

MODELLING THE FORMATION OF BLISTERS

A DISSERTATION SUBMITTED TO THE UNIVERSITY OF MANCHESTER
FOR THE DEGREE OF MASTER OF SCIENCE
IN THE FACULTY OF ENGINEERING AND PHYSICAL SCIENCES

2015

Gareth Wyn Molyneux
School of Mathematics

Contents

Abstract	6
Declaration	7
Intellectual Property Statement	8
Acknowledgements	9
1 Introduction	10
2 Methodology	13
2.1 Chemistry and Diffusion	13
2.1.1 Chemical Reactions and Law of Mass Actions	13
2.1.2 Fick's Laws of Diffusion and Reaction-Diffusion System	15
2.2 Continuum Mechanics	16
2.2.1 Displacement and Infinitesimal Strain Tensor	17
2.2.2 Deformation Gradient and the Constitutive Equations	19
2.2.3 Equations of Motion and Equilibrium	20
2.3 Coupling mechanics and Diffusion	20
3 Chemical induced stresses	23
3.1 " <i>Interaction Between Diffusion and Chemical Stresses</i> " by F.Yang . .	23
3.1.1 Governing Equation of Mechanical Equilibrium	24
3.1.2 Diffusion Equation	25
3.1.3 Correlation between normal stress and surface displacement . .	26
3.1.4 Development of Chemical stresses in a thin plate.	27

3.1.5	Steady State chemical stresses with constant surface concentrations.	28
3.1.6	Evolution of chemical stresses.	29
3.1.7	Summary	37
4	Polymer Swelling	43
4.1	Conservation of Mass and Balance of Linear and Angular Momentum. .	44
4.2	Balance of internal energy	46
4.3	Temperature Evolution	47
4.4	Helmholtz Energy	48
4.5	Diffusion and Heat conduction	49
4.6	Reformulation to 1 dimension.	50
4.7	Governing Equations	54
4.8	Boundary Conditions, Initial Conditions and Code Implementation . .	56
4.9	Polymer Swelling Results	64
4.10	Summary	65
5	Conclusion	67
A	Analytic Derivatives	71
B	Dimensional Analysis	72
B.1	Variable and Parameter dimensions	72
C	Code	74
C.1	Chapter 4: Constant Surface Concentration	74
C.2	Chapter 4: Fixed amount of solute deposited initially	76
C.3	Chapter 5: Case 4	78
	Bibliography	93

List of Tables

4.1 Table listing all the parameters used in the polymer swelling model by
Wilmer and Bargmann [53] 58

List of Figures

3.1	Concentration Profile for $\tilde{\alpha} = 0.01$	32
3.2	Concentration Profile for $\tilde{\alpha} = 0.1$	32
3.3	Concentration Profile for $\tilde{\alpha} = 1$	32
3.4	This is the evolution of the hydrostatic stress in a thin plate with a given constant surface concentration, with value of $\tilde{\alpha} = 0.1$	33
3.5	Concentration Profile for $\tilde{\alpha} = 0.01$ and an initially deposited solute. . .	35
3.6	Concentration Profile for $\tilde{\alpha} = 0.10$ and an initially deposited solute. . .	35
3.7	Concentration Profile for $\tilde{\alpha} = 1$ and an initially deposited solute. . . .	35
3.8	This is the evolution of the hydrostatic stress in a thin plate with a fixed amount of surface concentration initially deposited, with $\tilde{\alpha} = 0.1$. . .	37
4.1	The geometry of the polymer is assumed to have a cuboid shape, with the boundary conditions applied on the small face, with the concentra- tion diffusing in the x direction	51
4.2	Plot of \tilde{C} against the position coordinate, \tilde{X}	63
4.3	Plot of $\tilde{\theta}$ against the undeformed position, \tilde{X}	63
4.4	Plot of \tilde{x} against the undeformed position coordinate, \tilde{X}	63

Abstract

In this dissertation an investigation of the coupling between thermoelasticity and chemical diffusion was undertaken to develop a basis of understanding for the formation of uranium hydride blisters on a bed of uranium. Two research papers that couple deformation and diffusion of a chemical were investigated, namely the research paper regarding chemical-induced stresses in metals by F.Yang, "*Interaction between diffusion and chemical stresses*", and a detailed view into the numerical modelling of Case II diffusion in polymeric glasses, by J.Wilmers and S.Bargmann, "*A continuum mechanical model for the description of solvent induced swelling in polymeric glasses*". A review of Fick's laws of diffusion as well as continuum mechanics was undertaken, with a brief overview of the numerical solution technique of finite differencing. Code was developed to reproduce results given in Yang's chemical stresses paper, and a one-dimensional reformulation of the governing equations present in the polymer swelling paper was undertaken. Gradually constructing code to solve these reformulated one dimensional equations was done by introducing forcing terms and testing against analytic solutions, although even after nondimensionalizing these equations the numerical solutions were unsatisfactory. Analysis of how these examples of coupling thermoelasticity and diffusion can be applied to our blistering problems was also undertaken.

Declaration

No portion of the work referred to in the dissertation has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Intellectual Property Statement

- i. The author of this dissertation (including any appendices and/or schedules to this dissertation) owns certain copyright or related rights in it (the “Copyright”) and s/he has given The University of Manchester certain rights to use such Copyright, including for administrative purposes.
- ii. Copies of this dissertation, either in full or in extracts and whether in hard or electronic copy, may be made **only** in accordance with the Copyright, Designs and Patents Act 1988 (as amended) and regulations issued under it or, where appropriate, in accordance with licensing agreements which the University has entered into. This page must form part of any such copies made.
- iii. The ownership of certain Copyright, patents, designs, trade marks and other intellectual property (the “Intellectual Property”) and any reproductions of copyright works in the dissertation, for example graphs and tables (“Reproductions”), which may be described in this dissertation, may not be owned by the author and may be owned by third parties. Such Intellectual Property and Reproductions cannot and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property and/or Reproductions.
- iv. Further information on the conditions under which disclosure, publication and commercialisation of this dissertation, the Copyright and any Intellectual Property and/or Reproductions described in it may take place is available in the University IP Policy (see <http://documents.manchester.ac.uk/DocuInfo.aspx?DocID=487>), in any relevant Dissertation restriction declarations deposited in the University Library, The University Library’s regulations (see <http://www.manchester.ac.uk/library/aboutus/regulations>) and in The University’s Guidance on Presentation of Dissertations.

Acknowledgements

First and foremost I would like to thank my parents and my family for their everlasting support over these past summer months.

Secondly I would like to thank AWE and Phil Monks for the sponsorship and opportunity to tackle this interesting problem at hand.

Last but not least, I would like to extend my sincerest thanks and appreciation to Dr. Andrew Hazel for his patience, help and continuous support for the duration of this dissertation.

Chapter 1

Introduction

The aim for this research project is to formulate a basis of understanding needed in order to construct a reliable model that predicts the formation of Uranium Hydride blisters and any key properties which dictate the growth of these blisters. The Uranium Hydride blisters are formed when a bed of Uranium is exposed to a gaseous form of Hydrogen. Initially, the gaseous hydrogen to which the Uranium is exposed to diffuses into the surface. Once the concentrations of the hydrogen reach a critical value, this hydride corrosion product precipitates beneath the surface [43] and forms a product of Uranium Hydride. This chemical process produces a force which exerts on the surface due to the volume expansion at the surface - which occurs after the formation of the product. As the corrosion reaction proceeds, this precipitate continues to grow until it ruptures the surface and forms break-through sites. A detailed view into the very initial stages of hydride formation on metals was undertaken by Benamar et al.[6], where they discovered that the initial development of hydrides on hydrogen exposed metals displayed complex behaviour with two possible surface-associated stages. One of the possible hydride precipitates was identified to be a dense pattern of tiny blisters or spots, which form immediately after the metal (which in this given paper was gadolinium) is exposed to hydrogen, ceasing further notable development in size. The other type of hydride precipitation occurred following this previous stage; given a certain amount of time, development of "growth centres" of hydriding areas spread over the surface, which would eventually lead to a massive hydriding stage. Although initially our interests lie on the formation of the uranium hydride blisters, we will be interested eventually in the main causes as to what properties leads to the break out

of the blisters, rupturing the metal surface. With the exposure to hydrogen, initially it is a matter of diffusion process which further leads on to a reaction - diffusion system. Therefore an understanding of the basics of reaction-diffusion systems proves to be crucial; by first looking at the basics present in reaction-diffusion systems, we will then proceed to see how these reaction-diffusion systems are formulated in the models we are examining.

By taking a mechanical viewpoint of the problem at hand, as the chemical product is formed, the volume expansion causes compressive stress in the surrounding material of the surface. Given the mechanics involved in the formation of the blister, it would be wise to summarize basic results and concepts which are readily available in the literature regarding continuum mechanics and thermoelasticity. We will look at two examples in the research of current papers which investigate coupling between thermoelasticity and diffusion and the properties which are present. Both of the papers have a common modeling approach of coupling thermomechanics and diffusion. Therefore a detailed review into these models consisting important parameters, constitutive laws and key properties which govern both of the models underlining key differences as well as similarities will prove beneficial to helping us understand the blister forming problem at hand.

We will first aim to reproduce the results present in F.Yang's paper, *Interaction between diffusion and chemical stresses*, [54] and determine key equations which play an integral part in modelling the diffusion of a chemical through a metal material. In doing so, we will hope to produce code which enables us to easily modify the present parameters, also giving us a solid foundation on both understanding the problem at hand and a crucial first step into creating code which we hope to use to solve our metal blistering problem.

The second research paper we review investigates polymers which swell due to the presence of solvents; the paper written by J.Wilmers, S.Bargmann [53] "*A continuum mechanical model for the description of solvent induced swelling in polymeric glasses*", is the paper we will be looking at which couples the deformation mechanics and the diffusion of the solvent, which travels along the polymer causing it to swell. The diffusion observed in polymers do not follow the usual Fickian laws[17] of diffusion, which are often named Case I diffusion. Case II diffusion is common in the diffusion of solvents

through polymers and numerical modelling of Case II diffusion in polymeric glasses is the focus in this polymer swelling paper, where Case II diffusion is characterised by a strong coupling between the diffusion and deformation and is heavily dependent on the temperature. Thus, a general continuum mechanical framework governing a three way coupling of thermomechanics and diffusion is adapted to Case II diffusion, where equations governing the evolution of the deformed system (which describes the swelling), the evolution of the temperature and the diffusion are formulated. For this polymer swelling paper, we will be reformulating the governing equations to one dimension and hope to produce code which numerically solves these reformulated one dimensional equations which couple the concentration, temperature and deformation of the polymer.

Chapter 2

Methodology

In this chapter we will begin by describing reaction-diffusion systems as this will be used in reference to the hydrogen diffusion through the metal (in this case the Uranium) to cause a deformation of the material surface. Given we are dealing with deformations - and at that small deformations - also we describe key concepts present in the work of thermoelasticity theory and some basic results. Eventually we will relate these two fields by first observing research cases which couple thermomechanics and diffusion, in both the polymer swelling paper by J.Wilmers,S.Bargmann (2015)[53], and the general interaction between diffusion and chemical stresses by F.Yang (2005)[54].

2.1 Chemistry and Diffusion

2.1.1 Chemical Reactions and Law of Mass Actions

Basic reaction-diffusion theory and its equations are present in even the most simplest of chemical reactions. We begin by supposing a straightforward chemical process, where a chemical, A , were to mix with a chemical B , to produce a product, C . This results in the following process



For this type of process, with each chemical we would have to consider the source terms and how each chemical interacts with each other; for example, in some cases the product C would react with the reactants A or B to produce another compound or produce more of one of the three existing chemicals. For now we assume that the

product does not react with the reactants leaving with the linear reaction above in equation (2.1). The first step in formulating mathematical equations which describe these types of chemical reactions is by making the use of the law of mass actions. The law of mass actions is not necessary a law but more of a mathematical model [32]. Considering the simple irreversible reaction in equation (2.1), suppose the reaction rate of this particular chemical reaction is given by k , that is



The assumption we make here is the change of product in time corresponds to the number of collisions between molecules A and B , multiplied by the probability that a reaction happens upon collision of these two chemicals. Let a , b and c denote the concentrations of the chemicals A , B and C respectively, and let Δc denote the change of c - the concentration of C - in time. The change of concentration of the chemical C is defined as

$$\Delta c = abk\Delta t, \quad (2.3)$$

where Δt denotes the change in time. By taking the limit of $\Delta t \rightarrow 0$, we obtain the following ordinary differential equation (ODE)[51] for the concentration c ;

$$\frac{dc}{dt} = kab. \quad (2.4)$$

Consider introducing a reversible reaction, with forward reaction rates of k_+ , and backward reaction rates of k_- for the same chemical reaction given above in (2.2)



By making use of the law of mass actions, this chemical reaction leads to a system of ordinary differential equations (ODEs) given by

$$\frac{dc}{dt} = k_+ab - k_-c, \quad \frac{da}{dt} = k_-c - k_+ab, \quad \frac{db}{dt} = k_-c - k_+ab. \quad (2.6)$$

Given that we are interested in the diffusion of hydrogen through a metal (in this case Uranium) causing a reaction, we must look at how to go about formulating a general reaction-diffusion system.

2.1.2 Fick's Laws of Diffusion and Reaction-Diffusion System

The governing laws of diffusion were first formulated by Adolf Fick (1829-1901), in which the concept of diffusion was introduced in his paper "*Ueber Diffusion*"[17] ("*On liquid diffusion*"). Here Fick formulates an equation which relates the diffusive flux to the concentration, which is often named Fick's first law of diffusion. Suppose the concentration of the diffusing chemical is denoted by $u = u(\mathbf{x}, t)$, where the concentration is a function of space, \mathbf{x} , and time, t . Let \mathbf{J} denote the diffusion flux vector, and $\nabla = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z})$, denotes the grad or gradient operator[48] in terms of Cartesian coordinates. Fick's first law of diffusion is given by the following relation,

$$\mathbf{J} = -D(u, \mathbf{x})\nabla u(\mathbf{x}, t). \quad (2.7)$$

Here, $D(u, \mathbf{x})$ represents the diffusion coefficient or diffusivity of the concentration and can depend on the concentration itself as well as space - this is the leading term that dictates the rate of diffusion. The presence of the minus sign on the right hand side represents that the solute or diffusing chemical moves from an area with a high concentration of solute to a location with low concentration of solute, which is being driven by the concentration gradient, ∇u .

Having formally defined Fick's first law, with the use of Fick's second law, we can define the Diffusion equation which will be crucial in our understanding of the problem. Fick's second law is derived from both Fick's first law and the law of mass conservation. Consider a differential form of the continuity equation or the law of mass conservation[40],

$$\frac{\partial u}{\partial t} + \nabla \cdot \mathbf{J} = 0. \quad (2.8)$$

By making use of Fick's first law above and moving the divergence term to the right hand side, we obtain the following diffusion equation

$$\frac{\partial u}{\partial t} = \nabla \cdot [D(\mathbf{x}, u)\nabla u(\mathbf{x}, t)]. \quad (2.9)$$

After introduction of a reaction term, $f(\mathbf{x}, u, \nabla u)$, we obtain a reaction-diffusion system. Hence, a general reaction-diffusion system is of the form

$$\frac{\partial u}{\partial t} = \nabla \cdot [D(\mathbf{x}, u)\nabla u(\mathbf{x}, t)] + f(\mathbf{x}, u, \nabla u). \quad (2.10)$$

In many cases the diffusion coefficient matrix is independent of both space and concentration, leading to a simpler model of the form

$$\frac{\partial u}{\partial t} = D\nabla^2 u(\mathbf{x}, t) + f(\mathbf{x}, u, \nabla u). \quad (2.11)$$

Reaction terms tend to include processes which affect the system in some way. In our case it can be used to represent chemical reaction, but in systems which regard populations for example, the reaction term can include the affects of birth, death or diseases, including parameters which dictate the rate of these. Recall the chemical reaction in the system given by equation (2.5). If we now consider the case of chemical A , with corresponding concentration a , the source term present in the reaction-diffusion equation would give

$$f(\mathbf{x}, a, b, c) = k_-c - k_+ab, \quad (2.12)$$

which would lead to the system (assuming the diffusion coefficient is constant or independent of space, \mathbf{x})

$$\frac{\partial a}{\partial t} = D\nabla^2 a + k_-c - k_+ab. \quad (2.13)$$

Analytic solutions for a system such as equation (2.10) are difficult to come by, but there are specific examples which can lead to analytical solutions - many cases require the source term, $f(t, \mathbf{x}, u, \nabla u)$ to be zero, reducing it to simply the heat equation[49]. One way to solve such equations is numerically via the finite difference method[33], which will be discussed in greater detail later. Now having discussed laws of diffusion as well as how they can be used in chemical systems, we will look into the Continuum mechanics present in such a system, as well as methods of coupling both diffusion and mechanics.

2.2 Continuum Mechanics

Continuum mechanics is a branch of mechanics concerned with the analysis of the kinematics and mechanical behaviour of materials as one whole continuous mass as opposed to classical mechanics which is mainly concerned with the discrete particles of a body. Given that the surface of the uranium bed undergoes deformation and forms blisters, we shall begin with defining deformation, and the definitions needed. There are two classic descriptions in order to measure the position of a material point of a

body, the Lagrangian description and the Eulerian description. Suppose a body exists originally at the original configuration Ω_0 with volume, V_0 and a surface S_0 . At a later time, t , the same body now occupies a different region of space given by the current configuration, Ω_t with volume V_t and surface S_t .

Haupt(2000a)[25] defines a reference, or original position by the vector \mathbf{r} which is defined in our original or undeformed configuration, Ω_0 . At a given time, t , this position now occupies a current position defined by the vector \mathbf{R} in the current configuration, Ω_t . If we were to treat the current position, \mathbf{R} as a function of the original position and time (t) that is, of the form

$$\mathbf{R} = \mathbf{R}(\mathbf{r}, t), \quad (2.14)$$

this would be considered a Lagrangian or material description, and in this description we follow the evolution of individual material particles with time, where this particular viewpoint would be used in classical particle mechanics due to the interest in the behaviour of each individual particle. Alternatively, we could describe the undeformed or original position of a material point as a function of its current position and time, given as

$$\mathbf{r} = \mathbf{r}(\mathbf{R}, t). \quad (2.15)$$

This would be considered as an Eulerian or spatial description, where this method of description is more commonplace in fields such as fluid mechanics, where the original location of individual fluid particles is not of interest. In many models, the assumption of linear elasticity is common.

In the following sections we introduce the fundamentals of linear elasticity, which are needed in order to describe a linear elastic body [16]; the displacement vector, strain tensor, deformation gradient and stress tensor fields are introduced to define a linear elastic body, which in turn satisfies many strain-displacement relations. The introduction of constitutive relations as well as equations of motions help further describe the model, where the constitutive relations play a key role.

2.2.1 Displacement and Infinitesimal Strain Tensor

Given descriptions of both current and original material particle descriptions in the previous section, \mathbf{R} and \mathbf{r} respectively, we define the *displacement* vector as the change

in position of a material point within the body between the original configuration, Ω_0 and current configuration, Ω_t as

$$\mathbf{u} = \mathbf{R} - \mathbf{r}. \quad (2.16)$$

Note that this definition of the displacement can be written as a function of either the deformed or undeformed configurations, (Haupt(2000b)[26]), for example if we were to consider the displacement as a function in the Lagrangian viewpoint only, we obtain the following

$$\mathbf{u}(\mathbf{r}, t) = \mathbf{R}(\mathbf{r}, t) - \mathbf{r}, \quad (2.17)$$

where $\mathbf{r} = (x_1, x_2, x_3)$. Given a body of continuous material, the shape of this material body will change if any material points are displaced relative to each other. If all material points of a body are displaced to another location but the distances between individual material points remain constant relative to each other, then this body will simply have undergone a rigid body motion, that is, no deformation has taken place and the body has simply moved from one location to another. Deformation thus only occurs when particles of a continuous substance move so that the distances between particles are changed. Once given a displacement of a particle by \mathbf{u} - with each coordinate given by u_i , $i = 1, 2, 3$ - Boley and Weiner [7](1960, Chapter 1, Section 1.3) defined the infinitesimal strain tensor with components ε_{ij} as

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right), \quad (2.18)$$

where x_i are given by the original configuration of the particles, $\mathbf{r} = (x_1, x_2, x_3)$. This can be alternatively written as

$$\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}), \quad (2.19)$$

where $u_{i,j}$ denotes the derivative of the i th component of the displacement with respect to the j th undeformed coordinate, x_j , and hence $u_{i,j} = \frac{\partial u_i}{\partial x_j}$.

This strain-stress tensor is a measure of deformation in a continuous body, which represents the displacement between particles in the body relative to the original configuration. Although this definition of the infinitesimal strain tensor is often conveniently calculated, the main disadvantage of this method of measuring deformation are the restrictions it imposes on the constitutive equations governing the material model; it is only useful when there exist small deformations in the material. Given

that the problem we have at hand consists of small deformations, it would be wise to assume linear elasticity for the time being.

2.2.2 Deformation Gradient and the Constitutive Equations

With the above definitions for the strain tensor as well as displacement vector, let us now define the deformation gradient. The deformation gradient given by \mathbf{F} is the derivative of each component of the deformed coordinate vector, \mathbf{R} , with respect to each component of the reference vector, \mathbf{r} . Let us denote the deformed coordinates by X_i , meanwhile the undeformed or original coordinates are defined by x_i , where $i = 1, 2, 3$, and the original coordinates are Cartesian coordinates. The deformation gradient is a tensor with each component of the tensor defined as

$$F_{i,j} = \frac{\partial X_i}{\partial x_j}. \quad (2.20)$$

This deformation gradient is an important measure of how the continuum body is deformed, thus plays an integral part in the deformation of continuum bodies. Earlier we assumed the materials we are concerned with are linearly elastic, now let us assume it is also isotropic. For such materials in linear thermoelasticity, the infinitesimal strain tensor, ε_{ij} is related to the stress tensor, σ_{ij} by the following governing constitutive equation [5]

$$\varepsilon_{ij} = \frac{1+\nu}{E}\sigma_{ij} - \frac{\nu}{E}\sigma_{jj}\delta_{ij} + \alpha\Delta T\delta_{ij}. \quad (2.21)$$

Note that the presence of the repeated subscript, σ_{jj} actually represents $\sigma_{jj} = \sigma_{11} + \sigma_{22} + \sigma_{33}$, as we are following Einstein summation convention[44]. The stress tensor, or Cauchy stress tensor $\langle\sigma\rangle$ consists of 9 components (in a 3 dimensional basis) σ_{ij} , where the j th component of the traction vector is acting on the body with a normal component in the i th direction.[28]. The other terms in the governing equation are given by the Kronecker delta[50], δ_{ij} , the elastic or Young's modulus, E , which measures the elastic modulus and thus how elastic a material is. We also have the Poisson ratio given by ν , which is the fraction of expansion divided by the fraction of compression, as well as α , the isotropic coefficient of thermal expansion. Finally we have ΔT , which represents the change in temperature. Equation (2.12) can be manipulated to give us the stress in terms of the infinitesimal strain tensor (the inverse relation),

$$\sigma_{ij} = \frac{E}{1+\nu} \left(\varepsilon_{ij} + \frac{\nu}{1-2\nu} \varepsilon_{kk} \delta_{ij} \right) - \frac{E}{1-2\nu} \alpha \Delta T \delta_{ij}. \quad (2.22)$$

Given that for many models calculating the stress leads to modelling deformations, this inverse relation will be the most useful form to us and is common in the literature.

2.2.3 Equations of Motion and Equilibrium

Now let us generalize Newton's laws of motion, both linear and angular momentum, to a deformable solid [8]. Let ρ be the mass density of the deformed solid (and such, ρ_0 is the mass density of the undeformed or original solid). Assume that the solid is subject to a body force $\mathbf{b} = (b_1, b_2, b_3)$ and the acceleration of a material particle at position x_i in the deformed solid is represented by $\mathbf{a} = (a_1, a_2, a_3)$. Newton's third law of motion can be expressed as

$$\frac{\partial \sigma_{ij}}{\partial x_i} + \rho b_j = \rho a_j, \quad (2.23)$$

with $j = 1, 2, 3$, thus resulting in a system of three equations. Conservation of angular momentum for a continuum requires the Cauchy stress tensor to be symmetric, that is to say,

$$\sigma_{ji} = \sigma_{ij}, \quad (2.24)$$

where the full derivation of this is given by Bower(2010)[8]. In many systems, these equations are in fact equilibrium equations as the whole body tends not to undergo motion, resulting in the following

$$\frac{\partial \sigma_{ij}}{\partial x_i} + \rho b_j = 0, \quad (2.25)$$

which proves useful to measure both force and stress in a system.

2.3 Coupling mechanics and Diffusion

With the above equations we are able to model deformable solids assuming linear elasticity. For our model, the following question rises; which equations present would we alter and modify to help us in modelling our blistering problem? The definition of displacement and the infinitesimal strain tensor largely stays the same, regardless of the system we are modelling; the main changes to the stress-strain tensor are dependent on the displacement vector. Equations of motion and equilibrium remain consistent

from model to model which leaves with the constitutive relation;

$$\varepsilon_{ij} = \frac{1 + \nu}{E} \sigma_{ij} - \frac{\nu}{E} \sigma_{jj} \delta_{ij} + \alpha \Delta T \delta_{ij}. \quad (2.26)$$

By first looking at the work done by Prussin(1961) [41], in which Prussin focuses on stresses which are generated by diffusion rather than heat, Yang(2005) [54] extends Prussin's one dimensional model to the 3 dimensional case, and replaces the final term (the term dictated by temperature) in equation (2.17) with a term involving the concentration of the diffusing solute,

$$\varepsilon_{ij} = \frac{1 + \nu}{E} \sigma_{ij} - \frac{\nu}{E} \sigma_{jj} \delta_{ij} + \frac{C\Omega}{3} \delta_{ij}. \quad (2.27)$$

Here , Ω is the partial molar volume of solute (m^3/mol) and C is the concentration (moles/m^3)¹ of the diffusion component. This formulation of the constitutive law is one of the main reasons we are so interested in investigating Yang's paper; it is the first step in formulating our model of the problem which couples thermoelasticity and diffusion, leading to deformation. Therefore investigating the key results and the main focus and predictions of Yang's paper will prove beneficial. Although the diffusion in the chemical stresses paper is driven by the choice of the chemical potential, μ , the diffusion coefficient which appears in the polymer swelling paper presented by Wilmers and Bargmann [53] is where the coupling of diffusion and thermomechanics is present. Consider the choice of the diffusion coefficient,

$$\mathbf{D}(C, \theta, J) = \mathbf{D}_0 [1 - \phi_S]^2 [1 - 2\chi\phi_S] \exp \left(-\frac{E_A}{R\theta} + \delta \left[\frac{C}{C_{eq}} - 0.5 \right] \right), \quad (2.28)$$

where $\phi_S = C/J\rho_S$. Here, C denotes the concentration of the solvent diffusing through the polymer, while J is the determinant[46] of the deformation gradient, \mathbf{F} , given by $J = \det \mathbf{F}$. For now let us not concern ourselves with the other parameters present in the model as they are defined later when we take a detailed look into the polymer swelling model. The concentration given by C , the temperature, given by θ , and the deformation of the polymer described by the deformation gradient, \mathbf{F} (via J) are all present in the diffusion coefficient and dictate the diffusion through the polymer.

¹Note that the concentration and the partial molar volume of solute have the measurement of moles, which is the international system of units (SI) unit of the amount of substance, equal to the quantity containing as many elementary units as there are atoms in 0.012kg of carbon-12. More information can be found at *International Bureau of Weights and Measures* (2006), The International System of Units (SI) (PDF) (8th ed.), pp. 114–15, ISBN 92-822-2213-6

These are but two examples which we can easily see the coupling of both diffusion and thermomechanics, but one thing we need to consider is how and why the model dictates the constitutive relation or the diffusion coefficient which allows this coupling.

Chapter 3

Chemical induced stresses

By reviewing previous related research papers, we hope to further help our understanding of the problem at hand. The models we will be looking at successfully couple both thermomechanics and diffusion, where the diffusing chemical or substance alters the material body. We will begin by taking a look at F.Yang's (2005) paper, [54], "*Interaction between diffusion and chemical stresses*", in which Yang formulates a relation between hydrostatic stress and concentration of solute atoms in the model.

3.1 "*Interaction Between Diffusion and Chemical Stresses*" by F.Yang

Diffusion of atoms in materials which lead to the evolution of local stresses are named chemical stresses or diffusion-induced stresses. Specifically, diffusion of hydrogen into metals can cause hydrogen-induced damage, with extensive examples given in the book edited by R.Gangloff and B.Somerday(2012) et al[19]. Yang builds upon the work first analyzed by Prussin(1961)[41], specifically focusing on the coupling effect of the distribution of concentration of solute atoms in a thin plate, formulating both an analytical solution of the steady-state concentration in a plate and numerical solutions for an unsteady concentration in the plate. We will proceed to identify the key equations used in Yang's model and how we deem this relevant to our work, as well as the advantages and disadvantages of following a similar approach in modelling the formation of blisters.

3.1.1 Governing Equation of Mechanical Equilibrium

Earlier, we gave Yang's formulation of the constitutive relations as an example of how to alter a model to suit our needs. Starting with the work done by Prussin[41], Yang extended Prussin's one dimensional case to the three dimensional case, resulting in the following linear stress-strain relation,

$$\varepsilon_{ij} = \frac{1 + \nu}{E} \sigma_{ij} - \frac{\nu}{E} \sigma_{kk} \delta_{ij} + \frac{C\Omega}{3} \delta_{ij}, \quad (3.1)$$

which is analogous to classic linear thermoelasticity, but with chemical concentration playing the role of temperature. As a reminder, ε_{ij} represents the components of the strain tensor, σ_{ij} represents the components of the stress tensor, Ω is the partial molar volume of the solute (m^3/mol) and C is the concentration of the diffusing component (moles/m^3). Both the constants E and ν represent the Young's modulus and the Poisson's ratio respectively, where both of these constants depend on the material which is under stress, and thus differs from material to material.

After formulating this stress-strain relationship, Yang makes use of the equilibrium equations (originating from Cauchy's Momentum equation, Haupt(2000e)[29]) to formulate a relationship between the hydrostatic stress - which is simply the average of the three normal stress components of the stress tensor - and the concentration of solute atoms present. This is first done by introducing the equilibrium equations, given by

$$\sum_{i=1}^3 \frac{\partial \sigma_{ij}}{\partial x_i} + F_j = 0, \quad (3.2)$$

where F_j represents the components of body force, \mathbf{F} along the corresponding direction, $j = 1, 2, 3$. The reason no acceleration terms are used in this form of Cauchy's momentum equation is due to the rate of diffusion compared to the elastic deformation. Compared to diffusion of atoms in solids, the time for elastic deformation of solids is much smaller than that for atomic migration, hence mechanical equilibrium is built up much sooner than the diffusion process and equilibrium is assumed to be attained almost instantaneously, resulting in equation (4.2). Yang introduced the constitutive relation relating the stress, strain and concentration given by equation (4.1) into the equilibrium equation given by equation (4.2) to formulate a relationship between the hydrostatic stress and the concentration of solute atoms. The equilibrium equations

were then rewritten as

$$G\nabla^2 u_j + \frac{G}{1-2\nu} \sum_{i=1}^3 \frac{\partial^2 u_i}{\partial x_j \partial x_i} = K\Omega \frac{\partial C}{\partial x_j} - F_j \quad (j = 1, 2, 3), \quad (3.3)$$

where G and K are the shear and bulk moduli of the solid[27], related to Young's modulus, E , by

$$G = \frac{E}{2(1+\nu)} \text{ and } K = \frac{E}{3(1-2\nu)}. \quad (3.4)$$

Introducing the definition of the volumetric strain, ϵ as

$$\epsilon = \frac{\partial u_i}{\partial x_i}, \quad (3.5)$$

keeping in mind the use of Einstein summation notation[44], as well as the hydrostatic stress, σ , as

$$\sigma = \frac{\sigma_{ii}}{3}, \quad (3.6)$$

allowed a relation between the hydrostatic stress and the concentration to be formed, once the equilibrium equations had been manipulated to give

$$\nabla^2(\sigma + \alpha C) = 0, \quad (3.7)$$

in which α is a constant containing the Young's modulus E , Poisson's ratio, ν and the partial molar volume of solute, Ω , related by

$$\alpha = \frac{2E\Omega}{9(1-\nu)}. \quad (3.8)$$

Hence, the Laplacian of the hydrostatic stress is proportional to the Laplacian of the concentration of solute atoms. Here the constant α will be heavily dependent on the choice of material used, due to the presence of both Young's modulus and Poisson's ratio. In the one dimensional case, after the introduction of boundary conditions for both the hydrostatic stress as well as the concentration, a linear relation can be formed between the hydrostatic stress and concentration, which we will see later.

3.1.2 Diffusion Equation

The diffusion equation formulated here requires the chemical potential given by J.C.M.Li (1978)[37], which in an ideal solid solution is defined as

$$\mu = \mu_0 + R\theta \ln C - \sigma\Omega, \quad (3.9)$$

where μ_0 is a constant; R is the universal gas constant[21], θ is the absolute temperature, σ is the hydrostatic stress defined above as well as Ω , the partial molar volume of solute. Note that in general the chemical potential is a form of potential energy that can be either absorbed or released during a chemical reaction. In the original work of A.Fick(1855)[17], he described a salt-water system undergoing diffusion, and proposed the concept of the diffusion coefficient driven by chemical potentials[2]. From Fick's first law [39], the diffusion flux is proportional to the gradient of the chemical potential and considering the chemical potential given in Yang's paper, is expressed as

$$\mathbf{J} = -D_0 \left(\nabla C - \frac{\Omega C}{R\theta} \nabla \sigma \right), \quad (3.10)$$

where \mathbf{J} is the vector of the diffusion flux, D_0 is the diffusivity of solute atoms in a stress-free solid, and also remembering that ∇ is the gradient vector field in Cartesians, $\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$. Finally by making use of the law of mass conservation[40],

$$\nabla \cdot \mathbf{J} = -\frac{\partial C}{\partial t}, \quad (3.11)$$

we obtain the diffusion equation considering the effect of stress-induced diffusion,

$$D_0 \left[\nabla^2 C - \frac{\Omega}{R\theta} \nabla C \cdot \nabla \sigma - \frac{\Omega C}{R\theta} \nabla^2 \sigma \right] = \frac{\partial C}{\partial t}. \quad (3.12)$$

3.1.3 Correlation between normal stress and surface displacement

Let \mathbf{n} and \mathbf{t} be both the unit normal and tangent vectors of an undeformed surface (given by $\tilde{\Omega}$) respectively. By defining the surface gradient operator as $\nabla_S = \nabla - \mathbf{n}(\mathbf{n} \cdot \nabla)$, making use of the constitutive relation for an elastic solid given by equation (4.1) and by defining the displacement vector on the surface given by

$$\mathbf{u} = u_n \mathbf{n} + u_s \mathbf{t}, \quad (3.13)$$

Yang derives a relation between the normal stress and surface displacement, given by

$$\sigma_n = 3 \frac{1-\nu}{1+\nu} \sigma - 2G \nabla_S \cdot (u_s \mathbf{t}) - 2\mu u_n \kappa - \frac{\Omega C E}{3(1-2\nu)}. \quad (3.14)$$

Here, $\kappa = \nabla_S \cdot \mathbf{n}$ is twice the mean curvature of the undeformed surface. Overall, the normal stress is a function of the hydrostatic stress, the tangential displacement

component, and the normal component of the surface displacement. If we were to consider an initially flat surface, then $\kappa = 0$. With this information and a few boundary conditions - which will be discussed in the next section - we have the necessary equations in order to model the development of chemical stresses in a thin plate.

3.1.4 Development of Chemical stresses in a thin plate.

After formulating the governing equations and the constitutive relations, Yang's model is as follows. Consider a thin plate of isotropic material in the region $-a \leq x \leq a$. Suppose this thin plate is constrained in both the y and z directions, with no stresses applied to the surfaces in the x direction. Let the surface concentrations, the concentration of the solute to which the thin plate is exposed to, be functions of time only, independent of space, therefore $C = C(t)$ at both $x = \pm a$. As mentioned before, the diffusion is driven by the gradient of chemical potential, but in this thin plate the surface concentrations diffuse from both sides of the plate. Hence the above equations now become

$$\frac{\partial^2}{\partial x^2}(\sigma + \alpha C) = 0, \quad (3.15)$$

$$D_0 \left[\frac{\partial^2 C}{\partial x^2} - \frac{\Omega}{R\theta} \frac{\partial C}{\partial x} \cdot \frac{\partial \sigma}{\partial x} - \frac{\Omega C}{R\theta} \frac{\partial^2 \sigma}{\partial x^2} \right] = \frac{\partial C}{\partial t}. \quad (3.16)$$

On both the surfaces of the plate, there is no normal stress in the x direction and no tangential displacement, u_S , hence

$$\sigma_{xx} = 0 \text{ at } x = \pm a, \quad (3.17)$$

$$u_S = 0 \text{ at } x = \pm a, \quad (3.18)$$

meanwhile the in-plane symmetry about the y and z axes leads to $\sigma_{yy} = \sigma_{zz}$. In the previous section the normal stress component, σ_n is derived in Yang's paper to give the following relation

$$\sigma_n = 3 \frac{1 - \nu}{1 + \nu} \sigma - 2G \nabla_S \cdot (u_S \mathbf{t}) - 2\mu u_n \kappa - \frac{\Omega C E}{3(1 - 2\nu)}. \quad (3.19)$$

Remember, ∇_S is the surface gradient operator, \mathbf{n} and \mathbf{t} are the unit normal and unit tangent vectors of an undeformed surface, u_n and u_S are the local normal displacement and tangent displacement respectively, meanwhile $\kappa = \nabla_S \cdot \mathbf{n}$ is twice the mean curvature of the undeformed surface. Given that we are dealing with an initially flat

surface ($\kappa = 0$) and no tangential displacement as well as no normal stress at the boundary, from equations (4.17)-(4.19), we obtain the following boundary conditions for the hydrostatic stress

$$\sigma = \frac{1 + \nu}{9(1 - \nu)} \frac{E\Omega C}{1 - 2\nu} \text{ at } x = \pm a. \quad (3.20)$$

By first defining $C_1 = C|_{x=-a}$ and $C_2 = C|_{x=a}$, we have enough information to define the linear relationship between the hydrostatic stress and the concentration by solving equation (4.15);

$$\sigma = -\frac{2E\Omega C}{9(1 - \nu)} + \frac{E\Omega(C_2 - C_1)}{6(1 - 2\nu)} \frac{x}{a} + \frac{E\Omega(C_2 + C_1)}{6(1 - 2\nu)} \text{ for } -a \leq x \leq a. \quad (3.21)$$

Three special cases were then considered for the model. The first case was the steady state chemical stresses with constant surface concentrations.

3.1.5 Steady State chemical stresses with constant surface concentrations.

With the introduction of the dimensionless variable, $\tilde{x} = x/a$, an analytic solution was found for the case of steady concentrations,

$$\frac{\partial^2 C}{\partial \tilde{x}^2} - \frac{\Omega}{R\theta} \frac{\partial C}{\partial \tilde{x}} \cdot \frac{\partial \sigma}{\partial \tilde{x}} - \frac{\Omega C}{R\theta} \frac{\partial^2 \sigma}{\partial \tilde{x}^2} = 0. \quad (3.22)$$

Substitution of equation (4.21) into equation (4.22) led to the equation given by

$$\left(1 + \frac{\alpha\Omega C}{R\theta}\right) \frac{\partial^2 C}{\partial \tilde{x}^2} + \frac{\alpha\Omega}{R\theta} \left(\frac{\partial C}{\partial \tilde{x}}\right)^2 - \frac{\beta\Omega}{R\theta} \frac{\partial C}{\partial \tilde{x}} = 0, \quad (3.23)$$

where β is defined to be

$$\beta = \frac{E\Omega(C_2 - C_1)}{6(1 - 2\nu)}. \quad (3.24)$$

Following analysis of the steady state chemical stresses case, it was found that nonlinear distribution of concentration is observed. Also, the interaction between diffusion and chemical stresses was found to have a very strong influence on the diffusion of solute atoms and the distribution of solute in materials. Analysis of the parameter $\beta\Omega/R\theta$ found to have interesting results; the larger the value of this parameter (whether from a smaller value of ν or a larger difference in the concentrations on both sides of the plate), the more severe nonlinear distribution of solute atoms in the plate,

which in turn dictates the evolution of chemical stresses. With the same surface concentrations, the concentration of solute atoms for larger $\beta\Omega/R\theta$ is less than that for smaller $\beta\Omega/R\theta$. This is due to the faster diffusion (due to larger $\beta\Omega/R\theta$) resulting in smaller local dilatation or smaller local stretches.

The profiles of the hydrostatic stress were also plotted with different ratios of surface concentration, C_1/C_2 . Yang observed that as the ratio of the surface concentrations increased, the chemical stress also increased, with both the maximum and minimum stresses on either surface of the plate; hence to reduce the effect of chemical stresses on this thin plate, reduction of the difference between surface concentrations is needed. Consideration of this property regarding the surface concentration differences is undertaken in the more important case; the evolution of chemical stresses.

3.1.6 Evolution of chemical stresses.

Here the surface concentrations on both sides of the thin plate, $x = \pm a$ were considered to be equal, hence $\beta = 0$. Given that the surface concentrations were equal on both sides, only one case needed to be observed, hence the thin plate was only considered over the region $0 \leq x \leq a$. For simplification, Yang introduced the following dimensionless parameters

$$\tilde{t} = \frac{D_0 t}{a^2}, \quad \tilde{C} = \frac{C}{C_0}, \quad \tilde{\alpha} = \frac{\alpha \Omega C_0}{RT}. \quad (3.25)$$

The last two equations in (4.25) are for a constant surface concentration, C_0 , meanwhile for a fixed amount of solute deposited initially on the surface, C_{av} (the average concentration over the thin plate) is used rather than the constant surface concentration, C_0 , where the last two equations in (4.25) now become

$$\tilde{C} = \frac{C}{C_{av}} \quad \text{and} \quad \tilde{\alpha} = \frac{\alpha \Omega C_{av}}{R\theta}. \quad (3.26)$$

After redefining the parameters involved, the diffusion equation (equation (4.16)) now simplifies to the following equation

$$(1 + \tilde{\alpha}\tilde{C}) \frac{\partial^2 \tilde{C}}{\partial \tilde{x}^2} + \tilde{\alpha} \left(\frac{\partial \tilde{C}}{\partial \tilde{x}} \right)^2 = \frac{\partial \tilde{C}}{\partial \tilde{t}}. \quad (3.27)$$

Using the finite difference approach mentioned before, and focusing on the explicit difference scheme (due to the nonlinearity caused by the final term on the left hand

side), the scheme becomes

$$\tilde{C}_{i+1,j} = \tilde{C}_{i,j} + \Delta\tilde{t} \left[(1 + \tilde{\alpha}\tilde{C}_{i,j}) \frac{\tilde{C}_{i,j+1} - 2\tilde{C}_{i,j} + \tilde{C}_{i,j-1}}{(\Delta\tilde{x})^2} + \tilde{\alpha} \left(\frac{\tilde{C}_{i,j+1} - \tilde{C}_{i,j-1}}{2\Delta\tilde{x}} \right)^2 \right]. \quad (3.28)$$

Here, $\tilde{C}_{i+1,j} = \tilde{C}(\tilde{t}_i + \Delta\tilde{t}, \tilde{x}_j)$, where $\tilde{t}_i = i\Delta\tilde{t}$, $i \geq 0$ and $\tilde{x}_j = j\Delta\tilde{x}$, with $\tilde{C}_{i,j+1} = \tilde{C}(\tilde{t}_i, \tilde{x}_j + \Delta\tilde{x})$. Note that the spatial domain is defined on $0 \leq \tilde{x} \leq 1$, and the time domain is defined to have an upper limit given by some finite choice of $t_{final} = T$. The spatial domain is divided into $n = 101$ steps, hence $\Delta\tilde{x} = 0.01$ and $0 \leq j \leq 101$.

Given that we are dealing with the Explicit scheme in finite differencing, we need to take into care where numerical instabilities occur. Considering the case of the heat equation (see Chapter 3),

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} \longrightarrow U_{i+1,j} = U_{i,j} + \mu(U_{i,j+1} - 2U_{i,j} + U_{i,j-1}), \quad (3.29)$$

this scheme is only numerically stable if $\mu = \Delta t / (\Delta x)^2 \leq \frac{1}{2}$. The coefficient of the second derivative with respect to x in equation (4.23) given by $(1 + \tilde{\alpha}\tilde{C})$ now also affects the numerical stability of this scheme. Suppose now

$$\frac{\partial u}{\partial t} = f(x, t, u) \frac{\partial^2 u}{\partial x^2}, \quad (3.30)$$

this coefficient must also be implemented into the numerical stability property and a careful choice of Δt must follow, that is

$$f(x, t, u)\mu = f(x, t, u) \frac{\Delta t}{(\Delta x)^2} \leq \frac{1}{2}. \quad (3.31)$$

Returning to the diffusion equation which is present in Yang's paper, the different values of $\tilde{\alpha}$ considered were $\tilde{\alpha} = 0.01, 0.1$ and 1 . By definition of $\tilde{C} = C/C_0$ the max value is at the boundary, $\tilde{C} = 1$ as $C = C_0$. Now with maximum values of both the coefficient $\tilde{\alpha}$ as well as the concentration, \tilde{C} , we can determine the max value of the coefficient and implement this into the numerical stability property to determine which values of Δt would produce sensible results;

$$\max(1 + \tilde{\alpha}\tilde{C}) = 2 \implies \Delta t \leq \frac{(\Delta\tilde{x})^2}{4}. \quad (3.32)$$

After ensuring numerical stability (albeit, conditional numerical stability), we look into greater detail the two different cases; one case with a constant surface concentration and the other being a fixed amount of solute deposited initially on the surfaces.

Constant Surface Concentration

In this particular case, the choice of C_0 doesn't interest us if we are observing the development of \tilde{C} over time. Here the two boundary conditions are of the utmost importance, as they are in most mathematical models. The boundary condition we consider at the lower boundary condition, that is at $x = 0 \implies \tilde{x} = 0$, is that of a Neumann boundary condition,

$$\frac{\partial \tilde{C}}{\partial \tilde{x}} = 0 \text{ at } \tilde{x} = 0, \quad (3.33)$$

hence in the finite difference scheme, ghost points have to be implemented. For the upper boundary condition, $x = a \implies \tilde{x} = 1$ the boundary condition $\tilde{C} = 1$ was simply used, and can be easily implemented into the scheme. Given the choice of the spatial step, $\Delta x = 0.01$, this leaves us with a miniscule timestep to be chosen,

$$\Delta t \leq \frac{1}{40000}. \quad (3.34)$$

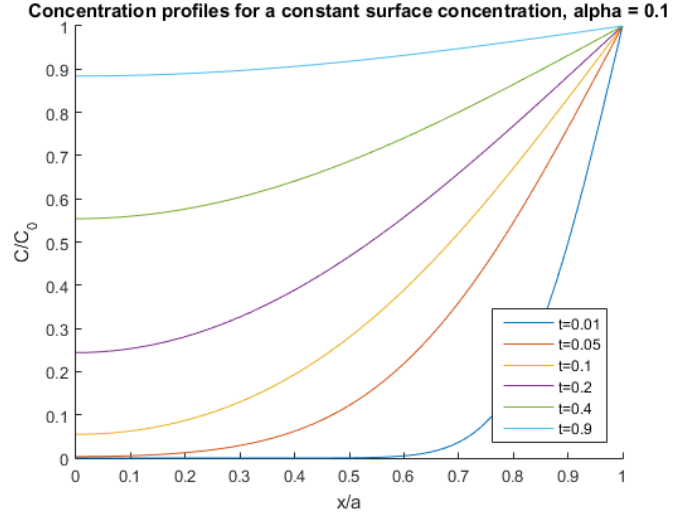
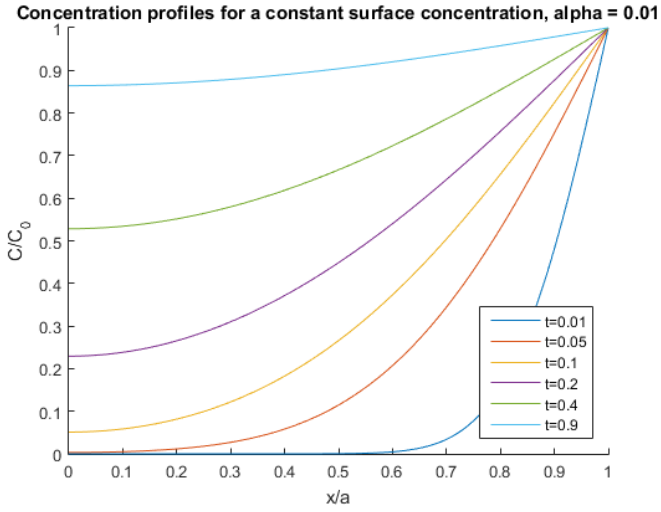
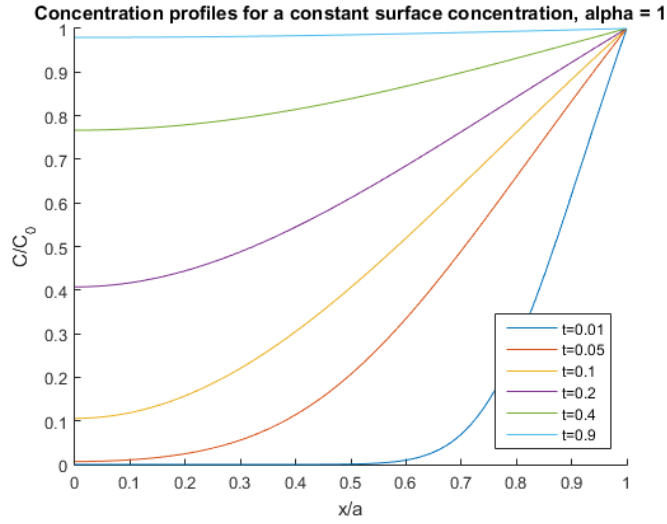
The profiles of the concentration in the thin plate at different times (in terms of \tilde{t}) are plotted in figures (3.1 - 3.3) for different values of $\tilde{\alpha}$. At the exact same time and location in the plate, higher concentration is observed for a larger value of $\tilde{\alpha}$, which is expected as the larger the value of $\tilde{\alpha}$, the larger the diffusivity of the material. For small enough $\tilde{\alpha}$, the parameter has little to no influence on the concentration profiles, which Yang observed to be consistent with the work done by Chu and Lee(1994) [11], in which they observed that in an isotropic solid, the effective diffusivity arising from the chemical stresses is proportional to the concentration.

Given the size of the timestep, originally code was developed to store every piece of information in this model, but due to the time it took an alternative but more efficient code was developed, and the code used to produce these results can be seen in Appendix (C): Constant Surface Concentration. After the assumption that mechanical equilibrium is easily attained, Yang derived a linear relationship between the hydrostatic stress and the solvent concentration. The relation was given by

$$\sigma = -\frac{2E\Omega C}{9(1-\nu)} + \frac{E\Omega(C_2 - C_1)}{6(1-2\nu)} \frac{x}{a} + \frac{E\Omega(C_2 + C_1)}{6(1-2\nu)} \text{ for } -a \leq x \leq a. \quad (3.35)$$

where the boundary conditions for the stress are given as

$$\sigma = \frac{1+\nu}{9(1-\nu)} \frac{E\Omega C}{1-2\nu} \text{ at } x = \pm a, \quad (3.36)$$

Figure 3.1: Concentration Profile for $\tilde{\alpha} = 0.01$ Figure 3.2: Concentration Profile for $\tilde{\alpha} = 0.1$ Figure 3.3: Concentration Profile for $\tilde{\alpha} = 1$

with $C_1 = C|_{x=-a}$ and $C_2 = C|_{x=a}$. The assumption that the given constant concentration at the surfaces is equal at both $x = \pm a$ leads to $C_1 = C_2 = C_0$, and by introducing the dimensionless parameter

$$\tilde{\sigma} = \frac{\sigma}{E\Omega C_0}, \quad (3.37)$$

the relation for the stress given by equation (4.35) reduces to

$$\tilde{\sigma} = -\frac{2\tilde{C}}{9(1-\nu)} + \frac{2}{6(1-2\nu)}, \text{ for } -a \leq x \leq a, \quad (3.38)$$

with the boundary condition at $\tilde{x} = 1$ being

$$\tilde{\sigma}|_{\tilde{x}=1} = \frac{1+\nu}{9(1-\nu)} \frac{\tilde{C}}{1-2\nu}. \quad (3.39)$$

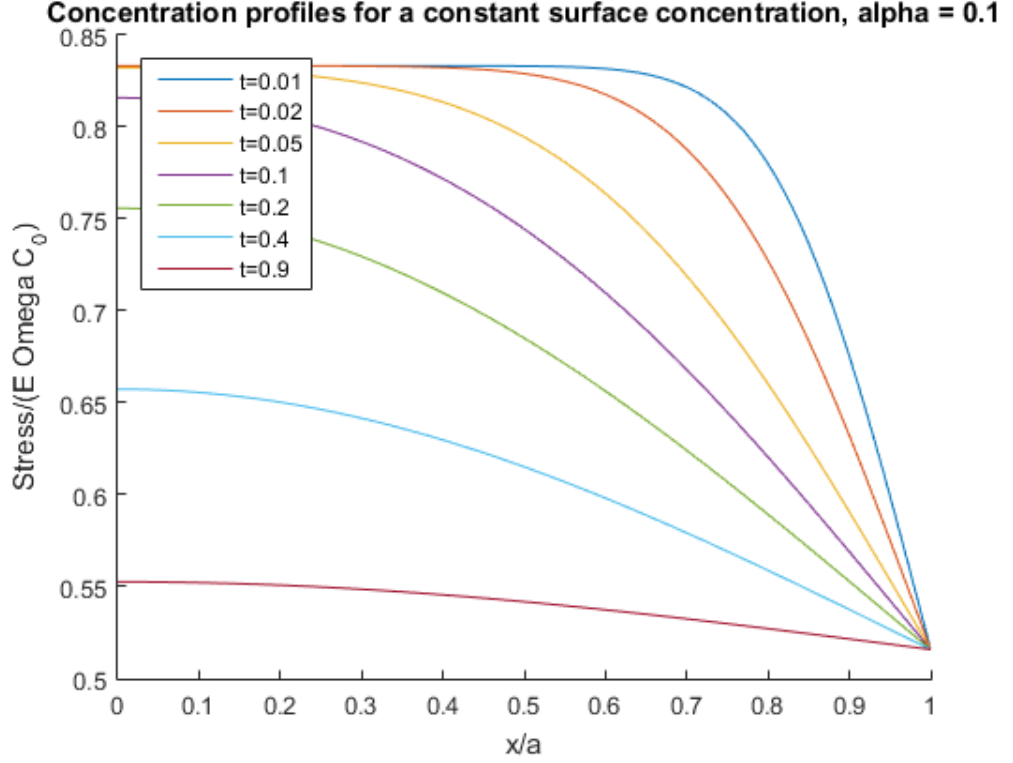


Figure 3.4: This is the evolution of the hydrostatic stress in a thin plate with a given constant surface concentration, with value of $\tilde{\alpha} = 0.1$.

Given that the inner boundary condition is the middle of the thin plate, and the system is assumed to be symmetric, a homogeneous Neumann boundary condition was applied,

$$\frac{\partial \tilde{\sigma}}{\partial \tilde{x}} = 0 \quad \text{at} \quad \tilde{x} = 0. \quad (3.40)$$

Plots of the dimensionless stress $\tilde{\sigma}$ against the position \tilde{x} can be seen in figure (3.4). By setting a value of $\nu = 0.3$ for Poisson's ratio, and by setting $t_{final} = T = 1$, i.e., the terminal time of the numerical solution, we see that the maximum stress occurs at the centre of the plate at the beginning of diffusion. Note that the plate is subjected to tension due to the constraint that $u_S = 0$, that is, the tangential displacement is equal to zero. We find that stresses are present at the centre of the plate for a short time of diffusion, even though the solute has not fully diffused to the centre, implying that there is no direct correlation between the gradient of concentration and stresses. When the concentration diffuses across the thin plate and the uniform distribution of concentration is reached, the hydrostatic stress reaches a constant given in equation (4.39), which is proportional to the equilibrium concentration achieved. Next we will

consider the case of having a fixed amount of solute which is deposited initially on both the surfaces.

Fixed amount of solute deposited initially

For this case, as opposed to having a constant concentration at the surface such as the previous case, we have a set amount of concentration deposited initially, and over time this concentration will diffuse through the thin metal, where the code can be seen in Appendix C. By taking the dimensionless parameters as

$$\tilde{C} = \frac{C}{C_{av}}, \quad \tilde{\alpha} = \frac{\alpha \Omega C_{av}}{R\theta}, \quad (3.41)$$

we follow the same analysis as before, but we must change the boundary conditions which have been applied in the previous system. In the previous system we took the boundary condition for the concentration to be $\tilde{C} = 1$ at $\tilde{x} = 1$ for all time, now we take $\tilde{C} = 1$ at $\tilde{x} = 1$ as the initial condition only, in terms of the finite difference scheme this means

$$\tilde{C}_{i=0,j=J} = 1, \quad \tilde{C}_{i=0,j \neq J} = 0. \quad (3.42)$$

Now we consider taking homogeneous Neumann boundary conditions at both sides of the plate, $\tilde{x} = 0$ and $\tilde{x} = 1$ and this gives us enough information to plot the concentration profiles for an initially deposited solute, which can be seen in figures (3.5) - (3.7). Initially, it seems that the change in $\tilde{\alpha}$ has little to no affect, but after closer observation, we see that near the surfaces, less amount of solute is found for a larger value of $\tilde{\alpha}$, meanwhile in the centre of the plate, a larger amount of solute is observed for larger $\tilde{\alpha}$ due to the fast diffusion speeds associated with higher values of $\tilde{\alpha}$. Similarly to before, a uniform distribution of concentration is observed which is independent of the interaction between the chemical stresses and diffusion.

Now we move to analyse the evolution of stresses present in the thin plate for a fixed amount of solute deposited initially on the surfaces. Due to the constraint of no tangential displacement imposed earlier, $u_S = 0$, the plate is always subjected to tension.

Once again the value chosen for Poisson's ratio is $\nu = 0.3$, and the dimensionless hydrostatic stress is given by

$$\tilde{\sigma} = \frac{\sigma}{E\Omega C_{av}}. \quad (3.43)$$

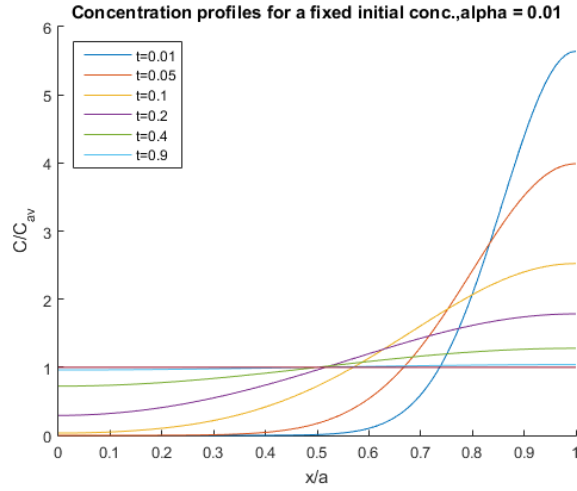


Figure 3.5: Concentration Profile for $\tilde{\alpha} = 0.01$ and an initially deposited solute.

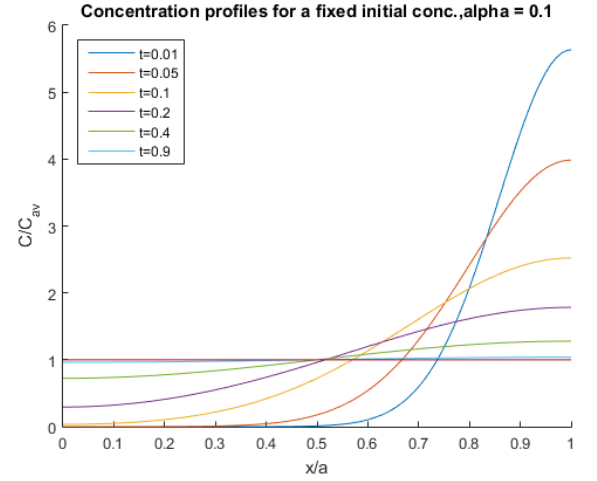


Figure 3.6: Concentration Profile for $\tilde{\alpha} = 0.10$ and an initially deposited solute.

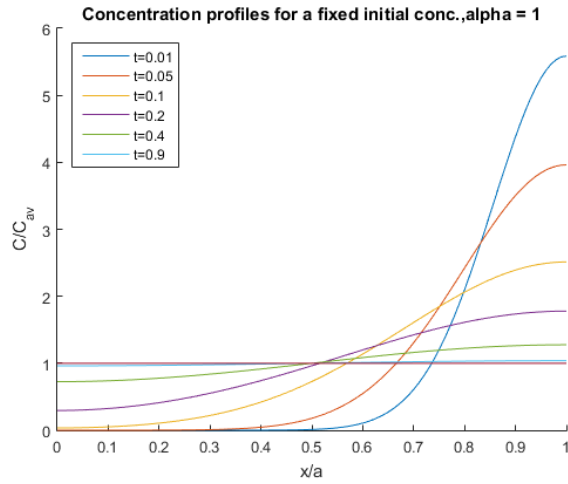


Figure 3.7: Concentration Profile for $\tilde{\alpha} = 1$ and an initially deposited solute.

Due to the linear relation between the hydrostatic stress and the concentrations, the changes to the model will also take affect on the boundary conditions applied to the concentrations as well as the hydrostatic stress, $\tilde{\sigma}$, defined on $0 \leq \tilde{x} \leq 1$. By first noting that the modified boundary condition of the hydrostatic stress in the previous case is

$$\tilde{\sigma} = \frac{1 + \nu}{9(1 - \nu)} \frac{\tilde{C}}{1 - 2\nu} \quad \text{at} \quad \tilde{x} = 1, \quad (3.44)$$

we notice that this largely remains the same, the equation we need to take care is the definition of the hydrostatic stress in the domain , $0 \leq \tilde{x} \leq 1$;

$$\sigma = \frac{2E\Omega(C_2)}{6(1 - 2\nu)} - \frac{2E\Omega C}{9(1 - \nu)}. \quad (3.45)$$

Note that $C_1 = C_2$, leading to the middle term in equation (4.21) equating to zero. In the previous case where the thin metal plate was exposed to a constant surface concentration, C_0 , the value we chose for C_1 would have been simply C_0 , i.e. $C_1 = C_0$, and hence after rearrangement we were able to get $\tilde{\sigma} = \sigma/E\Omega C_0$. In this case where a fixed amount of solute is deposited initially on the surfaces, the concentration at the boundary is gradually decreasing over time, due to the solute diffusing through the metal material. Hence, the values we choose for the boundary concentration, C_2 , are the values of concentration we calculated from the diffusion equation evaluated at the boundary, hence $C_2 = \tilde{C}(\tilde{x} = 1, \tilde{t} = \tilde{t}_i)$, where \tilde{t}_i is a given time. Thus equation (4.45) now becomes

$$\tilde{\sigma} = \frac{2\tilde{C}(\tilde{x} = 1, \tilde{t}_i)}{6(1 - 2\nu)} - \frac{2\tilde{C}}{9(1 - \nu)}, \quad (3.46)$$

after the introduction of the dimensionless variable $\tilde{C} = C/C_{av}$ of course. As a reminder, we should remember that both the concentration and hydrostatic stress here are functions of both the dimensionless space and time, $\tilde{\sigma} = \tilde{\sigma}(\tilde{x}, \tilde{t})$ and $\tilde{C} = \tilde{C}(\tilde{x}, \tilde{t})$. The evolution of the hydrostatic stress in the plate against position is given by figure (3.8), for given values $\nu = 0.3$ and $\tilde{\alpha} = 0.1$. As we can see, the maximum stress is occurring at the centre at the beginning of the diffusion. Previous work done by Li[37] shows that stresses are present at the centre of the plate for a short time of diffusion, even before the concentration has diffused to the centre of the plate. We see a similar result in our plot for the hydrostatic stress, which is consistent with the results we found out in the previous section with the case of a constant surface concentration, hence there is no direct correlation between the gradient of concentration and stresses.

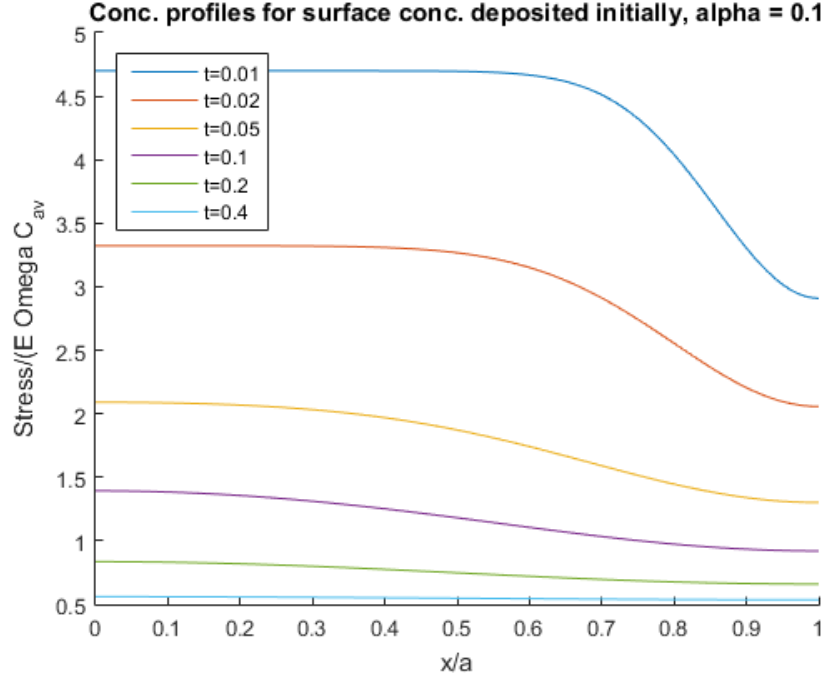


Figure 3.8: This is the evolution of the hydrostatic stress in a thin plate with a fixed amount of surface concentration initially deposited, with $\tilde{\alpha} = 0.1$.

Higher stress is developed in the centre of the plate in the case with a fixed amount of solute deposited initially than that of the constant surface concentration, but in both cases the stresses developed in the plate decrease with time and reach constant values which is determined by the uniform concentration in the plate.

3.1.7 Summary

Having discussed the results of F.Yang's paper of chemical induced stresses, we will recap the important equations involved, as well as key parameters and properties present. The first assumption was that the material behaves like an isotropic elastic solid, and that we are only concerned with small deformations. With small deformations we need to define the strain tensor as well as the constitutive law that is present for this particular model;

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right), \quad \varepsilon_{ij} = \frac{1}{E} [(1 + \nu)\sigma_{ij} - \nu\sigma_{kk}\delta_{ij}] + \frac{C\Omega}{3}\delta_{ij}, \quad (3.47)$$

remembering that ε_{ij} , σ_{ij} are components of the strain and stress tensor respectively, u_i is the i th component of the displacement vector \mathbf{u} and both ν and E are Poisson's

and Young's ratio of the material respectively. We then have the concentration, C , the partial molar volume of solute given by Ω , δ_{ij} is the Kronecker delta function and finally x_i are the spatial Cartesian coordinates given by $\mathbf{x} = (x_1, x_2, x_3)$. The constitutive law in (4.47) was formulated by previous work done by Prussin[41] and extended to three dimensions here.

In this model, the mechanical equilibrium is assumed to be attained much faster than the diffusion process, and hence it is assumed to be attained instantaneously, resulting in Cauchy's equation of momentum (in one dimension) with the absence of acceleration terms represented by

$$\sum_{i=1}^3 \frac{\partial \sigma_{ij}}{\partial x_i} + F_j = 0, \quad (j = 1, 2, 3). \quad (3.48)$$

Here F_j are the components of body force which depend from model to model where usually gravity is taken into account. This equation was then substituted and manipulated to formulate a relation between the hydrostatic stress given by σ and the concentration of the solute, resulting in the following relation

$$\nabla^2(\sigma + \alpha C) = 0, \quad \text{where} \quad \alpha = \frac{2E\Omega}{9(1-\nu)}. \quad (3.49)$$

Here α is largely dependent on the properties of the material as both Poisson's ratio, ν as well as Young's modulus, E are present. The diffusion equation was formulated by introducing the chemical potential given by μ [37] and making use of Fick's[17] first law, which states

$$\mathbf{J} = -MC\nabla\mu = -D_0 \left(\nabla C - \frac{\Omega C}{R\theta} \nabla \sigma \right), \quad \text{where} \quad \mu = \mu_0 + R\theta \ln C - \sigma\Omega. \quad (3.50)$$

Here \mathbf{J} is the diffusion flux, μ_0 and R are a constant and gas constant respectively, θ is the absolute temperature and D_0 is the diffusivity of solute atoms, with $M = D_0/R\theta$. Then by making use of the law of mass conservation

$$\nabla \cdot \mathbf{J} = -\frac{\partial C}{\partial t}, \quad (3.51)$$

the diffusion equation which couples the stress and the concentration was defined to be

$$D_0 \left[\nabla^2 C - \frac{\Omega}{R\theta} \nabla C \cdot \nabla \sigma - \frac{\Omega C}{R\theta} \nabla^2 \sigma \right] = \frac{\partial C}{\partial t}. \quad (3.52)$$

So far we have equations to solve for the hydrostatic stress, concentration of the solute which include the presence of temperature, although it is assumed here that the

temperature is given. Further derivation leads to the definition of the normal stress component, σ_n , given by

$$\sigma_n = 3\frac{1-\nu}{1+\nu}\sigma - 2G\nabla_S \cdot (u_S \mathbf{t}) - 2\mu u_n \kappa - \frac{\Omega CE}{3(1-2\nu)}. \quad (3.53)$$

Here $G = E/2(1+\nu)$ is defined as the shear modulus of the solid, ∇_S is the surface gradient operator, \mathbf{t} is the tangent vector to the surface, meanwhile μ is the chemical potential defined earlier, u_n is the local normal displacement and $\kappa = \nabla_S \cdot \mathbf{n}$ is twice the mean curvature of the undeformed surface.

With these equations, a model for the development of chemical stresses in a thin plate of isotropic metal material was developed. The surfaces of the plate in both the y and z direction were assumed to be constrained as well as having no additional stresses applied to the surfaces in the x direction. Although the concentration in the plate is assumed to be a function of both space and time, $C = C(x, t)$, the concentration at the surface was assumed to be a function of time only. At the surfaces of the plate, the assumption of no tangential displacement, $u_S = 0$, and no normal stress in the x direction, σ_{xx} , were imposed.

Three individual cases were considered as well as the affects the parameters played in dictating the distribution of concentration in the plate. The first case was that of the steady state, where $\partial C/\partial t = 0$. After formulating the relationship between the hydrostatic stress and the concentration of the solute (equation (4.35)), this was substituted into the diffusion equation and an analytic solution was formed. To simplify the model, the parameter β was introduced;

$$\beta = \frac{E\Omega(C_2 - C_1)}{6(1-2\nu)}. \quad (3.54)$$

Here the differences between the two surface concentrations given by $C_1 = C|_{x=-a}$ and $C_2 = C|_{x=a}$ influenced the model; the larger the difference between the two the more nonlinear distribution there seemed to be. Analysis into the parameter $\beta\Omega/RT$ led to the conclusion that the larger this parameter was, the more severe nonlinear distribution of the solute concentration there was in the plate - which directly effects the evolution of chemical stresses. This should not surprise us as we noticed that the larger the difference of surface concentrations there was, the more nonlinear the distribution of the concentration. Hence, the chemical stress increases with the ratio

C_1/C_2 (the difference between the surface concentrations), with both the maximum and minimum stresses on the surfaces of the plate.

The last two cases considered were the more interesting cases. Here the surface concentrations are considered to be the same ($\beta = 0$) and hence only half of the plate was considered as it was symmetric. Introduction of dimensionless parameters led to the dimensionless diffusion equation

$$(1 + \tilde{\alpha}\tilde{C})\frac{\partial^2\tilde{C}}{\partial\tilde{x}^2} + \tilde{\alpha}\left(\frac{\partial\tilde{C}}{\partial\tilde{x}}\right)^2 = \frac{\partial\tilde{C}}{\partial\tilde{t}}, \quad (3.55)$$

which required numerical solutions. The choices for \tilde{x} and \tilde{t} can be seen in Section 4.1.6: Evolution of chemical stresses. The difference between the two cases came in the choices of how the surface concentration was distributed. The first case considered was that of a constant surface concentration for all time, hence the boundary condition at the surface was constant for all time. With this boundary condition set, different choices of $\tilde{\alpha} = \alpha\Omega C_0/R\theta$ were chosen and higher concentrations were observed for larger values of $\tilde{\alpha}$, which is expected as larger $\tilde{\alpha}$ means higher local diffusivity. Stresses are present in the centre of the plate prior to diffusion, with the maximum stress occuring at the centre of the plate when the plate is subjected to tension due to the constraint of no tangential displacement, $u_S = 0$. This suggests that there is no direct correlation between the gradient of concentration and stresses, although once a uniform concentration is reached, the hydrostatic stress reaches a constant proportional to the concentration.

The last case considered was having a fixed amount of solute which is initially deposited on the surface, as opposed to having a constant concentration at the surface for all time. Due to the difference in the model, care was taken in formulating the relation between the stress and the concentration. In a similar fashion to before, different values of $\tilde{\alpha}$ were chosen and this led to less solute being present at the surfaces for a larger value of $\tilde{\alpha}$. This was due to the fact that the solute was diffusing through the material much more quickly and led to a larger amount of solute observed in the central portion of the plate, until a uniform concentration is reached which is independent of the interaction between chemical stresses and diffusion. Once again, the maximum stress occurs at the centre at the beginning of diffusion with stresses being present for a short time of diffusion. Although the solute has not diffused to

the centre of the plate, much higher stresses were observed at the centre of the plate than that of the case of constant surface concentration. The stresses developed in both cases decrease with time, and reach constant values once uniform distribution of concentration is reached. This conclusion was found to be consistent with the finding in the previous case in which suggests there is no direct correlation between the gradient of concentration and stresses.

We see that the model at hand shows clearly that there is always a non-linear distribution of solute atoms due to the interaction between the chemical stresses and the diffusion. This investigation was achieved by assuming a linear relation between the diffusion induced strain and the concentration of solute. The linear relationship formulated between the hydrostatic stress and concentration allowed further insight to the stresses developing in the model, which are present (due to the tension) before the diffusion occurs.

For our model, assuming a linear relation between the strain and the concentration of the solute atoms similar to Yang's model would be a good start; the formulation of the relationship between the hydrostatic stress and concentration is clear and concise which proves useful when solving the diffusion equation further along the line. The choice of chemical potential is dependent on the model, which in this case the chemical potential is chosen to represent that of an ideal solid solution. The chemical potential plays an important part in formulating the diffusion equation, therefore further research into whether this choice of μ would be an accurate representation of the chemical potential present in our model must be undertaken. With the appropriate choice of μ and the derivation of the diffusion equation describing the evolution of the concentration, C , in the plate, values for the hydrostatic stress can be calculated for our model with this formulation.

Unlike in Yang's model, we would ideally have a metal which has only one surface exposed to a concentration of solute atoms. We would then have these solute atoms precipitate under the surface, which leads to the metal being exposed by two chemicals from either sides; one concentration from the precipitate and one concentration from the surface. For our model though we would have to consider the concentration that has already diffused into the metal before precipitating at a given point, and whether this concentration of solute atoms present in the precipitate diffuses further into the

metal. After this consideration, we could then formulate a relationship between the chemicals present and the hydrostatic stress to predict the development of blisters due to the displacement of the metal. In the next chapter we will consider the paper written by Wilmers and Bargmann[53], in which they investigate the swelling of a polymer after exposure to a diffusing solvent.

Chapter 4

Polymer Swelling

Following a detailed look into the chemical stresses paper, we now turn our attention to the paper given by J.Wilmers and S.Bargmann(2015)[53], "*A continuum mechanical model for the description of solvent induced swelling in polymeric glasses*", where a detailed look will be into the numerical modelling of Case II diffusion in polymeric glasses. Case II diffusion differs from traditional diffusion in many ways; traditional diffusion is modelled by Ficks law and is often called Fickian diffusion, or Case I diffusion. The diffusion of solvent through a polymer causing it to swell is best described by Case II diffusion, which was first defined by Alfrey, Gurnee and Lloyd(1966) [1] where diffusion of small molecules into or through polymers often follow a more complicated pattern than that described by Fick's Laws. Diffusion in glassy polymers exhibits anomalous behaviour and Case II behaviour is characterized by a number of several phenomena, not just one property;

1. A sharp front forms between the plasticised and the dry region of the polymer.
2. Behind this front which is formed, a constant concentration as well as an equilibrium state of swelling is achieved, where the swelling remains and does not return to its original state.
3. The sharp front moves with a constant velocity which is independent of time and concentration.
4. Slightly ahead of the front, a Fickian precursor of varying size occurs, where the precursor is a compound that participates in the chemical reaction that produces

in another compound. The reason for this is that a small amount of the solvent diffuses into the free volume of the polymeric glass.

5. Not every aspect of Case II diffusion is free of Fickian's laws, the desorption process - the process where a substance is released from or through the surface front - follows Fickian diffusion kinetics.

Case II behaviour occurs only when all of these characteristics are present as many of these properties are present in a variety of diffusion processes. More detailed overview of models describing Case II diffusion kinetics as well as other diffusion processes that don't fully follow Fickian's laws are given by De Kee et al. [14] and Bargmann et al. (2011) [4]. There are a number of examples in the literature coupling Case II diffusion and deformation, for example the work done by Govindjee and Simo (1993) [22] constructs a continuum mechanical framework which couples concentration and displacement where Case II diffusion occurs. However, in this paper, Wilmers and Bargmann propose a numerical model for Case II diffusion based on the equations given in the work by McBride et al. (2011) [38], where the work done by Govindjee and Simo is coupled to thermomechanics. In doing so, formulations for the diffusion flux law as well as the free energy of mixing are presented which describe the diffusion kinetics and swelling behaviour present in Case II diffusion. Here we will discuss the governing equations present in this polymer swelling model.

4.1 Conservation of Mass and Balance of Linear and Angular Momentum.

The approach taken in the paper is not to differentiate between the solvent and the polymer, but to describe this mixture as a continuum. By treating the mixture as a continuum, we will have to examine results from continuum mechanics which we have done in Chapter 2: Methodology. Consider first the deformation gradient, \mathbf{F} . If we were given a motion, $\boldsymbol{\psi}$ that maps a reference configuration, B_0 , to the current configuration defined by $B_t = \boldsymbol{\psi}(B_0(\mathbf{X}, t))$, the deformation gradient is defined to be

$$\mathbf{F}(\mathbf{X}, t) = \nabla \boldsymbol{\psi}(\mathbf{X}, t). \quad (4.1)$$

Here ∇ denotes the gradient in space with respect to the reference Cartesian coordinates, \mathbf{X} . For this section let us define the position of the deformed coordinates by \mathbf{x} and the reference Cartesian coordinates as \mathbf{X} . Note that this notation is slightly different to that we've used in the previous sections; the reason this new notation is used is to closely follow the notation given by the paper. The first governing equation we consider is the conservation of mass. In the reference setting given by B_0 , a continuum body has a reference mass density given by ρ_0 , meanwhile in the current configuration, B_t , the density here is given by ρ_t where the mass density refers to mass per volume of the whole mixture. Following standard arguments,

$$\rho_0 = J\rho_t, \quad \text{where } J = \det \mathbf{F}, \quad (4.2)$$

where \det represents the determinant operator. Here the balance of mass is formulated by the consideration of the concentration, C_t , which is defined as the mass of solvent per volume of the mixture;

$$\frac{d}{dt} \int_{B_t} C_t dV_t = - \int_{\partial B_t} \mathbf{j} \cdot \mathbf{n} dA_t + \int_{B_t} w dV_t. \quad (4.3)$$

Here \mathbf{j} denotes the diffusion flux over the boundary of the configuration, given by ∂B and w is the internal sources of solvent molecules, where V_t and A_t are the volume and surface area of the current configuration. Here the conservation of mass is given in the current configuration B_t which is a function of time. By redefining these equations in terms of the reference configuration, we are able to take the time derivative on the left hand side through the integral due to the reference configuration's (B_0) independence of time. By making use of the Divergence Theorem[47] on the surface integral, we obtain the following equation for the conservation of mass

$$\frac{\partial C_0}{\partial t} = -\nabla \cdot \mathbf{J} + W. \quad (4.4)$$

Here \mathbf{J} denotes the diffusion flux over the reference configurations boundary given by ∂B_0 , W is the internal sources of solvent molecules in this reference configuration, meanwhile we note that $C_0 = C_t J$, hence every term is defined in this reference configuration.

Consider now the balance of linear and angular momentum. The balance of linear momentum is given by

$$\rho_0 \frac{\partial^2 \mathbf{x}}{\partial t^2} = \nabla \cdot \mathbf{P} + \rho_0 \mathbf{b}. \quad (4.5)$$

The term on the left hand side represents the acceleration of the current coordinates, given by \mathbf{x} , where ρ_0 represents the mass density of the original configuration body. \mathbf{P} represents the first Piola-Kirchhoff stress tensor which relates momentary forces to the reference area, and \mathbf{b} is the body force density. The first Piola-Kirchhoff[28] stress tensor relates forces in the present or current configuration with areas in the reference or original configuration, and is defined in terms of the Cauchy stress tensor, $\boldsymbol{\sigma}$, and the deformation gradient, \mathbf{F} , where J is defined as above;

$$\mathbf{P} = J\boldsymbol{\sigma}\mathbf{F}^{-T}. \quad (4.6)$$

The evaluation of the balance of angular momentum shows that the second Piola-Kirchhoff stress tensor, in terms of $\mathbf{S} = \mathbf{F}^{-1} \cdot \mathbf{P}$ is symmetric, thus the relation $\mathbf{P} \cdot \mathbf{F}^{-T} = \mathbf{F} \cdot \mathbf{P}^{-T}$ is true. Next we consider the balance of internal energy.

4.2 Balance of internal energy

In a diffusion process, the diffusing solvent contributes to the internal energy, ϵ [30], of the mixture. Here the first law of thermodynamics is the law of conservation of energy, adapted to thermodynamical systems, in which we have to consider the internal energy of the mixture. Before we define an equation for the local balance of internal energy, we must define an equation of state for the chemical potential of the mixture. Let us define the chemical potential of the mixture μ_S as

$$\mu_S = \Phi_S - \theta\eta_S, \quad (4.7)$$

where θ is the absolute temperature and Φ_S , η_S denote the specific enthalpy and specific entropy (respectively) contributed to the system by mixing. Here only Φ_S , the enthalpic part of the chemical potential contributes to the total internal energy. Both the enthalpy and entropy are introduced to the system via the introduction of the solvent uptake, and thus are directly related to the flux of the solvent through the polymer. The local balance of internal energy is given by

$$\rho_0 \dot{\epsilon} = \mathbf{P} : \dot{\mathbf{F}} - \nabla \cdot (\mathbf{Q} + \Phi_S \mathbf{J}) + \rho_0 r + \Phi_S W. \quad (4.8)$$

Here $\dot{\epsilon}$ represents the derivative of the internal energy with respect to time, \mathbf{Q} is the heat flux and the changes in internal energy caused by the sources of heat and diffusing species are given by $\rho_0 r$ and $\Phi_S W$ respectively.

The balance of entropy is defined as

$$\rho_0 \dot{\eta} = -\nabla \cdot \left(\frac{\mathbf{Q}}{\theta} + \eta_S \mathbf{J} \right) + \frac{\rho_0 r}{\theta} + \eta_S W + \frac{1}{\theta} \Gamma_0, \quad (4.9)$$

where $\Gamma_0 \geq 0$ is the dissipation energy. By applying a specific Helmholtz free energy of the form $\Psi = \epsilon - \theta \eta$ and introducing the coupled effective term, $\mathbf{H}_{eff} = \mathbf{Q}/\theta + \nu_S \mathbf{J}$, we obtain the balance of entropy in its Clausius-Duhem form,

$$\mathbf{P} : \dot{\mathbf{F}} - \rho_0 \dot{\Psi} - \rho_0 \eta \dot{\theta} - \mathbf{H}_{eff} \cdot \nabla \theta - \mathbf{J} \cdot \nabla \mu_S + \mu_S \dot{C}_0 \geq 0. \quad (4.10)$$

Once again note that the dot above the symbol denotes a derivative with respect to time, e.g. $\dot{a} = \partial a / \partial t$. After choosing the Helmholtz energy to be a function of the form $\Psi = \Psi(\mathbf{C}, C_0, \theta, \Xi; \mathbf{X})$, where Ξ denotes the set of internal variables, and $\mathbf{C} = \mathbf{F}^T \mathbf{F}$ represents the right Cauchy Green tensor which introduces the dependence of the Helmholtz energy on the deformation gradient. Following the Coleman-Noll [23] procedure we obtain

$$\mathbf{P} = 2\rho_0 \mathbf{F} \cdot \frac{\partial \Psi}{\partial \mathbf{C}}, \quad \mu_S = \rho_0 \frac{\partial \Psi}{\partial C_0}, \quad \eta = -\frac{\partial \Psi}{\partial \theta}, \quad (4.11)$$

which leads to the reduced dissipation inequality

$$-\mathbf{J} \cdot \nabla \mu_S - \mathbf{H}_{eff} \cdot \nabla \theta - \rho_0 \frac{\partial \Psi}{\partial \Xi} \cdot \dot{\Xi} \geq 0. \quad (4.12)$$

4.3 Temperature Evolution

The evolution of the temperature is derived from the energy balance equations given in equation (4.10) in its localized form as well as the constitutive relations for the entropy density given in the previous section, equation (4.11). Combining these equations defines an equation for the evolution of the temperature

$$-\rho_0 \theta \frac{\partial^2 \Psi}{\partial \theta^2} \dot{\theta} = -\mathbf{J} \cdot \nabla \mu_S - \nabla \cdot (\theta \mathbf{H}_{eff}) + \theta H_{eff} - \rho_0 \frac{\partial \Psi}{\partial \Xi} \cdot \dot{\Xi} + \theta \frac{\partial}{\partial \theta} \left[\mathbf{P} : \dot{\mathbf{F}} + \mu_S \dot{C}_0 + \rho_0 \frac{\partial \Psi}{\partial \Xi} \cdot \dot{\Xi} \right] \quad (4.13)$$

Here we can define $H_{eff} = \rho_0 r / \theta + \eta_S W$ and the specific heat capacity given by C_p as $C_p = -\theta \frac{\partial^2 \Psi}{\partial \theta^2}$. In this equation the coupling between the temperature evolution and the deformation of the polymer is incorporated through $\mathbf{P} : \dot{\mathbf{F}}$, the thermal derivative of the stress power. The framework we have so far describes a general system which

diffusion, heat conduction and deformation are coupled. In this next section, we will be introducing the model specific Helmholtz energy as well as diffusion laws which are needed in order to apply this general framework to that of Case II diffusion present in the swelling of the polymer.

4.4 Helmholtz Energy

Helmholtz free energy measures the useful work obtainable from a closed thermodynamic system with a given constant temperature and volume, which differs from the Gibbs free energy which measures the work obtainable from a thermodynamic system at a given constant temperature and pressure[3]. Working from the choice of Helmholtz free energy given by Govindjee and Simo (1993)[22], the free energy was decomposed into three parts;

$$\Psi = \Psi^{eq}(\mathbf{C}, \theta) + \Psi^{neq}(\mathbf{C}, \theta, \Xi) + \Psi^{mix}(\mathbf{C}, C_0, \theta), \quad (4.14)$$

where Ψ^{eq} is the free energy of an elastic material, Ψ^{neq} represents the non-equilibrium contributions and Ψ^{mix} is the free energy of mixing. A Neo-Hookean material model is chosen to represent the free energy of the polymer in the paper given by Wilmers and Bargmann,

$$\rho_0 \Psi^{eq} = \frac{\mu}{2} [\mathbf{C} - \mathbf{I}] : \mathbf{I} + \frac{\lambda}{2} \ln^2 J - \mu \ln J + \rho_0 C_p \left[\theta - \theta_0 - \theta \ln \frac{\theta}{\theta_0} \right] - 3\alpha \left[\lambda + \frac{2}{3}\mu \right] [\theta - \theta_0] \frac{\ln J}{J}, \quad (4.15)$$

meanwhile in our model we will consider a linearly elastic model. Here ρ_0 is the mass density of the polymer, meanwhile μ and λ are given Lamé constants and θ_0 is the reference temperature which is to be chosen. The non-equilibrium contribution of the material behaviour is described by

$$\frac{\partial \Psi^{neq}}{\partial \mathbf{C}} = \int_{\infty}^t \beta \exp \left(-\frac{t-s}{\tau_{relax}(s)} \right) \frac{d}{ds} \left[\frac{\partial \Psi^{eq}}{\partial \mathbf{C}}(s) \right] ds. \quad (4.16)$$

Here the parameter given by β is dimensionless, and describes the ratio of Young's moduli in the glassy and rubbery state, meanwhile τ_{relax} is the visco-elastic relaxation time of the polymer. Wilmers and Bargmann derive the mixing contribution of the free energy, Ψ^{mix} , with the use of Flory-Huggins theory of polymer mixtures[18]. From the balance of entropy via the Coleman-Noll procedure, the chemical potential is simply

$$\mu_S = \rho_0 \frac{\partial \Psi}{\partial C_0} = \rho_0 \frac{\partial \Psi^{mix}}{\partial C_0}, \quad (4.17)$$

given that the mixing contribution to the Helmholtz potential is the only term dependent on the concentration, C_0 . Thus the chemical potential can be integrated to give the mixing contribution to the Helmholtz potential,

$$\Psi^{mix} = \frac{k_B \theta}{\rho_0^2 V_0} \left[C_0 \chi \frac{1}{J} + C_0 \ln \left(\frac{C_0}{C_0 + \rho_0 \frac{m_S}{m_P}} \right) + \rho_0 \frac{m_S}{r m_P} \ln \left(\frac{C_0 + \rho_0 \frac{m_S}{m_P}}{\rho_0 \frac{m_S}{m_P}} \right) \right] + \gamma. \quad (4.18)$$

Here k_B is the Boltzmann constant[9], m_P is the mass of the polymer chain segment, m_S is the mass of a single solvent molecule, V_0 is the reference volume of the unswollen polymer, meanwhile χ represents the dimensionless Flory-Huggins interaction parameter. Finally the last constant given by γ is an independent value that accounts for the difference between the Gibbs free energy and the Helmholtz free energy per amount of solvent - the chemical potential is a Gibbs potential, but in this model it is assumed to be zero, $\gamma = 0$. Now with the Helmholtz free energy defined, the last two governing equations to define are concentration diffusion and heat conduction equations

4.5 Diffusion and Heat conduction

As mentioned before, Case II diffusion cannot be described by Fick's law. This is due to the wave-like solvent propagation with a constant diffusion front. In previous work done by Wilmers and Bargmann (2014)[52], an extension to Fick's first law was derived in order to describe this non-classical behaviour;

$$\mathbf{J}(\mathbf{X}, t + \tau_j) = -\mathbf{D}(C_0, \theta, J) \cdot \nabla C_0(\mathbf{X}, t + \tau_c), \quad (4.19)$$

where τ_j and τ_c denote retardation times representing the delay in formation of the concentration gradient and the flux due to molecular interactions. Although this expression for the diffusion flux does not guarantee that the dissipation inequality is fulfilled, the fulfillment of this inequality is checked in the appendix of this polymer swelling paper. The diffusion coefficient, \mathbf{D} , is where the coupling of the diffusion behaviour as well as the temperature and the deformation is accounted for. The diffusion coefficient is defined as

$$\mathbf{D}(C_0, \theta, J) = \mathbf{D}_0 [1 - \phi_S]^2 [1 - 2\chi\phi_S] \exp \left(-\frac{E_A}{R\theta} + \delta \left[\frac{C_0}{C_{eq}} - 0.5 \right] \right). \quad (4.20)$$

In Chapter 2: Methodology we defined the diffusion coefficient as well as ϕ_S noting that ϕ_S is the volume fraction of the solvent, given by $\phi_S = \frac{C_0}{J\rho_s}$. The activation

energy of the system is given by E_A meanwhile the constant δ , which is present in the exponential term, is valid for a number of Case II systems and is responsible for the sharp front in the model. By making use of the extended Fick's law above in equation (5.19), substituting this into the conservation of mass given by equation (5.4) with the assumption that no solvent molecules are created or destroyed within the polymer, $W = 0$, we obtain the following diffusion law governing Case II diffusion in a glassy polymer,

$$\dot{C}_0 + \tau_j \ddot{C}_0 = \nabla \cdot (\mathbf{D} \cdot \nabla C_0) + \tau_c \nabla \cdot (\mathbf{D} \cdot \nabla \dot{C}_0), \quad (4.21)$$

where we must remember the dependencies of the diffusion coefficient, \mathbf{D} , and with this diffusion equation now defined, this can be used to describe the wave-like propagation which exhibits a constant front velocity. Finally, the heat conduction in polymers follows Fourier's law, given by

$$\mathbf{Q} = -\mathbf{K} \cdot \nabla \theta, \quad (4.22)$$

where \mathbf{K} denotes the material's heat conductivity, which is required in the temperature evolution equation.

To numerically solve these equations in the simple one dimensional case, we now consider converting these three dimensional equations for the diffusion, temperature evolution as well as the linear momentum equation - which is used to calculate the location of the deformed coordinates, \mathbf{x} - into one dimensional equations which can be simplified and be numerically solved by the finite difference method.

4.6 Reformulation to 1 dimension.

In this paper, the diffusion of toluene in polystyrene is examined, which exhibits Case II diffusion. All the parameters used can be seen in table (4.1), where we must take care with all the different scalings which are present in the paper. The two way coupling of this system between the diffusion and deformation arises from the plasticisation of the material by the absorbed solvent. The diffusion front travels along the polymer in a wave like form, where after the solvent has diffused through the polymer, the polymer swells and changes from its rigid glassy state into its plasticised state. Hence before the diffusion front, the polymer remains in its rigid glassy state and has different mechanical behaviour to that of the plasticised state, thus the parameters

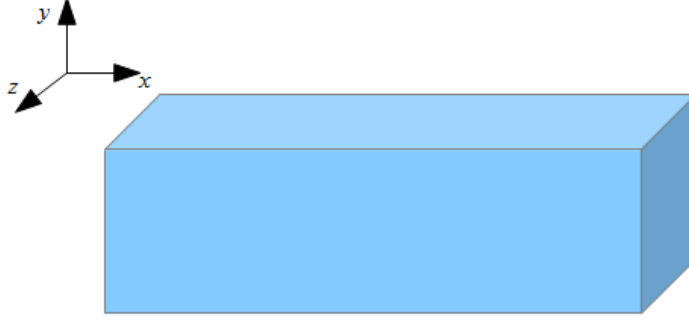


Figure 4.1: The geometry of the polymer is assumed to have a cuboid shape, with the boundary conditions applied on the small face, with the concentration diffusing in the x direction

which depend on the properties of the materials must be different ahead and behind this solvent front. Besides this change in the material's mechanical behaviour, coupling is also introduced into the system via dependence of the diffusion coefficient on the volume fraction of the solvent, as well as the Helmholtz free energy of mixing, Ψ^{mix} .

For the calculation of numerical solutions, a cuboidal geometry is assumed as seen in figure (4.1), where the solvent front diffuses in the X direction. The displacement of the cuboid is constrained on the three adjacent faces, where Dirichlet boundary conditions for both the concentration and temperature are only applied on one of these small faces. The boundary condition chosen for the concentration was the equilibrium concentration, denoted by C_{eq} , meanwhile the face at this boundary has an imposed heat of up to $\theta = 333.15\text{K}$, meanwhile the reference temperature throughout the polymer is given by $\theta_0 = 293.15\text{K}$ - where K is the measurement of temperature in the S.I. unit of Kelvins - and the value for the concentration present in the polymer everywhere except the boundary is chosen to be $C(X \neq 0, t) = 0.01C_{eq}$. Finally for every surface, the concentration and temperature fluxes are assumed to vanish, as we are only considered with the distribution of concentration and temperature within the cuboid.

Now we have the information required to numerically solve the polymer swelling model, we will proceed to rewrite and simplify these equations so that they may be numerically solved, where we shall assume linear elasticity for the model. We begin with the balance of linear momentum, or Cauchy's equation of momentum. This equation will be used to calculate the deformation of the swollen polymer from the

original position after diffusion of the solvent through the polymer;

$$\rho_0 \frac{\partial^2 x}{\partial t^2} = \frac{\partial \sigma_{XX}}{\partial X} + \rho_0 b. \quad (4.23)$$

Here x denotes the deformed coordinate or position, X is the reference position and σ is the Cauchy stress tensor. Here the Cauchy stress tensor replaces the Piola-Kirchhoff stress tensor due to the assumption of linear elasticity, which may be too restrictive. With values of the deformed position calculated, given that we are working in one dimension the determinant of the deformation gradient (\mathbf{F}) is simply given as

$$J = \det \mathbf{F} = \frac{\partial x}{\partial X}, \quad (4.24)$$

therefore for every value of the deformed coordinate that is calculated, we must update the determinant of the deformation gradient, J . In order to calculate the stress tensor, the following relation between the stress, σ and strain ε (see Chapter 2, Section 2.2.2.) was used in the previous chapter regarding Yang's chemical stresses paper;

$$\sigma_{ij} = \frac{E}{1+\nu} \left(\varepsilon_{ij} + \frac{\nu}{1-2\nu} \varepsilon_{kk} \delta_{ij} \right) + \frac{E}{1-2\nu} \alpha \Delta \theta \delta_{ij}. \quad (4.25)$$

Here, E is Young's modulus of the material, ν is Poisson's ratio, δ_{ij} represents the Kronecker delta function, $\Delta \theta$ is the difference in temperature while α is the thermal expansion coefficient. We can rewrite these equations as

$$\boldsymbol{\sigma} = 2\mu\boldsymbol{\varepsilon} + \left(\lambda \text{tr}(\boldsymbol{\varepsilon}) - \frac{E}{(1-2\nu)} \alpha \Delta \theta \right) \mathbf{I}, \quad \Delta \theta = \theta(x, t) - \theta_0. \quad (4.26)$$

The Lamé constants are given by μ and λ , meanwhile the stress and strain tensor is given by $\boldsymbol{\sigma}$ and $\boldsymbol{\varepsilon}$ respectively, with \mathbf{I} being the identity matrix - note that different Lamé constants are chosen in both the glassy and the plasticised state of the polymer. Now we have equations solving the deformed coordinates, which in turn solve the determinant of the deformation gradient, J , we consider the two equations which govern the temperature, θ , and the diffusion of the concentration, C_0 ;

$$-\rho_0 \theta \frac{\partial^2 \Psi}{\partial \theta^2} \dot{\theta} = -\mathbf{J} \cdot \nabla \mu_S - \nabla \cdot (\theta \mathbf{H}_{eff}) + \theta H_{eff} - \rho_0 \frac{\partial \Psi}{\partial \boldsymbol{\Xi}} \cdot \boldsymbol{\Xi} + \theta \frac{\partial}{\partial \theta} \left[\mathbf{P} : \dot{\mathbf{F}} + \mu_S \dot{C}_0 + \rho_0 \frac{\partial \Psi}{\partial \boldsymbol{\Xi}} \cdot \boldsymbol{\Xi} \right] \quad (4.27)$$

$$\dot{C}_0 + \tau_j \ddot{C}_0 = \nabla \cdot (\mathbf{D} \cdot \nabla C_0) + \tau_c \nabla \cdot (\mathbf{D} \cdot \nabla \dot{C}_0), \quad (4.28)$$

In one dimension, the equation governing the evolution of temperature (equation (5.27)) simplifies dramatically. We first consider that the constitutive relations are

without the history variables (or independent of the set of internal variables given by Ξ), hence

$$-\rho_0\theta\frac{\partial^2\Psi}{\partial\theta^2}\dot{\theta} = -\mathbf{J} \cdot \nabla\mu_S - \nabla \cdot (\theta\mathbf{H}_{eff}) + \theta H_{eff} + \theta\frac{\partial}{\partial\theta} [\mathbf{P} : \dot{\mathbf{F}} + \mu_S\dot{C}_0]. \quad (4.29)$$

Now we consider the term defined by \mathbf{H}_{eff} ,

$$\mathbf{H}_{eff} = \frac{1}{\theta}\mathbf{Q} + \eta_S\mathbf{J}. \quad (4.30)$$

This coupled effective term includes the diffusion flux given by \mathbf{J} , and the heat flux given by \mathbf{Q} , which are defined as

$$\mathbf{J} = -\mathbf{D} \cdot \nabla C_0, \quad \mathbf{Q} = -\mathbf{K} \cdot \nabla\theta. \quad (4.31)$$

By denoting the X coordinate or direction of these vectors with the subscript X , in one dimension these reduce to

$$J_X = -D\frac{\partial C_0}{\partial X}, \quad Q_X = -K\frac{\partial\theta}{\partial X}, \quad (4.32)$$

where the X coordinate of the diffusion coefficient $\mathbf{D} = \mathbf{D}(C_0, \theta, J)$ is given by

$$D(C_0, \theta, J) = D_0[1 - \phi_S]^2[1 - 2\chi\phi_S] \exp\left(-\frac{E_A}{R\theta} + \delta\left[\frac{C_0}{C_{eq}} - 0.5\right]\right). \quad (4.33)$$

In the example given in this paper, the maximum diffusion coefficient is given by $D_0 = 4.50714 \cdot 10^{-8}\text{cm}^2/\text{min}$. By substituting (5.31) into equation (5.30) and taking the X coordinate of the coupled effective term, \mathbf{H}_{eff} , we obtain the following;

$$[\mathbf{H}_{eff}]_X = \frac{-K}{\theta}\frac{\partial\theta}{\partial X} - \eta_SD\frac{\partial C_0}{\partial X}. \quad (4.34)$$

The reason we have denoted the X coordinate of the term \mathbf{H}_{eff} differently to before is to avoid confusion with the already present term $H_{eff} = \rho_0 r/\theta + \eta_S W$. Referring back to equation (5.29), the simplified temperature evolution equation, we recall our earlier definition of the specific heat capacity of the material,

$$C_p = -\theta\frac{\partial^2\Psi}{\partial\theta^2}. \quad (4.35)$$

If we were to take the second derivative of the Helmholtz free energy with respect to temperature, we would reach the following equation,

$$\frac{\partial^2\Psi}{\partial\theta^2} = \frac{\partial^2\Psi^{eq}}{\partial\theta^2} + \frac{\partial^2\Psi^{mix}}{\partial\theta^2}, \quad (4.36)$$

and given that the free energy of the mixing contribution, Ψ^{mix} is linear in θ , this leaves us with the free energy term alone, $\partial^2 \Psi^{eq} / \partial \theta^2$, which after differentiation leads us to this relation given in (5.35). Consider the term $\mathbf{P} : \dot{\mathbf{F}}$, in the one dimensional case this would simply be

$$\sigma_{XX} \frac{\partial v}{\partial X}, \quad (4.37)$$

where v is the velocity of the deformed coordinate, x , meanwhile X is the undeformed coordinate mentioned before. Note once again we have assumed linear elasticity allowing us to easily interchange the Piola-Kirchhoff stress tensor, \mathbf{P} with the Cauchy stress tensor, $\boldsymbol{\sigma}$. Gathering these terms gives us the following relation,

$$\rho_0 C_p \dot{\theta} = D \frac{\partial C_0}{\partial X} \frac{\partial \mu_S}{\partial X} + K \frac{\partial^2 \theta}{\partial X^2} + \frac{\partial}{\partial X} \left(\theta \eta_S D \frac{\partial C_0}{\partial X} \right) + \theta H_{eff} + \theta \frac{\partial}{\partial \theta} \left[\sigma_{XX} \frac{\partial v}{\partial X} + \mu_S \dot{C}_0 \right]. \quad (4.38)$$

By remembering $\dot{\theta} = \partial \theta / \partial t$, and following the derivative of θ through in the last term, we now have a simplified equation for evolution of temperature;

$$\rho_0 C_p \dot{\theta} = D \frac{\partial C_0}{\partial X} \frac{\partial \mu_S}{\partial X} + K \frac{\partial^2 \theta}{\partial X^2} + \frac{\partial}{\partial X} \left(\theta \eta_S D \frac{\partial C_0}{\partial X} \right) + \theta H_{eff} + \theta \frac{\partial \sigma_{XX}}{\partial \theta} \frac{\partial v}{\partial X} + \theta \frac{\partial \mu_S}{\partial \theta} \dot{C}_0. \quad (4.39)$$

Note that here $H_{eff} = (\rho_0 r / \theta) + \eta_S W$, but the assumption that no internal sources of heat are present gives us $H_{eff} = 0$. Let us now gather the governing equations which we have simplified from the 3 dimensional polymer swelling model to the one dimensional model.

4.7 Governing Equations

Here we summarize the governing equations which are in the polymer swelling paper, which have been reformulated to one dimension. The undeformed or reference coordinates are defined by X , meanwhile the time variable is given as t . The parameters have been assigned the values given in table (4.1), where we are working on the centimetres scale (10^{-2} m) as well as the time scale of minutes, therefore the parameters present as well as the position X , which is in terms of μm should be scaled accordingly. We begin with the equation which governs the diffusion of concentration through the polymer, by rewriting the concentration as $C_0 = C$;

$$\frac{\partial C}{\partial t} + \tau_j \frac{\partial^2 C}{\partial t^2} = \frac{\partial}{\partial X} \left(D \frac{\partial C}{\partial X} \right) + \tau_c \frac{\partial}{\partial X} \left(D \frac{\partial^2 C}{\partial t \partial X} \right). \quad (4.40)$$

Here the diffusion coefficient is given by D , where τ_j is the retardation time representing the delay in the formation of the concentration gradient, meanwhile τ_c denotes the retardation time representing the delay of the flux due to molecular interactions. The diffusion coefficient is defined in one dimension and is a function of the concentration, C , temperature, θ , and the deformation gradient, \mathbf{F} , through $J = \det \mathbf{F}$;

$$D(C, \theta, J) = D_0[1 - \phi_S]^2[1 - 2\chi\phi_S] \exp\left(-\frac{E_A}{R\theta} + \delta\left[\frac{C}{C_{eq}} - 0.5\right]\right), \text{ where } \phi_S = \frac{C}{J\rho_s}. \quad (4.41)$$

Here ϕ_S is the volume fraction of the solvent, D_0 represents the maximum diffusion coefficient, E_A represents the activation energy, R is the universal gas constant, C_{eq} is the equilibrium concentration which is obtained through the polymer, χ represents the Flory interaction parameter, δ represents the variation parameter of concentration dependence and finally ρ_s represents the mass density of the solvent. The simplified one dimensional temperature evolution equation we have derived is defined as

$$\rho_0 C_p \dot{\theta} = D \frac{\partial C}{\partial X} \frac{\partial \mu_S}{\partial X} + K \frac{\partial^2 \theta}{\partial X^2} + \frac{\partial}{\partial X} \left(\theta \eta_S D \frac{\partial C}{\partial X} \right) + \theta \frac{\partial \sigma_{XX}}{\partial \theta} \frac{\partial v}{\partial X} + \theta \frac{\partial \mu_S}{\partial \theta} \dot{C}. \quad (4.42)$$

Here the undefined parameters are ρ_0 , the mass density of the polymer, the specific heat capacity given by C_p , K is the heat conductivity of the material, meanwhile μ_S and η_S represent the chemical potential and specific entropy respectively. Given that we are assuming temperature dependence on the stress in the normal X direction, let us define the derivative here

$$\frac{\partial \sigma_{XX}}{\partial \theta} = \frac{\partial}{\partial \theta} \left[(2\mu + \lambda) \varepsilon_{XX} + \frac{E}{(1 - 2\nu)} \alpha(\theta(x, t) - \theta_0) \right] = \frac{E\alpha}{(1 - 2\nu)}. \quad (4.43)$$

Recall that μ and λ are Lamé constants, ε_{XX} is the normal strain in the X direction, E is Young's modulus, ν is Poisson's ratio of the material, meanwhile α is the thermal expansion coefficient. The choice for the chemical potential was derived to be

$$\mu_S = \Phi_S - \theta \eta_S, \text{ where } \Phi_S = \frac{k_B \theta}{\rho_0 V} \chi, \quad (4.44)$$

where Φ_S represents the specific enthalpy of the system, meanwhile the specific entropy (η_S) present in the chemical potential is derived by Wilmers and Bargmann in the appendix of this paper [53] as

$$\eta_S = -\frac{k_B}{\rho_0 V} \left[\ln \left(\frac{C}{C + \xi} \right) + \left[1 - \frac{1}{r} \right] \frac{\xi}{C + \xi} \right], \text{ where } \xi = \rho_0 \frac{m_S}{m_P}. \quad (4.45)$$

Care must be taken when the chemical potential and specific entropy is substituted into the equation governing temperature evolution, (4.42). The mass of the polymer chain segment and the solvent molecule are given by m_P and m_S respectively meanwhile k_B is the Boltzmann constant [9]. Recall the balance of linear momentum to be

$$\rho_0 \frac{\partial^2 x}{\partial t^2} = \frac{\partial \sigma_{XX}}{\partial X} + \rho_0 b, \quad (4.46)$$

where $\rho_0 b$ is the mass force density of the system, x is the deformed coordinate which is a function of the undeformed coordinate and time, $x = x(X, t)$, meanwhile σ_{XX} is the normal Cauchy stress in the X direction. With the equations present in the model simplified to the equations given by (4.40)-(4.46), after imposing appropriate boundary and initial conditions in the model, we now have the equations which need to be discretized in order to be numerically solved.

4.8 Boundary Conditions, Initial Conditions and Code Implementation

Here we introduce the boundary and initial conditions we impose on the reformulated one dimensional model, where we begin with the concentration, C . At $X = 3$ the boundary condition of no concentration flux was used $\partial C / \partial X = 0$, meanwhile at $X = 0$, the boundary condition $C = C_{eq}$ was applied, and we have assumed that the concentration has diffused slightly through the polymer at the very initial stages, therefore the initial condition is given as $C_{i=0,j=0} = C_{eq}$ and $C_{i=1,j \neq 0} = 0.01 C_{eq}$, where $j = 0 \implies X = 0$. If we were to choose the initial condition that $C = 0$ everywhere, the given value of η_S would blow up due to the $\ln(C/C + \xi)$ term where $\xi = \rho_0 m_s / m_p$. Given the definition of B , this constant value for C at the boundary and through the polymer gives the initial condition that $B_{i=0,j} = 0$ throughout the whole polymer. Let us recall that $J = \det \mathbf{F}$, and in one dimension this is simply

$$J = \frac{\partial x}{\partial X}. \quad (4.47)$$

Initially there is no deformation, hence $J = 1$, and $x = X$ for all values of X . More formally, initially there is no displacement (See Chapter 2: Methodology) and hence

the initial condition we can apply is

$$u = 0 \text{ at } t = 0, \quad (4.48)$$

for all X , $0 \leq X \leq 3$, where u represents the displacement, $u = x - X$. Initially the polymer is at a reference temperature of $\theta_0 = 293.15\text{K}$ throughout the polymer, except at the boundary $X = 0$. At this boundary, the face of the polymer is heated up to 333.15K for all time, hence $\theta(X = 0, t) = 333.15\text{K}$, meanwhile at $X = 3$ no temperature flux was applied, $\partial\theta/\partial X = 0$ for all times. Having defined initial and boundary condition, for ease of reference let us gather all these conditions, starting with initial conditions.

Initial Conditions The initial conditions for the concentration, temperature and displacement (and thus current coordinate, x) are given by;

$$\begin{aligned} C(X = 0, t = 0) &= C_{eq}, & C(X \neq 0, t = 0) &= (0.01)C_{eq}, \\ \theta(X = 0, t = 0) &= 333.15\text{K}, & \theta(X \neq 0, t = 0) &= 293.15\text{K}, \\ u(X, t = 0) &= 0, & \text{where } u(X, t) &= x(X, t) - X, \end{aligned}$$

respectively. Now lets consider the boundary conditions which we imposed on the

Boundary Conditions

$$\begin{aligned} C(X = 0, t) &= C_{eq}, & \left(\frac{\partial C}{\partial X} \right)_{X=3} &= 0, \\ \theta(X = 0, t) &= 333.15\text{K}, & \left(\frac{\partial \theta}{\partial X} \right)_{X=3} &= 0. \end{aligned}$$

.

Polymer Swelling Case

Let us consider the non-dimensionalization of the governing equations. Suppose A represents a variable or parameter. Introduce non-dimensional variables by \tilde{A} , and constants of the same dimension as the given variable and parameters by \hat{A} hence

$$\tilde{C} = \frac{C}{\hat{C}}, \quad \tilde{\theta} = \frac{\theta}{\hat{\theta}}, \quad \tilde{x} = \frac{x}{\hat{x}}. \quad (4.49)$$

Now consider nondimensionalizing the independent variables which represent space and time, given by X and t respectively,

$$\tilde{X} = \frac{X}{\hat{X}}, \quad \tilde{t} = \frac{t}{\hat{t}}. \quad (4.50)$$

Table 4.1: Table listing all the parameters used in the polymer swelling model by Wilmers and Bargmann [53]

Parameter	Symbol	Value	Source
Equilibrium Concentration	C_{eq}	0.13 g/ cm ³	[20]
Maximum diffusion coefficient	D_0	$4.50714 \cdot 10^{-8}$ cm ² /min	[20]
Activation Energy	E_A	1.13 eV	[20]
Variation of conc. dependence	δ	5	[52]
Flory interaction parameter	χ	0.133	[42]
Retardation time (flux)	τ_j	6732.45min	
Retardation time (gradient)	τ_c	50min	
Mass density of the polymer	ρ_0	1.04g/cm ³	[15]
Mass density of the solvent	ρ_S	0.8669 g/cm ³	
Number of polymer segments	r	3500	[20]
Mass polymer chain segment	m_p	$1.73 \cdot 10^{-25}$ kg	
Mass solvent molecule	m_s	$1.53 \cdot 10^{-25}$ kg	
Lamé constants (glassy)	λ_g	2.8GPa	
	μ_g	1.2GPa	
Lamé constants (plasticised)	λ_p	0.14GPa	
	μ_p	0.06GPa	
Viscoelastic relaxation time	τ_{rel}	$5 \cdot 10^3$ min	[22]
Specific heat capacity	C_p	1250J/(kg K)	
Thermal expansion coefficient	α	$9.0 \cdot 10^{-5}$ 1/K	[15]
Heat conductivity	K	0.17W/(m K)	

A list of the units and dimensions are given in the appendix, B, as well as the derivatives for time and space. The governing equations now become

$$\frac{\partial \tilde{C}}{\partial \tilde{t}} + \delta_1 \frac{\partial^2 \tilde{C}}{\partial \tilde{t}^2} = \delta_2 \frac{\partial}{\partial \tilde{X}} \left[\tilde{D} \frac{\partial \tilde{C}}{\partial \tilde{X}} \right] - \delta_3 \frac{\partial}{\partial \tilde{X}} \left[\tilde{D} \frac{\partial^2 \tilde{C}}{\partial \tilde{t} \partial \tilde{X}} \right], \quad (4.51)$$

$$\frac{\partial \tilde{\theta}}{\partial \tilde{t}} = \gamma_1 \tilde{D} \frac{\partial \tilde{C}}{\partial \tilde{X}} \frac{\partial \tilde{\mu}_S}{\partial \tilde{X}} + \gamma_2 \frac{\partial^2 \tilde{\theta}}{\partial \tilde{X}^2} + \gamma_3 \frac{\partial}{\partial \tilde{X}} \left(\tilde{\theta} \tilde{\eta}_S \tilde{D} \frac{\partial \tilde{C}}{\partial \tilde{X}} \right) + \gamma_4 \tilde{\theta} \frac{\partial \tilde{\sigma}_{XX}}{\partial \tilde{\theta}} \frac{\partial^2 x}{\partial \tilde{t} \partial \tilde{X}} + \gamma_5 \frac{\partial \tilde{\mu}_S}{\partial \tilde{\theta}} \frac{\partial \tilde{C}}{\partial \tilde{t}}, \quad (4.52)$$

$$\frac{\partial^2 \tilde{x}}{\partial \tilde{t}^2} = \omega_1 \frac{\partial^2 \tilde{x}}{\partial \tilde{X}^2} + \omega_2 \frac{\partial \tilde{\theta}}{\partial \tilde{X}}. \quad (4.53)$$

where we recall both $\partial v / \partial X = \partial^2 x / \partial t \partial X$ and $\partial \tilde{\sigma}_{XX} / \partial \tilde{\theta} = E\alpha / (1 - 2\nu)$. Given that we are given the Lamé constants, μ and λ , but not the values of Young's modulus and Poisson's ratio given by E and ν respectively, this can be calculated by the following relationship

$$\nu = \frac{1}{2} \left(\frac{\lambda}{\lambda + \mu} \right), \quad E = \frac{\mu}{\mu + \lambda} (2\mu + 3\lambda). \quad (4.54)$$

First let us define the coefficients which are present in the concentration diffusion

equation,

$$\delta_1 = \frac{\tau_j}{\hat{t}}, \quad \delta_2 = \frac{\hat{t}\hat{D}}{(\hat{X})^2}, \quad \delta_3 = \frac{\tau_c\hat{D}}{(\hat{X})^2}. \quad (4.55)$$

Now we define the coefficients in the temperature evolution equation;

$$\gamma_1 = \frac{\hat{D}\hat{C}\hat{\mu}_S\hat{t}}{\rho_0 C_p \hat{\theta} (\hat{X})^2}, \quad \gamma_2 = \frac{K\hat{t}}{\rho_0 C_p (\hat{X})^2}, \quad \gamma_3 = \frac{\hat{\eta}_S \hat{D} \hat{C} \hat{t}}{\rho_0 C_p (\hat{X})^2}, \quad \gamma_4 = \frac{\hat{x} E \alpha}{\hat{X} \rho_0 C_p (1 - 2\nu)}, \quad \gamma_5 = \frac{\hat{\mu}_S \hat{C}}{\rho_0 C_p \hat{\theta}} \quad (4.56)$$

meanwhile the coefficient in the balance of linear momentum is given by

$$\omega_1 = \frac{(2\mu + \lambda)\hat{t}^2}{\rho_0 (\hat{X})^2}, \quad \omega_2 = \frac{E \alpha \hat{\theta} (\hat{t})^2}{\rho_0 \hat{x} (1 - 2\nu) \hat{x} \hat{X}}. \quad (4.57)$$

Note here that the Lamé constants change depending on \tilde{C} ; if $\tilde{C} > 0.5$, the Lamé constants for the plasticised state are used, otherwise the Lamé constants for the glassy state of the polymer are used. The main problem we have now is defining the dimensional parameters (which we denoted by \hat{A}) which can be substituted into these equations. Here we denote the values chosen for our \hat{A} parameters, as well as the dimensionless parameters given by \tilde{A} . We first note that we rescale our reference coordinate by

$$X = \hat{X} \tilde{X}, \text{ where } \hat{X} = 3 \cdot 10^{-4} \text{cm}, \quad 0 \leq \tilde{X} \leq 1. \quad (4.58)$$

Now we will introduce the dimensionless variables and scales for the concentration C , temperature θ , deformed coordinate x , the chemical potential μ_S , the specific enthalpy Φ_S and finally the specific entropy, η_S . Note we also need to define the derivative $\partial\mu_S/\partial\theta$. Beginning with the concentration, here we chose

$$\tilde{C} = \frac{C}{\hat{C}}, \text{ where } \hat{C} = C_{eq} = 0.13 \text{g/cm}^3. \quad (4.59)$$

Given that the concentration diffuses through the polymer until it reaches an equilibrium concentration of C_{eq} , this choice for \hat{C} gives us the dimensionless concentration, \tilde{C} defined on $0 \leq \tilde{C} \leq 1$. Although the reference temperature through the polymer is given by $\theta_0 = 293.15\text{K}$, our choice of $\hat{\theta}$ is determined by the temperature at which one side of the polymer is heated. In this first case, the polymer is heated to $\theta = 333.15\text{K}$ at the boundary $\tilde{X} = 0$, thus the dimensionless temperature is defined to be

$$\tilde{\theta} = \frac{\theta}{\hat{\theta}}, \text{ where } \hat{\theta} = 333.15\text{K}. \quad (4.60)$$

Although we have defined the dimensionless spatial variable, \tilde{X} , we have yet to define our dimensionless time variable, \tilde{t} . We have a few choices for the value of \hat{t} , but for now from equation (4.51), we set

$$\delta_1 = 1 \implies \hat{t} = \tau_j, \quad (4.61)$$

thus,

$$\tilde{t} = \frac{t}{\hat{t}}, \text{ where } \hat{t} = \tau_j = 6732.45 \text{min.} \quad (4.62)$$

We obtain the dimensionless deformed coordinate given by x from the determinant of the deformation gradient, where

$$J = \frac{\partial x}{\partial X} \implies \hat{x} = \hat{X}, \text{ where } \hat{X} = 3 \cdot 10^{-4} \text{cm.} \quad (4.63)$$

thus for our dimensionless deformed coordinate,

$$\tilde{x} = \frac{x}{\hat{x}}, \text{ where } \hat{x} = 3 \cdot 10^{-4} \text{cm.} \quad (4.64)$$

Now we consider nondimensionalizing the chemical potential μ_S , specific enthalpy Φ_S and specific entropy η_S , as well as the one dimensional diffusion coefficient, D . Let us begin with the specific entropy, given by η_S . By choosing the constant coefficient present in the definition of the specific entropy, (4.45), the dimensionless specific entropy equation becomes

$$\tilde{\eta}_S = \frac{\eta_S}{\hat{\eta}_S}, \text{ where } \hat{\eta}_S = -\frac{k_B}{\rho_0 V_0}, \quad (4.65)$$

hence

$$\tilde{\eta}_S = \ln \left(\frac{C}{C + \rho_0 \xi} + \left[1 - \frac{1}{r} \right] \frac{\xi}{C + \xi} \right), \quad (4.66)$$

recalling the fact that $\xi = \rho_0 m_s / m_p$, where we can use the earlier defined $C = \hat{C} \tilde{C}$, noting that V_0 is the reference or undeformed volume of the polymer and all the parameter values are given in the table (4.1). Next we consider the specific enthalpy, given by Φ_S . From (4.44), let us introduce $\Phi_S = \hat{\Phi}_S \tilde{\Phi}_S$, as well as $\theta = \hat{\theta} \tilde{\theta}$, into this definition of Φ_S ;

$$\hat{\Phi}_S \tilde{\Phi}_S = \frac{k_B \chi}{\rho_0 V_0 J} \hat{\theta} \tilde{\theta}. \quad (4.67)$$

Therefore the choice of the dimensionless specific enthalpy is given by

$$\tilde{\Phi}_S = \frac{\chi}{J} \tilde{\theta}, \text{ where } \hat{\Phi}_S = \frac{k_B \hat{\theta}}{\rho_0 V_0}. \quad (4.68)$$

4.8. BOUNDARY CONDITIONS, INITIAL CONDITIONS AND CODE IMPLEMENTATION

With the dimensionless specific enthalpy now defined, we can define the dimensionless chemical potential by

$$\hat{\mu}_S \tilde{\mu}_S = \hat{\Phi}_S \tilde{\Phi}_S - \hat{\theta} \tilde{\theta} \hat{\eta}_S \tilde{\eta}_S. \quad (4.69)$$

This then implies that

$$\tilde{\mu}_S = \tilde{\Phi}_S - \tilde{\theta} \tilde{\eta}_S, \text{ where } \hat{\mu}_S = \frac{k_B \hat{\theta}}{\rho_0 V_0}. \quad (4.70)$$

The dimensionless term we need to calculate which involves the chemical potential is $\partial \mu_S / \partial \theta$, but due to the linearity of the variable $\tilde{\theta}$, this simply becomes

$$\frac{\partial \tilde{\mu}_S}{\partial \tilde{\theta}} = \frac{\chi}{J} - \tilde{\eta}_S. \quad (4.71)$$

The final dimensionless parameter we need to define is the diffusion coefficient, given by

$$D = D_0 [1 - \phi_S]^2 [1 - 2\chi\phi_S] \exp \left(-\frac{E_A}{R\theta} + \delta \left[\frac{C}{C_{eq}} - 0.5 \right] \right) \quad (4.72)$$

By making the choice $\hat{D} = D_0$, this gives us

$$\tilde{D} = [1 - \phi_S]^2 [1 - 2\chi\phi_S] \exp \left(-\frac{E_A}{R\tilde{\theta}\hat{\theta}} + \delta [\tilde{C} - 0.5] \right), \text{ where } \hat{D} = D_0 = 4.50714 \cdot 10^{-8} \text{ cm}^2/\text{min} \quad (4.73)$$

Having defined all the scaling terms above we can calculate the coefficients which are present in the dimensionless governing equations, with the approximate values for the coefficients were calculated to be

$$\begin{aligned} \delta_1 \approx 1, \quad \delta_2 \approx 3371.57, \quad \delta_3 \approx 25.04 \quad \gamma_1 \approx -2.21 \cdot (10^{-24}), \quad \gamma_2 \approx 9.8 \cdot 10^6, \\ \gamma_3 \approx -4.42 \cdot 10^{-21} \cdot (10^{-20}), \quad \gamma_4 \approx \frac{E\alpha}{\rho_0 C_p (1 - 2\nu)}, \quad \gamma_5 \approx 4.42 \cdot 10^{-25}. \end{aligned}$$

For both the plasticised and glassy state of the polymer, different values of ω_1 were calculated,

$$\omega_1^g \approx 2.9433 \cdot 10^{15}, \quad \omega_1^p \approx 5.8867 \cdot 10^{17}, \quad \omega_2 = \frac{E\alpha\hat{\theta}(\hat{t})^2}{\rho_0 \hat{x} \hat{X} (1 - 2\nu)}.$$

where if $\tilde{C} \geq 0.5$, the value $\omega_1 = \omega_1^g$ is chosen, otherwise $\omega_1 = \omega_1^p$. Now we will define the initial and boundary conditions we have imposed for the dimensionless variables, beginning with the concentration, \tilde{C} .

Initial and Boundary Conditions

As mentioned above, all the dimensionless variables and scaling parameters are given in appendix (B). Dirichlet boundary conditions were chosen for the concentration at $\tilde{X} = 0$ meanwhile at the boundary $\tilde{X} = 1$, Neumann boundary conditions were chosen;

$$\tilde{C}(\tilde{X} = 0, \tilde{t}) = 1, \quad \left(\frac{\partial \tilde{C}}{\partial \tilde{X}} \right)_{\tilde{X}=1} = 0. \quad (4.74)$$

Initially, we assume the concentration is diffusing from $\tilde{X} = 0$ to the rest of the polymer, and assume a small concentration of the solvent has already diffused through the polymer

$$\tilde{C}(\tilde{X} = 0, \tilde{t} = 0) = 1, \quad \tilde{C}(\tilde{X} \neq 0, \tilde{t} = 0) = 0.01. \quad (4.75)$$

Similar boundary conditions were chosen for the temperature which diffuses through the material. Dirichlet boundary conditions were imposed at $\tilde{X} = 0$, meanwhile Neumann boundary conditions were imposed at $\tilde{X} = 1$;

$$\tilde{\theta}(\tilde{X} = 0, \tilde{t}) = 1, \quad \left(\frac{\partial \tilde{\theta}}{\partial \tilde{X}} \right)_{\tilde{X}=1} = 0. \quad (4.76)$$

The reference temperature throughout the polymer was given to be $\theta_0 = 293.15\text{K}$, meanwhile the boundary at $\tilde{X} = 0$ was heated to $\theta = 333.15\text{K}$. Therefore by setting $\hat{\theta} = 333.15\text{K}$, the initial conditions for the temperature now become

$$\tilde{\theta} = (\tilde{X} = 0, \tilde{t} = 0) = 1, \quad \tilde{\theta}(\tilde{X} \neq 0, \tilde{t} = 0) = \frac{293.15}{333.15}. \quad (4.77)$$

Now consider the position of the deformed X coordinate, $\tilde{x}(\tilde{X}, \tilde{t})$. Recall that the displacement is defined to be $u = \tilde{x} - X$, hence $\tilde{u} = \tilde{x} - \tilde{X}$ (where $\hat{u} = \hat{x} = \hat{X}$), we impose the initial condition

$$\tilde{u} = 0, \text{ at } t = 0. \quad (4.78)$$

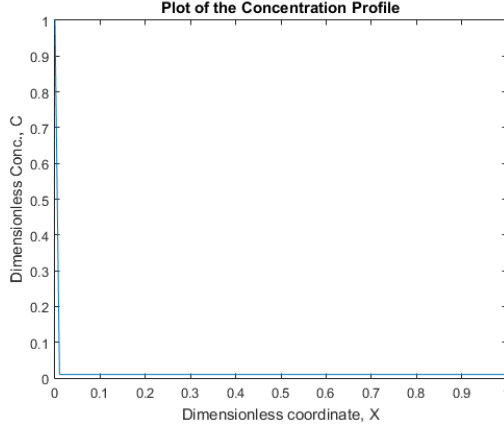
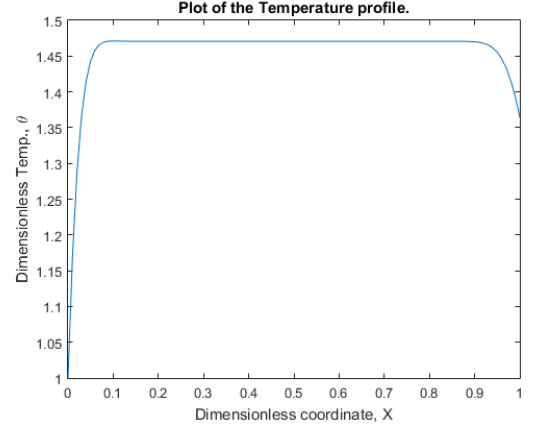
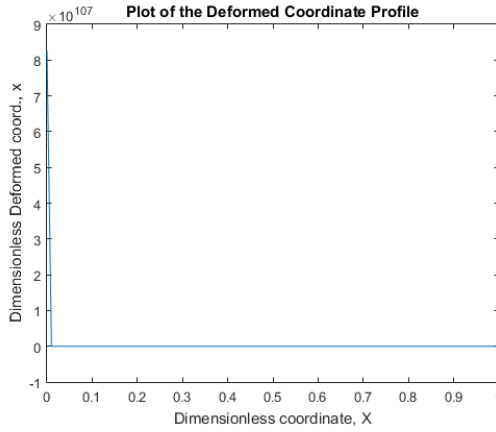
Given that we are working in only one dimension, J is simply

$$J = \frac{\partial x}{\partial X}. \quad (4.79)$$

Therefore for this initial condition for the displacement we are able to obtain an initial condition for the determinant of the deformation gradient

$$J = 1 \text{ for } t = 0. \quad (4.80)$$

We now have the boundary and initial conditions needed to solve our code. By setting the forcing terms and rewriting the equations in the code to the dimensionless code

Figure 4.2: Plot of \tilde{C} against the position coordinate, \tilde{X} Figure 4.3: Plot of $\tilde{\theta}$ against the undeformed position, \tilde{X} Figure 4.4: Plot of \tilde{x} against the undeformed position coordinate, \tilde{X}

the results obtained were unsatisfactory. Given the reformulation of the polymer swelling code we expected somewhat similar results given to the paper. The only reasonable plots we obtained were the given fixed initial and boundary conditions for the concentration profile, although this was only after a few iterations, which can be seen in (4.2). Further iterations caused the value of concentration to blow up, for a scheme with a very small timestep ($\Delta t = 10^{-6}$). Having noticed this term blowing up rapidly we then set our sights on whether the temperature and deformed coordinate plots were sensible. For the same number of iterations as the concentration profile was plotted, the figures (4.3) and (4.4) show the dimensionless temperature, $\tilde{\theta}$ and the dimensionless deformed coordinate, \tilde{x} . From the approximate values of the coefficients we have calculated, we should not be surprised that our explicit solver was unsuccessful. Due to the large separation in timescales which is present in the

governing equations, an explicit finite difference scheme would never have worked. In the previous chemical-induced stresses paper given by Yang, the assumption of mechanical equilibrium was made. Here due to the coupling this would lead to no thermoelastic effects unless these were included in the model, which we neglected initially assuming linear elasticity with the omission of thermoelastic affects. In order to attempt solve these equations, we must first reintroduce thermoelastic affects which we neglected and reformulate the one dimensional equations which we derived. Then we could solve this problem by introducing an implicit solver due to the implicit solvers' ability to deal with multiple timescales which differ drastically. Although further work needs to be done regarding the numerical solutions of the reformulated one dimensional equations which are present in the polymer swelling paper, it would prove beneficial to analyse the main results in the paper given by Wilmers and Bargmann.

4.9 Polymer Swelling Results

The geometry of the 3 dimensional polymer used in the paper followed the same geometry as (4.1). The concentration diffuses from the small face of the cuboid with an imposed heating of up to 333.15K on the same face. The solvent diffuses down this cuboid in a wave-like front down the x direction given in (4.1), after this front the polymer swells considerably while almost no deformation besides the thermal expansion occurs in the low concentration region ahead of the front. Directly ahead of this front where the polymer is in its glassy state and unable to deform, tensile stresses were observed, meanwhile behind this front due to the swelling and the adjacent rigid glassy state compressive strains are observed. For Case II diffusion, heat conduction is orders of magnitude faster than the solvent transport, hence by heating one face of the polymer a homogeneous temperature (in this case, $\theta = 333.15\text{K}$) is achieved much quicker through the polymer.

Different temperatures were applied to the small face of the polymer to investigate the coupling between the temperature as well as the diffusion and swelling. As the temperature in the material increases, different diffusion front velocities were observed, leading to faster concentration diffusion through the plate. With higher imposed temperatures, the solvent front widens due to the relation between the diffusivity

and the temperature - the larger the value of the imposed heating, the larger the diffusion coefficient becomes and thus the solvent diffuses much more quickly. Finally the relationship between the volume of the swollen sample and the temperature was investigated; a linear relation exists between increasing temperature and the volume change of the polymer - although this is not due to thermal expansion as the thermal expansion only accounts for a minimal percentage of the volume increase. Although small pre-deformation of the polymer material has little influence on the modelled diffusion behaviour, large pre-deformation was observed by Harmon et al.(1987)[24] to cause a transition from Case II behaviour of diffusion to that of a more Fickian or Case I behaviour.

4.10 Summary

For this chapter we have investigated the Polymer swelling paper given by Wilmers and Bargmann(2015)[53], *A Continuum Mechanical Model for the Description of Solvent Induced Swelling In Polymeric Glasses: Thermomechanics coupled with diffusion*. A definition of Case II solvent diffusion in polymers was given as Case II diffusion occurs rather than Case I or Fickian diffusion. Then a general formulation which coupled diffusion, heat conduction and deformation were coupled before Helmholtz energy, diffusion laws and heat conduction laws were introduced in order to transition this general framework to a framework that describes Case II diffusion. In doing this, governing equations and their derivations were considered, where equations governing the concentration diffusion, the temperature evolution and the balance of linear momentum were derived. A reformulation of the 3 dimensional equations to one dimension under given assumptions was formulated, with an attempt to numerically solve these equations. After a failed first attempt to numerically solve these equations, nondimensionalization of the governing equations was undertaken which revealed large differences in timestep, which cannot be easily solved with the explicit finite difference scheme we have implemented. For the future we may consider analysing further the reasons why this code had failed, including wrong formulation, incorrect parameter scalings as well as time scalings and choice of finite difference scheme. Although the results obtained from the numerical solutions was unsatisfactory, a detailed look into

the polymer swelling paper and interesting properties of Case II diffusion was undertaken, namely the development of stresses and a further investigation of the coupling between the concentration, temperature and deformation of the polymer.

Although a lot of the specifics of this model are not directly relevant to the formation of uranium hydride blisters, a general framework which couples diffusion, heat conduction and deformation was formulated. Having formulated this general framework, Case II specific laws of diffusion and heat conduction were implemented - further investigation of how these Case II specific laws were derived could help further our understanding and develop our own metal material specific diffusion and heat conduction laws, taking into consideration unique properties of the uranium hydride blister formation.

Chapter 5

Conclusion

The aim of this dissertation was to help further our understanding of the formation of uranium hydride blisters on a bed of uranium exposed to gaseous hydrogen. If a material body is exposed to a diffusing solvent causing it to deform, we must consider coupling both the fields of thermomechanics and diffusion theory. In order to investigate coupling between thermomechanics and diffusion, a basis of understanding was needed in both continuum mechanics, chemistry and diffusion. A brief discussion of chemistry and the use of law of mass actions was undertaken. Following the derivation of Fick's laws of diffusion as well as defining reaction-diffusion systems, we turned our attention towards defining the laws needed in continuum mechanics. Basic definitions from continuum mechanics were defined, as well as various tensors governing the infinitesimal strain and stress. Constitutive relations relating the strain, and thus the deformation, and stress were defined, as well as relevant equations of motion and equilibrium. Brief insight as to how continuum mechanics and diffusion could be coupled was observed, namely the coupling terms which are present in the two research papers we investigated into greater detail later on. Given the complexities of the coupled equations we would come across, an overview of the different finite difference methods available at our disposal and their use in formulating numerical solutions was undertaken, with an emphasis on explicit difference scheme as this was our difference scheme of choice for the remainder of the project.

We investigated two different research papers that successfully couple thermomechanics and diffusion. The first of these was "*Interaction between diffusion and chemical stresses*" by F. Yang[54]. First, Yang formulates a relationship between the hydrostatic stress and the concentration of solute atoms present in the metal; for a solid free of external body forces, the Laplacian of the hydrostatic stress is proportional to the Laplacian of the concentration of solute atoms. Then a general relationship among surface concentration of solute atoms, normal stress and surface deformation is also derived, where the normal stress is dependent on the mean curvature of the undeformed surface and the tangential components of the surface displacement. A model of a thin sheet of metal exposed to chemical concentrations on both sides of the plate was developed. Given the assumption of a steady state chemical stresses as well as a constant surface concentration, an analytical solution is formed as well as numerical solutions to the more interesting and relevant case which governs the evolution of chemical stresses. For a metal plate with two surfaces exposed to a chemical concentration, nonlinear distribution of concentration was observed for larger differences in the concentration chemicals at either side of the plate in the case of steady state concentrations. After assuming the concentration surfaces of the plate are the same, analysis was undertaken into the non-steady state of the system with two particular cases; the first case with a constant surface concentration, and the other case with an initially deposited surface concentration. Similar results were obtained for the two cases, once the thin plate was initially exposed to concentration, the highest stresses were observed at the centre of the plate, even though no solvent had diffused to the centre. Although over time the stresses decreased in time after initial exposure, a constant value of stress was reached once a uniform distribution was reached; this value of stress was due to the relationship derived between the concentration and the hydrostatic stress earlier in the paper. Given Yang's results, assuming a linear relation between the strain and concentration for our model would not be a terrible idea. Unlike Yang's model though, we would ideally have a metal which has only one surface exposed to a concentration of solute atoms, which the solute atoms would then precipitate into the metal or under the surface, forming a more complicated model. Although this model is clear and easy to follow, given the geometry of blisters, we would be interested in more than developing a relationship between the hydrostatic

stress and the concentration, introducing reaction terms which would then formulate blisters.

The second of these papers proved to be a much more complicated model than that of Yang's chemical stresses paper. Wilmers and Bargmann's paper [53] undertook a detailed view into the numerical solution of Case II diffusion through polymers. A general framework which coupled diffusion, heat conduction and deformation was formed in three dimensions, before being extended and altered for Case II diffusion and its governing laws of diffusion. Hence governing equations and their derivations were considered, where equations which govern the diffusion of concentration, temperature evolution and deformation were defined. Reformulation of these three dimensional equations to one dimensional equations with certain assumptions was undertaken, with an aim to numerically solve these equations. Code was gradually built up to solve these equations and after an unsuccessful attempt, we considered nondimensionalizing the reformulated governing equations. The results obtained from this were unsatisfactory - it was perhaps somewhat naive to attempt to numerically solve these complicated equations with an explicit difference scheme, due to the complications that arise with numerical stability, particularly with large differences in timescale. Although Wilmers and Bargmann's paper successfully predict and describe Case II diffusion in a polymer exposed to a solvent, they are somewhat vague as to how they went about solving these governing equations and were unclear with the choice of scalings and inconsistent with the parameters involved. Due to these variety of scales introduced in the parameters we had to rescale a few of these parameters to ensure consistency in the model, which could be a major leading factor as to why the code was unsuccessful. For future work better numerical solvers should be used to solve these reformulated equations, as well as a careful rescaling of the parameters which are present. Even though we are interested mainly in the deformation of metals once exposed to chemical solvents, a detailed look into Wilmers and Bargmann's paper proves to be beneficial as a general framework which couples diffusion, temperature and deformation are formed which can be used to our advantage.

Our aim of the current dissertation was to get a good grounding on coupling the effects of diffusion and thermomechanics. Yang's research paper proves to be simple to follow and formulates a linear relationship between the hydrostatic stresses which

develop in a plate, and the chemical concentration the metal material is exposed to. If we were to extend Yang's model to suit our needs we would need to consider and investigate the relationship between each of the components of the Cauchy stress tensor, σ_{ij} , with the concentration as Yang's model only considers hydrostatic stress, which is the average of the three normal stress components. With this further investigation, we would hope to introduce reaction terms which would lead to the formation of uranium hydride blisters. Regarding the work undertaken in the polymer swelling paper, the first thing we would have to do would be to develop a more complicated or advanced solver to solve the reformulated solutions we have derived. Once this has been done, a very detailed look into the choice of parameters and making use of the correct scalings is of the utmost importance. We would then have the understanding to further research the work which has been done in order to formulate these diffusion and heat conduction laws for Case II diffusion and see whether laws could be developed for our blister formation problem, where we would like to include reaction terms in the appropriate equations which govern the development of blisters.

Appendix A

Analytic Derivatives

Here $\partial D/\partial X$ for Case 4 in Section 5.7: Numerical solutions in the final section of Chapter 5 is given by

$$\frac{\partial D}{\partial X} = D_0 \frac{\partial f(\phi_s)}{\partial X} \exp(g(C, \theta)) + Df(\phi_s) \frac{\partial g}{\partial X} \exp(g(C, \theta)), \quad (\text{A.1})$$

where $f = [1 - \phi_s]^2[1 - 2\chi\phi_s]$, $\phi_s = C/J\rho_s$ and

$$\frac{\partial f}{\partial X} = [2(\phi_s - 1)(1 - 2\chi\phi_s) - 2\chi(1 - \phi_s)^2] \left[\frac{1}{J} \frac{\partial C}{\partial X} - \frac{C}{J^2} \frac{\partial J}{\partial X} \right] \quad (\text{A.2})$$

where $C = 0.1 + 0.01X \sin t$, $J = 1 + Xt^2$, and the function $g(C, \theta)$ is defined by

$$g(C, \theta) = -\frac{E_A}{R\theta} + \delta \left[\frac{C}{C_{eq}} - 0.5 \right], \quad \frac{\partial g}{\partial X} = \frac{\delta}{C_{eq}} \frac{\partial C}{\partial X} + \frac{E_A}{R\theta^2} \frac{\partial \theta}{\partial X}, \quad (\text{A.3})$$

where the analytic solution for the temperature is defined to be $\theta = 1 + X^2 \sin t/2$.

We move onto the other derivatives, $\partial\eta_s/\partial X$, $\partial\mu_s/\partial X$ and $\partial\mu_s/\partial\theta$, which are in the forcing terms. Beginning with $\partial\eta_s/\partial X$,

$$\frac{\partial\eta_s}{\partial X} = \frac{\partial\eta_s}{\partial C} \frac{\partial C}{\partial X}, \quad \text{where} \quad \frac{\partial\eta_s}{\partial C} = -\frac{k_B}{\rho_0 V} \left[\frac{\xi}{C(C + \xi)} - \left(1 - \frac{1}{r}\right) \frac{\xi}{(C + \xi)^2} \right], \quad (\text{A.4})$$

recalling $\xi = \rho_0 m_s/m_p$. In order to define $\partial\mu_s/\partial X$, let us first define the derivatives $\partial\mu_s/\partial C$, $\partial\mu_s/\partial\theta$ as well as $\partial\mu_s/\partial J$.

$$\frac{\partial\mu_s}{\partial C} = -\theta \frac{\partial\eta_s}{\partial C}, \quad \frac{\partial\mu_s}{\partial\theta} = \left(\frac{k_B \chi}{\rho_0 V J} - \eta_s \right), \quad \frac{\partial\mu_s}{\partial J} = -\frac{k_B \chi}{\rho_0 V J^2}. \quad (\text{A.5})$$

With these defined, simply via the chain rule we get

$$\frac{\partial\mu_s}{\partial X} = \frac{\partial\mu_s}{\partial C} \frac{\partial C}{\partial X} + \frac{\partial\mu_s}{\partial\theta} \frac{\partial\theta}{\partial X} + \frac{\partial\mu_s}{\partial J} \frac{\partial J}{\partial X}. \quad (\text{A.6})$$

Appendix B

Dimensional Analysis

Here let us consider first the dependent variables present, the concentration, temperature and the position of the deformed coordinate. Suppose A represents a variable or parameter. We introduce non-dimensional variables by \tilde{A} , and constants of the same dimension as the given variable and parameters by \hat{A} . To nondimensionalize the dependent variables, we introduce the following

$$\tilde{C} = \frac{C}{\hat{C}}, \quad \tilde{\theta} = \frac{\theta}{\hat{\theta}}, \quad \tilde{x} = \frac{x}{\hat{x}}. \quad (\text{B.1})$$

Now consider nondimensionalizing the independent variables which represent space and time, given by X and t respectively.

$$\tilde{X} = \frac{X}{\hat{X}}, \quad \tilde{t} = \frac{t}{\hat{t}}. \quad (\text{B.2})$$

These derivatives thus become

$$\frac{\partial}{\partial X} = \frac{1}{\hat{X}} \frac{\partial}{\partial \tilde{X}}, \quad \text{and} \quad \frac{\partial}{\partial t} = \frac{1}{\hat{t}} \frac{\partial}{\partial \tilde{t}}. \quad (\text{B.3})$$

With the dimensionless variables now defined, as well as the derivatives, these can be substituted into the governing equations and can be nondimensionalized, in order to ensure the dimensions are correct, let define the dimensions of the parameters involved.

B.1 Variable and Parameter dimensions

First of all, let us define the dimensions; L is the length dimension, T is the time dimension, M represents mass meanwhile Θ represents the temperature. Obviously

$[X] = L$, $[x] = L$, $[t] = T$ as well as $[\theta] = \Theta$. The concentration here is defined as the mass of solvent per volume of the mixture, hence $[C] = M/L^3$. Having given dimensions to the independent and dependent variables, let us define the dimensions of all the parameters which is present;

$$\begin{aligned}
 &\text{Mass density; } [\rho_0] = \frac{M}{L^3}, \quad \text{Specific Heat Capacity; } [C_p] = \frac{L^2}{\Theta T^2} \\
 &\text{Diffusion Coefficient; } [D] = \frac{L^2}{T}, \quad \text{Chemical Potential; } [\mu_s] = \frac{L^2}{T^2} \\
 &\quad \text{Specific Enthalpy; } [\Phi] = \frac{L^2}{T^2}, \quad \text{Specific Entropy; } [\eta_s] = \frac{L^2}{\Theta T^2} \\
 &\text{Heat Conductivity; } [K] = \frac{ML}{\Theta T^3}, \quad \text{Acceleration force; } [b] = \frac{L}{T^2}, \\
 &\text{Stress; } [\sigma] = \frac{M}{LT^2}, \quad \text{Thermal Expansion Coefficient; } [\alpha] = \frac{1}{\Theta}.
 \end{aligned}$$

Note care must be taking with the Specific heat capacity, specific enthalpy and specific entropy; the dimensions of these parameters given in the model differ from the heat capacity, enthalpy and entropy. With the dimensions of these parameters defined, we see that the dimensionless equations now governing the concentration, temperature and deformed coordinate are consistent.

Appendix C

Code

C.1 Chapter 4: Constant Surface Concentration

```
%Code for implementing the numerical solutions of Yang's Paper
%We want to solve
%  $(1 + \alpha C)C_{xx} + \alpha (C_x)^2 = C_t$ 
%Where  $C_{xx}$  is the 2nd derivative w.r.t.  $x$ ,  $C_t$  is 1st derivative w.r.t  $t$ 
%etc.
clear all
%First, we define the parameters needed for this solution.
J=100; %Number of steps
dx = 1/J; %Size of spatial steps
dt = (dx^2)/5 ; %Size of time steps (altered!)
mu = dt/(dx^2); %mu < 1/2 is necessary for explicit stability
Timestep = 1.0/dt; %Number of timesteps
alpha=0.01;
nu = 0.3; %Poisson's ratio of the material

%Defining x and Boundary conditions of plate
for k=1:J+1
    x(k)=(k-1)*dx;
    C0(k) = 0;
    if k == J+1
        C0(k) = 1;
    end
end
```

```

end

hold on

for i=1:Timestep           %Time loop
    t(i)=i*dt;             %Defining t(i)

    if i==1                %Implementing initial conditions
        ConcOld = C0;
    else
        ConcOld = ConcNew;
    end

    for j=1:J+1            %Spatial Loop
        if j==1            %Implement Neumann Boundary condition
            source = 0;
            diffusion = (1+alpha*ConcOld(j))*((2*ConcOld(j+1) - 2*ConcOld(j))/(dx^2));
        elseif j==J+1
            source =0;
            diffusion =0;
            ConcNew(j)=C0(J+1);
            Stress(j) = [(1+nu)*ConcNew(j)]/[9*(1-nu)*(1-2*nu)];
        else
            source = alpha*((ConcOld(j+1)-ConcOld(j-1))/(2*dx))^2;
            diffusion = (1+alpha*ConcOld(j))*(ConcOld(j+1)-2*ConcOld(j)+ConcOld(j-1));
        end
        ConcNew(j) = ConcOld(j) + dt*[diffusion + source];
        Stress(j) = 2*(1/(6*(1-2*nu)) - ConcNew(j)/(1-nu));
    end

    if t(i)==0.01
        plot(x,ConcOld)
        axis([0,1,0,1])
    end

    if t(i)==0.05
        plot(x,ConcOld)
        axis([0,1,0,1])
    end

    if t(i)==0.1
        plot(x,ConcOld)
    end

```

```

axis([0,1,0,1])
end
if t(i)==0.2
    plot(x,ConcOld)
end
if t(i)==0.4
    plot(x,ConcOld)
end
if t(i)==0.9
    plot(x,ConcOld)
end
end
legend('t=0.01','t=0.05','t=0.1','t=0.2','t=0.4','t=0.9','Location','southeast')
title('Concentration profiles for a constant surface concentration, alpha = 0.01')
xlabel('x/a')
ylabel('C/C_{0}')
hold off

```

C.2 Chapter 4: Fixed amount of solute deposited initially

```

%Code for implementing the numerical solutions of Yang's Paper
%We want to solve
%  $(1 + \alpha * C) * C_{xx} + \alpha * (C_x)^2 = C_t$ 
%Where  $C_{xx}$  is the 2nd derivative w.r.t.  $x$  ,  $C_t$  is 1st derivative w.r.t  $t$ 
%etc.
clear all
%First, we define the parameters needed for this solution.
J=100; %Number of steps
dx = 1/J; %Size of spatial steps
dt = (dx^2)/5 ; %Size of time steps (altered!)
mu = dt/(dx^2); %mu < 1/2 is necessary for explicit stability
Timestep = 1.0/dt; %Number of timesteps
alpha=0.01;
nu = 0.3; %Poisson's ratio of the material
for k=1:J+1

```

```

x(k)=(k-1)*dx;
C0(k) = 0;
if k == J+1
C0(k)= 1;
end
end

hold on

for i=1:Timestep           %Time loop
t(i)=i*dt;                %Defining t(i)
%Defining x and Boundary conditions of plate
    if i==1                %Implementing initial conditions
        ConcOld = C0;
    else
        ConcOld = ConcNew;
    end
    for j=1:J+1            %Spatial Loop
        if j==1            %Implement Neumann Boundary condition
            source = 0;
            diffusion = (1+[alpha*ConcOld(j)])*((2*ConcOld(j+1) - 2*ConcOld(j))/(dx^2));
        elseif j==J+1
            source = 0;
            diffusion = (1+[alpha*ConcOld(j)])*((2*ConcOld(j-1)-2*ConcOld(j))/(dx^2));
        else
            source = [alpha]*(((ConcOld(j+1)- ConcOld(j-1))/(2*dx))^2);
            diffusion = (1+[alpha*ConcOld(j)])*((ConcOld(j+1)-2*ConcOld(j)+ConcOld(j-1))/(dx^2));
        end
        ConcNew(j) = ConcOld(j) + dt*[diffusion + source];
        Stress(j) = 2*(1/(6*(1-2*nu)) - ConcOld(j)/(1-nu));
    end
    if t(i)==0.01
        int = 0.5 *dx * [ ConcOld(1) + ConcOld(J+1) + 2 *sum(ConcOld(2:J))];
        plot(x,ConcNew/int);
    end
    if t(i)==0.02
        int = 0.5 *dx * [ ConcOld(1) + ConcOld(J+1) + 2 *sum(ConcOld(2:J))];
        plot(x,ConcNew/int);
    end
end

```

```

end
if t(i)==0.05
    int = 0.5 *dx * [ ConcOld(1) + ConcOld(J+1) + 2 *sum(ConcOld(2:J))] ;
    plot(x,ConcNew/int);
end
if t(i)==0.1
    int = 0.5 *dx * [ ConcOld(1) + ConcOld(J+1) + 2 *sum(ConcOld(2:J))] ;
    plot(x,ConcNew/int);

end
if t(i)==0.2
    int = 0.5 *dx * [ ConcOld(1) + ConcOld(J+1) + 2 *sum(ConcOld(2:J))] ;
    plot(x,ConcNew/int);
end
if t(i)==0.4
    int = 0.5 *dx * [ ConcOld(1) + ConcOld(J+1) + 2 *sum(ConcOld(2:J))] ;
    plot(x,ConcNew/int);
end
if t(i)==0.9
    int = 0.5 *dx * [ ConcOld(1) + ConcOld(J+1) + 2 *sum(ConcOld(2:J))] ;
    plot(x,ConcNew/int);
end
end
legend('t=0.01','t=0.05','t=0.1','t=0.2','t=0.4','t=0.9','Location','northwest')
title('Concentration profiles for a fixed initial conc.,alpha = 0.01')
xlabel('x/a')
ylabel('C/C_{av}')
hold off

```

C.3 Chapter 5: Case 4

```

%Here is some code to test whether or not the assumption used in the
%Polymer Swelling code is accurate.
%We will be solving  $C(x,t) = x \sin(t)$ ,  $F = x \cos(t) - \sin(t)$ .
%We will be solving  $dc/dt + \tau_{uj} d^2c/dt^2 = d/dx(D dc/dx) + \tau_{uc} d/dx(D dc/dx) + F$ .
%as well as  $C_p dT/dt = D dc/dx + k d^2 T / d x^2 + dD/dx * dc/dx +$ 
%D*d^2c/dx^2 + T*dc/dt + R

```

%Note here we follow the notation given in the Polymer swelling paper.
 %although we have defined the undeformed coordinates here as x and the
 %deformed as X , in the figures we need to plot the deformed coordinates
 %givne in the paper by x , and the undeformed by X.

%Note this code for test5 doesn't quite work but not sure why.
 %Hence I moved on to a new code, Test6.

clear all;

```
J = 100; %Number of spatial steps
Domain = 3; %Size of the domain, micrometers
dx = Domain/J; %Spatial step
dt = (dx^2)/18; %Time step
mu = dt / (dx^2); %mu = dt/dx^2
Timestep = 1/dt;
tau_c = 50; %Retardation time gradient
tau_j = 6732.45; %Retardation time flux
C_p = 1250; %Specific heat capacity
K=0.17; %Heat conductivity
E_A = 1.13; %Activation Energy
C_eq = 0.13; %Eq. Conc.
```

%Note if C_eq = 0.13 like the polymer swelling paper the diffusion
 %coefficient blows up drastically, hence we need to redefine our
 %concentration to fit this value of concentration - keeping in mind that
 %the max value of the concentration in the polymer paper is 0.13!!

```
D_0 = 4.50714*(10^(-8)); %Max diffusion coeff. in micrometers
delta = 5 ; %Variaton parameter
chi=0.133; %Flory interaction parameter
rho_0 =(1.04); %Mass density of the polymer
rho_s = 0.8669; %Mass density of the solvent
r = 3500; %Number of polymer segments
m_p = 1.73*(10^(-25)); %Mass polymer chain segment
m_s = 1.53*(10^(-25)); %Mass solvent molecule
lamb_g = 2.8; %Lame constants, glassy
```

```

mu_g = 1.2; %Lame constants, glass
lambda_p = 0.14; %Lame constants, polymer
mu_p = 0.06; %Lame constants, polymer
tau_relax = 5*(10^3); %Viscoelastic relaxation time
alpha = 9*(10^(-5)); %Thermal expansion coefficient
R = 8.3144621; %universal gas const.
k_B = 1.3806488*(10^(-23)); %Boltzmann const.
V = 1; %Volume, chosen 1 for now
G = rho_0*(m_s/m_p); %Constant simplified for nu_s

%First define the spatial domains
for k=1:J+1
    x(k)=(k-1)*dx;

    %Initial values for conc (from analytic soln) C
    C0(k) = 0.1;

    %Initial values for deriv. conc (analytic) B
    B0(k) = (0.01)*x(k);

    %Initial value for theta, (analytic).
    theta_0(k) = 1;

    %Initial value for the deformed coord, X
    X_0(k) = x(k);

    %Initial value of Y = dX/dt
    Y_0(k) = 0;

    %Initial value for det. of def. grad. J
    J_0(k) = 1;
end

%Defining the time domain
for p=1:Timestep+1
    t(p)=(p-1)*dt;
end

hold on

```



```

%Time Loop
for i=1:Timestep+1
    %Spatial Loop
    for j=1:J+1
        i
        %Analytic Solutions

        %Given Concentration, C
        C1(i,j) = 0.1 + ((0.01)*x(j))*sin(t(i));

        %Given conc. derivative, B = dC/dt
        B1(i,j) = ((0.01)*x(j))*cos(t(i));

        %Given temperature , theta.
        theta1(i,j) = 1 + (0.5)*(x(j)^2)*sin(t(i));

        %Given deformed coord, X
        X1(i,j) = x(j) + 0.5*(x(j)^2)*(t(i)^2);

        %Given deformed coord, Y = dX/dt
        Y1(i,j) = t(i)*(x(j)^2);

        %Given det. of the deform. grad., J
        J1(i,j) = 1 + x(j)*(t(i)^2);

    end

    %Applying initial conditions
    if i==1
        %Initial condition for conc, C
        C_Old = C0;

        %Initial condition for conc. derivative, B
        B_Old = B0;

        %Initial condition for the temperature.
        theta_Old = theta_0;
    end
end

```

```

%Initial condition for the deformed coord, X
X_Old = X_0;

%Initial condition of Y = dX/dt
Y_Old = Y_0;

%Applying "final" time conditions
elseif i==Timestep+1
    %Applying the analytic soln for the final time, C
    C_New = C1(Timestep+1,:);

    %Applying the analytic soln for the final time, B
    B_New = B1(Timestep+1,:);

    %Applying the analytic soln for the final time, theta
    theta_New = theta1(Timestep+1,:);

    %Applying the analytic soln for the final time, X
    X_New = X1(Timestep+1,:);

    %Applying the analytic solution for the final time, Y
    Y_New = Y1(Timestep+1,:);

    return

%Applying the updating of vectors
else
    %Updating B=dC/dt
    B_Old = B_New;

    %Updating C
    C_Old = C_New;

    %Updating the temperature, theta
    theta_Old = theta_New;

    %Updating the deformed coord, X
    X_Old = X_New;

```

```

    %Updating the deformed coord, Y = dX/dt
    Y_Old = Y_New;
end

%Defining the diffusion coefficient and the forcing term
for p=1:J+1

    %Defining the calculated det. of the def. grad., J
    if p==J+1
        J_curr(p) = (1/dx)*(X_Old(p-1)-X_Old(p));
    else
        J_curr(p) = (1/dx)*(X_Old(p+1)-X_Old(p));
    end

    %Defining the exact det. of the def. grad., J
    J_curr1(p) = 1 + x(p)*(t(i)^2);

    %Defining the calculated volume fraction phi_s
    phi_s(p) = (C_Old(p)/(J_curr(p)*rho_s));

    %Defining the exact volume fraction phi_s1
    phi_s1(p) = (C1(i,p)/(J_curr1(p)*rho_s));

    %Defining the numerically calculated diffusion coefficient
    D_curr(p) = D_0*((1-phi_s(p))^2)*(1-2*chi*phi_s(p))*exp(-(E_A/(R*theta_Old(p))));

    %Defining the numerically calculated specific entropy eta_s
    eta_s(p) = -(k_B/(rho_0*V))*(log(C_Old(p)/(C_Old(p)+G)) + (1-(1/r))*(G/(C_Old(p)+G)));

    %Defining the numerically calculated chemical potential, mu_s
    mu_s(p) = ((k_B*theta_Old(p)*chi)/(rho_0*V*J_curr(p))) - theta_Old(p)*eta_s(p);

    %Defining the numerically calculated derivative of mu_s w.r.t theta
    mu_stheta(p) = (k_B*chi/(rho_0*V*J_curr(p))) - eta_s(p);

```

```

%Rather than have the complicated terms derivatives everywhere in the code,
%let us define and calculate them here before putting them in the
%forcing term

%Remember that these are all exact analytic functions - we evaluate
%these in the forcing terms.

%Focusing first on the diffusion coefficient,  $D = D_0 * f * \exp(g)$ ;

%Defining the function  $f=f(\phi_s = C / \rho_s J)$ 
f(p) = ((1-phi_sl(p))^2)*(1-2*chi*phi_sl(p));

%Defining the deriv of f w.r.t. x, where  $D = D_0 * f * \exp(g)$ 
fwrtx(p) = (2*(phi_sl(p) - 1)*(1-2*chi*phi_sl(p)) - 2*chi*((1-phi_sl(p))^2))*((0.01/J

%Defining the function  $g=g(C, \theta)$ 
g(p) = -(E_A)/(R*thetal(i,p)) + delta*((C1(i,p)/C_eq) - 0.5);

%Defining the derivative of g, dg/dx
gwrtx(p) = (delta/C_eq)*0.01*sin(t(i)) + (E_A/(R*(thetal(i,p)^2)))*x(p)*sin(t(i));

%Defining the analytic diffusion coefficient, D
D_curr1(p) = D_0*f(p)*exp(g(p));

%Defining dD/dx , the diffusion coeff. w.r.t. x
Dwrtx(p) = D_0*fwrtx(p)*exp(g(p)) + D_0*f(p)*gwrtx(p)*exp(g(p));

%With the derivative of the diffusion coefficient defined, let us
%define the deriv. of the entropy, eta_s, and the chem potential, mu

%Defining the exact value of the entropy, eta_sl
eta_sl(p) = -(k_B/(rho_0*V))*(log(C1(i,p)/(C1(i,p)+G)) + (1-(1/r))*(G/(C1(i,p)+G)));

%Defining the exact value of the chemical potential, mu_sl
mu_sl(p) = ((k_B*thetal(i,p)*chi)/(rho_0*V*J_curr1(p))) - thetal(i,p)*eta_sl(p);

%Defining the deriv. of eta_sl w.r.t. the conc, C
etawrtC(p) = -(k_B/(rho_0*V))*((G/(C1(i,p)*(C1(i,p)+G))) - (1-(1/r))*(G/((C1(i,p)+G)^2

```

```

%Defining the deriv of eta_s1 w.r.t x
etawrtx(p) = etawrtC(p)*0.01*sin(t(i));

%Defining the deriv of mu_s1 w.r.t. theta
muwrttheta(p) = (k_B*chi/(rho_0*V*J_curr1(p))) - eta_s1(p);
%Defining the deriv of mu_s1 w.r.t. x
muwrtx(p) = -theta1(i,p)*etawrtx(p) + (muwrttheta(p))*x(p)*sin(t(i))
- (k_B*chi/(rho_0*V*(J_curr1(p)^2)))*(t(i)^2);

%Now we have all the analytic derivatives needed to input into the
%forcing terms.

%Defining the Forcing term present in the diffusion equation, F
F_curr(p) = B1(i,p) - tau_j*0.01*x(p)*sin(t(i)) - Dwrtx(p)*0.01*sin(t(i)) -

%Defining the Forcing term present in the temperature equation, R.
R_curr(p) = 0.5*rho_0*C_p*(x(p)^2)*cos(t(i)) - D_curr1(p)*0.01*sin(t(i))*mu

%Defining the forcing term present in the deformed coord equation, b
b_curr(p) = (x(p)^2) - (2*mu_g + lamb_g)*(t(i)^2);

end

for k=1:J+1

    %Applying boundary conditions at x=0
    if k==1

        %B.C. for C at x=0, t=(i)*dt
        C_Old(k) = 0.1 + (0.01)*x(k)*sin(t(i));

        %B.C. for C at x=0, t=(i+1)*dt
        C_New(k) = 0.1 + (0.01)*x(k)*sin(t(i+1));

        %B.C. for B at x=0, t=(i)*dt
        B_Old(k) = (0.01)*x(k)*cos(t(i));

```

```

%B.C. for B at x=0, t=(i+1)*dt
B_New(k) = (0.01)*x(k)*cos(t(i+1));

%B.C. for theta at x=0, t=(i)*dt
theta_Old(k) = 1 + 0.5*(x(k)^2)*sin(t(i));

%B.C. for theta at x=0, t=(i+1)*dt
theta_New(k) = 1 + 0.5*(x(k)^2)*sin(t(i+1));

%B.C. for X at x=0, t=(i)*dt
X_Old(k) = x(k) + 0.5*(x(k)^2)*(t(i)^2);

%B.C. for X at x=0, t=(i+1)*dt
X_New(k) = x(k) + 0.5*(x(k)^2)*(t(i+1)^2);

%B.C. for Y=dX/dt at x=0, t=(i)*dt
Y_Old(k) = x(k)*(t(i)^2);

%B.C. for Y = dX/dt at x=0, t=(i+1)*dt
Y_New(k) = x(k)*(t(i+1)^2);

%B.c. for J at x=0, t=(i)*dt
J_curr(k) = 1 + x(k)*(t(i)^2);

%Calculating the error at timestep i, between numeric and
%analytic C
C_Error(k) = abs(C_Old(k) - C1(i,k));

%Calculating the error at timestep i, between numeric and analytic
%theta
theta_Error(k) = abs(theta_Old(k) - theta1(i,k));

%Calculating the error at timestep i, between numeric and analytic
%deformed coordinate, x
X_Error(k) = abs(X_Old(k) - X1(i,k));

```

```

elseif k==J+1

    %B.C. for C at x=3, t=(i)*dt
    C_Old(k) = 0.1 + (0.01)*x(k)*sin(t(i));

    %B.C. for C at x=3, t=(i+1)*dt
    C_New(k) = 0.1 + (0.01)*x(k)*sin(t(i+1));

    %B.C. for B at x=3, t=(i)*dt
    B_Old(k) = (0.01)*x(k)*cos(t(i));

    %B.C. for B at x=3, t=(i+1)*dt
    B_New(k) = (0.01)*x(k)*cos(t(i+1));

    %B.C. for theta at x=3, t=(i)*dt
    theta_Old(k) = 1 + 0.5*(x(k)^2)*sin(t(i));

    %B.C. for theta at x=3, t=(i+1)*dt
    theta_New(k) = 1 + 0.5*(x(k)^2)*sin(t(i+1));

    %B.C. for X at x=3, t=(i)*dt
    X_Old(k) = x(k) + 0.5*(x(k)^2)*(t(i)^2);

    %B.C. for X at x=3, t=(i+1)*dt
    X_New(k) = x(k) + 0.5*(x(k)^2)*(t(i+1)^2);

    %B.C. for Y=dX/dt at x=3, t=(i)*dt
    Y_Old(k) = x(k)*(t(i)^2);

    %B.C. for Y=dX/dt at x=3, t=(i+1)*dt
    Y_New(k) = x(k)*(t(i+1)^2);

    %B.c. for J at x=3, t=(i)*dt
    J_curr(k) = 1 + x(k)*(t(i)^2);

```

```

%Calculating the error at timestep i, between numeric and
%analytic C
C_Error(k) = abs(C_Old(k) - C1(i,k));

%Calculating the error at timestep i, between numeric and analytic
%theta
theta_Error(k) = abs(theta_Old(k) - theta1(i,k));

%Calculating the error at timestep i, between numeric and analytic
%deformed coordinate, x
X_Error(k) = abs(X_Old(k) - X1(i,k));

else

%Calculating B at timestep (i+1)
B_New(k) = B_Old(k) * ( 1 - (dt/tau_j)) + (mu/tau_j) * (D_curr(k+1) - D_curr(k)) * (C_Old(k) - C1(i,k));

%Calculating C at timestep (i+1)
C_New(k) = C_Old(k) + dt*B_Old(k);

%Calculating the error at timestep i, between numeric and
%analytic C
C_Error(k) = abs(C_Old(k) - C1(i,k));

%Calculating theta at timestep (i+1) (note this needs C_New(k)!)
theta_New(k) = theta_Old(k) + (D_curr(k) / (rho_0*C_p)) * (mu) * (C_Old(k+1) - C_Old(k)) * (mu_0 - mu_1);

%Calculating X at timestep (i+1)
X_New(k) = X_Old(k) + dt*Y_Old(k);

%Calculating Y at timestep (i+1)
Y_New(k) = Y_Old(k) + (2*mu_g + lamb_g) * (mu/rho_0) * (X_Old(k+1) - 2*X_Old(k) + X_Old(k-1)));

%Calculating the error at timestep i, between numeric and
%analytic C
C_Error(k) = abs(C_Old(k) - C1(i,k));

```



```

%Calculating the error at timestep i, between numeric and analytic
%theta
theta_Error(k) = abs(theta_Old(k) - theta1(i,k));

%Calculating the error at timestep i, between numeric and analytic
%deformed coordinate, x
X_Error(k) = abs(X_Old(k) - X1(i,k));

%                               %Plotting the Numeric Soln. and Analytic Soln. of Conc.
%   if           i == 2000           %Plotting t=0.1
%       hold all
%       plot(x,C_Old)
%       plot(x,C1(i,:), '-o')
%   elseif      i == 5000           %Plotting t = 0.25
%       plot(x,C_Old)
%       plot(x,C1(i,:), '-o')
%   elseif      i == 10000          %Plotting t=0.5
%       plot(x,C_Old)
%       plot(x,C1(i,:), '-o')
%   elseif      i == 15000          %Plotting t=0.75
%       plot(x,C_Old)
%       plot(x,C1(i,:), '-o')
%   elseif      i== 20000           %Plotting t=1
%       plot(x,C_Old)
%       plot(x,C1(i,:), '-o')
%
%       legend('Numerical, t=0.1','Analytic, t=0.1','Numerical, t=0.25','Analytic, t=0.25')
%       xlabel('Position, X [\mu m]')
%       ylabel('Concentration, C')
%       title('Numerical and Analytic Solution of Conc., Case 4')
%       return

%       Plotting the Error between the Analytic Soln. and Numeric Soln.
%       if   i == 2000           %Plotting t=0.1
%           hold all
%           plot(x,C_Error)
%
%       elseif      i == 5000           %Plotting t = 0.25

```

```

%           plot(x,C_Error)
%   elseif   i == 10000           %Plotting t=0.5
%           plot(x,C_Error)
%   elseif   i == 15000           %Plotting t=0.75
%           plot(x,C_Error)
%   elseif   i== 20000           %Plotting t=1
%           plot(x,C_Error)
%
%   legend('t=0.1','t=0.25','t=0.5','t=0.75','t=1','Location','Northwest')
%   xlabel('Position, X [\mu m]')
%   ylabel('Abs .Error between the Real and Numeric Solution of Conc.')
%   title('Plot of the concentration error vs. x , Case 4')
%   return

%Plotting the Numeric Soln. and Analytic Soln. of temp, theta
%   if       i == 2000           %Plotting t=0.1
%       hold all
%       plot(x,theta_Old)
%       plot(x,theta1(i,:), '-o')
%   elseif   i == 5000           %Plotting t = 0.25
%       plot(x,theta_Old)
%       plot(x,theta1(i,:), '-o')
%   elseif   i == 10000          %Plotting t=0.5
%       plot(x,theta_Old)
%       plot(x,theta1(i,:), '-o')
%   elseif   i == 15000          %Plotting t=0.75
%       plot(x,theta_Old)
%       plot(x,theta1(i,:), '-o')
%   elseif   i== 20000           %Plotting t=1
%       plot(x,theta_Old)
%       plot(x,theta1(i,:), '-o')
%
%   legend('Numerical, t=0.1','Analytic, t=0.1','Numerical, t=0.25','Analytic, t=0.25',
%   xlabel('Position, X [\mu m]')
%   ylabel('Temperature, \theta')
%   title('Numerical and Analytic Solution for temperature \theta, Case 4')
%   return

%Plotting the Error between the Analytic Soln. and Numeric Soln.

```

```

        %for theta
        if            i == 2000                %Plotting t=0.1
            hold all
            plot(x,theta_Error)

elseif i == 5000                %Plotting t = 0.25
            plot(x,theta_Error)
elseif i == 10000            %Plotting t=0.5
            plot(x,theta_Error)
elseif i == 15000            %Plotting t=0.75
            plot(x,theta_Error)
elseif i== 20000            %Plotting t=1
            plot(x,theta_Error)

legend('t=0.1','t=0.25','t=0.5','t=0.75','t=1','Location','Northwest')
xlabel('Position, X [\mu m]')
ylabel('Error between the Analytic and Numerical Solution of temp, \theta')
title('Plot of the abs. temperature error vs. X , Case 4')
return

        %Plotting the Numeric Soln. and Analytic Soln. of deform. coord, x
%   if            i == 2000                %Plotting t=0.1
%       hold all
%       plot(x,X_Old)
%       plot(x,X1(i,:), '-o')
%   elseif i == 5000                %Plotting t = 0.25
%       plot(x,X_Old)
%       plot(x,X1(i,:), '-o')
%   elseif i == 10000            %Plotting t=0.5
%       plot(x,X_Old)
%       plot(x,X1(i,:), '-o')
%   elseif i == 15000            %Plotting t=0.75
%       plot(x,X_Old)
%       plot(x,X1(i,:), '-o')
%   elseif i== 20000            %Plotting t=1
%       plot(x,X_Old)
%       plot(x,X1(i,:), '-o')
%
%       legend('Numerical, t=0.1','Analytic, t=0.1','Numerical, t=0.25','Analytic, t=0.25')

```

```

%       xlabel('Position, X [\mu m]')
%       ylabel('Deformed coord, x')
%       title('Numerical and Analytic Solution for deformed coord, x, Case 4')
%       return

%Plotting the Error between the Analytic Soln. and Numeric Soln.
    %for x
%       if          i == 2000          %Plotting t=0.1
%           hold all
%           plot(x,X_Error)
%
%       elseif      i == 5000          %Plotting t = 0.25
%           plot(x,X_Error)
%       elseif      i == 10000         %Plotting t=0.5
%           plot(x,X_Error)
%       elseif      i == 15000         %Plotting t=0.75
%           plot(x,X_Error)
%       elseif      i== 20000          %Plotting t=1
%           plot(x,X_Error)
%
%       legend('t=0.1','t=0.25','t=0.5','t=0.75','t=1','Location','Northwest')
%       xlabel('Position, X [\mu m]')
%       ylabel('Abs. Error between the real and exact Soln, of deformed coord., x')
%       title('Plot of the abs. def. coord error vs. X , Case 4')
%       return

end
end
end
end

```

Bibliography

- [1] Alfrey, T., Gurnee, E.F., Lloyd, W.G., (1966) *Diffusion in Glassy Polymers*, Journal of Polymer Science: Part C, No 12, p249-261.
- [2] Atkins, P., de Paula, J., (2006)a, *Atkins' Physical Chemistry*, Section 3.6: The chemical potential of liquids , First Edition, Oxford, Oxford University Press,p143-147.
- [3] Atkins, P., de Paula, J., (2006)b, *Atkins' Physical Chemistry*, Section 3.5: The Helmholtz and Gibbs Free Energies, First Edition, Oxford, Oxford University Press,p95- 100.
- [4] Bargmann, S., McBride, A.T., Steinmenn, P., 2011. *Models of solvent penetration in glassy polymers with an emphasis on Case II diffusion. A comparative review*, Appl. Mech. Rev. 64 (1). 010803-1-010803-13.
- [5] Begley, M.R. , Begley, J.A., Landis, C.M., (2012) *Gaseous Hydrogen embrittlement of materials in energy technologies* Volume 2: Mechanisms, modelling and future developments, Chapter 10: Continuum Mechanics modelling of Hydrogen Embrittlement, Oxford Cambridge Philadelphia New Delhi, Woodhead Publishing.
- [6] Benamar, G., Schweke, D., Bloch, J., Livneh, T., Mintz, M.H., (2009) *The very initial stage of hydride formation on polycrystalline gadolinium*, Journal of Alloys and Compounds 477, p188-192.
- [7] Boley, B.A., Weiner, J.H., (1960) *Theory of Thermal Stresses* New York, Dover Publications,Inc.
- [8] Bower, A.F., (2010) *Applied Mechanics of Solids*, Chapter 2, Section 2.3: Equations

- of Motion and Equilibrium for Deformable Solids, Boca Raton London New York, CRC Press, p49-53.
- [9] Boltzmann constant. 2015. Encyclopædia Britannica Online. Retrieved 30 August, 2015, from <http://www.britannica.com/science/Boltzmann-constant>
- [10] Cannon, J.R., *The One-Dimensional Heat Equation* Cambridge, UK, Cambridge University Press.
- [11] Chu, J.L., Lee, S.B., (1994) *The effect of chemical stresses on diffusion*, J.Appl. Phys. 75, p2823
- [12] Crank, J. (1975) *The Mathematics of Diffusion*, Chapter 8: Numerical Methods, Section 8.4: Finite-Difference solution : explicit method, Oxford UK , Clarendon Press / Oxford University Press , p141-142
- [13] Crank, J. , Nicolson, P., (1947) *A practical method for numerical evaluation of solutions of partial differential equations of the heat-conduction type*, Proc. Camb. Phil. Soc. 43, p50-67.
- [14] De Kee, D., Liu, Q., Hinestroza, J., 2005, *Viscoelastic (non-Fickian) diffusion*. Can. J. Chem. Eng. 83 (6) p913-929.
- [15] DeLassus, P. T. and Whiteman, N. F. 2003. Physical and Mechanical Properties of Some Important Polymers. Wiley Database of Polymer Properties.
- [16] Eslami, M.R., Hetnarski, R.B., Ignaczak, J. , Noda, N., Sumi, N., Tanigawa, Y., (2013). Chapter 2 : Fundamentals of Linear Elasticity. In: Gladwell, G.M.L. *Theory of Elasticity and Thermal Stresses*. Dordrecht Heidelberg New York London: Springer. p35-36.
- [17] Fick, A., (1855) *Ueber Diffusion*, Annalen der Physik, Volume 170, Issue 1, p59-86 - NOTE An English translation is given by the Journal of Membrane Science : Fick, A., (1995) *On liquid diffusion*, Journal of Membrane Science 100, p35-38
- [18] Flory, P.J., 1970, *Fifteenth spiels memorial lecture, Thermodynamics of Polymer solutions*, Discuss Faraday Soc, 49. p7-29.

- [19] Gangloff, R.P., Somerday, B.P., (2012) *Gaseous hydrogen embrittlement of materials in energy technologies*, Oxford Cambridge Philadelphia New Delhi, Woodhead Publishing Limited.
- [20] Gall, T.P., Kramer, E.J., 1991, *Diffusion of deuterated toluene in polystyrene*. Polymer Volume 32, Issue 2, p265-271
- [21] (Molar) Gas constant, 2015, Encyclopædia Britannica Online. Retrieved 30 August, 2015, from <http://www.britannica.com/science/molar-gas-constant>
- [22] Govindjee, S., Simo, J.C., 1993. *Coupled stress-diffusion Case II*. J.Mech.Phys. Solids 41 (5), p863-887.
- [23] Gurtin, M.E., Fried, E., Anand, L., (2010), *The Mechanics and Thermodynamics of Continua*, Thermodynamics and Constitutive Restrictions, Cambridge, Cambridge University Press, p232-234
- [24] Harmon, J.P., Lee, S., Li, J.C.M., (1987) *Methanol transport in PMMA: The Effect of Mechanical Deformation*, Journal of Polymer Sciences Part A: Polymer Chemistry, Volume 25, Issue 12, p3215-3229.
- [25] Haupt, P. (2000)a *Continuum Mechanics and Theory of Materials*, Chapter 1: Kinetics, Section 1.2: Material and Spatial Representation, Springer, New York, p19-23
- [26] Haupt, P. (2000)b *Continuum Mechanics and Theory of Materials*, Chapter 1: Kinetics, Section 1.1: Material Bodies, Springer, New York, p7-19
- [27] Haupt, P. (2000)c *Continuum Mechanics and Theory of Materials*, Chapter 5: Classical Theories of Continuum Mechanics, Section 5.4: Linear Elastic Solid, Springer, New York, p185-188
- [28] Haupt, P. (2000)d *Continuum Mechanics and Theory of Materials*, Chapter 2: Balance Relations of Mechanics, Section 2.3.2: Stress Tensors, Springer, New York, p90-95

- [29] Haupt, P. (2000)e *Continuum Mechanics and Theory of Materials*, Chapter 2: Balance Relations of Mechanics, Section 2.3.4: Local Formulation of the Balance of Linear Momentum and Rotational Momentum, Springer, New York, p95-101
- [30] Haupt, P. (2000)f *Continuum Mechanics and Theory of Materials*, Chapter 13: Constitutive Models in Continuum Mechanics, Section 13.1: Thermomechanical Consistency, Springer, New York, p487-491
- [31] Isaacson, E., Keller, H.B., (1994), *Analysis of Numerical Methods*, Chapter 4: Heat Equation, New York, Dover Publications, p521.
- [32] Kuttler, C. (2011) , *Reaction-Diffusion equations with applications*, Section 1.2.5 Chemical reactions, p5-9, Website: (http://www-m6.ma.tum.de/~kuttler/script_reaktdiff.pdf)
- [33] LeVeque, R.J., (2007) *Finite Difference Methods for Ordinary and Partial Differential Equations* Chapter 2, Section 2.4: "A Simple Finite Difference Method", Philadelphia : Society for Industrial and Applied Mathematics.
- [34] LeVeque, R.J., (2007) *Finite Difference Methods for Ordinary and Partial Differential Equations* Chapter 2, Section 2.1: *The Heat Equation*, Philadelphia : Society for Industrial and Applied Mathematics., p13-17.
- [35] LeVeque, R.J., (2007) *Finite Difference Methods for Ordinary and Partial Differential Equations* Chapter 5, Section 5.3: *Some Basic Numerical Methods*, Philadelphia : Society for Industrial and Applied Mathematics., p120-121.
- [36] LeVeque, R.J., (2007) *Finite Difference Methods for Ordinary and Partial Differential Equations* Chapter 2, Section 2.12: *Neumann boundary conditions*, Philadelphia : Society for Industrial and Applied Mathematics., p29-32.
- [37] Li, J.C.M., (1978) *Physical chemistry of some microstructural phenomena*, Metallurgical Transactions A, Volume 9, Issue 10, p1353-1380.
- [38] McBride, A.T., Bargmann, S., Steinmann, P., 2011 *Geometrically Nonlinear Continuum Thermomechanics Coupled to Diffusion: a Framework for Case II Diffusion*, In: Volume 59 of Lecture Notes in Applied and Computational Mechanics. Springer. Berlin Heidelberg, p89-107 book section 5.

- [39] Mehrer, H., (2007) *Diffusion in Solids : Fundamentals, Materials, Diffusion-Controlled Processes*, Chapter 2 : Continuum Theory of Diffusion., Springer Series in Solid-State Sciences , p27-29
- [40] Pozrikidis, C., (2009), *Fluid Dynamics; Theory, Computation, and Numerical Simulation*, Chapter 2 Section 2.7.3. The Continuity Equation, New York, Springer, ISBN: 978-0-387-95869-9, e-ISBN: 978-0-387-95871-2, DOI: 10.1007/978-0-387-95871-2 , p95-96
- [41] Prussin, S., (1961) *Generation and Distribution of Dislocations by Solute Diffusion*, Journal of Applied Physics, Volume 32, p1876
- [42] Schuld, N., Wolf, B.A., 1999, Polymer-solvent interaction parameter found in : Brandrup, J., Immergut, E.H., Grulke, E.A., *Polymer Handbook*, Fourth Edition, Wiley, New York.
- [43] Taylor, C.D., Lillard, R.S., (2009) *Ab-initio calculations of the hydrogen-uranium system: Surface phenomena, absorption, transport and trapping*, Acta Materialia 57, p4707-4715.
- [44] Stover, Christopher and Weisstein, Eric W. "Einstein Summation." From MathWorld—A Wolfram Web Resource. <http://mathworld.wolfram.com/EinsteinSummation.html>
- [45] Swift, R.J., Wirkus, S.A., (2007) *A Course in Ordinary Differential Equations*, Boca Raton, Chapman and Hall/CRC.
- [46] Weisstein, Eric W. "Determinant." From MathWorld—A Wolfram Web Resource. <http://mathworld.wolfram.com/Determinant.html>
- [47] Weisstein, Eric W. "Divergence Theorem." From MathWorld—A Wolfram Web Resource. <http://mathworld.wolfram.com/DivergenceTheorem.html>
- [48] Weisstein, Eric W. "Gradient." From MathWorld—A Wolfram Web Resource. <http://mathworld.wolfram.com/Gradient.html>
- [49] Weisstein, Eric W. "Heat Conduction Equation." From MathWorld—A Wolfram Web Resource. <http://mathworld.wolfram.com/HeatConductionEquation.html>

- [50] Weisstein, Eric W. "Kronecker Delta." From MathWorld—A Wolfram Web Resource. <http://mathworld.wolfram.com/KroneckerDelta.html>
- [51] Weisstein, Eric W. "Ordinary Differential Equation." From MathWorld—A Wolfram Web Resource. <http://mathworld.wolfram.com/OrdinaryDifferentialEquation.html>
- [52] Wilmers, J., Bargmann, S., 2014, *Simulation of non-classical diffusion in polymers*, Heat Mass Transf, p1-10.
- [53] Wilmers, J. , Bargmann, S. , (2015) *A continuum mechanical model for the description of solvent induced swelling in polymeric glasses: Thermomechanics coupled with diffusion*, European Journal of Mechanics A/Solids 53, p10-18.
- [54] Yang, F. (2005) *Interaction between diffusion and chemical stresses.*, Materials Science and Engineering A 409, p153-159.