonequilibrium thermodynamics. The model is formulated for a general case of an n-component system. Then the governing equations will be derived for a two-component system i.e., a polymer and a solvent. It will be shown that how the local equilibrium hypothesis enables us to use the Gibbs fundamental equation of classical thermodynamics to derive the heat and mass fluxes in an evaporating polymer solution using Prigogine’s theorem for systems in mechanical equilibrium and Onsager’s reciprocity relations. The mutual diffusion coefficient, thermal diffusion coefficient and thermal conductivity enter the governing equations in terms of entries of Onsager’s matrix.
2.1 Governing Equations

We consider a non-reacting multi-component mixture in which non-convective mass diffusion and heat conduction occur. The system is considered to be in one phase, far from the critical region of phase separation and above its glass transition temperature during the course of evaporation which happens only at the surface. We also assume no change in volume upon mixing and consider the system to be in mechanical equilibrium.

The hypothesis of local equilibrium allows the fundamental equation of classical thermodynamics to be valid for every volume element in the system, although the whole system is not in equilibrium [13,14]. Equation (2.1) states the fundamental equation per unit volume of a mixture;

\[ de = T ds + \sum_{i=1}^{k} \mu_i dn_i, \]  

(2.1)

where \( T, s, e, \mu_i \) and \( n_i \) are absolute temperature, entropy per unit volume, enthalpy per unit volume, chemical potential of component \( i \) and moles of component \( i \) per unit volume, respectively. One can rewrite Eq. (2.1), using the mass concentration of the components and take a derivative with respect to time to find
\[
T \frac{ds}{dt} = \frac{de}{dt} = \sum_{i=1}^{k} \frac{\mu_i}{M_i} \frac{dc_i}{dt},
\]

(2.2)

where \( c_i \) and \( M_i \) are the mass concentration and molecular weight of component \( i \), respectively.

Time derivatives in Eq. (2.2) are substantial time derivatives given by

\[
\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla.
\]

(2.3)

Here, \( \mathbf{v} \) is the mean velocity of the components. The time derivatives of \( e \) and \( c_i \) in Eq. (2.3) are related to the divergence of heat and non-convective mass fluxes,

\[
\frac{de}{dt} = -\nabla \cdot J_e,
\]

(2.4)

\[
\frac{dc_i}{dt} = -\nabla \cdot J_i.
\]

(2.5)

According to Prigogine’s theorem, for systems in mechanical equilibrium an arbitrary frame of reference can be chosen [14]. The non-convective mass flux of the component \( i \) in this frame of reference which moves with the mean velocity \( \mathbf{v} \) is given by

\[
J_i = \rho_i \varphi_i (v_i - \mathbf{v}),
\]

(2.6)

where \( \rho_i \), \( \varphi_i \), and \( v_i \) are mass density, volume fraction and the velocity of component \( i \), respectively and the mean velocity \( \mathbf{v} \) is expressed as

\[
\mathbf{v} = \sum_{i=1}^{k} \varphi_i v_i.
\]

(2.7)

It follows from Eqs. (2.6) and (2.7) that the fluxes are not independent and their dependency is given by
\[ \sum_{i=1}^{k} \frac{j_i}{\rho_i} = 0. \]  

(2.8)

Rewriting Eq. (2.2) for a two-component system and replacing \( \frac{de}{dt} \) and \( \frac{dc_i}{dt} \) with the divergences of the associated fluxes given by Eqs. (2.4) and (2.5), we obtain

\[ T \frac{ds}{dt} = -\nabla \cdot J_q + \frac{\mu_1}{M_1} \nabla \cdot J_1 + \frac{\mu_2}{M_2} \nabla \cdot J_2. \]  

(2.9)

Hereafter, subscripts 1 and 2 are attributed to solvent and polymer respectively, and \( \varphi \) represents the volume fraction of the former.

Equation (2.9) can be reduced after applying the constraint between fluxes given by Eq. (2.8) to the form

\[ T \frac{ds}{dt} = -\nabla \cdot J_q + \mu \nabla \cdot J_1, \]  

(2.10)

where \( \mu \) is expressed as

\[ \mu = \frac{\mu_1 - \rho_2 \mu_2}{M_1 \rho_1 M_2}. \]  

(2.11)

We can rewrite Eq. (2.10) by replacing the right hand side with an equivalent form and dividing both sides by \( T \),

\[ \frac{ds}{dt} = -\frac{1}{T} \nabla \cdot \left( J_q - \mu J_1 \right) - \frac{1}{T} \frac{1}{T} J_1 \nabla \mu. \]  

(2.12)

The first term of the right hand side of Eq. (2.12) can be manipulated to an equivalent form so that

\[ \frac{ds}{dt} = -\nabla \cdot \left( \frac{J_q - \mu J_1}{T} \right) - \frac{1}{T^2} \nabla T \cdot \left( J_q - \mu J_1 \right) - \frac{1}{T} \frac{1}{T} J_1 \nabla \mu. \]  

(2.13)

We can write Eq. (2.13) in the following form
\[
\frac{ds}{dt} = -\nabla \cdot J_s + \sigma, \quad (2.14)
\]

where \( J_s \) is the entropy flux and \( \sigma \) is the rate of entropy production per unit volume of the system

\[
J_s = \frac{1}{T} \left( J_q - \mu J_1 \right), \quad (2.15)
\]

\[
\sigma = -\frac{1}{T} J_1 \cdot \nabla \mu - \frac{1}{T^2} \nabla T \cdot \left( J_q - \mu J_1 \right). \quad (2.16)
\]

One can see that \( \sigma \) is a bilinear form of fluxes \( J_1 \) and \( \left( J_q - \mu J_1 \right) \) and thermodynamic forces \(-\frac{1}{T} \nabla \mu \) and \(-\frac{1}{T^2} \nabla T \).

In the linear region of nonequilibrium thermodynamics, the fluxes can be written in terms of the forces as shown in Eqs. (2.17) and (2.18) which in matrix presentation would yield Eq. (2.19)

\[
J_1 = l_{11} \left( -\frac{1}{T} \nabla \mu \right) + l_{12} \left( -\frac{1}{T^2} \nabla T \right), \quad (2.17)
\]

\[
J_q - \mu J_1 = l_{21} \left( -\frac{1}{T} \nabla \mu \right) + l_{22} \left( -\frac{1}{T^2} \nabla T \right), \quad (2.18)
\]

\[
\begin{pmatrix}
J_1 \\
J_q - \mu J_1
\end{pmatrix} =
\begin{pmatrix}
l_{11} & l_{12} \\
l_{21} & l_{22}
\end{pmatrix}
\begin{pmatrix}
-\frac{1}{T} \nabla \mu \\
-\frac{1}{T^2} \nabla T
\end{pmatrix}. \quad (2.19)
\]

Entries of matrix \( L = (l_{ij})_{2 \times 2} \) are Onsager’s coefficients and based on Onsager’s reciprocity relations, off-diagonal entries of matrix \( L \) are identical [16].
In conditions for which linear flux-force relations are valid, rate of entropy production takes the quadratic form [16]

$$
\sigma = l_{11} \left(-\frac{1}{T} \nabla \mu \right)^2 + (l_{12} + l_{21}) \left(-\frac{1}{T} \nabla \mu \right) \left(-\frac{1}{T^2} \nabla T \right) + l_{22} \left(-\frac{1}{T^2} \nabla T \right)^2 > 0. \tag{2.20}
$$

Matrix $L = (l_{ij})_{2 \times 2}$ which satisfies Eq. (2.20) should be positive definite and to be so, its entries should satisfy the conditions

$$
l_{11} > 0, \ l_{22} > 0, \ l_{12} > (l_{12})^2. \tag{2.21}
$$

It is interesting to note that, if we let $\frac{l_{11}}{T} = \alpha$, $\frac{l_{12}}{T^2} = \beta$, $\frac{l_{21}}{T} = \delta$ and $\frac{l_{22}}{T^2} = \gamma$, we can recast Eqs. (2.17) and (2.18) in the same way presented by Landau [17]. Doing so, keeping in mind that $\delta$ can be replaced with $\beta T$ because of equality of $l_{12}$ and $l_{21}$, and replacing $\nabla \mu$ with the right hand side of Eq. (2.22), knowing the fact that chemical potential is a function of concentration (volume fraction of solvent $\phi$) and temperature, we find

$$
\nabla \mu = \left(\frac{\partial \mu}{\partial \phi} \right)_T \nabla \phi + \left(\frac{\partial \mu}{\partial T} \right)_\phi \nabla T, \tag{2.22}
$$

$$
J_1 = -\alpha \left(\frac{\partial \mu}{\partial \phi} \right)_T \nabla \phi - \left[\alpha \left(\frac{\partial \mu}{\partial T} \right)_\phi + \beta\right] \nabla T, \tag{2.23}
$$

$$
J_q = \left(\mu + \frac{\beta}{\alpha} T\right) J_1 - \left(\gamma - \frac{\beta^2}{\alpha} T\right) \nabla T. \tag{2.24}
$$

In order to preserve the positive definiteness of matrix $L$, the following conditions should be satisfied:

$$
\alpha > 0, \ \gamma > 0, \ \beta < \sqrt{\alpha \gamma T^{-1}}. \tag{2.25}
$$

After deriving the heat and mass fluxes, we obtain the governing equations
\[ \rho \frac{d\varphi}{dt} = \nabla \cdot \left\{ \alpha \frac{\partial \mu}{\partial \varphi} + \beta \left[ \alpha \frac{\partial \mu}{\partial T} + \beta \right] \nabla T \right\}, \] (2.26)

\[ \rho c_p \frac{dT}{dt} = -\nabla \cdot \left\{ \left( \mu + \frac{\beta T}{\alpha} \right) J_1 - \left( \gamma - \frac{\beta^2 T}{\alpha} \right) \nabla T \right\}, \] (2.27)

where \( \rho \) and \( c_p \) are the mass density and isobaric specific heat capacity of the solution respectively and are assumed to be constant.

It should be noted that \( \alpha \frac{\partial \mu}{\partial \varphi} \), \( \left[ \alpha \frac{\partial \mu}{\partial T} + \beta \right] \) and \( \gamma - \frac{\beta^2 T}{\alpha} \) are the mutual diffusion coefficient \( D_m \), thermal diffusion coefficient \( D_t \) and thermal conductivity, respectively.

In general, phenomenological coefficients \( \alpha \), \( \beta \) and \( \gamma \) can be functions of temperature and concentration. Since we do not have any theoretical knowledge of these functions, the simplest functions shall be considered for the numerical computations based on the constraints mentioned earlier due to positive definiteness of matrix \( L \), dimensional analysis and the important asymptotic behavior of mutual and thermal diffusion coefficients at very small concentrations \( (\varphi \to 0) \) where the former tends to a finite constant and the latter tends to zero.

To satisfy the constraint \( \beta < \sqrt{\alpha \gamma T^{-1}} \), we let \( \beta \) be zero and \( \alpha \) and \( \gamma \) are given by

\[ \alpha = \frac{D_m \rho \varphi (1 - \varphi)}{RT}, \] (2.28)

\[ \gamma = \gamma_0 \frac{T_r^{6/5} (1 - T_r)^{0.38}}{M_1 T_r^{1/6}} T_r^{1/6}, \] (2.29)
where $D_0$ and $\gamma_0$ are two constant parameters, $T_b$ and $T_c$ are boiling and critical points of the solvent and $T_r$ is the reduced temperature [18].

In fact, here we ignore correlation effects between the non-convective mass flux $J_1$ and reduced heat flux $J_q - \mu J_1$. Therefore the off-diagonal entries of Onsager matrix, which are given by the Green-Kubo relation in terms of integral of time correlation functions of the mentioned fluxes, are reduced to zero.

$\mu$ can be calculated via Eq. (2.11) while chemical potentials of the solvent $\mu_1$ and polymer $\mu_2$ are expressed as [19]

$$
\mu_1 = \mu_1^0 + RT \left[ \ln(\varphi) + (1-\varphi) \left(1 - \frac{1}{N} \right) + \chi (1-\varphi)^2 \right], 
$$

$$
\mu_2 = \mu_2^0 + RT \left[ \ln(1-\varphi) + \varphi (1-N) + \chi N \varphi^2 \right], 
$$

where $\mu_1^0$, $\mu_2^0$, $R$ and $\chi$ are chemical potential of pure solvent, chemical potential of the pure liquid polymer, universal gas constant and the Flory-Huggins interaction parameter.

Finally, $N$ is the ratio of the molar volumes of polymer and solvent.

Assuming molecular weight of polymer to be very high as compared to that of solvent, we express $\mu$ as

$$
\mu = \frac{\mu_1^0}{M_1} + \frac{RT}{M_1} \left[ \ln(\varphi) + 1 + \chi (1-2\varphi) \right]. 
$$

The chemical potential of the pure solvent is assumed to be a linear function of temperature and is given by

$$
\mu_1^0(T) = a + b(T - T_0), 
$$
where \( a \) is the chemical potential at temperature \( T_0 \) and \( b \) is the temperature coefficient.

2.2 Initial and Boundary Conditions for a 1-D Problem

In this section the derived governing equations will be used to numerically simulate the drying process of a thin polymer solution film on a substrate while the whole system is exposed to a laminar flow of air with temperature \( T_\infty \) (Figure 1.1). The film is thin in the sense that its dimensions in the plane of surface, which is perpendicular to the \( y \)-axis, are large compared to the thickness, and hence the diffusion is a 1-D process to a good approximation.

For each governing equation, two boundary conditions and an initial condition are needed to solve the problem. The initial conditions are fulfilled by starting with uniform concentration and temperature profiles

\[
\varphi(y, t = 0) = \varphi_0, \quad \text{(2.34)}
\]

\[
T(y, t = 0) = T_0. \quad \text{(2.35)}
\]
Boundary conditions at the surface \( w(t) \) of the solution are

\[
(J_i)_{lab,w(t)} - c_i(w(t),t) \frac{dw(t)}{dt} = C_s,
\]

(2.36)

\[
(J_q)_{lab,w(t)} = \langle h \rangle (T - T_\infty) + \Delta H_s C_s,
\]

(2.37)

where \( C_s \), \( \langle h \rangle \) and \( \Delta H_s \) are the evaporating solvent flux, averaged heat transfer coefficient and heat of evaporation of solvent, respectively. The calculation of \( \langle h \rangle \) and \( C_s \) is shown in Appendix A. Subscript ‘lab’ denotes laboratory frame of reference.

It should be noted that mass and heat fluxes have been derived in a frame of reference which moves with the velocity given by Eq. (2.7); hence boundary conditions should be...
expressed in the same frame of reference. After deriving the equation for the moving boundary $w(t)$, it will be shown that the fluxes at the boundaries are the same in both the laboratory and moving frame of references.

Boundary conditions at the substrate for the mass and heat equations are

$$\left( J_1 \right)_{lab} = 0, \quad (2.38)$$

$$\left( J_a \right)_{lab} = -k \frac{\partial T_{sub}}{\partial y}, \quad (2.39)$$

where $k$ and $T_{sub}$ are the thermal conductivity and absolute temperature of substrate.

Transient heat conduction in the substrate along with associated initial and boundary conditions are given by

$$\frac{\partial T_{sub}}{\partial t} = \kappa \frac{\partial^2 T_{sub}}{\partial y^2}, \quad (2.40)$$

$$T_{sub}(y, t = 0) = T_0, \quad (2.41)$$

$$\langle h \rangle (T_\infty - T_{sub}) = -k \frac{\partial T_{sub}}{\partial y}, \quad (2.42)$$

The boundary condition at the interface between substrate and polymer solution is satisfied by a continuity condition in temperature.

In this problem the location of the surface of the solution $w(t)$ is not known a priori and it must be determined as part of the problem. Considering the fact that polymer does not evaporate, the conservation of polymer mass during evaporation yields

$$\frac{d}{dt} \int_0^{w(t)} \varphi(y, t) dy = 0. \quad (2.43)$$

Equation (2.43) can be expanded in terms of volume fraction of solvent as
\[
(1 - \varphi_w) \frac{dw(t)}{dt} - \int_0^{w(t)} \frac{\partial \varphi}{\partial t} dy = 0,
\]

where \( \varphi_w \), represents the volume fraction of solvent at the moving boundary.

Replacing \( \frac{\partial \varphi}{\partial t} \) with \( -\frac{1}{\rho_1} \frac{\partial (J_{i,lab,w(t)})}{\partial y} \) leads to

\[
(1 - \varphi_w) \frac{dw(t)}{dt} = -\frac{1}{\rho_1} (J_{i,lab,w(t)}).
\]

The equation of the moving boundary can then be found from Eqs. (2.36) and (2.45),

\[
\frac{dw(t)}{dt} = -\frac{C_i}{\rho_1}.
\]

The non-convective mass flux of the component \( i \) in the laboratory frame of reference is given by

\[
(J_{i,lab}) = c_i v_i,
\]

where \( c_i \) and \( v_i \) are the mass concentration and the velocity of component \( i \), respectively.

The non-convective mass flux of component \( i \) in the moving and laboratory frame of references can be related by

\[
J_i = (J_{i,lab}) - c_i v.
\]

The velocity of the moving frame of reference at the surface of the solution \( v \) is given by

\[
v = v_i \varphi + \frac{dw(t)}{dt} (1 - \varphi).
\]

The velocity \( \frac{dw(t)}{dt} \) of polymer at the surface can be calculated from Eq. (2.36) for the mass flux of polymer. Writing Eq. (2.48) for the solvent and using Eqs. (2.46) and (2.49),
one can show that the mass flux at the surface of the film is the same in both laboratory and moving frame of references. The same condition would be found for the mass flux at the substrate using Eqs. (2.38), (2.47) and (2.48).

In the case of heat flux, it can be shown that for slow processes such as diffusion, the heat flux is invariant to a change in reference velocity [20] which means that

\[
(J_q)_{lab} = J_q, \tag{2.50}
\]

holds for both boundaries.

It should be noted that Eqs. (2.26) and (2.27) are thermodynamically constant governing equations to describe the evolution of concentration and temperature in polymer solutions under any initial and boundary conditions. Therefore, the result of this theoretical work can be used for any mass and heat transfer problem of polymer solutions by applying initial and boundary conditions associated to the problem at hand.

In Chapter III, the derived governing equations will be solved numerically for a 1-D solution casting problem using an explicit finite difference and front-fixing approach to deal with the moving boundary.
CHAPTER III

NUMERICAL SOLUTION PROCEDURE

3.1 Brief Review of the Problem

The governing equations derived for mass diffusion and heat conduction form a system of coupled nonlinear partial differential equations. By plugging $J_1$ from Eq. (2.23) into Eq. (2.27) and letting $\beta$ be zero, as mentioned in Chapter II, and writing Eqs. (2.26) and (2.27) for a 1-D evaporation problem (Figure 1.1) we find

$$\rho_i \frac{d\phi}{dt} = \frac{\partial}{\partial y} \left\{ \alpha \left( \frac{\partial \mu}{\partial \phi} \right)_T \frac{\partial \phi}{\partial y} + \alpha \left( \frac{\partial \mu}{\partial T} \right)_\phi \frac{\partial T}{\partial y} \right\},$$

(3.1)

$$\rho c_p \frac{dT}{dt} = \frac{\partial}{\partial y} \left\{ \alpha \mu \left( \frac{\partial \mu}{\partial \phi} \right)_T \frac{\partial \phi}{\partial y} + \left( \alpha \mu \left( \frac{\partial \mu}{\partial T} \right)_\phi + \gamma \right) \frac{\partial T}{\partial y} \right\}.$$ 

(3.2)

We solve Eqs. (3.1) and (3.2) under initial and boundary conditions described in Chapter II using an explicit finite difference scheme. A front-fixing approach is adopted to deal with the moving boundary. The aim of numerical computations is to visualize the evolution of concentration and temperature predicted by the derived governing equations for the mass diffusion and heat conduction. The physical properties and parameters used for the computations are given in Appendix B.
3.2 Nondimensionalization of Equations

A time scale can be derived from the equation of moving boundary, Eq. (2.46). By plugging the equation for evaporating solvent flux, \( C_s \), derived in Appendix A, we can recast Eq. (2.46) as

\[
\frac{dw(t)}{dt} = -\left( \frac{K_c}{\rho} \right) \left( \frac{P_{50}^p M_1}{RT_w} \right) \exp \left[ -\frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \exp \left[ \ln(\phi) + (1-\phi) + \chi (1-\phi)^2 \right]. \tag{3.3}
\]

Considering initial thickness of polymer solution, \( w_0 \), as a scale for thickness, we define the time scale

\[
t^* = \frac{\rho w_0 RT_w}{\left( \frac{K_c}{P_{50}^p M_1} \right)}. \tag{3.4}
\]

All the variables in both dimensional and nondimensional form are given in Table 1.3. Hereafter, all the dimensionless quantities are shown with tilde. Therefore, the equation for moving boundary in dimensionless form is given by:

\[
\frac{d\tilde{w}(\tilde{t})}{d\tilde{t}} = -\tilde{p}(\phi, \theta), \tag{3.5}
\]

with the initial condition

\[
\tilde{w}(\tilde{t} = 0) = 1, \tag{3.6}
\]

where \( \tilde{p}(\phi, \theta) \) is a dimensionless function of temperature and volume fraction of solvent

\[
\tilde{p}(\phi, \theta) = \exp \left[ -\frac{\Delta H}{RT_0} \left( \frac{1}{\theta} - \frac{1}{\theta_{boiling}} \right) \right] \exp \left[ \ln(\phi) + (1-\phi) + \chi (1-\phi)^2 \right]. \tag{3.7}
\]
Table 3.1: Variables and scales have been used for nondimensionalization.

<table>
<thead>
<tr>
<th>Dimensional variable</th>
<th>Scale</th>
<th>Dimensionless variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t )</td>
<td>( t^* = \frac{\rho_1 w_1 R T_\infty}{\langle K_c \rangle P_{st}^* M_1} )</td>
<td>( \tilde{t} )</td>
</tr>
<tr>
<td>( c_1 )</td>
<td>( \rho_1 )</td>
<td>( \varphi )</td>
</tr>
<tr>
<td>( T )</td>
<td>( T_0 )</td>
<td>( \theta )</td>
</tr>
<tr>
<td>( T_\infty )</td>
<td>( T_0 )</td>
<td>( \theta_\infty )</td>
</tr>
<tr>
<td>( y )</td>
<td>( w_0 )</td>
<td>( \tilde{y} )</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>( \gamma_0 )</td>
<td>( \tilde{\gamma} )</td>
</tr>
<tr>
<td>( w(t) )</td>
<td>( w_0 )</td>
<td>( \tilde{w}(\tilde{t}) )</td>
</tr>
</tbody>
</table>

The dimensionless form of Eq. (3.1) is

\[
NG1 \frac{d\varphi}{dt} = \frac{\partial}{\partial y} \left( ME1(\varphi) \right) \frac{\partial \varphi}{\partial y} + ME1(\varphi) \frac{\partial^2 \varphi}{\partial y^2} + \frac{\partial}{\partial y} \left( ME3(\varphi, \theta) \right) \frac{\partial \theta}{\partial y} + ME3(\varphi, \theta) \frac{\partial^2 \theta}{\partial y^2},
\]

(3.8)

where \( NG1, ME1(\varphi) \) and \( ME3(\varphi, \theta) \) are the dimensionless functions

\[
NG1 = \left( \frac{\langle K_c \rangle P_{st}^* M_1 w_0}{RT_\infty} \right) \left( \frac{1}{D_0 \rho_1} \right),
\]

(3.9)

\[
ME1(\varphi) = (1 - \varphi)(1 - 2\chi \varphi),
\]

(3.10)

\[
\frac{\varphi(1 - \varphi)}{\theta} \left( \frac{b}{R} + \left[ \ln(\varphi) + 1 + \chi(1 - 2\varphi) \right] \right) = ME3(\varphi, \theta).
\]

(3.11)
The initial condition for Eq. (3.8) is
\[
\phi(\tilde{y}, \tilde{t} = 0) = \phi_0, \tag{3.12}
\]

The bottom boundary condition, at the substrate, is
\[
(1 - 2\chi\phi) \frac{\partial \phi}{\partial \tilde{y}} + ME2(\phi, \theta) \frac{\partial \theta}{\partial \tilde{y}} = 0, \tag{3.13}
\]
where \( ME2(\phi, \theta) \) is a dimensionless function
\[
\frac{\phi}{\theta} \left(\frac{b}{R} + \left[\ln(\phi) + 1 + \chi(1 - 2\phi)\right]\right) = ME2(\phi, \theta). \tag{3.14}
\]

The boundary condition at the evaporating boundary is
\[
-ME1(\phi) \frac{\partial \phi}{\partial \tilde{y}} - ME3(\phi, \theta) \frac{\partial \theta}{\partial \tilde{y}} - NG1\phi|_{y(t)} \frac{d\tilde{y}(\tilde{t})}{d\tilde{t}} = NG1\bar{p}(\phi, \theta). \tag{3.15}
\]

The dimensionless form of Eq. (3.2) is
\[
NG2 \frac{d\theta}{dt} = \frac{\partial}{\partial \tilde{y}} (HE1(\phi, \theta)) \frac{\partial \phi}{\partial \tilde{y}} + HE1(\phi, \theta) \frac{\partial^2 \phi}{\partial \tilde{y}^2} + \frac{\partial}{\partial \tilde{y}} (HE2(\phi, \theta)) \frac{\partial \theta}{\partial \tilde{y}} + HE2(\phi, \theta) \frac{\partial^2 \theta}{\partial \tilde{y}^2} + NG3 \left(\frac{\partial \gamma}{\partial \tilde{y}} \frac{\partial \phi}{\partial \tilde{y}} \frac{\partial \theta}{\partial \tilde{y}} + \frac{\partial^2 \theta}{\partial \tilde{y}^2}\right), \tag{3.16}
\]
where \( NG2, HE1(\phi, \theta), HE2(\phi, \theta) \) and \( NG3 \) are the dimensionless groups and functions
\[
NG2 = \rho c_p \frac{\left(K_c \right) P_{\infty}^* w_0 M_1}{\rho \gamma RT} \left(\frac{M_1}{D_0 \rho R}\right), \tag{3.17}
\]
\[
HE1(\phi, \theta) = (1 - \phi) \left(\frac{a}{RT_0} + \frac{b(\theta - 1)}{R}\right) + \theta \left[\ln(\phi) + 1 + \chi(1 - 2\phi)\right] (1 - 2\chi\phi), \tag{3.18}
\]
\[
HE2(\phi, \theta) = \left[\frac{\phi(1 - \phi)}{\theta}\right] \left(\frac{a}{RT_0} + \frac{b(\theta - 1)}{R}\right) + \theta \left[\ln(\phi) + 1 + \chi(1 - 2\phi)\right] \left(\frac{b}{R} + \left[\ln(\phi) + 1 + \chi(1 - 2\phi)\right]\right). \tag{3.19}
\]
The initial condition for Eq. (3.16) is
\[ \theta(\bar{y}, \tilde{t} = 0) = 1. \]  

The boundary condition at the evaporating boundary is
\[ -HE1(\varphi, \theta) \frac{\partial \varphi}{\partial \bar{y}} - HE2(\varphi, \theta) \frac{\partial \theta}{\partial \bar{y}} - NG3\varphi \frac{\partial \theta}{\partial \bar{y}} = NG4(\theta - \theta_e) + NG5\bar{p}(\varphi), \]  

where \( NG4 \) and \( NG5 \) are the dimensionless groups
\[ NG4 = \left( \frac{M_1w_0}{D_0\rho_1R} \right), \]  
\[ NG5 = \left( \frac{\Delta H_e (K_e) M_1 w_0}{D_0\rho_1 RT_0} \right) \left( \frac{P^*_{20} M_1}{RT_e} \right). \]

The bottom boundary condition, at the substrate, is
\[ -HE1(\varphi, \theta) \frac{\partial \varphi}{\partial \bar{y}} - HE2(\varphi, \theta) \frac{\partial \theta}{\partial \bar{y}} - NG3\varphi \frac{\partial \theta}{\partial \bar{y}} = -NG6 \frac{\partial \theta_{\text{sub}}}{\partial \bar{y}}, \]  

where \( NG6 \) is a dimensionless group
\[ NG6 = \left( \frac{kM_1w_0}{D_0\rho_1Rl_0} \right). \]

Heat transfer in the substrate is given by
\[ \frac{\partial \theta_{\text{sub}}}{\partial \bar{t}} = NG7 \frac{\partial^2 \theta_{\text{sub}}}{\partial \bar{y}^2}, \]  

where \( NG7 \) is the dimensionless group given by
\[ NG7 = \frac{\rho \omega_0 RT_u \kappa}{\langle K_c \rangle \overline{P_{so} M t_0}}. \]  

(3.28)

The initial condition for Eq. (3.27) is

\[ \theta_{sub}(\bar{y}, t = 0) = \theta_0, \]  

(3.29)

The boundary condition of the substrate in air is given by

\[ (\theta_{\infty} - \theta_{sub}) = -NG8 \frac{\partial \theta_{sub}}{\partial \bar{y}}, \]  

(3.30)

where \( NG8 \) is a dimensionless group

\[ NG8 = \frac{k}{l_0 \langle h \rangle}. \]  

(3.31)

For the boundary condition with polymer solution the continuity condition in temperature is used.

\[ \theta(\bar{y} = 0) = \theta_{sub}(\bar{y} = 0). \]  

(3.32)

3.3 Front-fixing Approach to Deal with the Moving Boundary

In many important cases of boundary-value problems, the domain is not known in the beginning and has to be determined as part of the solution. When the boundary is stationary and the problem is steady-state, these problems are called free-boundary problems. Moving boundaries, on the other hand are associated with time-dependent problems. Some authors prefer to use the term free-boundary problems for both types of problems [22]. One method to deal with a moving-boundary problem is the so-called front-fixing approach. In this approach the moving boundary will be fixed by a suitable
choice of new space coordinates. For example in case of a 1D problem, the following transformation fixes the moving boundary at

\[ \xi = \frac{\tilde{y}}{\tilde{w}(\tilde{t})}, \quad 0 \leq \xi \leq 1, \tag{3.33} \]

for all values of time. The transformation given by Eq. (3.33) was first proposed by Landau [23] and Crank used it in a finite-difference scheme [24].

By applying the so-called Landau transformation, we find the first and second derivatives of field variables with respect to position become [22]

\begin{align*}
\frac{\partial \phi}{\partial \tilde{y}} &= \frac{1}{\tilde{w}(\tilde{t})} \frac{\partial \phi}{\partial \xi}, & \frac{\partial^2 \phi}{\partial \tilde{y}^2} &= \frac{1}{[\tilde{w}(\tilde{t})]^2} \frac{\partial^2 \phi}{\partial \xi^2}, \tag{3.34} \\
\frac{\partial \theta}{\partial \tilde{y}} &= \frac{1}{\tilde{w}(\tilde{t})} \frac{\partial \theta}{\partial \xi}, & \frac{\partial^2 \theta}{\partial \tilde{y}^2} &= \frac{1}{[\tilde{w}(\tilde{t})]^2} \frac{\partial^2 \theta}{\partial \xi^2}. \tag{3.35}
\end{align*}

As shown in Appendix C, after transformation, time derivatives of field variables will be

\begin{align*}
\left( \frac{\partial \phi}{\partial \tilde{t}} \right)_{\tilde{y}} &= -\frac{\xi}{\tilde{w}(\tilde{t})} \frac{d\tilde{w}(\tilde{t})}{d\tilde{t}} \frac{\partial \phi}{\partial \xi} + \left( \frac{\partial \phi}{\partial \tilde{t}} \right)_{\xi}, \tag{3.36} \\
\left( \frac{\partial \theta}{\partial \tilde{t}} \right)_{\tilde{y}} &= -\frac{\xi}{\tilde{w}(\tilde{t})} \frac{d\tilde{w}(\tilde{t})}{d\tilde{t}} \frac{\partial \theta}{\partial \xi} + \left( \frac{\partial \theta}{\partial \tilde{t}} \right)_{\xi}. \tag{3.37}
\end{align*}

After coordinate transformation the equation for mass transfer, Eq. (3.8) will be

\begin{align*}
NG1\left( \frac{\partial \phi}{\partial \tilde{t}} \right)_{\xi} &= NG1\left( \frac{\xi}{\tilde{w}(\tilde{t})} \frac{d\tilde{w}(\tilde{t})}{d\tilde{t}} \frac{\partial \phi}{\partial \xi} + \frac{1}{[\tilde{w}(\tilde{t})]^2} \frac{\partial}{\partial \xi} (ME1(\phi)) \frac{\partial \phi}{\partial \xi} + \\
ME1(\phi) \frac{1}{[\tilde{w}(\tilde{t})]^2} \frac{\partial^2 \phi}{\partial \xi^2} + \frac{1}{[\tilde{w}(\tilde{t})]^2} \frac{\partial}{\partial \xi} (ME3(\phi, \theta)) \frac{\partial \theta}{\partial \xi} \right) \\
ME3(\phi, \theta) \frac{1}{[\tilde{w}(\tilde{t})]^2} \frac{\partial^2 \theta}{\partial \xi^2}. \tag{3.38}
\end{align*}
The initial condition, boundary condition at substrate and boundary condition at evaporating surface for Eq. (3.38) after transformation are

\[ \varphi(\xi, t = 0) = \varphi_0, \]  

\[ (1 - 2 \chi \varphi) \frac{\partial \varphi}{\partial \xi} + ME2(\varphi, \theta) \frac{\partial \theta}{\partial \xi} = 0, \]  

\[ -ME1(\varphi) \frac{1}{\tilde{w}(\tilde{t})} \frac{\partial \varphi}{\partial \tilde{\xi}} - ME3(\varphi, \theta) \frac{1}{\tilde{w}(\tilde{t})} \frac{\partial \theta}{\partial \tilde{\xi}} - NG1(\varphi) \left|_{\tilde{\xi} = 1} \right. \frac{d\tilde{\nu}(\tilde{t})}{dt} = NG1\dot{p}(\varphi). \]  

Eq. (3.16) after transformation will be

\[ NG2 \left( \frac{\partial \theta}{\partial \tilde{t}} \right) = NG2 - \frac{\xi}{\tilde{w}(\tilde{t})} \frac{d\tilde{w}(\tilde{t})}{dT} \frac{\partial \theta}{\partial \tilde{\xi}} + \frac{1}{\left[ \tilde{w}(\tilde{t}) \right]^2} \frac{\partial}{\partial \tilde{\xi}} \left( HE1(\varphi, \theta) \right) \frac{\partial \varphi}{\partial \tilde{\xi}} + \]  

\[ HE1(\varphi, \theta) \frac{1}{\left[ \tilde{w}(\tilde{t}) \right]^2} \frac{\partial^2 \varphi}{\partial \tilde{\xi}^2} + \frac{1}{\left[ \tilde{w}(\tilde{t}) \right]^2} \frac{\partial}{\partial \tilde{\xi}} \left( HE2(\varphi, \theta) \right) \frac{\partial \theta}{\partial \tilde{\xi}} + \]  

\[ HE2(\varphi, \theta) \frac{1}{\left[ \tilde{w}(\tilde{t}) \right]^2} \frac{\partial^2 \theta}{\partial \tilde{\xi}^2} + NG3 \frac{1}{\left[ \tilde{w}(\tilde{t}) \right]^2} \left( \frac{\partial^2 \varphi}{\partial \tilde{\xi}^2} + \gamma \frac{\partial^2 \theta}{\partial \tilde{\xi}^2} \right). \]  

The initial condition, boundary condition at substrate and boundary condition at evaporating surface for Eq. (3.38) after transformation are

\[ \theta(\xi, \tilde{t} = 0) = 1, \]  

\[ -HE1(\varphi, \theta) \frac{1}{\tilde{w}(\tilde{t})} \frac{\partial \varphi}{\partial \tilde{\xi}} - HE2(\varphi, \theta) \frac{1}{\tilde{w}(\tilde{t})} \frac{\partial \theta}{\partial \tilde{\xi}} - NG3\gamma \frac{1}{\tilde{w}(\tilde{t})} \frac{\partial \theta}{\partial \tilde{\xi}} = -NG6 \frac{\partial \theta_{ub}}{\partial \gamma}, \]  

\[ -HE1(\varphi, \theta) \frac{1}{\tilde{w}(\tilde{t})} \frac{\partial \varphi}{\partial \tilde{\xi}} - HE2(\varphi, \theta) \frac{1}{\tilde{w}(\tilde{t})} \frac{\partial \theta}{\partial \tilde{\xi}} - NG3\gamma \frac{1}{\tilde{w}(\tilde{t})} \frac{\partial \theta}{\partial \tilde{\xi}} = \]  

\[ NG4(\theta - \theta_{\infty}) + NG5 \dot{p}(\varphi, \theta). \]
3.4 Discretization of Dimensionless Equations

An explicit finite difference scheme was used to approximate a solution for the problem at hand. A grid of discrete points with the computational molecules shown in Figure 3.1 was used to discretize the equations.

Discretization in space will be shown by the index \( i \). Therefore, \( i-1 \) and \( i+1 \) represent the grid point to the left and the grid point to the right of the current grid point, respectively. \( i=1 \) represents the grid point on the bottom boundary (substrate) and \( i=i_{\text{max}} \) represents the grid points on the top boundary (evaporating surface).
Discretization in time will be displayed by $n$ where $n$ means the current point in time. Therefore, $n-1$ and $n+1$ are previous and next time steps. It should be noted that the unknowns are in the next time step, $n+1$, that will be calculated from the previous and current information.

We discretized the equations using central difference in space for all the interior points and forward space in time.

Bottom and top boundary conditions were discretized by (341) forward difference and (341) backward difference, respectively.

The first step for solving the problem is to solve the equation of moving boundary for the new dimensionless thickness of polymer solution. This was done by discretizing Eq. (3.5) which gives

$$\tilde{w}^{n+1} = -\tilde{p}(\phi^n, \theta^n) \Delta \tilde{t} + \tilde{w}^n,$$

where $\Delta \tilde{t}$ is the time interval for marching in time and track the evaporation process. In effect, the calculation will be continued until the whole solvent evaporates. This condition is invoked after reaching a tolerance in the computer program.

The discretized form of mass equation for calculation of volume fraction of solvent in the next time step of interior points is given by
Note that in Eq. (3.38) all the dimensionless ME groups are functions of field variables. It is expected that before discretization, the derivative of functions expanded in terms of their arguments. However, this process renders a lot of complexity and also increases the errors due to derivation process. Therefore, we avoided doing that and the discretization was done by considering ME functions in their compact form without expansion of derivatives.

The same procedure was performed in the case of HE functions in Eq. (3.42) to calculate dimensionless temperature in the next time step of interior points given by
The discretized bottom boundary conditions for mass and heat equations are

\[
\theta^{n+1} = \theta^n + \frac{\xi}{\bar{w}} (\bar{w}^{n+1} - \bar{w}^n) \left( \frac{\theta^n_{i+1} - \theta^n_{i-1}}{2\Delta \xi} \right) + \\
\frac{\Delta \tilde{t}}{NG2} \left( \frac{\text{HE}1(\phi^n_{i+1}, \theta^n_{i+1}) - \text{HE}1(\phi^n_{i-1}, \theta^n_{i-1})}{2\Delta \xi} \right) \left( \theta^n_{i+1} - \theta^n_{i-1} \right) + \\
\frac{\Delta \tilde{t}}{NG2} \left( \frac{\text{HE}2(\phi^n_{i+1}, \theta^n_{i+1}) - \text{HE}2(\phi^n_{i-1}, \theta^n_{i-1})}{2\Delta \xi} \right) \left( \theta^n_{i+1} - \theta^n_{i-1} \right) + \\
NG3 \left( \frac{\Delta \tilde{t}}{NG2} \left( \frac{\text{NG}2(\phi^n_{i+1}, \theta^n_{i+1}) - \text{NG}2(\phi^n_{i-1}, \theta^n_{i-1})}{2\Delta \xi} \right) \left( \theta^n_{i+1} - \theta^n_{i-1} \right) + \tilde{\chi}^n_1 \left( \theta^n_{i+1} - 2\theta^n_{i+1} + \theta^n_{i-1} \right) \right).
\]

The discretized bottom boundary conditions for mass and heat equations are

\[
\left(1 - 2\chi \phi^{n+1}_1\right) \left(-3\phi^{n+1}_1 + 4\phi^{n+1}_2 - \phi^{n+1}_3\right) + \\
\text{ME}2(\phi^{n+1}_1, \theta^{n+1}_1) \left(-3\phi^{n+1}_1 + 4\phi^{n+1}_2 - \theta^{n+1}_3\right) = 0,
\]

\[
\text{HE}1(\phi^{n+1}_1, \theta^{n+1}_1) \left(\frac{-3\phi^{n+1}_1 + 4\phi^{n+1}_2 - \phi^{n+1}_3}{2\Delta \xi}\right) = 0,
\]

\[
\text{HE}2(\phi^{n+1}_1, \theta^{n+1}_1) \left(\frac{-3\theta^{n+1}_1 + 4\theta^{n+1}_2 - \theta^{n+1}_3}{2\Delta \xi}\right) = 0,
\]

\[
\text{NG}3 \left(\frac{\Delta \tilde{t}}{NG2} \left(\frac{-3\theta^{n+1}_1 + 4\theta^{n+1}_2 - \theta^{n+1}_3}{2\Delta \xi}\right) \right) = 0,
\]

\[
\text{NG}6 \left(\frac{3\theta^{n+1}_{sub, i_{max}} - 4\theta^{n+1}_{sub, i_{max+1}} + \theta^{n+1}_{sub, i_{max-2}}}{2\Delta \tilde{y}}\right),
\]

respectively.
The discretized top boundary conditions for mass and heat equations are

\[-ME1(\varphi_{\text{max}}^{n+1}) \frac{1}{\tilde{W}^{n+1}} \left( \frac{3\varphi_{\text{max}}^{n+1} - 4\varphi_{\text{max}}^{n+1} + \varphi_{\text{max}}^{n+1}}{2\Delta \xi} \right) - \]

\[ME3(\varphi_{\text{max}}^{n+1}, \theta_{\text{max}}^{n+1}) \frac{1}{\tilde{W}^{n+1}} \left( \frac{3\theta_{\text{max}}^{n+1} - 4\theta_{\text{max}}^{n+1} + \theta_{\text{max}}^{n+1}}{2\Delta \xi} \right) \]  

(3.51)

\[-NG1\varphi_{\text{max}}^{n+1} \left( \tilde{W}^{n+1} - \tilde{W}^n \right) = NG1 \tilde{p}(\varphi_{\text{max}}^{n+1}, \theta_{\text{max}}^{n+1}) . \]

\[-HE1(\theta_{\text{max}}^{n+1}, \varphi_{\text{max}}^{n+1}) \frac{1}{\tilde{W}^{n+1}} \left( \frac{3\theta_{\text{max}}^{n+1} - 4\theta_{\text{max}}^{n+1} + \theta_{\text{max}}^{n+1}}{2\Delta \xi} \right) - \]

\[HE2(\varphi_{\text{max}}^{n+1}, \theta_{\text{max}}^{n+1}) \frac{1}{\tilde{W}^{n+1}} \left( \frac{3\theta_{\text{max}}^{n+1} - 4\theta_{\text{max}}^{n+1} + \theta_{\text{max}}^{n+1}}{2\Delta \xi} \right) - \]  

(3.52)

\[NG3\gamma_{\text{max}}^{n+1} \frac{1}{\tilde{W}^{n+1}} \left( \frac{3\theta_{\text{max}}^{n+1} - 4\theta_{\text{max}}^{n+1} + \theta_{\text{max}}^{n+1}}{2\Delta \xi} \right) = \]

\[NG4(\theta_{\text{max}}^{n+1} - \theta_0) + NG5 \tilde{p}(\varphi_{\text{max}}^{n+1}, \theta_{\text{max}}^{n+1}) . \]

At each boundary a system of nonlinear algebraic equations should be solved for the new values of concentration and temperature on the boundaries. For doing so, the globally convergent 2-D Newton’s method [25] was used to solve Eqs. (3.49) and (3.50) at the bottom boundary and Eqs. (3.51) and (3.52) at the top boundary.

The discretized equation for heat transfer in the substrate, boundary condition with polymer solution and boundary condition with air are

\[\theta_{\text{sub},i}^{n+1} = \theta_{\text{sub},i}^{n} + \Delta tNG7 \left( \frac{\theta_{\text{sub},i+1}^{n} - 2\theta_{\text{sub},i}^{n} + \theta_{\text{sub},i-1}^{n}}{(\Delta \tilde{y})^2} \right) , \]  

(3.53)

\[\theta_{\text{sub},i,\text{max}}^{n} = \theta_1^n , \text{ for all values of } n \]  

(3.54)
respectively. \( \bar{y} \) is the dimensionless coordinate at the substrate and \( \Delta \bar{y} \) is the special interval.

The Fortran 77 code written for the numerical computations is given in Appendix F. In order to keep the numerical computation stable a very low time step \( (\Delta t^* = 10^{-8}) \) was used. Table 3.2 shows the computation time for different levels of discretization using a machine with an Intel Core 2 Duo E8400 processor.

The concentration and temperature profiles associated with those discretization levels are shown in Appendix F. The simulation results for cases where \( \Delta \xi = 0.01 \) and \( \Delta \xi = 0.001 \) indicates that by refining the mesh no drastic difference is observed in the computation results. Therefore, in order to perform faster computations, \( \Delta \xi = 0.01 \) was used to run the code. The results of simulation are shown in Chapter IV.

Table 3.2: Computation time for different levels of discretization.

<table>
<thead>
<tr>
<th>( \Delta \xi )</th>
<th>Computation time for ( 10^5 \times \Delta t^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>00:00:27</td>
</tr>
<tr>
<td>0.01</td>
<td>00:03:06</td>
</tr>
<tr>
<td>0.001</td>
<td>00:30:15</td>
</tr>
</tbody>
</table>
CHAPTER IV

SIMULATION RESULTS

The results of simulations after running the computer program for different processing conditions are presented in this chapter.

As mentioned in Chapter II, we consider uniform profiles as initial conditions for concentration and temperature. After applying boundary conditions, the initial uniform profiles will be perturbed and concentration and temperature gradients develop in the system. Since polymers typically have positive thermal diffusion coefficient and therefore tend to migrate to cold regions when a polymer solution is exposed to a temperature gradient [21], an increase in the local concentration of solvent on the warm side of a temperature gradient is expected.

Figures 4.1-4.3 show concentration and temperature profiles at the onset of solvent evaporation for different values of $T_0$ and $T_\infty$. By concentration we mean volume fraction of the solvent $\phi$ and by temperature, dimensionless temperature $\theta$.

In all the concentration and temperature profiles $\phi$, $\theta$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 
Figure 4.1: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 298.15$ K, $V_\infty = 1.2$ m/s. $\phi$, $\theta$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 

$T_0$, $T_\infty = 298.15$ K, $V_\infty = 1.2$ m/s.

$\phi$, $\theta$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 

$T_0$, $T_\infty = 298.15$ K, $V_\infty = 1.2$ m/s.
Figure 4.2: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 318.15$ K, $V_\infty = 1.2$ m/s. $\varphi$, $\theta$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 
Figure 4.3: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0, T_\infty = 338.15$ K, $V_\infty = 1.2$ m/s. $\varphi, \theta, \tau^*$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $\tau^* = 0$. 

36
The important point observed in concentration profiles is the variation of volume fraction of the solvent in the vicinity of the substrate. As expected, by developing a temperature gradient in the polymer solution the local concentration of the solvent increases near the substrate which is the warm side of the temperature gradient.

The evolution of concentration near the substrate can clearly be observed in the magnified views of the concentration profiles shown in Figure 4.4. A comparison between concentration profiles shown in Figure 4.4 and their corresponding temperature profiles in Figures 4.1-4.3 indicates that migration of the solvent to the warm side of a temperature gradient is higher when the temperature gradient is steeper. Figure 4.3 with the steepest temperature gradient shows the highest values for $\phi$ near the substrate. The steepest temperature gradient is the result of evaporation at a high temperature as compared with Figures 4.1 and 4.2 where the temperature is lower. In effect, the trend of variation of concentration and temperature profiles shows that the model can describe the evolution of field variables qualitatively well.
Figure 4.4: Concentration profiles at the onset of evaporation of the solvent. a) $T_0$, $T_\infty = 298.15$ K, b) $T_0$, $T_\infty = 318.15$ K, c) $T_0$, $T_\infty = 338.15$ K, $V_\infty = 1.2$ m/s. $\phi$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 
The model is very sensitive in capturing the effect of thermal diffusion in polymer solutions. This can be observed by comparing the results of simulation of evaporation process at different air velocities. Figures 4.5-4.10 show concentration and temperature profiles for evaporation process at different temperatures and air velocities. The magnified view of concentration profiles for evaporation at different velocities has been compared in Figures 4.11-4.13. Although the difference between temperature gradient at different air velocities in a given initial temperature is not drastic, the model can show the effect of thermal diffusion by increasing the local concentration of solvent near the substrate which is the warm side of the temperature gradient.
Figure 4.5: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0, T_\infty = 298.15 \, \text{K}$, $V_\infty = 0.3 \, \text{m/s}$. $\varphi$, $\theta$, $\tau^*$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $\tau^* = 0$. 
Figure 4.6: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 298.15$ K, $V_\infty = 0.6$ m/s. $\phi$, $\theta$, $t^*$ and $\zeta$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\zeta = 0$ shows the substrate and $\zeta = 1$ represents the evaporating surface at $t^* = 0$. 
Figure 4.7: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 318.15$ K, $V_\infty = 0.3$ m/s. $\varphi$, $\theta$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 
Figure 4.8: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 318.15$ K, $V_\infty = 0.6$ m/s. $\phi$, $\theta$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 
Figure 4.9: Concentration and temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 338.15 \text{ K}$, $V_\infty = 0.3 \text{ m/s}$. $\varphi$, $\theta$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 
Figure 4.10: Concentration and temperature profiles at the onset of evaporation of the solvent. \(T_0, T_\infty = 338.15 \text{ K}, V_\infty = 0.6 \text{ m/s}\). \(\phi, \theta, \tau^*\) and \(\zeta\) are volume fraction of the solvent, dimensionless temperature, dimensionless time and dimensionless length. \(\zeta = 0\) shows the substrate and \(\zeta = 1\) represents the evaporating surface at \(\tau^* = 0\).
Figure 4.11: Concentration profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 298.15$ K. (a) $V_\infty = 0.3$ m/s, (b) $V_\infty = 0.6$ m/s. $\varphi$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 

46
Figure 4.12: Concentration profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 318.15$ K. (a) $V_\infty = 0.3$ m/s, (b) $V_\infty = 0.6$ m/s. $\varphi$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 
Figure 4.13: Concentration profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 338.15$ K. (a) $V_\infty = 0.3$ m/s, (b) $V_\infty = 0.6$ m/s. $\varphi^*$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 
The concentration profile and corresponding temperature profile for the entire time until complete evaporation in the solution casting process governed by Eqs. (3.1) and (3.2) are shown in Figures 4.14 and 4.15, respectively.

Figure 4.14: Concentration profile for the whole evaporation process, $T_0 = 298.15$ K, $T_\infty = 338.15$ K, $V_\infty = 1.2$ m/s. $\varphi$, $t^*$ and $\xi^*$ are volume fraction of the solvent, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 
Figure 4.15: Two views of temperature profile for the whole evaporation process. $T_0 = 298.15$ K, $T_\infty = 338.15$ K, $V_\infty = 1.2$ m/s. $\theta^*$ and $\xi$ are dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 
The evolution of solvent concentration near the substrate for the whole process of evaporation is shown in the magnified view of Figure 4.14.

The models formulated for the process of drying of polymer solutions neglect entropy production in the system. Therefore, governing equations derived in such models cannot describe thermal diffusion in polymer solutions (see i.e., Figure 4.16). Moreover, the coupling between mass and heat transfer equations in those models is only due to the temperature dependence of mutual diffusion coefficient.

![Figure 4.16: Concentration profiles of solvent in a polymer solution during evaporation. Profiles are shown in 10-s increments starting at t=0 when the solvent concentration is uniform. Reproduced with permission from ref. [5].](image-url)
CHAPTER V

MODEL PREDICTIONS FOR POLYMER THERMAL DIFFUSION

Thermal diffusion or Ludwig–Soret effect is the mass diffusion driven by applying a temperature gradient on multi-component systems [14]. Although during the past decade this effect in polymer solutions has been studied by some research groups [21,26-31], still no complete picture has been provided to explain experimental observations.

According to recent experiments, thermal diffusion coefficient in polymer solutions is found to be an increasing function of molecular weight, in case of short chains while reaching a plateau at high molecular weights [27-30]. It also has inverse dependence on the solvent viscosity [29]. Moreover, rigid polymer chains have higher thermal diffusion coefficients than more flexible ones [28,29,31].

The governing equations derived in Chapter II can be written in terms of polymer volume fraction, $\varphi_2$, and polymer mass flux, $J_2$

$$
\rho_2 \frac{d\varphi_2}{dt} = \nabla \cdot \left\{ \alpha \left( \frac{\partial \mu^*}{\partial \varphi_2} \right)_T \nabla \varphi_2 + \left[ \alpha \left( \frac{\partial \mu^*}{\partial T} \right)_{\varphi_2} + \beta \right] \nabla T \right\}, \tag{5.1}
$$

$$
\rho c_p \frac{dT}{dt} = -\nabla \cdot \left\{ \left( \mu^* + \frac{\beta}{\alpha} T \right) J_2 - \left( \gamma - \frac{\beta^2}{\alpha} T \right) \nabla T \right\}, \tag{5.2}
$$
where $\rho_2$ is the mass density of polymer and $\mu^*$ is given by

$$\mu^* = \frac{\mu_2}{M_2} - \frac{\rho_1}{\rho_2} \frac{\mu_i}{M_i}. \tag{5.3}$$

As mentioned in Chapter II, subscripts 1 and 2 are attributed to solvent and polymer, respectively.

According to the model, mutual and thermal diffusion coefficients are expressed by

$$D_M = \alpha \left( \frac{\partial \mu^*}{\partial \varphi_2} \right)_T, \tag{5.4}$$

$$D_T = \alpha \left( \frac{\partial \mu^*}{\partial T} \right)_{\varphi_2} + \beta. \tag{5.5}$$

Knowing that the difference between chemical potentials of a component in the mixture and in its pure state is given by partial molar Gibbs free energy of mixing, Eq. (5.3) can be rewritten as

$$\mu^* = \frac{1}{M_2} \left[ \mu_2^0 + \frac{\partial \Delta G_m}{\partial n_2} \right]_{T,P,n_i} - \frac{\rho_1}{\rho_2} \frac{1}{M_1} \left[ \mu_i^0 + \frac{\partial \Delta G_m}{\partial n_1} \right]_{T,P,n_2}, \tag{5.6}$$

where $\mu_2^0$ and $\mu_i^0$ are the chemical potentials of pure liquid polymer [19] and pure solvent, respectively and $\Delta G_m$ is the Gibbs free energy of the mixing. See Appendix D for calculation of $\mu^*$.

Chemical potential of component $i$ in its pure state which in general is a function of temperature and pressure can be presented by

$$\mu_i^0(T,P) = \mu_i^0(T_0,P) + \left( \frac{\partial \mu_i^0}{\partial T} \right)_{P,T_i} (T - T_0). \tag{5.7}$$
According to Maxwell relations, the derivative of chemical potential with respect to absolute temperature equals partial molar entropy with minus sign given by [32]

\[
\left( \frac{\partial \mu}{\partial T} \right)_{p,n} = - \left( \frac{\partial S}{\partial n} \right)_{T,P},
\]

(5.8)

Partial molar entropy of pure component \( i \) equals its molar entropy \( S_i \) which can be presented by following integration:

\[
\left( \frac{\partial S_i}{\partial n_i} \right)_{T_i,P_i} = \int_{T_0}^{T} \frac{C_p}{T} dT,
\]

(5.9)

where \( C_p \) is molar isobaric heat capacity. Using Eqs. (5.5) - (5.9), one can present the thermal diffusion coefficient as

\[
D_T = \alpha \left\{ S_T + \frac{\partial G_T}{\partial T} \right\} + \beta,
\]

(5.10)

where \( S_T \) and \( G_T \) are

\[
S_T = -S_2 + \frac{\rho_1}{\rho_2} S_1,\]

(5.11)

\[
G_T = \frac{1}{M_2} \left( \frac{\partial \Delta G_m}{\partial n_2} \right)_{T,P,n_1} - \frac{\rho_1}{\rho_2} \frac{1}{M_1} \left( \frac{\partial \Delta G_m}{\partial n_1} \right)_{T,P,n_1},
\]

(5.12)

respectively.

Eq. (5.10) indicates two independent contributions to thermal diffusion in polymer solutions. One contribution arises from temperature dependency of chemical potentials which is given by the first term on the right hand side of Eq. (5.10). Another one is expressed by phenomenological coefficient \( \beta \) which gives the drift velocity of polymer chains in a temperature gradient without considering temperature dependency of
chemical potentials. In fact in the process of development of the model, first, $\beta$ which is related to off-diagonal entries of Onsager matrix appeared as thermal diffusion coefficient and then gradient of chemical potential results in another contribution. Phenomenological coefficient $\alpha$ can be related to the friction coefficient and consequently solvent viscosity by making a comparison between Eq. (5.1) and the Smoluchowski equation [33] and also Eq. (5) and proposed equation for mutual diffusion coefficient in polymer solutions [34]. In general, one can approximate $\alpha$ with

$$\frac{f(\varphi)}{\zeta}$$

where $f(\varphi)$ is a concentration function and $\zeta$ is the friction coefficient of polymer beads, with radius $a$, which is related to solvent viscosity $\eta$ by

$$\zeta = 6\pi \eta a.$$  \hspace{1cm} (5.13)

Therefore, Eq. (5.10) can be written in the form

$$D_T = \frac{f(\varphi)}{6\pi \eta a} \left\{ \left( -\frac{S_2}{M_2} + \frac{\rho_1 S_1}{\rho_2 M_1} \right) g(\varphi) + \beta(\varphi, T) \right\}.$$  \hspace{1cm} (5.14)

The inverse dependence of $D_T$ on solvent viscosity [29] can be explained by the viscosity in the first term at the right hand side of Eq. (5.14).

Conformational entropy of liquid polymer chains in their reference state (melt state) which has the dominant contribution to polymer molar entropy [35] is lower for stiffer polymer chains than more flexible ones and therefore according to Eq. (12) since molar entropy is a positive quantity, by increasing polymer chain stiffness, $S_T$ will increase for a given polymer molecular weight and therefore results in higher $D_T$ values which is consistent with experimental observations [28,29].
Equation (5.14) indicates that $D_T$ is dependent on polymer molecular weight and upon increasing molecular weight, $D_T$ increases and finally gives a plateau at very high molecular weights. This behavior is in accord with experimental data observed in recent research [27-30].

As one can see, based on the proposed equation for thermal diffusion coefficient, it would be possible to explain the effects of solvent viscosity, polymer chain stiffness and polymer molecular weight on thermal diffusion coefficient in polymer solutions.
A thermodynamically consistent model was developed to describe evolution of concentration and temperature during evaporation of solvent from polymer solutions. The governing equations for mass and heat transfer were derived from rate of entropy production in the linear regime of nonequilibrium thermodynamics. The model was developed from the Gibbs equation using local equilibrium hypothesis, Onsager’s reciprocal relations and Prigogine’s theorem for systems in mechanical equilibrium. The model was formulated for a general case of multi-component system and then final governing equations were presented for a two-component system (polymer solution). Therefore, the governing equations for mass of components for multi-component system can be derived simply from the model. The governing equations form a system of coupled nonlinear partial differential equations with a complex connection between heat and non-convective mass fluxes in that, the mass flux contributes to the heat equation. This coupling between mass diffusion and heat conduction is not observed in the models proposed for drying polymer solutions without considering entropy production in the system. Mutual and thermal diffusion coefficients and thermal conductivity of the polymer solution appeared in governing equations in terms of phenomenological
coefficients which are bounded to some theoretical constraints. To perform numerical computations, phenomenological coefficients are approximated in a way that the theoretical constraints and the asymptotic behaviors of mutual and thermal diffusion coefficients are satisfied. The numerical simulation results indicate that the governing equations can show the evolution of concentration and temperature after applying the boundary conditions to the uniform concentration and temperature profiles in the system. Moreover, the model can capture the effect of thermal diffusion in polymer solutions in that, local concentration of solvent increases on the warm side of a temperature gradient during the solution casting process.

Although it has been assumed that the polymer system under consideration is in one phase, the model might be extended to the case where phase separation takes place. In effect, two important developments can be considered for the future work and extending the model. As described in Chapter II, the model assumed that the polymer solution is always in a temperature above glass transition temperature. In some conditions it might be possible that a skin forms during the evaporation process, in that case the effect of glass transition temperature and effect of skin on the evaporation of solvent becomes very important. Therefore, improvement of model for considering skin formation may be considered for future improvement of the model. Moreover, by evaporation of solvent, it is possible that the polymer solution experiences different regimes of concentration and in some case it is possible that phase separation occurs in the system. Considering different regimes of concentration and phase separation during evaporation is another step for improvement of the model in future.
In addition to theoretical improvements, it is worth developing an implicit numerical scheme to solve the governing equations. As explained in Chapter III, the numerical computation presented in this work is an explicit scheme.

“The law that entropy always increases holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations — then so much the worse for Maxwell's equations. If it is found to be contradicted by observation — well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation.”

Sir Arthur Eddington, The Nature of the Physical World


61


APPENDIX A

CALCULATION OF EVAPORATING SOLVENT FLUX

Evaporating solvent flux can be calculated via

$$C_x = \langle K_c \rangle (c_{sw} - c_{sw})$$, \hspace{.5cm} (A.1)

where $\langle K_c \rangle$ and $c_{sw}$ are the averaged mass transfer coefficient and mass concentration of solvent at the liquid-air interface. The mass concentration $c_{sw}$ of the solvent far from the interface will be assumed to be negligible.

Averaged transfer coefficients for a laminar flow of uniform velocity $v_\infty$ over a flat plate with the length of $x$ in the direction of flow are [9]

$$\langle h \rangle = \frac{\langle Nu \rangle k_{air}}{x}, \hspace{.5cm} (A.2)$$

$$\langle K_c \rangle = \frac{\langle Sh \rangle D_{AB}}{x}, \hspace{.5cm} (A.3)$$

where $k_{air}$, $D_{AB}$, $\langle Nu \rangle$ and $\langle Sh \rangle$ are the thermal conductivity of air, diffusion coefficient of solvent into air, and the averaged Nusselt and Sherwood numbers, respectively. These numbers can be approximated by [9]

$$\langle Nu \rangle = 0.664 \text{Re}^{1/2} \text{Pr}^{1/3}, \hspace{.5cm} (A.4)$$

$$\langle Sh \rangle = 0.664 \text{Re}^{1/2} \text{Sc}^{1/3}, \hspace{.5cm} (A.5)$$
where \( \text{Re}, \text{Pr} \) and \( \text{Sc} \) are the Reynolds, Prandtl and Schmidt numbers given by

\[
\text{Re} = \frac{\rho v L}{\eta},
\]

\[
\text{Pr} = \frac{\eta}{\rho \kappa},
\]

\[
\text{Sc} = \frac{\eta}{\rho D},
\]

respectively. Here \( \rho, v, L, \eta, \nu, \kappa \) and \( D \) are density of the fluid, mean velocity, characteristic linear dimension, viscosity, kinematic viscosity, thermal diffusivity and mass diffusivity, respectively.

Assuming ideal gas behavior for the solvent at the liquid-air interface, we calculate \( c_{sw} \) through the equation of state of ideal gas

\[
c_{sw} = \frac{P_s M_s}{RT_{\infty}}. \tag{A.9}
\]

According to the Flory–Huggins theory, the ratio of vapor pressure of solvent in polymer solution \( P_s \) to the vapor pressure of pure solvent \( P_s^* \) is given by [8]

\[
\frac{P_s}{P_s^*} = \exp \left[ \ln(\phi) + (1-\phi) + \chi (1-\phi)^2 \right]. \tag{A.10}
\]

The vapor pressure of pure solvent at a given temperature \( T \) can be estimated from a known value \( P_{s0}^* \) at a temperature \( T_0 \) by using the Clausius–Clapeyron equation

\[
\ln \left( \frac{P_s^*}{P_{s0}^*} \right) = -\frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right), \tag{A.11}
\]

where \( \Delta H \) is molar heat of evaporation.
APPENDIX B

PHYSICAL PROPERTIES USED FOR SIMULATION

\[ \rho_1 = 779 \text{kg.m}^{-3} \]
\[ M_1 = 84.16 \text{g.mol}^{-1} \]
\[ \rho_2 = 1050 \text{kg.m}^{-3} \]
\[ \chi = 0.35 \]
\[ R = 8.314 \text{J.K}^{-1} \text{mol}^{-1} \]
\[ T_b = 353.9 \text{K} \]
\[ T_c = 553.4 \text{K} \]
\[ a = 26.83 \times 10^3 \text{J.mol}^{-1} \]
\[ b = -204.10 \text{J.K}^{-1} \text{mol}^{-1} \]
\[ D_0 = 10^{-9} \text{m}^2 \text{.sec}^{-1} \]
\[ \gamma_0 = 0.03 \text{W.m}^{-1} \text{.K}^{-1} \]
\[ c_p = 1.251 \times 10^3 \text{J.kg}^{-1} \text{.K}^{-1} \]
\[ \Delta H_v = 0.38 \times 10^6 \text{J.kg}^{-1} \]
\[ \Delta H = 32 \times 10^3 \text{J.mol}^{-1} \]
\[ v_v = 1.2 \text{m.sec}^{-1} \]
\[ \phi_0 = 0.8 \]
APPENDIX C

TIME DERIVATIVE OF FIELD VARIABLES AFTER COORDINATE TRANSFORMATION

The time derivative of field variables like volume fraction in different coordinates is

\[
\left( \frac{\partial \phi}{\partial t} \right)_y = \frac{\partial \phi}{\partial \xi} \frac{\partial \xi}{\partial t} + \left( \frac{\partial \phi}{\partial \tilde{t}} \right)_{\xi}.
\] (C.1)

Using Eq. (3.34), we can recast the first term on the right hand side of Eq. (C.1) as

\[
\frac{\partial \phi}{\partial \xi} \frac{\partial \xi}{\partial t} = \frac{\tilde{y}}{\tilde{w}(\tilde{t})} \frac{d\tilde{w}(\tilde{t})}{d\tilde{t}} \frac{\partial \phi}{\partial \tilde{t}} \frac{\partial \tilde{t}}{\partial \xi}.
\] (C.2)

Therefore, with some manipulation Eq. (C.1) can be written as

\[
\left( \frac{\partial \phi}{\partial t} \right)_y = -\frac{\tilde{y}}{\tilde{w}(\tilde{t})} \frac{d\tilde{w}(\tilde{t})}{d\tilde{t}} \frac{\partial \phi}{\partial \tilde{t}} + \left( \frac{\partial \phi}{\partial \tilde{t}} \right)_{\xi} \left( \frac{\partial \xi}{\partial \tilde{t}} \right)_{\xi}.
\] (C.3)

By the same way the time derivative of dimensionless temperature in two coordinates is

\[
\left( \frac{\partial \theta}{\partial t} \right)_y = -\frac{\tilde{y}}{\tilde{w}(\tilde{t})} \frac{d\tilde{w}(\tilde{t})}{d\tilde{t}} \frac{\partial \theta}{\partial \tilde{t}} + \left( \frac{\partial \theta}{\partial \tilde{t}} \right)_{\xi} \left( \frac{\partial \xi}{\partial \tilde{t}} \right)_{\xi}.
\] (C.4)
APPENDIX D

CALCULATION OF CHEMICAL POTENTIAL

\[ \mu_1 = \mu_1^0 + RT \left\{ \ln(1 - \varphi_2) + \varphi_2 \left(1 - \frac{1}{N}\right) + \chi \varphi_2^2 \right\} \]

\[ \mu_2 = \mu_2^0 + RT \left\{ \ln(\varphi_2) + (1 - \varphi_2)(1 - N) + \chi N(1 - \varphi_2)^2 \right\} \]

\[ \mu^* = \frac{1}{M_2} \left[ \mu_2^0 + \left( \frac{\partial \Delta G_m}{\partial n_2} \right)_{T,P,n_i} \right] - \frac{\rho_1}{\rho_2} \frac{1}{M_1} \left[ \mu_1^0 + \left( \frac{\partial \Delta G_m}{\partial n_1} \right)_{T,P,n_i} \right] \]

\[ \left( \frac{\partial \Delta G_m}{\partial n_2} \right)_{T,P,n_i} = RT \left\{ \ln(\varphi_2) + (1 - \varphi_2)(1 - N) + \chi N(1 - \varphi_2)^2 \right\} \]

\[ \left( \frac{\partial \Delta G_m}{\partial n_1} \right)_{T,P,n_i} = RT \left\{ \ln(1 - \varphi_2) + \varphi_2 \left(1 - \frac{1}{N}\right) + \chi \varphi_2^2 \right\} \]

\[ \mu^* = \frac{1}{M_2} RT \left\{ \ln(\varphi_2) + (1 - \varphi_2)(1 - N) + \chi N(1 - \varphi_2)^2 \right\} - \frac{\rho_1}{\rho_2} \frac{1}{M_1} RT \left\{ \ln(1 - \varphi_2) + \varphi_2 \left(1 - \frac{1}{N}\right) + \chi \varphi_2^2 \right\} \]
## APPENDIX E
### NOTATION

<table>
<thead>
<tr>
<th>Variable or Parameter</th>
<th>Name</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( e )</td>
<td>Enthalpy per unit volume</td>
<td>( J \cdot m^3 )</td>
</tr>
<tr>
<td>( T )</td>
<td>Absolute temperature</td>
<td>( K )</td>
</tr>
<tr>
<td>( s )</td>
<td>Entropy per unit volume</td>
<td>( J \cdot K^{-1} \cdot m^{-3} )</td>
</tr>
<tr>
<td>( \mu_i )</td>
<td>Chemical potential of component ( i )</td>
<td>( J \cdot mol^{-1} )</td>
</tr>
<tr>
<td>( n_i )</td>
<td>Moles of component ( i ) per unit volume</td>
<td>( mol )</td>
</tr>
<tr>
<td>( t )</td>
<td>time</td>
<td>( sec )</td>
</tr>
<tr>
<td>( M_i )</td>
<td>Molecular weight of component ( i )</td>
<td>( kg \cdot mol^{-1} )</td>
</tr>
<tr>
<td>( c_i )</td>
<td>Mass concentration of component ( i )</td>
<td>( kg/m^3 )</td>
</tr>
<tr>
<td>( J_q )</td>
<td>Heat flux</td>
<td>( J \cdot m^{-2} \cdot sec^{-1} )</td>
</tr>
<tr>
<td>( J_i )</td>
<td>Non-convective mass flux of component ( i )</td>
<td>( kg/m^2 \cdot sec^{-1} )</td>
</tr>
<tr>
<td>( \rho_i )</td>
<td>Mass density of component ( i )</td>
<td>( kg/m^3 )</td>
</tr>
<tr>
<td>( v_i )</td>
<td>Velocity of component ( i )</td>
<td>( m/\text{sec} )</td>
</tr>
<tr>
<td>( v )</td>
<td>Mean velocity</td>
<td>( m/\text{sec} )</td>
</tr>
<tr>
<td>( J_s )</td>
<td>Entropy flux</td>
<td>( J \cdot K^{-1} \cdot m^{-2} \cdot sec^{-1} )</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Entropy production per unit volume</td>
<td>( J \cdot K^{-1} \cdot m^{-2} \cdot sec^{-1} )</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>Phenomenological coefficient</td>
<td>( kg \cdot m^{-1} \cdot sec )</td>
</tr>
<tr>
<td>( \beta )</td>
<td>Phenomenological coefficient</td>
<td>( kg \cdot m^{-1} \cdot K^{-1} \cdot sec^{-1} )</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>Thermal conductivity</td>
<td>( W \cdot m^{-1} \cdot K^{-1} )</td>
</tr>
<tr>
<td>( D_0 )</td>
<td>Fitting parameter</td>
<td>( m^2 \cdot \text{sec}^{-1} )</td>
</tr>
<tr>
<td>( R )</td>
<td>Universal gas constant</td>
<td>( J \cdot K^{-1} \cdot \text{mol}^{-1} )</td>
</tr>
<tr>
<td>( \gamma_0 )</td>
<td>parameter</td>
<td>( W \cdot m^{-1} \cdot K^{-1} )</td>
</tr>
<tr>
<td>( T_b )</td>
<td>Boiling point of solvent</td>
<td>( K )</td>
</tr>
<tr>
<td>( T_c )</td>
<td>Critical point of solvent</td>
<td>( K )</td>
</tr>
<tr>
<td>( \mu^0 )</td>
<td>Chemical potential of pure solvent</td>
<td>( J \cdot mol^{-1} )</td>
</tr>
<tr>
<td>Variable or Parameter</td>
<td>Name</td>
<td>Unit</td>
</tr>
<tr>
<td>-----------------------</td>
<td>----------------------------------------------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>$\Delta H_v$</td>
<td>Heat of evaporation of solvent</td>
<td>J kg$^{-1}$</td>
</tr>
<tr>
<td>$\langle K_c \rangle$</td>
<td>Averaged mass transfer coefficient</td>
<td>m sec$^{-1}$</td>
</tr>
<tr>
<td>$c_{sw}$</td>
<td>Mass concentration of solvent at the liquid-air interface</td>
<td>kg m$^{-3}$</td>
</tr>
<tr>
<td>$c_{svw}$</td>
<td>Mass concentration of the solvent far from the interface</td>
<td>kg m$^{-3}$</td>
</tr>
<tr>
<td>$k_{air}$</td>
<td>Thermal conductivity of air</td>
<td>W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$x$</td>
<td>Length of substrate in the direction of air flow</td>
<td>m</td>
</tr>
<tr>
<td>$D_{AB}$</td>
<td>Diffusion coefficient of solvent into air</td>
<td>m$^2$ sec$^{-1}$</td>
</tr>
<tr>
<td>$P_s$</td>
<td>Vapor pressure of solvent in polymer solution</td>
<td>Pa</td>
</tr>
<tr>
<td>$P_s^*$</td>
<td>Vapor pressure of pure solvent</td>
<td>Pa</td>
</tr>
<tr>
<td>$P_{s0}^*$</td>
<td>Vapor pressure of pure solvent at $T_0$</td>
<td>Pa</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>Molar heat of evaporation</td>
<td>J mol$^{-1}$</td>
</tr>
<tr>
<td>$k$</td>
<td>Thermal conductivity of substrate</td>
<td>W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$T_{sub}$</td>
<td>Absolute temperature of substrate</td>
<td>K</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Direction of evaporation</td>
<td>m</td>
</tr>
<tr>
<td>$T_0$</td>
<td>Initial temperature</td>
<td>K</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Chemical potential of pure solvent at $T_0$</td>
<td>J mol$^{-1}$</td>
</tr>
<tr>
<td>$b$</td>
<td>Temperature coefficient for chemical potential</td>
<td>J K$^{-1}$ mol$^{-1}$</td>
</tr>
<tr>
<td>$w(t)$</td>
<td>Thickness of the film</td>
<td>m</td>
</tr>
<tr>
<td>$C_s$</td>
<td>Evaporating solvent flux</td>
<td>kg m$^{-2}$ sec$^{-1}$</td>
</tr>
<tr>
<td>$\langle h \rangle$</td>
<td>Averaged heat transfer coefficient</td>
<td>W m$^{-2}$ K$^{-1}$</td>
</tr>
<tr>
<td>$T_\infty$</td>
<td>Temperature of flowing air</td>
<td>K</td>
</tr>
<tr>
<td>Dimensionless parameters</td>
<td>Name</td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>$\varphi_i$</td>
<td>Volume fraction of component $i$</td>
<td></td>
</tr>
<tr>
<td>$\varphi$</td>
<td>Volume fraction of solvent</td>
<td></td>
</tr>
<tr>
<td>$T_r$</td>
<td>Reduced temperature</td>
<td></td>
</tr>
<tr>
<td>$\chi$</td>
<td>Flory-Huggins interaction parameter</td>
<td></td>
</tr>
<tr>
<td>$N$</td>
<td>Ratio of the molar volumes of polymer and solvent</td>
<td></td>
</tr>
<tr>
<td>$\varphi_0$</td>
<td>Initial volume fraction of solvent</td>
<td></td>
</tr>
<tr>
<td>$\langle Nu \rangle$</td>
<td>Averaged Nusselt number</td>
<td></td>
</tr>
<tr>
<td>$\langle Sh \rangle$</td>
<td>Averaged Sherwood number</td>
<td></td>
</tr>
<tr>
<td>Re</td>
<td>Reynolds number</td>
<td></td>
</tr>
<tr>
<td>Pr</td>
<td>Prandtl number</td>
<td></td>
</tr>
<tr>
<td>Sc</td>
<td>Schmidt number</td>
<td></td>
</tr>
<tr>
<td>$\tilde{t}$</td>
<td>Dimensionless time</td>
<td></td>
</tr>
<tr>
<td>$\theta$</td>
<td>Dimensionless temperature</td>
<td></td>
</tr>
<tr>
<td>$\theta_{\infty}$</td>
<td>Dimensionless ambient temperature</td>
<td></td>
</tr>
<tr>
<td>$\tilde{y}$</td>
<td>Dimensionless space variable</td>
<td></td>
</tr>
<tr>
<td>$\tilde{\gamma}$</td>
<td>Dimensionless thermal conductivity</td>
<td></td>
</tr>
<tr>
<td>$\tilde{w}(\tilde{t})$</td>
<td>Dimensionless thickness</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX F

COMPUTER CODE

```fortran
PROGRAM MATH

C SIANAK SHAMS ES-HAGHI 06/19/12

C PROBLEM:

C CASTING OF POLYMER SOLUTION
C SYSTEM OF PDES
C MOVING BOUNDARY PROBLEM (FRONT-FIXING APPROACH)
C METHOD OF SOLUTION: FD IN TIME AND CD IN X
C BOTTOM BC : FD 341
C TOP BC : BD 341

C DECLARATION-----------------------------
C UNITS ARE IN SI.

C FOR PHI (VOLUME FRACTION OF SOLVENT)
C X FOR XI (SPATIAL VARIABLE)

IMPLICIT NONE

DOUBLE PRECISION C(1001,0:1),TS(1001,0:1),GV(1001,0:1)
DOUBLE PRECISION X(1001),W(1,0:1),GVIT(1000001)
DOUBLE PRECISION SFUX(1000000),TG(1001,0:1)
DOUBLE PRECISION Q(10000001),HH(10000001),ST(10000001)

INTEGER IFLAG(2,1),INTER(2,1)

C = VOLUME FRACTION OF SOLVENT (PHI IN EQUATIONS)
TS = NON-DIMENSIONALIZED TEMPERATURE (THETA IN EQUATIONS)
GV = GLOBAL VOLUME FRACTION OF SOLVENT
GVIT = ARRAY FOR SAVING GLOBAL VOLUME FRACTION
W = THICKNESS OF POLYMER SOLUTION
ST = SURFACE TEMPERATURE
SFUX = EVAPORATING SOLVENT FLUX
```

72
DOUBLE PRECISION RHOS, TBOILING
36 C MS = MASS OF SOLVENT
37 C MP = MASS OF POLYMER
38 C RHOS = DENSITY OF SOLVENT
39 C RHOP = DENSITY OF POLYMER
40 C TBOILING = BOILING TEMPERATURE OF SOLVENT

DOUBLE PRECISION CO, TS0, W0, WINF, DX, DT, D0, CP, HV, HMOLAR, GAMMA0
42 C CO = INITIAL VOLUME FRACTION OF SOLVENT
43 C TS0 = INITIAL TEMPERATURE
44 C W0 = INITIAL THICKNESS OF POLYMER SOLUTION
45 C WINF = THICKNESS OF POLYMERIC FILM
46 C DX = REPRESENTS DXI IN EQUATIONS; X = [0,1]
48 C DT = TIME STEP
49 C D0 = SELF-DIFFUSION COEFFICIENT OF SOLVENT
50 C TDS = THERMAL DIFFUSIVITY OF POLYMER SOLUTION
51 C CP = HEAT CAPACITY OF SOLVENT
52 C HV = HEAT OF VAPORIZATION OF SOLVENT (J/KG)
53 C HMOLAR = HEAT OF VAPORIZATION OF SOLVENT (J/MOL)
54 C GAMMA0 = PREFACTOR OF THERMAL CONDUCTIVITY OF SOLUTION

DOUBLE PRECISION RE, RHOAIR, VINF, L, MU, TDAIR, PR, SC, SH, DAB, NU, NUS
57 C RE = REYNOLDS NUMBER
58 C RHOB = DENSITY OF AIR
59 C VINF = VELOCITY OF AIR FLOW
60 C L = LENGTH OF THE PLATE
61 C MU = VISCOSITY OF AIR
62 C TDAIR = THERMAL DIFFUSIVITY OF AIR
63 C PR = PRANDTL NUMBER
64 C SC = SCHMIDT NUMBER
65 C SH = SHERWOOD NUMBER
66 C DAB = DIFFUSION COEFFICIENT OF SOLVENT IN AIR
67 C NU = KINEMATIC VISCOSITY OF AIR
69 C NUS = NUSSELT NUMBER

DOUBLE PRECISION KC, M1, P, TINF, KAIR, HAIR, PSZS, TCritical
70 C KC = INTERFACIAL MASS TRANSFER COEFFICIENT
71 C M1 = MOLECULAR WEIGHT OF THE SOLVENT
72 C R = GAS CONSTANT
73 C TINF = TEMPERATURE OF THE AIR FLOW
74 C KAIR = THERMAL CONDUCTIVITY OF AIR
75 C HAIR = CONVECTION COEFFICIENT OF AIR
77 C PSZS = PS0 STAR IN EQUATIONS
78 C TCritical = CRITICAL TEMPERATURE OF SOLVENT
DOUBLE PRECISION NG1,NG2,NG3,NG4,NG5,NG6,NG7,NG8
DOUBLE PRECISION TSTAR

DOUBLE PRECISION P,ME1,ME2,ME3,HE1,HE2,GAMMA
DOUBLE PRECISION PHI,THETA

INTEGER I,N,IMAX,M,J,S,PP(10000001),NP,NUM

INTEGER IMAXG

DOUBLE PRECISION S1,S2,S3,S4,S5,S6,S7,S8,S9,S10,S11
DOUBLE PRECISION H1,H2,H3,H4,H5,H6,H7,H8
DOUBLE PRECISION K1,K2,K3,K4,K5,K6,K7,K8
DOUBLE PRECISION K9,K10,K11,K12,K13
DOUBLE PRECISION RSHM,RSHH

C ---------------------------------------------

DOUBLE PRECISION ND11,ND12
DOUBLE PRECISION AA,BT

DOUBLE PRECISION P1,LAMBDA,LAMBDAT
DOUBLE PRECISION KF,K0,KM

C SUBSTRATE PARAMETERS
DOUBLE PRECISION K,DL,TDG,DXP
C K = THERMAL CONDUCTIVITY OF SUBSTRATE
C DL = THICKNESS OF SUBSTRATE

PARAMETER (NUM=2)
DOUBLE PRECISION Y(NUM),F(NUM)
LOGICAL CHECK
INTEGER ID

COMMON /FUN1/ HVMOULAR
COMMON /FUN2/ R
COMMON /FUN3/ BT
COMMON /FUN4/ AA
COMMON /FUN5/ TSO
COMMON /FUN6/ TBOILING
COMMON /FUN7/ TCritical
COMMON /FUN8/ K1,K2,K3,K4,K5,K6,K7,K8,K9,K10,K11,K12,K13
COMMON /FUN9/ ID
C
CHARACTER*1 CFLAG
CHARACTER*13 FLNAME
CHARACTER*3 CHAN3
INTEGER NP
NP = 10**6

WRITE(6,*) 'ENTER ID FLAG (1 CHARACTER)'
READ(5,77) CFLAG

77 FORMAT(A1)

RHCS = 0.779D3
TBOILING = 353.9D0
TCRITICAL = 553.4D0
C0 = 0.8D0
TS0 = 298.15D0
W0 = 0.2D-3
WINF = 1.0D0-C0
AA = 26.83D3
BT = -204.10D0

D0 = 1.D-9
CP = 1.251D3
HV = 0.38D6
HVMOLAR = 32.D3
GAMMA0 = 0.031D0

RHOAIR = 1.0085D0
VINF = 1.2D0
L = 0.1651D0
MU = 20.81D-6
TDAIR = 2.94D-5
DAB = 0.124D-4
NU = MU/RHOAIR
RE = (RHOAIR*VINF*L)/MU
PR = NU/TDAIR
SC = NU/DAB
M1 = 84.16D-3
R = 8.314D0
TINF = 298.15D0
PS2S = 101325.D0
KAIR = 29.7D-3
IMAX = 101
IMAXG = 51

SUBSTRATE
K = 0.96D0
IDG = 0.34D-6
DL = 1.5D-3
dxp = 1.D0/DFLOAT(IMAXG-1)

DX = 1.D-2
DT = 1.D-8

CALCULATION OF REGIME OF FLOW
IF (RE .LE. 5.D5) THEN
   LAMINAR REGIME
   SH = 0.664D0*(RE**0.5D0)*SC**2*(1.D0/3.D0)
   NUS = 0.664D0*(RE**0.5D0)*FR**2*(1.D0/3.D0)
ELSE IF ((RE .GT. 5.D5) .AND. (RE .LT. 1.D8)) THEN
   LAMINAR AND TURBULENT REGIME
   SH = (0.037D0*(RE**0.8D0)-871.D0)*SC**2*(1.D0/3.D0)
   NUS = (0.037D0*(RE**0.8D0)-571.D0)*FR**2*(1.D0/3.D0)
ELSE IF (RE .GT. 1.D8) THEN
   TURBULENT REGIME
   SH = 0.037D0*(RE**0.8D0)*SC**2*(1.D0/3.D0)
   NUS = 0.037D0*(RE**0.8D0)*FR**2*(1.D0/3.D0)
END IF

KC = (SH*DAB)/L
HAIR = (NUS*HAIR)/L

ISTAR = (RHOS*W0*R*TINF)/(KC*PSZS*M1)

NON-DIMENSIONAL GROUPS
NG1 = (KC*PSZS*M1*W0)/(R*TINF*DO*RHOS)
NG2 = (CP*KC*PSZS*W0*M1*ML)/(R*TINF*DO*RHOS*R)
NG3 = (M1*GAMMA)/(D0*RHOS*R)
NG4 = (M1*W0*HAIR)/(D0*RHOS*R)
NG5 = (R7*KC*M1*W0*PSZS*M1)/(D0*RHOS*R*T50*R*TINF)
NG6 = (M1*K*W0)/(D0*R*RHOS*DL)

NG7 & NG8 ARE RELATED TO SUBSTRATE
NG7 = (RHOS*W0*R*TINF*IDG)/(KC*PSZS*M1*(DL**2))
NG8 = K/(DL*HAIR)
C SPATIAL GRID

DO I=1,IMAX
   X(I) = 0.D0 + DFLOAT(I-1)*DX
END DO

DO I=1,IMAXG
   TS(I,0) = 1.D0
END DO

W(1,0) = 1.D0
GV(1,0) = C0

CALL OUTFN('CON',CHN3(N),CFLAG,1)
CALL OUTFN('TEM',CHN3(N),CFLAG,2)

DO I=1,IMAX
   HH(I) = W(1,0)*X(I)
   C(I,0) = C0
   TS(I,0) = 1.D0
   WRITE(I,*) 'HH(I),' ',0.D0,' ',C(I,0)
   WRITE(I,*) 'TS(I,0)'
END DO

CLOSE(1)
CLOSE(2)

NPP=0
W(1,1)=1.D0

N=1
M=NPP+1
S=1

W(1,0)=1.D0
PP(1)=1
Q(1)=W(1,0)*W0
ST(1) = T50-273.15D0

DO WHILE (W(1,1)*X(IMAX)-WINF .GE. 0.1D-5)
   W(1,1)=W(1,0)-2*(C(IMAX,0),TS(IMAX,0))*DI

C --------------------------------------------------------
CALCULATION OF NEW GLOBAL VOLUME FRACTION OF SOLVENT

\[ GV(1,1) = \frac{(GV(1,0) \times W(1,0)) - (W(1,0) - W(1,1))}{W(1,1)} \]

---

IF (S .EQ. 1) SFLUX(S) = -RHOS*(W(1,1) - W(1,0))/DT

---

SAVING DATA OF CALCULATED THICKNESS

IF (N .EQ. M) THEN
    S = S + 1
    M = M + N
    PR(S) = N
    Q(S) = W(1,1)*W0
END IF

---

SOLVENT CONCENTRATION AND TEMPERATURE AT NEXT TIME STEP

---

C(I,0) & TS(I,0) ARE OLD VALUES
C(I,1) & TS(I,1) ARE NEW VALUES

DO I=2, IMAX-1

    S1 = X(I)/W(1,0)
    S2 = W(1,1) - W(1,0)
    S3 = (C(I+1,0) - C(I-1,0)) / (2.0*D0*DX)
    S4 = DI/(NG1*(W(1,0)**2))
    S5 = (ME1(C(I+1,0)) - ME1(C(I-1,0)))/(2.0*D0*DX)
    S6 = ME1(C(I,0))
    S7 = (C(I+1,0) - 2.0*C(I,0) + C(I-1,0))/(DX**2)
    S8 = (ME3(C(I+1,0),TS(I+1,0)) - ME3(C(I-1,0),TS(I-1,0)))/ (2.0*D0*DX)
    S9 = (TS(I+1,0) - TS(I-1,0)) / (2.0*D0*DX)
    S10 = ME3(C(I,0),TS(I,0))
    S11 = (TS(I+1,0) - 2.0*TS(I,0) + TS(I-1,0))/(DX**2)

    RHSM = (S1*S2*S3) + (S4*S5*S3) + (S6*S4*S7) + (S4*S8*S9) + (S10*S4*S11)
    C(I,1) = C(I,0) + RHSM

    H1 = DI/(NG2*(W(1,0)**2))
    H2 = (HE1(C(I+1,0),TS(I+1,0)) - HE1(C(I-1,0),TS(I-1,0)))/ (2.0*D0*DX)
    H3 = HE1(C(I,0),TS(I,0))
    H4 = (HE2(C(I+1,0),TS(I+1,0)) - HE2(C(I-1,0),TS(I-1,0)))/ (2.0*D0*DX)

---

78
H5 = HE2(C(I,0),TS(I,0))
H6 = NG3*H1
H7 = (GAMMA(TS(I+1,0))-GAMMA(TS(I-1,0)))/(2.0*DX)
H8 = GAMMA(TS(I,0))

RSHH = (S1*S2*S9)+(H1*H2*S3)+(H3*H1*S7)+(H1*H4*S9)+
       (H5*H1*S11)+H6*{(H7*S9)+(H8*S11)}
TS(I,1) = TS(I,0)+RSHH

END DO

DO I=2,IMAXG-1
    TG(I,1) = TG(I,0)+((NG7*DI/(DXP**2)))*
              (TG(I+1,0)-2.0*TG(I,0)+TG(I-1,0))
END DO

IG(1,1) = ((TINF/TS0)+(NG8/(2.0*DXP)))*(4.0*IG(2,1)-IG(3,1))/
         ((3.0*NG8/(2.0*DXP))+1.0)

K1 = 4.0*C(2,1)-C(3,1)
K2 = 4.0*TS(2,1)-TS(3,1)
K3 = 1.0/(2.0*W(1,1)*DX)
K4 = NG3*K3
K5 = NG6/(2.0*DXP)
K6 = -4.0*IG(IMAXG-1,1)+IG(IMAXG-2,1)

C FIRST GUESS
Y(1)=C(1,0)
Y(2)=TS(1,0)
ID=1
CALL NEWT(Y,NUM,CHECK)
CALL FUNCV(NUM,Y,F)
IF (CHECK) THEN
    WRITE(*,*) 'CONVERGENCE PROBLEMS.'
ENDIF

C(1,1) = Y(1)
TS(1,1) = Y(2)

IG(IMAX,1) = TS(1,1)

C

K7 = -4.D0*C(IMAX-1,1)+C(IMAX-2,1)
K8 = -4.D0*TS(IMAX-1,1)+TS(IMAX-2,1)
K9 = NG1*(W(1,1)-W(1,0))/DT
K10 = NG1
K11 = NG4
K12 = TINF/TS0
K13 = NG5

FIRST GUESSES

Y(1)=C(IMAX,0)
Y(2)=TS(IMAX,0)

ID=2
CALL NEWI(Y,NUM,CHECK)
CALL FUNCV(NUM,Y,F)
IF (CHECK) THEN
WRITE(*,*) 'CONVERGENCE PROBLEMS.'
ENDIF

C(IMAX,1) = Y(1)
TS(IMAX,1) = Y(2)

IF (N .EQ. M) THEN
S=S+1
M=M+NF
PP(S) = N
Q(S) = W(1,1)*W0
ST(S) = TS(IMAX,1)*TS0-273.D0
GVT(S) = GV(1,1)
SFLUX(S) = -RHOS*(W(1,1)-W(1,0))/DT
ENDIF

IF (NF*((N+1)/NF) .EQ. N+1) THEN
NPP=NPP+1
CALL OUTFN('CON',CHAN3((N+1)/NF),CFLAS,1)
CALL OUTFN('TEM',CHAN3((N+1)/NF),CFLAS,2)

END IF

80
WRITE (*,*) N+1,'',CHAN3((N+1)/NP)
DO I=1,IMAX
   HH(I)=W(I,1)*X(I)
WRITE (1,*) HH(I),'',NPP,'',C(I,1)
WRITE (2,*) HH(I),'',NPP,'',TS(I,1)
END DO
CLOSE (1)
CLOSE (2)
END IF

DO I=1,IMAX
   C(I,0)=C(I,1)
   TS(I,0)=TS(I,1)
END DO
DO I=1,IMAXG
   TG(I,0)=TG(I,1)
END DO

W(1,0) = W(1,1)
GV(1,0) = GV(1,1)
N=N+1
END DO

OPEN (14,FILE='THICKNESS.OUT')
DO J=1,S
   WRITE (14,*) J,'',(PF(J)-1)*DT*TSTAR,'',Q(J)
END DO
CLOSE (14)

OPEN (10,FILE='SURFACE-TEMPERATURE.OUT')
DO J=1,S
   WRITE (10,*) J,'',(PF(J)-1)*DT*TSTAR,'',ST(J)
END DO
CLOSE (10)

OPEN (12,FILE='GLOBAL VOLUME FRACTION.OUT')
DO J=1,S
   WRITE (12,*) J,'',(PF(J)-1)*DT*TSTAR,'',1.0D-GVi(J)
END DO
CLOSE (12)

OPEN (13,FILE='SOLVENT FLUX.OUT')
DO J=1,S
WRITE(13,*) J,' ',(FP(J)-1)*DT*ISTAR,' ',SFLUX(J)
END DO
CLOSE(13)

OPEN(9,FILE='RANK.CUT')
WRITE(9,55) 'N','TIME','THICKNESS','SUR-TEMP','GLOBAL-VOL','SFLUX'
DO J=1,S
WRITE(9,66) J, (FP(J)-1)*DT*TSTAR, Q(J), ST(J), 1.DO-GVI(J), SFLUX(J)
END DO
FORMAT(T5, ' ')
FORMAT(I3,T5,' ',10(E14.6, ' '))
CLOSE(9)
STOP
END

SUBROUTINES-----------------------------

SUBROUTINE OUTFN(IFR,FID,CFLAG,LUN)

USAGE
TYPE *,' ENTER FILE ID'
ACCEPT (2A), ID
CALL OUTFN(ID,'I',1) CREATES OUTPUT FILE I'ID'.DAT
TAKEN FROM NAZANIN IMANI

CHARACTER*3 FID
CHARACTER*1 CFLAG
CHARACTER*3 FPR
INTEGER LUN
CHARACTER*20 FLNAME

FLNAME = FPR // 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
C 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

C  GLOBALLY CONVERGENT MULTI-DIMENSIONAL NEWTON'S METHOD
SUBROUTINE NEWT(X,N,CHECK)
INTEGER N,NN,NP,MAXITS
LOGICAL CHECK
DOUBLE PRECISION X(N),FVEC,TOLF,TOLMIN,TOLX,STPMX
PARAMETER (NP=40,MAXITS=200,TOLF=1.D-4,TOLMIN=1.D-6,TOLX=1.D-7,
STPMX=100.D0)
COMMON /NEWTV/ FVEC(NP),NN
SAVE /NEWTV/
USES FDJAC,FMIN,LNSRCH,LUBKSBLUDCNP
INTEGER I,ITS,J,INDEX(NP)
DOUBLE PRECISION D,DEP,F,FOLD,STPMAX,SUM,TEMP,TEST,FJAC(NP,NP),
STPM(NP),P(NP),XOLD(NP),FMIN
EXTERNAL FMIN

N=N
F=FMIN(X)
TEST=0.D0
DO 11 I=1,N
   IF (ABS(FVEC(I)) .GT. TEST) TEST=ABS(FVEC(I))
11   CONTINUE
IF (TEST.LT..01D0*TOLF) THEN
   CHECK=.FALSE.
   RETURN
ENDIF
SUM=0.D0
DO 12 I=1,N
   SUM=SUM+X(I)**2
12  CONTINUE
STPMAX=STPMX*MAX(SQRT(SUM),DFLOAT(N))
DO 21 ITS=1,MAXITS
   CALL FDJAC(N,X,FVEC,NP,FJAC)
21   CONTINUE
DO 14 I=1,N
SUM=0.D0
DO 13 J=1,N
   SUM=SUM+JAC(J,I)*FVEC(J)
13 CONTINUE
G(I)=SUM
CONTINUE
DO 15 I=1,N
   XOLD(I)=X(I)
15 CONTINUE
FOLD=F
DO 16 I=1,N
   F(I)=-FVEC(I)
16 CONTINUE
CALL LUDCMP(FJAC,N,NP,INDX,D)
CALL LUBKSB(FJAC,N,NP,INDX,F)
CALL LNSRCH(N,XOLD,FOLD,G,P,X,F,STPMAX,CHECK,FMIN)
TEST=0.D0
DO 17 I=1,N
   IF (ABS(FVEC(I)).GT.TEST) TEST=ABS(FVEC(I))
17 CONTINUE
IF (TEST.LT.TOLF) THEN
   CHECK=.FALSE.
   RETURN
ENDIF
IF (CHECK) THEN
   TEST=0.D0
   DEN=MAX(F,.5D0*N)
   DO 18 I=1,N
      TEMP=ABS(G(I))*MAX(ABS(X(I)),1.D0)/DEN
   18 CONTINUE
   IF (TEMP.GT.TEST) TEST=TEMP
   IF (TEST.LT.TOLM) THEN
      CHECK=.TRUE.
   ELSE
      CHECK=.FALSE.
   ENDIF
   RETURN
ENDIF
TEST=0.D0
DO 19 I=1,N
   TEMP=(ABS(X(I)-XOLD(I)))/MAX(ABS(X(I)),1.D0)
19 CONTINUE
IF (TEMP.GT.TEST) TEST=TEMP
IF (TEST.LT.TOLX) RETURN
CONTINUE
PAUSE 'MAXITS EXCEEDED IN NEWT'
END

C TAKEN FROM NUMERICAL RECIPES

C FINITE-DIFFERENCE JACOBIAN

SUBROUTINE FDJAC(N,X,FVEC,NE,DF)
INTEGER N,NE,NMAX
DOUBLE PRECISION DF(NE,NE),FVEC(N),X(N),EPS
PARAMETER (NMAX=40,EPS=1.D-4)
USES FUNCV

INTEGER I,J
DOUBLE PRECISION H,TEMP,F(NMAX)

DO 12 J=1,N
   TEMP=X(J)
   H=EPS*ABS(TEMP)
   IF (H.EQ.0.D0) H=EPS
   X(J)=TEMP+H
   H=X(J)-TEMP
   CALL FUNCV(N,X,F)
   X(J)=TEMPP
   DO 11 I=1,N
      DF(I,J)=(F(I)-FVEC(I))/H
      11 CONTINUE
      12 CONTINUE
RETURN
END

C TAKEN FROM NUMERICAL RECIPES

C NORM OF A VECTOR FUNCTION

FUNCTION FMIN(X)
INTEGER N,NE
DOUBLE PRECISION FMIN,X(*),FVEC
PARAMETER (NE=40)
COMMON /NEWTV/ FVEC(NE),N
SAVE /NEWTV/
USES FUNCV

INTEGER I
DOUBLE PRECISION SUM
CALL FUNCV(N,X,FVEC)
SUM=0.D0
DO 11 I=1,N
   SUM=SUM+FVEC(I)**2
      11 CONTINUE
FMIN=0.5D0*SUM
RETURN
END

C TAKEN FROM NUMERICAL RECIPES

C SEARCH ALONG A LINE

SUBROUTINE LNSRCH (N, X0LE, FOLD, G, P, X, F, STPMAX, CHECK, FUNC)
INTEGER N
LOGICAL CHECK
DOUBLE PRECISION F, FOLD, STPMAX, G(N), P(N), X(N), XOLD(N), FUNC, ALF,
* TOLX
PARAMETER (ALF=1.D-4, TOLX=1.D-7)
EXTERNAL FUNC
CU USES FUNC
INTEGER I
DOUBLE PRECISION A, ALAM, ALAM2, ALAMIN, B, DISC, F2, RHS1, RHS2, SLOPE,
* SUM, TEMP, TEST, TMPLAM
CHECK=.FALSE.
SUM=0.D0
DO 11 I=1, N
  SUM=SUM+P(I)*P(I)
11 CONTINUE
SUM=SQR(T(SUM))
IF (SUM.GT.STPMAX) THEN
  DO 12 I=1, N
    P(I)=P(I)*STPMAX/SUM
12 CONTINUE
ENDIF
SLOPE=0.D0
DO 13 I=1, N
  SLOPE=SLOPE+G(I)*P(I)
13 CONTINUE
IF (SLOPE.GE.0.D0) PAUSE 'ROUNDOFF PROBLEM IN LNSRCH'
TEST=0.D0
DO 14 I=1, N
  TEMP=ABS(P(I))/MAX(ABS(XOLD(I)), 1.D0)
  IF (TEMP.GT.TEST) TEST=TEMP
14 CONTINUE
ALAM=TOLX/TEST
ALAM=1.D0
CONTINUE
DO 15 I=1, N
  X(I)=XOLD(I)+ALAM*P(I)
15 CONTINUE
F=FUNC(X)
IF (ALAM.LT.ALAMIN) THEN
DO 16 I=1,N
   X(I)=XOLD(I)
   CONTINUE
   CHECK=.TRUE.
   RETURN
ELSE IF (F.LE.FOLD+ALF*ALAM*SLOPE) THEN
   RETURN
ELSE
   IF (ALAM.EQ.1.D0) THEN
      TMFLAM=-SLOPE/(2.D0*(F-FOLD-SLOPE))
   ELSE
      RHS1=F-FOLD-ALAM*SLOPE
      RHS2=F2-FOLD-ALAM2*SLOPE
      A=(RHS1/ALAM**2-RHS2/ALAM2**2)/(ALAM-ALAM2)
      B=(-ALAM2*RHS1/ALAM**2+ALAM*RHS2/ALAM2**2)/(ALAM-ALAM2)
      IF (A.EQ.0.D0) THEN
         TMFLAM=-SLOPE/(2.D0*B)
      ELSE
         DISC=B*B-3.D0*A*SLOPE
         IF (DISC.LT.0.D0) THEN
            TMFLAM=.5D0*ALAM
         ELSE IF (B.LE.0.D0) THEN
            TMFLAM=(-B+SQRT(DIS))/(3.D0*A)
         ELSE
            TMFLAM=-SLOPE/(B+SQRT(DIS))
         ENDIF
      ENDIF
      IF (TMFLAM.GT..5D0*ALAM) TMFLAM=.5D0*ALAM
   ENDIF
   ALAM2=ALAM
   F2=F
   ALAM=MAX(TMFLAM,.1D0*ALAM)
GOTO 1
END
C TAKEN FROM NUMERICAL RECIPES
C
C LINEAR EQUATION SOLUTION, BACKSUBSTITUTION
SUBROUTINE LUBKSB(A,N,NP,INDEX,B)
INTEGER N,NP,INDEX(N)
DOUBLE PRECISION A(NP,NP),B(N)
INTEGER I,II,J,LL
DO 12 I=1,N
   DO 12 12 I=1,N
Li=INDX(I)
SUM = B(LL)
B(LL) = B(I)
IF (II NE.0) THEN
   DO 11 J=II, I-1
      SUM = SUM - A(I, J) * B(J)
   11 CONTINUE
ELSE IF (SUM .NE. 0.) THEN
      II = I
END IF
B(I) = SUM
12 CONTINUE
DO 14 I=N, 1, -1
   SUM = B(I)
   DO 13 J=I+1, N
      SUM = SUM - A(I, J) * B(J)
   13 CONTINUE
B(I) = SUM / A(I, I)
14 CONTINUE
RETURN
END

C TAKEN FROM NUMERICAL RECIPES

C LINEAR EQUATION SOLUTION, LU DECOMPOSITION
SUBROUTINE LUDCMP(A, N, NP, INDX, D)
INTEGER N, NP, INDX(N), NMAX
DOUBLE PRECISION D, A(NP, NP), TINY
PARAMETER (NMAX=500, TINY=1.D-20)
INTEGER I, IMAX, J, K
DO 20 J=1, N
   D(J) = 1.D0
   AMAX = 0.D0
   DO 11 J=1, N
      IF (ABS(A(I, J)) .GT. AMAX) AMAX = ABS(A(I, J))
   11 CONTINUE
   IF (AMAX .EQ. 0.D0) PAUSE 'SINGULAR MATRIX IN LUDCMP'
   VV(I) = 1.D0 / AMAX
20 CONTINUE
DO 19 J=1, N
   DO 14 I=1, J-1
      SUM = A(I, J)
   14 CONTINUE
   DO 13 K=1, I-1
      SUM = SUM - A(I, K) * A(K, J)
   13 CONTINUE
   A(I, J) = SUM
19 CONTINUE
CONTINUE
AAMAX=0.DO
DO 16 I=J,N
   SUM=A(I,J)
   DO 15 K=1,J-1
      SUM=SUM-A(I,K)*A(K,J)
   CONTINUE
   A(I,J)=SUM
   DUM=VV(I)*ABS(SUM)
   IF (DUM.GE.AAMAX) THEN
      IMAX=I
      AAMAX=DUM
   ENDIF
CONTINUE
IF (J.NE.IMAX) THEN
   DO 17 K=1,N
      DUM=A(IMAX,K)
      A(IMAX,K)=A(J,K)
      A(J,K)=DUM
   CONTINUE
   D=-D
   VV(IMAX)=VV(J)
ENDIF
INDEX(J)=IMAX
IF(A(J,J).EQ.0.DO) A(J,J)=TINY
IF(J.NE.N) THEN
   DUM=1.DO/A(J,J)
   DO 18 I=J+1,N
      A(I,J)=A(I,J)*DUM
   CONTINUE
END
CONTINUE
RETURN
END

SUBROUTINE FUNCV(N,X,F)
  INTEGER N
  COMMON /FUN8/ K1,K2,K3,K4,K5,K6,K7,K8,K9,K10,K11,K12,K13
  COMMON /FUN9/ ID
  EXTERNAL ME1,ME2,ME3,HE1,HE2,GAMMA,P
  DOUBLE PRECISION ME1,ME2,ME3,HE1,HE2,GAMMA,P
  DOUBLE PRECISION K1,K2,K3,K4,K5,K6,K7,K8
  DOUBLE PRECISION K9,K10,K11,K12,K13

89
INTEGER ID
DOUBLE PRECISION X(N),F(N)
IF (ID.EQ.1) THEN
  F(1) = (1.0 - 2.0 * 0.35*D0*X(1)) * (-3.0*D0*X(1) + K1) +
        1
        ME2(X(1),X(2)) * (-3.0*D0*X(2) + K2)
  F(2) = -HE1(X(1),X(2)) * K3 * (-3.0*D0*X(1) + K1) -
        1
        HE2(X(1),X(2)) * K3 * (-3.0*D0*X(2) + K2) -
        1
        K4*GAMMA(X(2)) * (-3.0*D0*X(2) + K2) +
        1
        K5 * (3.0*D0*X(2) + K6)
END IF
IF (ID.EQ.2) THEN
  F(1) = -ME1(X(1)) * K3 * (3.0*D0*X(1) + K7) -
        1
        ME3(X(1),X(2)) * K3 * (3.0*D0*X(2) + K2) - K3*X(1) - K10*F(X(1),X(2))
  F(2) = -HE1(X(1),X(2)) * K3 * (3.0*D0*X(1) + K7) -
        1
        HE2(X(1),X(2)) * K3 * (3.0*D0*X(2) + K8) -
        1
        GAMMA(X(2)) * K4 * (3.0*D0*X(2) + K8) -
        1
        K11 * (X(2) - K12) - K13*F(X(1),X(2))
END IF
RETURN
END

FUNCTION P_PHI,THETA)

FUNCTION ME1_PHI)

IMPLICIT NONE
COMMON /FUN1/ HVMOULAR
COMMON /FUN2/ R
COMMON /FUN5/ TS0
COMMON /FUN6/ TBOILING
DOUBLE PRECISION P,PHI,THETA,HVMOULAR,R,TS0,TBOILING
P = EXP(- (HVMOULAR/R) * ((1.0/(TS0*THETA)) - (1.0/TBOILING))) *
    1
    EXP(DLOG(PHI) + (1.0 - PHI) + 0.35*D0*(((1.0 - PHI)**2)))
RETURN
END

FUNCTION ME1_PHI)

IMPLICIT NONE
DOUBLE PRECISION ME1, PHI
ME1 = (1.0-Phi)*(1.0-2.0*0.35D0*Phi)
RETURN
END

FUNCTION ME2(Phi, Theta)
IMPLICIT NONE
COMMON /FUN2/ R
COMMON /FUN3/ BI
DOUBLE PRECISION ME2, Phi, Theta, R, BI
ME2 = (Phi/Theta)*((BI/R)+DLOG(Phi)+1.0D0+0.35D0*(1.0D0-2.0D0*Phi))
RETURN
END

FUNCTION ME3(Phi, Theta)
IMPLICIT NONE
COMMON /FUN2/ R
COMMON /FUN3/ BI
DOUBLE PRECISION ME3, Phi, Theta, R, BI
ME3 = (Phi*(1.0D0-Phi)/Theta)*
1/(BI/R)+DLOG(Phi)+1.0D0+0.35D0*(1.0D0-2.0D0*Phi))
RETURN
END

FUNCTION HE1(Phi, Theta)
IMPLICIT NONE
COMMON /FUN2/ R
COMMON /FUN3/ BI
COMMON /FUN4/ AA
COMMON /FUN5/ TS0
DOUBLE PRECISION HE1, Phi, Theta, R, BI, AA, TS0
HE1 = (1.0D0-Phi)*(1.0D0-2.0D0*0.35D0*Phi)*
1/(AA/(R*TS0))+(BI*(Theta-1.0D0)/R)+
1/Theta*(DLOG(Phi)+1.0D0+0.35D0*(1.0D0-2.0D0*Phi))
RETURN
END

FUNCTION HE2(Phi, Theta)
IMPLICIT NONE
COMMON /FUN2/ R
COMMON /FUN3/ BI
COMMON /FUN4/ AA
COMMON /FUN5/ TS0
DOUBLE PRECISION HE2, Phi, Theta, R, BI, AA, TS0
HE2 = (PHI*(1.0D0-PHI)/THETA)*

1  ((AA/(R*T50))+(BT*(THETA-1.0D0)/R)+
1  THETA*(DLOG(PHI)+1.0D0+0.35D0*(1.0D0-2.0D0*PHI)))*
1  ((BT/R)+DLOG(PHI)+1.0D0+0.35D0*(1.0D0-2.0D0*PHI))

RETURN
END

FUNCTION GAMMA(THETA)
IMPLICIT NONE
COMMON /FUNS/ T50
COMMON /FUN6/ TBOILING
COMMON /FUN7/ TCritical
DOUBLE PRECISION GAMMA,THETA,TBOILING,TCritical,T50
GAMMA = (TBOILING***(6.0D0/5.0D0)/
1  (64.16D0*(TCritical**(1.0D0/6.0D0))))*
1  ((1.0D0-(THETA+T50/TCritical))**0.96D0)/
1  ((THETA+T50/TCritical)**(1.0D0/6.0D0))
RETURN
END
Figure F.1: Concentration profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 298.15$ K, $V_\infty = 1.2$ m/s. a) $\Delta \xi = 0.1$, b) $\Delta \xi = 0.01$, c) $\Delta \xi = 0.001$. $\phi$, $t^*$ and $\xi$ are volume fraction of the solvent, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 
Figure F.2: Temperature profiles at the onset of evaporation of the solvent. $T_0$, $T_\infty = 298.15$ K, $V_\infty = 1.2$ m/s. a) $\Delta \xi = 0.1$, b) $\Delta \xi = 0.01$, c) $\Delta \xi = 0.001$. $\theta$, $t^*$ and $\xi$ are dimensionless temperature, dimensionless time and dimensionless length. $\xi = 0$ shows the substrate and $\xi = 1$ represents the evaporating surface at $t^* = 0$. 