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MULTIPHYSICS PHASE FIELD MODELING OF ELECTROMIGRATION

By

Zachary J. Morgan

A DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

In Materials Science and Engineering

MICHIGAN TECHNOLOGICAL UNIVERSITY

2020

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This dissertation has been approved in partial fulfillment of the requirements for the Degree of DOCTOR OF PHILOSOPHY in Materials Science and Engineering.

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Preface

An efficient, parallel computer program package has been developed based on the multi-physics phase field model to simulate a wide range of electromigration behavior on high-performance supercomputers. The program can solve for the concurrent and coupled diffusion processes involving electrical conduction, heat transfer, and mechanical stress buildup in highly heterogeneous and anisotropic interconnects. The model is applied to pore and inclusion migration, as an example, subjected to various external loadings and internal microstructure-dependent fields. The simulation results are used to analyze pore and inclusion velocity and path. Interactions among defects and the important roles of anisotropy are also discussed. These simulations reveal and provide new insight into the microstructural processes in electromigration phenomena.

This work is divided into six chapters. The first is an introduction with background regarding electromigration behavior and summary of relevant materials of interest. In the second chapter, the modeling equations used to describe the multiphysical phenomena associated with electromigration are developed and discussed. In the next chapter, the development and implementation of the program used to simulate these behaviors is showcased. This includes the development of semi-implicit time integration methods and implementation of low-pass filtering methods. In addition, the algorithms used are discussed in some detail.

The fourth and fifth chapters showcase the modeling particularly on the migration of pores and inclusions. The first of these chapters deals with both heat and charge conduction. In this chapter, applications relevant to tin solders are described. In particular, those related to fundamental pore migration behaviors taking into account electrical conductivity anisotropy are discussed. The first part of the applications section has previously been published in

Z. J. Morgan and Y. M. Jin, “Phase field modeling of pore electromigration in anisotropic conducting polycrystals,” *Computational Materials Science*, vol. 172, p. 109362, Feb. 2020, doi: 10.1016/j.commatsci.2019.109362.

The last part dealing with pore-pore interactions is intended to be submitted, in part, to a journal. The next chapter deals with elasticity. It builds upon the previous chapter integrating the role of stress and its gradient on migration behavior. This work is also intended to be submitted, in part, to an appropriate journal. Finally, the last chapter briefly summarizes the modeling, simulation, and analysis work, and it suggests future directions.

The first appendix includes some example problems verified using the developed program. They are put here to be in one place for ease of review and to simplify the flow of each chapter. A brief description of each program is described in the next appendix. Note that not all of the code is provided here. The last appendix includes some lengthier derivations that would otherwise interrupt the flow of the content in chapters preceding it.

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To my running friends, once back home now far and wide, I look forward to our comeback

at a future Great Lakes Relay in the heat of summer and Michigan outback. A shoutout to Jack and Aaron. Here at Tech, I have met a great number of terrific people. In no way can I thank them all, but I want to thank those who have helped me out significantly, especially when I was down and out on my luck. In no particular order, they include Brady Burby, Lance Taylor, Alicia Steele, Zach Simpson, and Tyler Schwartz. Of course, I have to thank my girlfriend Catherine Galligan for all of our great time and adventures together. I also want to thank her for being often being my rubber duck as I try and debug code. A shoutout to her family, as well.

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Abstract

With the miniaturization of microelectronic devices, the reliability of solder interconnects is a significant concern. As size is reduced, the current density flowing through an interconnect becomes larger and exacerbates electromigration leading to microstructural changes and failure. Since most solder alloys are required to be lead-free over toxicity concerns, there are additional challenges to interconnect performance. Nearly all solder alloys are comprised with its majority component being tin due to its low melting temperature and economical cost. The typical metallic white tin phase has a body-centered tetragonal crystal structure which exhibits strong anisotropy in its physical properties. In particular, the electrical/thermal conductivity and elastic modulus are highly anisotropic. For this reason, the performance of solder bumps that contain only a few grains are sensitive to the orientation of each individual grain. Quantitative description of electromigration at such scales is required to understand the microstructure behavior impacting performance and degradation of interconnects.

Electromigration induced microstructure evolution in solder interconnects involves complicated multiphysical processes. It involves the diffusion of atoms driven by charge conduction which is also strongly affected by concurrent heat conduction and mechanical processes. A multiphysics phase field model is developed to investigate the diffusional processes in tin solder interconnects. The driving forces for electromigration are obtained

solving for current density and electric field in microstructures with inhomogeneous and anisotropic electrical conductivity using microscopic Ohm's law. Similarly, the driving forces caused by temperature gradients are obtained solving for heat flux using Fourier's law of conduction that accounts for inhomogeneous and anisotropic thermal conductivity. The model is capable of accounting for the generation of heat through Joule heating. Simulations of conduction driven pore and inclusion migration are discussed in terms of volume and surface diffusion mechanisms. Finally, the contribution of stress and its gradient are obtained through microelasticity modeling. From Hooke's law of elasticity, the modeling allows different external loading conditions to be considered and is capable of solving for internal stress concentrations in microstructures with structural and elastic property mismatches near defects including grain boundaries, voids, and precipitates. These internal stresses generated contribute to the diffusional processes through its gradient.

Chapter 1

Introduction

Electromigration is mass transport driven by the motion of charges in an electrical conductor [3]. It is a complicated multiphysical process that involves diffusion of atoms, conduction of electric charge and heat, as well as lattice deformations. It is an important issue and concern within the microelectronics industry that affects solder interconnects. Lead-tin solders are a common alloy used to join electronic components. It forms a simple binary eutectic with 75.8% Sn at 460 K at the eutectic point [4]. The major component tin has a melting temperature of 505.1 K, and lead melts at 600.6 K. Alloy compositions are chosen for its low melting temperature and desired mechanical properties and electromigration performance. However, lead is undesirable due to toxicity and mandates dictate that solder alloys are lead-free [5]. Common lead-free solder alloys, nearly all using tin as its major component, include gold, silver, copper, bismuth, indium, zinc, and antimony.

Of these, only bismuth-tin and zinc-tin form a simple binary eutectic system [5]. All others form systems with complicated intermetallic compounds. The copper-tin system is of particular importance since solder joints form interconnections between copper lines. Zinc is an inexpensive element but tends to form oxides during solder processes. Indium on the other hand, is expensive and generally not considered in broad applications. Antimony has concerns about being potentially harmful. Bismuth is primarily a byproduct of lead mining but is still considered to be a good candidate alloy. Shown in Fig. 1.1 are a collection of relevant binary systems [4, 6, 7, 8, 9, 10, 11].

(e) Zinc-tin

(f) Bismuth-tin

(g) Indium-tin

(h) Antimony-tin

Figure 1.1: Binary phase diagrams for common solder alloys

1.1 Motivation

Moore's law is the observation that the number of transistors in manufactured integrated circuits doubles approximately every two years [12]. Recognized by Gordon Moore in 1965, then co-founder of Fairchild Semiconductor and future co-founder of Intel, this observation drove the semiconductor industry to what it is today. However, the practical limits of

Moore's law is seen in 2016 where device features are already as small as 14 nm [13]. Despite this looming breakdown of Moore's law, there is still optimism that microprocessors will continue to improve. One technique includes reducing the size of integrated circuit packaging. This, however, brings about new challenges associated with electromigration.

Electromigration is mass transport in metals due to charge transport. Recognized as a failure mode in integrated circuits, James Black investigated the median time to failure $t_{1/2}$ of integrated circuit metallizations in the late 1960s and early 1970s [14, 15]. For his formative work, the semi-empirical equation

$$\frac{1}{t_{1/2}} = \frac{kj^n}{T} e^{-\frac{Q}{RT}} \quad (1.1)$$

bears his name. Here, Q is an activation energy related to the driving force for diffusion, R is the gas constant, T is temperature, and j is the current density. It should be noted that Eq. (1.1) is not a physical model but an engineering tool to help designers. Constants k and n are fitting parameters accounting for material, geometry, and environmental conditions. Black recognized that current density alone did not increase the driving force for diffusion. Factors such as gradients in temperature and current density also have an influence on the degradation of these metallizations. Joule heating due to current crowding increases temperature variations which alters the driving force for diffusion. In 1976, Ilan Blech and Conyers Herring showed that a critical current density exists below which gradients in stress and concentration oppose the electromigration driving force [16]. These

stress and concentration gradients form as a result of electromigration itself as atoms accumulate at the anode and deplete at the cathode. These coupled phenomena illustrate the difficulty in understanding electromigration. When considering integrated circuit solder interconnects, the complication increases further.

1.2 The copper-tin system

Copper and tin solders represent the simplest solder system formed by the joining of copper metallizations with pure tin. Many copper-tin-based solders also contain other alloying elements such as silver. The calculated copper-tin phase diagram

Table 1.1
Crystallographic properties of room-temperature copper-tin phases

	Cu	Cu ₃ Sn	Cu ₆ Sn ₅	Sn
Crystal system	Cubic	Orthorhombic	Monoclinic	Tetragonal
Space group	<i>Fm$\bar{3}m$</i>	<i>Cmcm</i>	<i>C2/c</i>	<i>I4₁/amd</i>
<i>a</i> [Å]	3.614	5.53	11.023	5.832
<i>b</i> [Å]	—	4.775	7.282	—
<i>c</i> [Å]	—	4.324	9.827	3.173
α [°]	90	90	90	90
β [°]	—	—	98.84	—
γ [°]	—	—	—	—
Ω [Å ³]	47.2	114.1	779.4	108.2

[6] is shown in Fig. 1.1b. For temperatures below $T = 461$ K (188 °C) and above $T = 286$ K (13 °C), four phases are stable; they are the α -Cu, ϵ -Cu₃Sn, η' -Cu₆Sn₅, and white Sn phase. White tin refers to the metallic allotrope to distinguish it from gray tin, the nonmetallic allotrope that transforms below 13 °C, albeit slowly. Similarly, cooling below 188 °C, the Cu₆Sn₅ phase undergoes a transformation from its simple superlattice η phase to its long-period superlattice η' phase structure. The crystallographic parameters [17, 18, 19, 20]

for these four phases are shown in Table 1.1. The unit cell Bravais lattice for each phase in this temperature range is summarized as follows: Cu is face-centered cubic, Cu₃Sn is base-centered orthorhombic, Cu₆Sn₅ is base-centered monoclinic, and Sn is body-centered tetragonal. In experimental observations of copper-tin solders, it is typical to observe all four phases existing at local equilibrium with respect to one another.

For the binary copper-tin system [6], the Gibbs function G_k for phase k with mole fraction X_j is given by

$$G_k = (1 - X_{\text{Sn}})\mu_{\text{Cu}}^k + X_{\text{Sn}}\mu_{\text{Sn}}^k \quad (1.2)$$

where μ_j^k is the chemical potential, or partial molar Gibbs free energy, of component j in phase k . The Cu phase is assumed to be a subregular solution. For a general solution phase, the chemical potential of the Cu component is

$$\begin{aligned} \mu_{\text{Cu}}^k = & {}^0G_{\text{Cu}}^k + RT \ln(1 - X_{\text{Sn}}) + X_{\text{Sn}}^2 L_0^k \\ & + X_{\text{Sn}}^2(3 - 4X_{\text{Sn}})L_1^k + X_{\text{Sn}}^2(5 - 16X_{\text{Sn}} + 12X_{\text{Sn}}^2)L_2^k \end{aligned} \quad (1.3)$$

and Sn component is

$$\begin{aligned} \mu_{\text{Sn}}^k = & {}^0G_{\text{Sn}}^k + RT \ln X_{\text{Sn}} + (1 - X_{\text{Sn}})^2 L_0^k \\ & + (1 - X_{\text{Sn}})^2(1 - 4X_{\text{Sn}})L_1^k + (1 - X_{\text{Sn}})^2(1 - 8X_{\text{Sn}} + 12X_{\text{Sn}}^2)L_2^k \end{aligned} \quad (1.4)$$

where ${}^0G_i^k$ is the standard Gibbs free energy [21] of component j in phase k , R is the gas constant, T is the temperature, and L_i^k are the solution parameters of a Redlich–Kister

polynomial. Since the Cu phase is subregular solution, L_2^α is zero while L_0^α and L_1^α are not necessarily zero. Tin is assumed to have no solubility such that its Gibbs function is simply its standard Gibbs free energy G_{Sn}^0 . Both Cu_3Sn and Cu_6Sn_5 are intermetallic compounds and assumed to have negligible solubility. Their compositions are fixed by stoichiometry and their Gibbs functions are

$$G_k = G_k^0 + (1 - X_{\text{Sn}})^0 G_{\text{Cu}}^\alpha + X_{\text{Sn}} G_{\text{Sn}}^0 \quad (1.5)$$

where G_k^0 is the standard Gibbs energy of formation for compound k . The Gibbs energy diagram at room temperature is shown in Fig. 1.2. The copper phase is the only one that shows any appreciable composition dependence.

Figure 1.2: Gibbs energy diagram of equilibrium copper-tin phases at $T = 298 \text{ K}$

The material properties of individual phases are all uniquely different. When considering the main electromigration phenomena, that is, mass diffusion, charge conduction, elastic deformation, thermal expansion, and heat conduction, the constitutive equations describing the phenomena relate two physical quantities that are directly proportional to one another by an appropriate material property. For the phenomena above, they are the chemical diffusivity, electrical conductivity, elastic moduli, thermal expansivity, and thermal conductivity, respectively. Isotropic average values [22, 23, 24, 25] for each phase are summarized in Table 1.2. Each describes how a material responds to some type of stimuli.

At room temperature, there is no clear trend in properties with respect to one another. The only exception is the electrical conductivity and thermal conductivity where all the phases have the same relative magnitude with respect to one another. For example, Cu and Cu₆Sn₅ are the most and least conductive of all phases, both electrically and thermally. This relationship between the two conductivity types can be

Table 1.2
Polycrystalline properties of room-temperature copper-tin phases

	Cu	Cu ₃ Sn	Cu ₆ Sn ₅	Sn	
D_{Cu}^0 [m ² s ⁻¹]	34	0.018	0.062	0.24	×10 ⁻⁶
Q_{Cu} [J mol ⁻¹]	195.6	78.8	80.5	33.02	×10 ³
D_{Sn}^0 [m ² s ⁻¹]	29.5	0.00079	0.59	0.0012	×10 ⁻⁶
Q_{Sn} [J mol ⁻¹]	177	79.7	85.2	43.89	×10 ³
σ [S m ⁻¹]	0.59	0.112	0.0571	0.087	×10 ⁸
E [Pa]	117	19	85.6	41	×10 ⁹
G [Pa]	46.8	42.1	50.2	15.4	×10 ⁹
α [K ⁻¹]	17.1	19	16.3	23	×10 ⁻⁶
k [W m ⁻¹ K ⁻¹]	398	70.4	34.1	67	

Table 1.3
Physical properties of room-temperature copper-tin phases

	Cu	Cu ₃ Sn	Cu ₆ Sn ₅	Sn	
ρ [kg m ⁻³]	8.94	8.97	8.31	7.29	×10 ³
c_p [J kg ⁻¹ K ⁻¹]	385	326	286	227	
M [kg mol ⁻¹]	63.5	309.3	974.7	118.7

Figure 1.3: Temperature-dependent diffusivity of copper and tin in each of the four equilibrium phases for $0 \leq T \leq 500$ K

resolved by recognizing that free electrons carry most of the heat in metals [26]. For all other properties there is no obvious relationship or trend. Included in Table 1.3 are the density ρ , specific heat capacity c_p , and molar mass M for each phase. Shown in Fig. 1.3a and Fig. 1.3b are the temperature dependent isotropic diffusivities for copper and tin in each of the four phases.

1.3 The physical properties of tin

All of the polycrystalline properties discussed are isotropic due to the mostly random orientation of grains. For individual grains, however, properties are generally anisotropic with directional dependence corresponding to the symmetry of its crystal structure. Other than the elastic modulus which is represented by either the fourth-rank stiffness or compliance tensor, the properties are second-rank tensors. Since copper is cubic, all of its

transport properties are isotropic excluding its compliance. The intermetallic compounds are expected to be anisotropic since Cu_3Sn is orthorhombic and Cu_6Sn_5 is monoclinic. Unfortunately, no experimental data of this anisotropy is available. Nevertheless, the grain size of these intermetallics is small which suggests they can be assumed to be isotropic. Considering that they have low volume fractions, this assumption is realistic. Tin, however, is highly anisotropic because it is tetragonal: all of its properties exhibit a preference either along its a -axis or c -axis. Furthermore, tin grains are relatively large in solder compared to the intermetallic compounds which suggests that grains are textured. The anisotropic properties of tin are not systematically preferred along just the a -axis or c -axis. To illustrate, the anisotropy surface [27] for each property is shown. These surfaces represent how magnitude of the property varies as a function of direction and should not be confused with the representation quadric or magnitude ellipsoid for second rank tensors [28]. These latter two define a surface which relates the directions of two fields. For example, the second rank tensor of electrical conductivity relates the current density to the electrical field. In this case, the magnitude ellipsoid traces out the current density relative magnitude and direction for a unit length of applied electric field. Conversely, the representation ellipsoid traces the relative magnitude and direction of the electric field for a given resolved current density direction of unit length. Finally, each property's dependence on temperature is provided up to the melting temperature of tin T_m 231.9°C, or 505.1K.

Figure 1.4: White tin, or β -tin, is stable at room temperature

Recalling from Table 1.1 that the structure is tetragonal, the room-temperature lattice parameters a and c are 5.832 Å and 3.173 Å, respectively. Shown in Fig. 1.4a is the crystal structure of tin. The white tin phase, often referred to as β -tin is the stable room temperature phase. Below 13.2 °C, the structure becomes the diamond cubic structure, the brittle grey tin phase referred to as α -tin. The unary phase diagram of tin is shown in Fig. 1.4b.

The chemical diffusivity D_{ij} for tin is completely described by two independent coefficients by symmetry. The anisotropy surface for the self-diffusion of tin is shown in Fig. 1.5a. The surface is an oblate spheroid indicating that tin prefers to self-diffuse perpendicular to its own c -axis [29]. Shown in Fig. 1.5b is a plot of these diffusion coefficients from 273 K to the melting temperature T_m which follows an Arrhenius relationship. Considering the interstitial diffusion of copper atoms in a tin lattice, the opposite is observed where diffusion of copper along the c -axis of tin is preferred [30]. The anisotropic surface is displayed in Fig. 1.6a where it is noted that the interstitial diffusion of copper in tin

(a) Visualization of anisotropic diffusivity at $T = 298\text{K}$

(b) Temperature-dependence of diffusivity for $273\text{ K} \leq T \leq T_m$

Figure 1.5: Anisotropic chemical diffusivity for self-diffusion of tin in tin

(a) Visualization of anisotropic diffusivity at $T = 298\text{K}^*$

(b) Temperature-dependence of diffusivity for $273\text{ K} \leq T \leq T_m$

Figure 1.6: Anisotropic chemical diffusivity for interstitial diffusion of copper in tin

along its c -axis is about 500 times larger than it is along its a -axis at room temperature and 12 orders of magnitude greater than observed for self-diffusion. The temperature dependence of the anisotropic diffusion coefficients for copper in tin follows an Arrhenius relationship is shown in Fig. 1.6b. Considering that the structure of tin in Fig. 1.4a, it is

*Not to scale

Figure 1.7: Anisotropic electrical conductivity of tin

clear that the smaller interstitial atoms of copper have more spacing to move along the c -axis direction compared to its basal plane.

The electrical conductivity σ_{ij} of tin is highly anisotropic: electrons prefer to conduct along directions perpendicular to the c -axis [31] as compared to the a -axis; this is illustrated in Fig. 1.7a. An electric field applied in the basal plane will result in a larger current density over a field applied along the c -axis. At room temperature, the ratio of conductivity for the a -axis to c -axis is about 1.5. The temperature dependence of the electrical conductivity is shown in Fig. 1.7b. The relationship with temperature is assumed to be linear which is typical for metals. Over the temperature range 273 K to T_m , the conductivity decreases, and the degree of anisotropy also decreases.

Similar to the electrical conductivity where the conduction of electrons is preferred along directions perpendicular to the c -axis, heat prefers to conduct in the same manner [32].

Figure 1.8: Anisotropic thermal conductivity of tin

A temperature gradient along the c -axis is more insulating to heat flux compared to that in the basal plane which is more conductive. The anisotropic surface for thermal conductivity κ_{ij} is shown in 1.8a. Up to the melting temperature, the magnitude of the two coefficients decreases with a slight decrease in anisotropy. This is consistent with what is observed for electrical conductivity.

Some of the peculiar mechanical properties of tin are due to its anisotropic elastic moduli. The elastic behavior of a crystal cannot be represented by a single surface, however. The variation of Young's modulus with direction, nonetheless, provides a good visualization of the elasticity. This surface is shown in Fig. 1.9a for tin [33]. The crystal is stiffest along its c -axis. Unlike the diffusivity, conductivity, and expansivity, the stiffness varies in the basal plane. For example, at 45° from the a -axis in the basal plane, the stiffness is softer than it is for the a -axis itself. The elastic properties of a crystal are given by a fourth-rank tensor using either the stiffness c_{ijkl} or compliance s_{ijkl} . Using Voigt notation, the

Figure 1.9: Anisotropic Young's modulus and elastic compliance of tin

tensors can be simplified to 36×36 matrices c_{ij} and s_{ij} , respectively. For tin, only six of the components are independent. The temperature dependence of the six compliance coefficients are shown in Fig. 1.9b. It is observed that only s_{11} and s_{12} appear to vary with temperature. The other four constants s_{33} , s_{31} , s_{44} and s_{66} are mostly constant over the temperature range 0°C to its melting temperature.

The thermal expansivity α_{ij} of tin is also anisotropic [34]. As a second-rank tensor, only two components are independent. For a uniform stress-free thermal strain, the temperature difference perpendicular to the c -axis is larger than it is parallel to the c -axis which is shown in Fig. 1.10a. The thermal expansivity as a function of temperature is provided in Fig. 1.10b. For increasing temperatures, the two thermal expansion coefficients also increase. The ratio of the two expansivities also increases with temperature. Under a uniform temperature change, the expansion strain along the c -axis will be larger than it is in its basal plane.

Figure 1.10: Anisotropic thermal expansivity of tin

Figure 1.11: Temperature-dependent specific heat capacity and density of tin
 $273\text{ K} \leq T \leq T_m$

Finally, the specific heat capacity and density of tin are shown in Fig. 1.11a and Fig. 1.11b, respectively [35, 36]. Under increasing temperature up to the melting point of tin, the specific heat capacity increases while the density decreases. This is typical behavior for metals.

1.4 Review of microstructural observations

As the size of integrated circuit packaging technology is expected to decrease, the understanding of solder microstructure and its role in electromigration performance will become more important. A typical solder microstructure [1] is shown in Fig. 1.12. This microstructure is formed by the soldering process performed at 250 °C for 45 minutes. At either end are the α -Cu phase substrates. Moving inward from the ends are the ε -Cu₃Sn and η' -Cu₆Sn₅ phases which have an average thickness of about 1.4 μm and 7.2 μm , respectively. The average radius of the Cu₆Sn₅ scallops is about 7.1 μm . The intermetallic layer thickness can be controlled: by soldering for longer times, the thickness of the layers increases as do the radii of the scallops. During solid-state aging, it is known that the Cu₆Sn₅ phases changes from a scallop-type to layer-type morphology [37]. If an electrical current is applied, the transformation occurs much faster. It is observed, however, that the Cu₆Sn₅ intermetallic phase dissolves into a layer at the cathode while it grows into a layer at the anode; this is intuitive by recalling that electrons flow from the cathode to the anode (which is opposite of conventional current).

The solder configuration in Fig. 1.12, which shows a low volume of tin, has not been extensively studied. In general, electromigration studies have focused on solder bumps which have a height of about 100 μm [38]. The intermetallic layers are still on the order of 10 microns in thickness leaving a large volume fraction of tin. In these studies, experiments

Figure 1.12: Multiphase solder microstructure (adapted from Huang [1])

are carried out at elevated temperatures near the transformation temperature of the η' phase. These temperatures are not typical of the actual operating conditions which alter the reaction kinetics. For the solder bump configurations and operating conditions, it is observed that voids nucleate at the Cu_6Sn_5 -Sn interface which is where the highest current density is expected. Similarly, lower temperature studies performed have shown the actual segregation of the Cu_6Sn_5 intermetallic into tin itself [39]. This has been attributed to both the combined effects of the current density and heat flow. The direction of heat flow is known to affect tin where the atoms tend to migrate from the cold end to the hot end [40].

When considering the smaller solder configurations as in Fig. 1.12, growth of the intermetallics subject to no electrical current does not necessarily follow the same trends as

the larger solder bumps. It has been observed that the tin is actually consumed by the intermetallics. The scallop morphology of the Cu_6Sn_5 phase is retained until the layers impinge upon one another [41]. Recent electromigration studies suggests that solder joints formed by soldering until the only remaining phase is Cu_3Sn have a higher resistance to electromigration failure than those which have initially unconsumed tin [22]. For the microstructures with tin, scallops at the anode grow into the cathode layer. Because the scallops are not uniform in thickness, large voids can develop as they run into the cathode layer. These large voids ultimately contribute to the poor performance of the solder interconnect. Clearly, the reactions and morphology of the joint are quite complicated.

Interest in the role of anisotropy of tin on electromigration performance has been growing over the past 10 years. These experimental studies have tried to understand the role of tin anisotropy in solder performance. For example, it is observed that in pure tin, grains will rotate under the influence of electric current [42]. It is believed that due to the anisotropy in the electrical conductivity, vacancies are transported along the grain boundaries giving rise to stresses that can cause the grains to rotate. This grain rotation leads to a drop in resistance in the direction of current flow. In addition, the anisotropy is known to play a significant role in the fatigue behavior of tin undergoing large temperature changes [43, 44]. Due to thermal expansion misfit, large stresses at grain boundaries form and contribute to grain boundary sliding and decohesion. The role of grain orientation has also been extensively studied in solder bumps comprised of a high volume of tin with intermetallics present. For instance, it has been observed that when the c -axis of large

tin grains is aligned with the current direction, the interstitial diffusion of copper leads to significant damage [45, 46]. Conversely, when the *c*-axis is perpendicular to the direction of current flow, the damage occurs much slower. It has been suggested that this slower damage rate is due to the interstitial diffusion of tin. However, this explanation does not resolve the issue that interstitial diffusion of copper in tin along the *c*-axis is about 500 times larger than it is for the *a*-axis and 12 orders of magnitude greater than it is for the self-diffusion of tin at room temperature. Another study revealed the Cu_6Sn_5 phase can be formed within the bulk of tin due to differences in the orientation of adjacent grains; this gives rise to a net flux of copper atoms to a particular grain allowing the Cu_6Sn_5 phase to form and grow [47]. The role of grain size has also been investigated. Through repeated soldering, the average size of the tin grains becomes smaller; it has been shown that this improves the electromigration reliability and is attributed to the averaging out of anisotropy effects [48]. It could be argued that this increased performance is due to the random orientation of the grains. However, because tin is tetragonal, it should not necessarily be expected that grains are randomly oriented. In fact, the above study showed that most of the grain boundaries form together at small angles less than 20° or at 60° twin boundaries. Regarding this observation, it would appear that this textured arrangement is preferred to minimize misfit between grains. That is, the random orientation of tin grains is not preferred.

Finally, the interest in void, or pore, migration is of rising interest due to smaller bump sizes. The anisotropy of tin grains is an important factor in electromigration performance

where it has been observed that only several grains are present within the bump [49, 50, 51]. In particular, the role of anisotropy on pore migration path and velocity has yet to be examined where pore formation, growth, and coalescence has been observed due to high current densities [52].

1.5 Review of pore and inclusion migration

Motivated by observations of helium-filled bubbles migrating in nuclear fuel materials, Shewmon first analyzed the motion of spherical inclusions under a temperature gradient [53]. Assuming the bubble as a mostly insoluble precipitate, the motion is analyzed in terms of three mechanisms: surface diffusion, volume diffusion, and vapor transport. For each of the three cases, it is assumed the crystal has isotropic properties and is being subjected to some driving force in terms of irreversible thermodynamics. In the case of surface diffusion, atoms or vacancies move from one side of the bubble to the other along its surface. Thus, the bubble (of insoluble gas or vacancies) moves in the direction opposite to that of the force exerted on the atoms. For vapor transport, it is assumed the gas is ideal, and therefore, the diffusivity of the gas varies inversely with pressure. In the case of volume diffusion, the bubble moves through vacancy formation on the trailing edge and moves through the lattice of the matrix where vacancy annihilation occurs on the leading edge. Considering the bubble as a remote, nonconducting inclusion, the driving force acting on the atoms is assumed to be uniform. From irreversible thermodynamics, the

driving force is proportional to the temperature gradient in thermomigration or electric field in electromigration [54]. In general, any ellipsoidal inclusion with homogeneous and isotropic properties embedded in a matrix that also has homogeneous and isotropic properties gives rise to a uniform temperature gradient or electric field when subjected to a corresponding remote field [55, 56]. Given the uniform driving force, the velocity of the bubble will be in the direction of — and with magnitude proportional to — the applied field.

In the above analysis, the sphere is assumed to be rigid under motion and nonconducting. Further work extended the analysis without assuming a rigid or nonconducting inclusion for surface [57], volume [58], and vapor [59] mechanisms. Further generalizations were carried out for motions induced by both a thermal gradient and direct current [60] as well as for cylindrical inclusions. In general, the behavior of spherical and cylindrical pores is similar. Both types migrate with a velocity independent of radius for the volume and vapor mechanisms and with a velocity inversely proportional to radius for the surface diffusion mechanism. By analyzing the interface motion of the inclusion, it is shown that it will migrate without changing shape. For the volume diffusion mechanism, an inclusion with identical conductivity (thermal or electrical) to that of the surrounding matrix will not migrate relative to a coordinate system fixed to the lattice. At one limit where the inclusion becomes a nonconducting pore, void, or bubble, it will migrate at a velocity higher than that of the lattice due to either contributions due to volume or surface diffusion. In particular, a pore will migrate at a velocity twice the velocity of the lattice

for the volume diffusion mechanism. In the limit where the inclusion is a good (perfect) conductor compared to the matrix, motion is dominated by volume diffusion and approaches an equal but opposite of the lattice velocity.

The terminology used to describe pore and inclusion migration is briefly summarized [61]. Although many of the terms can be interchanged, two general terms are used: pore and inclusion. Pores describe an absence of material within another material. Common terms include voids, bubbles, holes, and cavities. The general characteristics and meanings are summarized below and by no means is definitive:

- ▶ Void — has relatively low vapor pressure
- ▶ Bubble — has relatively high vapor pressure
- ▶ Hole — exposed to a free surface
- ▶ Cavity — enclosed in a volume

Similarly, an inclusion is distinguished from a pore and describes a region of material within another material. Common examples of inclusions include inhomogeneities, precipitates, particles, and markers. Again the terminology used is neither exhaustive or definitive but generally mean the following:

- ▶ Inhomogeneity — has different structural properties or elastic response
- ▶ Precipitate — is in solution with another phase
- ▶ Particle — is not in solution with another phase
- ▶ Marker — does not participate in diffusion

In addition to movement of pores and inclusions by electric fields and temperature gradients, stress influences their evolution with respect to their size, path, and shape. The migration of spherical bubbles has been analyzed and available analytical solutions for their migration is known [2, 62]. Following the work of [62], bubbles in uniaxial stress gradient will move upwards with the gradient whether or not it is due to tension or compression. Shown in Fig. 1.13 is the expansion of the normal velocity of a pore or inclusion into zeroth order dilation, first order translation, and higher order distortion modes [2]. The figure is adapted for a cylindrical pore using Chebyshev polynomials of the first kind [63] instead of Legendre polynomials for a sphere. From this analysis, stress gradients are responsible for migration at constant volume and shape while stress itself is responsible for distortions at constant volume and fixed center. The equilibrium shapes of distorted pores can be analyzed [64, 65] from minimum free energy by accounting for the surface energy due to shape and the change in potential energy due to loading. It is found that there is a critical loading and aspect ratio that can be established beyond which the growth of elliptical pores grow unstably into cracks.

Figure 1.13: Evolution of a pore/inclusion due to interface normal velocity expanded in terms of Chebyshev polynomials (adapted from Olander [2])

A phase field model of pore migration driven by temperature gradient has been developed for nuclear fuel materials [66]. This model only considers isotropic properties, but provides a good benchmark for volume and surface diffusion mechanisms. A phase field focusing on incorporating the effects of homogeneous stress on the evolution of copper-tin phases has also been developed [67]. However, the model does not incorporate the influence of external stress gradients which also contribute to the migration of phases. In the interest of fundamental electromigration behaviors, a complete multiphysics model accounting for the concurrent driving forces affecting the diffusional processes including charge and heat conduction along with elastic deformation is developed. In particular, special care is taken to account for anisotropy, especially with regard to the electrical conductivity of tin. In addition, the phase field model incorporates microelasticity modeling and special care is made to account for external stress gradient driven migration. Finally, all of this work is analyzed for simpler cases of pore and inclusion migration behaviors. The basic idea is to focus on tractable problems to not only verify the new models, but to also demonstrate behaviors and explain their underlying mechanisms. A model is only as good as it is useful; simply emulating real behavior is not the goal. Instead, the fundamental equations and simulations are used to demonstrate and explain these behaviors.

Chapter 2

Modeling

Multiphysical processes involving the migration of atoms driven by electric fields, temperature gradients, and stress gradients. Appropriate modeling for mass diffusion, charge conduction, heat conduction, and elastic deformation is developed taking special care to account for inhomogeneous and anisotropic properties. In addition, migration in a binary system is developed with emphasis on surface and volume diffusion mechanisms.

2.1 Mass diffusion

The net movement of atoms arising from their thermal motions is the process of diffusion. These motions can be characterized as random due to initially non-random distribution of

atoms and/or nonrandom due to driving forces acting on the atoms [68]. To characterize these motions, it is necessary to define a flux for each component.

2.1.1 Fick's law of diffusion and conservation of chemical species

The mass flux J_k of a component k is related to its concentration c_k and velocity $\mathbf{v}_k$ [69] which is defined by

$$J_k \equiv c_k \mathbf{v}_k. \quad (2.1)$$

Conservation of mass requires that continuity equation be satisfied for each component k . In spatial coordinates (laboratory reference frame), the continuity equation is

$$\frac{\partial c_k}{\partial t} = -\nabla \cdot J_k \quad (2.2)$$

Here, it is assumed there are no sources or sinks of component k . If there are chemical reactions, Eq. (2.2) can be written to take into account the generation/annihilation of component k [69]. In defining a velocity, a reference frame must be chosen to make these measurements. Observers in different laboratory reference frames may obtain different fluxes and velocities of a given component based on the choice of a reference point to measure from. These laboratory frames are commonly chosen out of convenience which are characterized by a set of points that remain fixed relative to all other points over time. A common example is to choose one end of a sample as the reference point. However,

choosing one end of the sample will result in different measurements of the fluxes and velocities compared to the other end. For these reasons, a reference frame that is independent of the observer is desired. One convention is to choose a *mean velocity reference frame* to overcome the difficulties in using laboratory reference frames [68]. The basic idea is to take a weighted average of all component velocities measured in a laboratory frame to obtain a mean velocity frame. There are various choices in weighting the velocities. For example, the center of mass of each component can be chosen. Another is the mean molar (also called number-fixed) reference frame which is chosen using the mole fraction as the weight where the sum of all n mole fractions for each component k is equal to one

$$\sum_k^n X_k = 1. \quad (2.3)$$

The mole fraction X_k of component k is defined by the ratio of composition c_k for each component k to the total molar concentration c_0

$$X_k = \frac{c_k}{c_0} \quad (2.4)$$

such that summing all individual compositions gives the total overall composition

$$\sum_k^n c_k = c_0. \quad (2.5)$$

The velocity of the mean molar reference frame measured relative to the laboratory frame is weighted using the mole fractions defined by

$$\mathbf{v} \equiv \sum_k^n X_k \mathbf{v}_k \quad (2.6)$$

where $\mathbf{v}_k$ is the velocity of component k measured in a given laboratory frame. A new mean molar flux can be defined $J'_k \equiv c_k(\mathbf{v}_k - \mathbf{v})$. Rearranging Eq. (2.1) and substituting into Eq. (2.6) gives flux constraint

$$\sum_k^n J'_k = 0. \quad (2.7)$$

Due to the constraint Eq. (2.3), only $n-1$ conservation equations are required to completely describe the diffusion. For a two component binary system with components j and k , only one conservation equation is needed since $X_j + X_k = 1$. However, it is difficult to distinguish between what is participating in diffusion or moving due to bulk flow due to movement of all other components. Therefore, special care must be taken when defining reference frames. There is distinction between flux of a certain component relative to all other components and flux due to bulk flow of all components at the same rate and direction. A reference frame that moves with the bulk flow is called the “inert marker” (also called lattice-fixed) reference frame; fluxes J_k^* measured in this frame are due to diffusion only [68]. These fluxes are related to the mean molar by

$$J'_k = J_k^* - X_k \sum_i^n J_i^*. \quad (2.8)$$

For a binary system the fluxes are $J'_j = X_k J_j^* - (1 - X_k) J_k^*$ and $J'_k = -X_k J_j^* + (1 - X_k) J_k^*$ [70].

The driving force F_k from component k is due to the negative gradient of its chemical potential variations μ_k

$$F_k = -\nabla \mu_k. \quad (2.9)$$

In practice, the chemical potential is not a simple quantity to measure. From a historical perspective, Fick's laws of diffusion are written in terms of concentration (or composition) gradients with corresponding diffusion coefficients. From a practical point of view, compositions are much simpler to measure experimentally. In addition, solutions that are ideal simplify the chemical potential gradient in terms of the concentration gradient. From the chain rule, the relationship between chemical potential gradient of a component k follows

$$\nabla \mu_k = \frac{\partial \mu_k}{\partial c_k} \nabla c_k. \quad (2.10)$$

The chemical potential of a component in a solution can be written as

$$\mu_k = G_k^0 + RT \ln a_k = \underbrace{G_k^0 + RT \ln X_k}_{\text{ideal}} + \underbrace{RT \ln \gamma_k}_{\text{excess}} \quad (2.11)$$

R is the gas constant, T is temperature, $a_k = \gamma_k X_k$ is the activity of component k , and γ_k is the activity coefficient which is used to describe the deviation from ideal behavior, or excess chemical potential [71]. In general, the activity coefficient can be a function

of composition $\gamma_k = \gamma_k(X_k)$. If the component is nearly pure, $X_k \rightarrow 1$ and Raoult's law applies where $\gamma_k = 1$ which characterizes an ideal solution. Conversely, if the component is dilute $X_k \rightarrow 0$ and Henry's law applies where $\gamma_k = \text{constant} \neq 1$ which characterizes a non-ideal solution. The partial derivative of the chemical potential with respect to the composition results in

$$\frac{c_k}{RT} \frac{\partial \mu_k}{\partial c_k} = \begin{cases} 1 & \text{ideal} \\ 1 + \frac{\partial \ln \gamma_k}{\partial \ln X_k} & \text{non-ideal} \end{cases} \quad (2.12)$$

The latter term is called the thermodynamic factor and can be multiplied by the tracer diffusion coefficient to give the intrinsic diffusion coefficient. The mobility as a function of diffusion coefficient is

$$M_{kk} = \frac{D_k c_k}{RT} \quad (2.13)$$

which gives the standard form of $-D_k \nabla c_k$. From the concentration gradient, a wide variety of solutions for nonsteady and steady state diffusion problems can be utilized [72]. However, these solutions are not adequate to describe the behavior in many other systems. In general, the driving force due to component k affects all fluxes including the flow of itself. In addition, gradients are independent of the reference frame chosen. From the principle of microscopic reversibility [73, 74], Onsager's reciprocal relations [75, 76, 77] hold for the linear combination of thermodynamic forces for the flow of each component. Considering one-dimensional fluxes and driving forces each flux, there are n mobility coefficients for

each of the n fluxes; that is,

$$J_i = \sum_j^n M_{ij} F_j \quad i = 0, 1, \dots, n \quad (2.14)$$

for a total of n^2 coefficients. Onsager's reciprocal relation requires that $M_{ij} = M_{ji}$ if $j \neq k$ which simplifies the number of independent coefficients to $n(n+1)/2$. This applies to any reference frame chosen. However, a further restriction is imposed if a mean velocity reference frame is used. For the number-fixed frame [Eq. \(2.7\)](#) holds. Going back to vector notation and assuming isotropic mobilities for convenience (anisotropic mobility coefficients can be considered but the notation is cumbersome), the fluxes for the binary system are

$$\mathbf{J}'_j = M'_{jj} \mathbf{F}_j + M'_{jk} \mathbf{F}_k \quad \mathbf{J}'_k = M'_{kj} \mathbf{F}_j + M'_{kk} \mathbf{F}_k \quad \text{number-fixed} \quad (2.15)$$

$$\mathbf{J}^*_j = M^*_{jj} \mathbf{F}_j + M^*_{jk} \mathbf{F}_k \quad \mathbf{J}^*_k = M^*_{kj} \mathbf{F}_j + M^*_{kk} \mathbf{F}_k \quad \text{lattice-fixed} \quad (2.16)$$

Recalling the Gibbs–Duhem equation at constant temperature and pressure

$$\sum_k^n X_k d\mu_k = 0, \quad (2.17)$$

the binary relationship $X_j d\mu_j + X_k d\mu_k = 0$ can be used to obtain

$$(1 - X_k) \nabla \mu_j + X_k \nabla \mu_k = 0 \quad (2.18)$$

such that $F_j = -(X_k/X_j)F_k$ and $F_k = -(X_j/X_k)F_j$ [78]. Using Eq. (2.7) with Eq. (2.17), the number-fixed frame (and any mean velocity reference frame) only has $(n-1)(n)/2$ coefficients [68] which greatly reduces the number of independent mobility coefficients. For example, a binary system only has one independent coefficient. Using these results from Eq. (2.18), the mean molar fluxes can be written as

$$J'_j = \left(-\frac{X_k}{1-X_k} M'_{jj} + M'_{jk} \right) F_k \quad \text{and} \quad J'_k = \left(-\frac{X_k}{1-X_k} M'_{kj} + M'_{kk} \right) F_k. \quad (2.19)$$

Since $J'_j + J'_k = 0$ and $M'_{jk} = M'_{kj}$, only one mobility coefficient is needed to describe the diffusional processes $M \equiv M'_{jj} = M'_{kk} = -M'_{jk} = -M'_{kj}$. Applying the same procedure to the inert marker reference frame, the corresponding fluxes are

$$J_j^* = \left(-\frac{X_k}{1-X_k} M_{jj}^* + M_{jk}^* \right) F_k \quad \text{and} \quad J_k^* = \left(-\frac{X_k}{1-X_k} M_{kj}^* + M_{kk}^* \right) F_k. \quad (2.20)$$

Using the result of Eq. (2.8) gives mean molar flux in terms of the inert marker reference frame

$$J'_j = -\frac{1}{1-X_k} \left(X_k^2 M_{jj}^* - 2X_k(1-X_k)M_{jk}^* + (1-X_k)^2 M_{kk}^* \right) F_k \quad (2.21)$$

$$J'_k = \frac{1}{1-X_k} \left(X_k^2 M_{jj}^* - 2X_k(1-X_k)M_{kj}^* + (1-X_k)^2 M_{kk}^* \right) F_k \quad (2.22)$$

such that $M = (1-X_k)(X_k^2 M_{jj}^* - 2X_k(1-X_k)M_{jk}^* + (1-X_k)^2 M_{kk}^*)$. Choosing principal mobility coefficients $M_{kk}^* = M_k X_k$ and $M_{jj}^* = M_j X_j$ while ignoring the cross terms $M_{jk}^* = M_{kj}^* = 0$,

Eq. (2.19) and Eq. (2.21) gives interdiffusion mobility with composition dependence [71] given by

$$M = X(1 - X)(XM_j + (1 - X)M_k). \quad (2.23)$$

where $X \equiv X_k$. Further simplifications can be achieved using $c \equiv c_k$ and letting $\mu \equiv \mu_k - \mu_j$ such that a new driving force can be defined for the binary system $F \equiv -\nabla\mu = -\nabla(\mu_k - \mu_j)$.

The mass conservation continuity equation for the binary system is

$$\frac{\partial c}{\partial t} = -\nabla \cdot J \quad (2.24)$$

in material coordinates where $J = J_k$. Fick's law of diffusion for the binary system [79] states that the mass flux J of a component is proportional to the driving force F acting on by the mobility

$$J_i = M_{ij}F_j \quad (2.25)$$

where the mobility $M_{ij} = M_{ij}(D_{ij}, X, T)$ is a function of diffusion coefficient D_{ij} , mole fraction X , and temperature T , which simplifies to Eq. (2.23) when the diffusion coefficient is isotropic. In general, the anisotropic mobility of each component is proportional to the diffusion coefficient D_{ij} according to

$$M_{ij} = \frac{D_{ij}c_0}{RT} \quad (2.26)$$

where M_{ij} and D_{ij} are symmetric second-rank tensors. For isotropic (or cubic) materials

the diffusion coefficient can be described by a single term $D_{ij} = D\delta_{ij}$ where δ_{ij} is the Kronecker delta. It can be shown that the mobility in Eq. (2.26) accounts for both surface and volume diffusion dominated mechanisms. For dilute solutions with equal diffusion coefficients $D = D_k = D_j$, the mobility is proportional to the composition of the solute [80]: it is the product of coefficient involving the diffusivity with the low concentration of the minor diffusing species. For example, where $X \rightarrow 0$, Eq. (2.23) and Eq. (2.26) simplify to

$$M = \frac{Dc_0}{RT}X \quad \text{volume} \quad (2.27)$$

Similarly applied to $X \rightarrow 1$, the mobility reduces to

$$M = \frac{Dc_0}{RT}(1 - X) \quad \text{volume} \quad (2.28)$$

The same proportionality coefficient Dc_0/RT is common between both cases. For surface dominated diffusion [80, 81], the mobility is confined to a small composition band near $X \approx 0.5$ and can be written as

$$M = \frac{Dc_0}{RT}X(1 - X) \quad \text{surface} \quad (2.29)$$

which has the same proportionality coefficient as the volume diffusion mechanisms. As the solution becomes more dilute, that is, where $X \rightarrow 0$ or $X \rightarrow 1$ the mobility tends to

Figure 2.1: Composition dependent mobility

zero. Defining the non-dimensional parameter $\zeta = M_k/M_j$, the maximum mobility can be found at mole fraction

$$X = \frac{(4\zeta - 2) - \sqrt{(2 - 4\zeta)^2 - 4\zeta(\zeta - 3)}}{2(3\zeta - 3)} \quad (2.30)$$

for $\zeta \neq 1$ and $X = 1/2$ for $\zeta = 1$. Shown in Fig. 2.1a is an illustration of the composition dependent mobility for a binary system with two unequal diffusion coefficients. For small compositions, the mobility approximates volume diffusion mechanism while over large compositions, the mobility is maximum at the interface composition consistent with surface diffusion mechanism. Similarly, in Fig. 2.1b is the composition dependent mobility for various ratios of diffusion coefficients and the shift in maximum mobility as a function of mole fraction.

The chemical free energy F can be described [82, 83] by a functional

$$F = c_0 \int_{\Omega} \left\{ f(X) + \frac{1}{2} \kappa (\nabla X)^2 \right\} d^3 \mathbf{r} \quad (2.31)$$

where $f(X)$ is the bulk free energy of the coexisting α and β phases and the gradient term describes the interfacial free energy due to the formation of interfaces between them where κ is the gradient coefficient. The bulk free energy term as a function of mole fraction is related to the chemical potential of each component μ_j and μ_k

$$f(X) = (1 - X)\mu_j(X) + X\mu_k(X) \quad (2.32)$$

and can be modified according to

$$f_0(X) = (1 - X)[\mu_j(X) - \mu_j(X^\alpha)] + X[\mu_k(X) - \mu_k(X^\beta)] \quad (2.33)$$

which refers to an equilibrium mixture of α and β decomposed from an overall composition of c_0 [82]. Shown in Fig. 2.2a is an example of a bulk free energy curve $f(X)$. The intersection of the tangent line with the curve gives the equilibrium phase compositions X^α and X^β of phases α and β , respectively, with overall composition $f(X^0)$. Subtracting the tangent line from the bulk curve gives Eq. (2.33) which is shown in Fig. 2.2b. A

fourth-order Taylor expansion can be used to approximate this free energy curve

$$f_0(X) \approx 16f_0(X^0) \left[\frac{X^\beta - X}{X^\beta - X^\alpha} \right]^2 \left[\frac{X - X^\alpha}{X^\beta - X^\alpha} \right]^2. \quad (2.34)$$

where $f_0(X^0)$ is the height of the free energy barrier of this double-well potential. The phase fractions of α and β are described by

$$x_\alpha = \frac{X^\beta - X}{X^\beta - X^\alpha} \quad \text{and} \quad x_\beta = \frac{X - X^\alpha}{X^\beta - X^\alpha} \quad (2.35)$$

such that the polynomial may be rewritten as $f_0(X) \approx 16f_0(X^0)x_\alpha^2x_\beta^2$. Since $x_\alpha + x_\beta = 1$, the notation may be further simplified according to $16f_0(X^0)(1-x)^2x^2$ where $x \equiv x^\beta$. Using a simpler polynomial approximation allows the functional derivative of [Eq. \(2.31\)](#)

(a) Illustration of a nonuniform system comprised of phases α and β (Redlich-Kister polynomial)

(b) Solution referenced to its equilibrium state with overall mole fraction X_k^0 and fourth order polynomial approximation

Figure 2.2: Free energy of a binary system as a function of the mole fraction for component k

to be carried out and facilitates its analysis for further investigation. In addition, it is numerically more efficient to implement in a computer program. The functional derivative of the chemical free energy is the chemical potential

$$\frac{\delta F}{\delta c(\mathbf{r})} = \frac{1}{c_0} \frac{\delta F}{\delta X(\mathbf{r})} = \mu(\mathbf{r}); \quad (2.36)$$

evaluating Eq. (2.31), the functional derivative is

$$\frac{1}{c_0} \frac{\delta F}{\delta X(\mathbf{r})} = \frac{\partial f}{\partial X} - \kappa \nabla^2 X. \quad (2.37)$$

2.1.2 Driving forces for diffusion: conduction and deformation

Driving forces for migration [84] include the influences of charge and heat conduction due to electric [85] and thermal driving force [86] fields. These driving forces are related to these fields by material interference properties. In terms of elasticity, the chemical potential is affected by the elastic fields [87, 88]. The resulting driving force is more or less related to the stress gradient [89]. Considering electromigration, the flux of components j and k in the mean molar frame can be expanded to include the influence of the electric field E . Again considering only isotropic properties to simplify notation, the fluxes with

current density $\mathbf{j}$ are

$$\mathbf{J}'_j = L_{jj}\mathbf{F}_j + L_{jk}\mathbf{F}_k + L_{je}\mathbf{E} \quad (2.38)$$

$$\mathbf{J}'_k = L_{kj}\mathbf{F}_j + L_{kk}\mathbf{F}_k + L_{ke}\mathbf{E} \quad (2.39)$$

$$\mathbf{j} = L_{ej}\mathbf{F}_j + L_{ek}\mathbf{F}_k + L_{ee}\mathbf{E} \quad (2.40)$$

where the mobility $M \equiv L_{jj} = L_{kk} = -L_{jk} = -L_{kj}$ is consistent with the previous analysis and $\sigma \equiv L_{ee}$ is the electrical conductivity by definition [90]. Here e refers to the flow of electric charge which can be thought of as an additional component. Onsager's reciprocal relations require the cross effects be symmetric such that $L_{je} = L_{ej}$ and $L_{ke} = L_{ek}$. Summing Eq. (2.38) and Eq. (2.39), it is clear that $L_{je} + L_{ke} = 0$. In the case where there is no electric field present, $\mathbf{E} = \mathbf{0}$. The off-diagonal coefficients are defined by $L_{ej} = eN_A(L_{jj}Z_j^* + L_{jk}Z_k^*)$ and $L_{ek} = eN_A(L_{kj}Z_j^* + L_{kk}Z_k^*)$ such that the current density is $\mathbf{j} = eN_A(Z_j^*\mathbf{J}'_j + Z_k^*\mathbf{J}'_k)$ where Z_j^* and Z_k^* are the effective charge numbers of components j and k . Here, N_A is Avogadro's constant and e is the elementary charge. The driving force for diffusion accounting for electric coupling becomes

$$F_i = -\frac{\partial\mu}{\partial x_i} + eN_A Z_{ij}^* E_j \quad \text{electrical} \quad (2.41)$$

where Z_{ij}^* is the effective charge number difference tensor between components k and j . For each component, the contributions to the effective charge number include two components: $Z^* = \text{electrostatic} + \text{wind}$ where each term represents a different mechanism

acting on the atom. The electrostatic term represents the electric field effect of the atomic valence. The so-called "wind" term represents the interaction of moving electrons with the atom [84]. For heat conduction, the fluxes with heat flux $\mathbf{q}$ are

$$\mathbf{J}'_j = L_{jj}\mathbf{F}_j + L_{jk}\mathbf{F}_k + L_{jh}T^{-1}\mathbf{X} \quad (2.42)$$

$$\mathbf{J}'_k = L_{kj}\mathbf{F}_j + L_{kk}\mathbf{F}_k + L_{kh}T^{-1}\mathbf{X} \quad (2.43)$$

$$\mathbf{q} = L_{hj}\mathbf{F}_j + L_{hk}\mathbf{F}_k + L_{hh}T^{-1}\mathbf{X} \quad (2.44)$$

where the thermal driving force $\mathbf{X}$ is the negative temperature gradient [91]. In the context of irreversible processes, the driving force is related to $T^{-1}\mathbf{X}$ responsible the rate of entropy production [92] where Onsager's reciprocal relations hold with new diagonal term related to the thermal conductivity $\kappa \equiv T^{-1}L_{hh}$. Here h refers to the flow of heat (enthalpy) again considered as an additional component. Similar to the electrical analysis, $L_{hj} = T^{-1}N_A(L_{jj}Q_j^* + L_{jk}Q_k^*)$ and $L_{hk} = T^{-1}N_A(L_{kj}Q_j^* + L_{kk}Q_k^*)$ such that the current density is $\mathbf{q} = T^{-1}N_A(Q_j^*\mathbf{J}'_j + Q_k^*\mathbf{J}'_k)$ where Q_j^* and Q_k^* are the heats of transport of components j and k . The new driving force for diffusion is therefore

$$F_i = -\frac{\partial\mu}{\partial x_i} + \frac{1}{T}N_A Q_{ij}^* X_j \quad \text{thermal} \quad (2.45)$$

where Q_{ij}^* is the heat of transport difference tensor between components k and j . For each component, the heat of transport can be represented by three terms: $Q^* = \text{intrinsic} + \text{electron} + \text{phonon}$. The first represents the intrinsic transport of energy by an atomic

jump; the latter two represent the interactions of phonons and electrons with the atom due to heat conduction [84]. For each component, *negative values* of either Z^* or Q^* indicate the component diffuses in a direction that is *opposite* to the external field.

The elastic strain energy is arguably one of the most important considerations in understanding microstructure evolution. Unlike conduction, elastic deformation is an equilibrium property. Starting with the combined first and second law of thermodynamics for an open system

$$dU_v = \sigma_{ij} d\epsilon_{ij} + T dS_v + \sum_k^n \mu_k dc_k \quad (2.46)$$

where U_v is the internal energy density (per unit volume), σ_{ij} is the stress, ϵ_{ij} is the total strain, T is temperature, S_v is entropy density, and for component k , μ_k and c_k are the chemical potential and concentration, respectively [28]. The Gibbs free energy density is the Legendre transform of the internal energy $G_v = U_v - \sigma_{ij} \epsilon_{ij} - TS_v$. For a binary system, $c_0 = c_k + c_j$ where $dc_0 = 0$ such that the infinitesimal reversible change of Gibbs free energy density is

$$dG_v = -\epsilon_{ij} d\sigma_{ij} - S_v dT + \mu dc. \quad (2.47)$$

From the definition of partial derivatives, the strain, entropy, and chemical potential difference are defined by the partial differentials

$$-\left(\frac{\partial G_v}{\partial \sigma_{ij}}\right) = \epsilon_{ij}, \quad -\left(\frac{\partial G_v}{\partial T}\right) = S_v, \quad \text{and} \quad \left(\frac{\partial G_v}{\partial c}\right) = \mu. \quad (2.48)$$

Maxwell's relations can be used to define a new parameter that accounts for the interaction of stress and composition. The symmetry of second derivatives of the Gibbs free energy density with respect to stress and atomic fraction gives parameter

$$-\left(\frac{\partial^2 G_v}{\partial \sigma_{ij} \partial X}\right) = \left(\frac{\partial \varepsilon_{ij}}{\partial X}\right) = -\left(\frac{\partial^2 G_v}{\partial X \partial \sigma_{ij}}\right) = -c_0 \left(\frac{\partial \mu}{\partial \sigma_{ij}}\right) = \eta_{ij} \quad (2.49)$$

which is a tensor with units of strain (dimensionless or length per length). The total strain is the sum of elastic strain due to stress with the inelastic stress-free strain related to change in composition. Similarly, the total chemical potential difference in the binary system can be split into an internal term due to interactions between components j and k and an external term due to stress. Incorporation of the parameter η_{ij} into the strain and chemical potential may as well be

$$\varepsilon_{ij} = s_{ijkl} \sigma_{kl} + \eta_{ij}(X - X_0) \quad \text{and} \quad \mu = RT \ln\left(\frac{\zeta X}{1 - X}\right) - \frac{1}{c_0} \eta_{ij} \sigma_{ij} \quad (2.50)$$

where s_{ijkl} is the compliance tensor, X_0 is the reference state of the overall solution, and $\zeta = \gamma_k/\gamma_j$ is the ratio of activity coefficients [93]. The stress-free strain ε_{ij}^0 therefore is

$$\varepsilon_{ij}^0 = \eta_{ij}(X - X_0) \quad (2.51)$$

where η_{ij} is the “chemical” expansivity. For a crystal with orthogonal lattice parameters a , b , and c ($\alpha = \beta = \gamma = 90^\circ$), the principal components of the expansion tensor [93] are

given by

$$\eta_{11} = \frac{\partial \ln a}{\partial X} = \frac{1}{a} \frac{\partial a}{\partial X} \quad \eta_{22} = \frac{\partial \ln b}{\partial X} = \frac{1}{b} \frac{\partial b}{\partial X} \quad \eta_{33} = \frac{\partial \ln c}{\partial X} = \frac{1}{c} \frac{\partial c}{\partial X} \quad (2.52)$$

These relations should also hold for hexagonal and trigonal crystals where $a = b$ and $\gamma = 90^\circ$; the principal coefficients are $\eta_{11} = \eta_{22}$ and no off-diagonal coefficients. The composition dependence of the lattice parameter between phases α and β may follow Vegard's law which follows a simple rule of mixtures

$$a = (1 - X)a_\alpha + Xa_\beta \quad b = (1 - X)b_\alpha + Xb_\beta \quad c = (1 - X)c_\alpha + Xc_\beta \quad (2.53)$$

and not expected to follow for monoclinic or triclinic crystals since they have nonzero off-diagonal expansion coefficients. The driving for diffusion is therefore

$$F_i = -\frac{\partial(\mu_0 - \eta_{jk}\sigma_{jk})}{\partial x_i} \quad \text{elastic} \quad (2.54)$$

where $\mu_0 = RT \ln[\zeta X/(1 - X)]$ is now defined as the chemical potential without stress effects. It is then possible to combine for each effect for electrical, thermal, and mechanical effects by summing each contribution:

$$F_i = \underbrace{-\frac{\partial(\mu_0 - \eta_{kl}\sigma_{kl})}{\partial x_i}}_{\text{chemical+mechanical}} + \underbrace{N_A e Z_{ij}^* E_j}_{\text{electrical}} - \underbrace{N_A Q_{ij}^* \frac{1}{T} \frac{\partial T}{\partial x_j}}_{\text{thermal}}$$

2.2 Charge conduction

The flow of charge in conductors as electrical current is due to collisions and momentum transfers between charged particles driven by voltage, or electric potential difference [26]. Conductors are characterized by mobile charges including electrons in metals, holes in semiconductors, and cations and/or anions electrolytes. Nonconductors, or insulators have very few mobile charges. Conduction is especially enhanced by metallic bonding in metals where free electrons are shared in a “sea of electrons” which gives rise to high electrical and thermal conductivity. Of all the metals, silver has the highest electrical conductivity. To solve the conduction problem, it is necessary to take into account the long-range interactions of the electric field due to inhomogeneous charge density distribution [94, 95].

2.2.1 Ohm’s law of conduction and conservation of charge

Ohm’s law of conduction states that the free current $\mathbf{j}$ is proportional to the electric field $\mathbf{E}$ by the conductivity

$$j_i = \sigma_{ij} E_j \quad (2.55)$$

where σ_{ij} is the electrical conductivity tensor. The electric field is decomposed into two parts: one that is spatially homogeneous $\bar{\mathbf{E}}$ and the other that is spatially inhomogeneous

$\delta E(\mathbf{r})$ where

$$\mathbf{E}(\mathbf{r}) = \bar{\mathbf{E}} + \delta \mathbf{E}(\mathbf{r}) . \quad (2.56)$$

The homogeneous part is the spatial average of the total electric field

$$\bar{\mathbf{E}} = \frac{1}{V} \int_{\Omega} \mathbf{E}(\mathbf{r}) d^3 \mathbf{r} \quad (2.57)$$

which represents an applied external field $\bar{\mathbf{E}} = \mathbf{E}^{\infty}$ where $\mathbf{E}^{\infty}$ is the remotely applied field.

The inhomogeneous part is spatially variable

$$\delta \mathbf{E}(\mathbf{r}) = -\nabla \phi \quad (2.58)$$

which represents the internal electric field due to the negative gradient of the electrostatic potential ϕ . Charge-charge interactions are Coulombic such that the potential energy U of an electrostatic field [96] is given by the double integral functional

$$U = \frac{1}{8\pi\epsilon_0} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r} d^3 \mathbf{r}' \quad (2.59)$$

where ρ is the charge density and ϵ_0 is the vacuum permittivity. Taking the functional derivative with respect to the charge density field gives the electrostatic potential

$$\frac{\delta U}{\delta \rho(\mathbf{r})} = \phi(\mathbf{r}). \quad (2.60)$$

Evaluating Eq. (2.59) gives

$$\phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' . \quad (2.61)$$

Conservation of charge requires that continuity equation be satisfied

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \mathbf{j} \quad (2.62)$$

where the time rate of change of charge density equals the convergence of the current density field. This equation can be derived from Maxwell's equations, specifically Ampère's circuital law and Gauss's law for electricity [97].

2.3 Heat conduction

The transfer of heat by conduction is likely one of the most straightforward of the transport phenomena. Despite being similar to diffusion, its simple physical description results in a rich variety of mathematical tools. Fourier's study of heat gave rise to not only the eponymous law of conduction, but also Fourier series and the Fourier transform. Specifically, heat conduction is the transfer of internal energy through a material driven by temperature gradients. For a solid, the transfer of energy is carried by a combination of phonons (lattice vibrations) and free electrons [26]. Conduction is distinguished by two

other heat transfer modes which include *convection* where heat is carried by the relative motion of a material mainly observed in fluids and *radiation* where heat is transferred between disconnected over a distance by electromagnetic waves [55].

2.3.1 Fourier's law of conduction and conservation of energy

Fourier's law of conduction states that the heat flux $\mathbf{q}$ is proportional to the thermal driving force $\mathbf{X}$ by the conductivity

$$q_i = \kappa_{ij} X_j \quad (2.63)$$

where κ_{ij} is the thermal conductivity tensor. The thermal driving force is decomposed into two parts: one that is spatially homogeneous $\bar{X}$ and the other that is spatially inhomogeneous $\delta X(\mathbf{r})$ where

$$X(\mathbf{r}) = \bar{X} + \delta X(\mathbf{r}). \quad (2.64)$$

The homogeneous part is the spatial average of the total thermal driving force

$$\bar{X} = \frac{1}{V} \int_{\Omega} X(\mathbf{r}) d^3\mathbf{r} \quad (2.65)$$

which represents an applied external field $\bar{X} = X^\infty$ where X^∞ is the remotely applied field. The inhomogeneous part is spatially variable

$$\delta X(\mathbf{r}) = -\nabla T \quad (2.66)$$

which represents the internal thermal driving force due to the negative gradient of the temperature T .

Conservation of energy requires that continuity equation be satisfied

$$\rho \frac{\partial u}{\partial t} = -\nabla \cdot \mathbf{q} + \varphi \quad (2.67)$$

where ρ is the density, u is the change specific internal energy, and φ is a term accounting for sinks or sources of heat. One example of heat generation is due to Joule heating where $\varphi = \mathbf{j} \cdot \mathbf{E}$ which depends on current density $\mathbf{j}$ and electric field $\mathbf{E}$ [98]. Another is due to viscous dissipation where $\varphi = \sigma_{ij} D_{ij}$ which depends on the state of stress σ_{ij} and rate of deformation D_{ij} [99]. The left-hand side of Eq. (2.67) can be simplified if an equation of state is known for the specific internal energy. An alternative approach is to use the definition of specific enthalpy change

$$h = u + \frac{p}{\rho} \quad (2.68)$$

where p is the pressure. Rearranging and substituting Eq. (2.68) into Eq. (2.67) gives an alternative equation that expresses the conservation of energy

$$\rho \frac{\partial h}{\partial t} - \frac{\partial p}{\partial t} = -\nabla \cdot \mathbf{q} + \varphi. \quad (2.69)$$

Here, an equation of state for the specific enthalpy and pressure is needed. A common

simplification for solids is to assume constant pressure $\partial p / \partial t = 0$ such that the change in enthalpy is due to temperature changes only given by the integral

$$h = \int_{T_0}^{T(t)} c_p(T) dT \quad (2.70)$$

where c_p is the specific heat capacity. Using the Leibniz integral rule

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial t} \int_{T_0}^{T(t)} c_p(T) dT = c_p(T) \frac{\partial T}{\partial t}, \quad (2.71)$$

it can be shown that

$$\rho c_p \frac{\partial T}{\partial t} = -\nabla \cdot \mathbf{q} + \varphi. \quad (2.72)$$

This is a common expression for conservation of energy applicable to heat transfer in solids.

2.4 Elastic deformation

Solving the internal stress field for any given arbitrary inhomogeneous and anisotropic microstructure is important for analyzing microstructural phenomena and material properties but often overlooked due to its difficulty. Elastic deformations are long-range and act through — and are transferred by — the medium. This makes the problem more difficult than electromagnetic interactions which are also long-range but act in disregard to

the medium. For example, the electrostatic potential in Eq. (2.61) depends only on the distribution of charge density field. Both of the fields do not depend explicitly on the medium or its properties. Similar integrals exist for the solution of electric and magnetic field in terms of polarization and magnetization densities, respectively, which also do not rely on the medium. This means the electromagnetic fields can be solved for any inhomogeneous and anisotropic microstructures. For elasticity, there is no explicit solution of the elastic fields in terms of the deformations in a body that can be used for any type of microstructure. One of the only explicit solutions exists for a uniform isotropic body; this is known as the Kelvin solution which gives the displacement field $\mathbf{u}$ in terms of any arbitrary distribution of forces in the body $\mathbf{F}$ given by

$$u_i(\mathbf{r}) = \frac{1}{16\pi\mu(1-\nu)} \int \left\{ \frac{(3-4\nu)\delta_{ij}}{|\mathbf{r}-\mathbf{r}'|} + \frac{(x_i-x'_i)(x_j-x'_j)}{|\mathbf{r}-\mathbf{r}'|^3} \right\} F_j(\mathbf{r}') d^3\mathbf{r}' \quad (2.73)$$

where μ is the shear modulus (Lamé's second parameter) and ν is Poisson's ratio [100]. However, many deformations are due to stress-free strains that are not due to a body force in Eq. (2.73). In 1957, Eshelby determined the elastic fields inside and outside of an ellipsoidal *elastic* inclusion embedded in an isotropic matrix with prescribed uniform stress-free strain by relating the Kelvin state solution of elastic fields due to a body point force to virtual relaxation, transformation, and restoration operations on the inclusion [101, 102]. Eshelby showed that for ellipsoidal inclusions, the stress inside is uniform. In principal, the force term in Eq. (2.73) is replaced with a stress-free strain deformation

which gives the integral

$$u_i(\mathbf{r}) = \frac{1}{8\pi(1-\nu)} \int \left\{ \frac{(1-2\nu)[\delta_{ij}(x_k - x'_k) + \delta_{ik}(x_j - x'_j) - \delta_{jk}(x_i - x'_i)]}{|\mathbf{r} - \mathbf{r}'|^3} + \frac{3(x_i - x'_i)(x_j - x'_j)(x_k - x'_k)}{|\mathbf{r} - \mathbf{r}'|^5} \right\} \varepsilon_{jk}^0(\mathbf{r}') d^3\mathbf{r}' \quad (2.74)$$

where ε_{ij}^0 is the stress-free strain. Due to elasticity being linear, an ellipsoidal *structural* inclusion with different properties of the surrounding matrix can be replaced by an equivalent homogeneous problem. Replacing the structural inhomogeneity having different properties than the surrounding matrix with an elastic inhomogeneity having the same properties as the matrix gives rise to what is known as the equivalent inclusion method. By 1967, Khachaturyan solved the inhomogeneity problem for inclusions of

Figure 2.3: Determining the elastic fields due to the presence of inhomogeneity

arbitrary shape and anisotropy using Fourier transform integrals [100]. However, the development of phase field microelasticity theory and modeling allowed for the capability of solving the stress field of arbitrary microstructures with structural and elastic inhomogeneities [103]. Phase field microelasticity modeling is one technique that provides

such a capability and can be integrated into computational studies of microstructure evolution and material properties such as voids and cracks in polycrystals [104], dislocation dynamics [105, 106, 107], martensitic transformations [108, 109], ferromagnetic domains [110], and ferroelectric domains [111]. The problem of phase field microelasticity modeling comes down to numerically solving for the eigenstrain that equivalently represents the structural and elastic inhomogeneities of the inhomogeneous system in the homogeneous system.

2.4.1 Hooke's law of elasticity and mechanical equilibrium

Hooke's law of elasticity states that the Cauchy stress tensor σ_{ij} is proportional to the infinitesimal elastic strain $e_{ij} = \varepsilon_{ij} - \varepsilon_{ij}^0$ by the stiffness tensor c_{ijkl}

$$\sigma_{ij} = c_{ijkl}(\varepsilon_{kl} - \varepsilon_{kl}^0) \quad (2.75)$$

where the total infinitesimal strain is ε_{ij} and stress-free strain is ε_{ij}^0 [112]. Stress is a symmetric tensor $\sigma_{ij} = \sigma_{ji}$ by virtue of conservation of angular momentum as are the strain tensors $\varepsilon_{ij} = \varepsilon_{ji}$, $e_{ij} = e_{ji}$, and $\varepsilon_{ij}^0 = \varepsilon_{ji}^0$ by definition. Strain is the symmetrical part of the displacement gradient that describes deformation including change in lengths and angles while rotations are described the antisymmetrical part [99]. The inhomogeneous stiffness has major symmetries $c_{ijkl} = c_{klij}$ from Maxwell's relations, specifically the symmetry of

second derivatives for internal strain energy density with respect to the strain [27, 28].

In addition, the minor symmetries $c_{ijkl} = c_{jikl}$ and $c_{ijkl} = c_{ijlk}$ are due to the symmetry of the stress and strain tensors, respectively. The stiffness can be decomposed into two parts: a positive definite, invertible reference stiffness tensor c_{ijkl}^0 with inverse compliance $s_{ijkl}^0 = (c_{ijkl}^0)^{-1}$ and a remaining inhomogeneous part $\delta c_{ijkl}(\mathbf{r})$ which sum to

$$c_{ijkl}(\mathbf{r}) = c_{ijkl}^0 + \delta c_{ijkl}(\mathbf{r}). \quad (2.76)$$

The total strain can be decomposed into two parts: a spatially homogeneous $\bar{\varepsilon}_{ij}$ and inhomogeneous part $\delta \varepsilon_{ij}(\mathbf{r})$ where

$$\varepsilon_{ij}(\mathbf{r}) = \bar{\varepsilon}_{ij} + \delta \varepsilon_{ij}(\mathbf{r}). \quad (2.77)$$

The homogeneous part is the spatial average of the total strain

$$\bar{\varepsilon}_{ij} = \frac{1}{V} \int_{\Omega} \varepsilon_{ij}(\mathbf{r}) d^3\mathbf{r} \quad (2.78)$$

and variable part is related to the gradient of displacement according to

$$\delta \varepsilon_{ij}(\mathbf{r}) = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right). \quad (2.79)$$

Conservation of linear momentum is given by Cauchy's equation of motion [99] which

is a statement Newton's second law of motion for a continuum body relating the rate of change of momentum to the acting surface and body forces; it is given by

$$\rho \frac{\partial^2 u_i}{\partial t^2} = \frac{\partial \sigma_{ij}}{\partial x_j} + F_j \quad (2.80)$$

in material coordinates where ρ is the density, $\mathbf{u}$ is the displacement vector field, and $\mathbf{F}$ is the body force term. In the context of linear elastostatics, the inertia term $\rho \partial^2 \mathbf{u} / \partial t^2$ goes to zero since the acceleration $\mathbf{a}$ everywhere in the body is zero $\mathbf{a} = \partial^2 \mathbf{u} / \partial t^2 = \mathbf{0}$;

Eq. (2.80) simplifies to

$$\frac{\partial \sigma_{ij}}{\partial x_j} + F_j = 0. \quad (2.81)$$

Body forces like gravity are often neglected since they are usually insignificant, especially when the local density differences are small. The equilibrium equation is

$$\frac{\partial \sigma_{ij}}{\partial x_j} = 0. \quad (2.82)$$

The reference stiffness tensor forms the equivalent homogeneous system. The stress in the inhomogeneous system can be equivalently represented in the homogeneous system by

$$\sigma_{ij} = c_{ijkl}^0 (\bar{\varepsilon}_{kl} + \delta \varepsilon_{kl} - \varepsilon_{kl}^*) \quad (2.83)$$

where the eigenstrain ε_{ij}^0 is introduced to account for the inhomogeneous problem. The

average eigenstrain accounts for either external stress or strain fields according to

$$\bar{\varepsilon}_{ij} = \begin{cases} \bar{\varepsilon}_{ij}^0 + s_{ijkl}^0 \sigma_{kl}^\infty & \text{stress-controlled} \\ \bar{\varepsilon}_{ij}^0 + \varepsilon_{ij}^\infty & \text{strain-controlled} \end{cases} \quad \bar{\varepsilon}_{ij}^0 = \frac{1}{V} \int_{\Omega} \varepsilon_{ij}^0(\mathbf{r}) d^3\mathbf{r} \quad (2.84)$$

where the remote stress is σ_{ij}^∞ and strain is ε_{ij}^∞ . The divergence of the stress in Eq. (2.83)

is equal to the zero vector from Eq. (2.82) in the equilibrium case such that

$$c_{ijkl}^0 \frac{\partial^2 u_k}{\partial x_j \partial x_l} = c_{ijkl}^0 \frac{\partial \varepsilon_{kl}^0}{\partial x_j} \quad (2.85)$$

where the eigenstress is $\sigma_{ij}^0 = c_{ijkl}^0 \varepsilon_{kl}^0$. Taking the Fourier transform of Eq. (2.85) results in

$$-k_j k_l c_{ijkl}^0 u_k(\mathbf{k}) = i k_j c_{ijkl}^0 \varepsilon_{kl}^0(\mathbf{k}). \quad (2.86)$$

Denoting $G_{ik}^{-1}(\mathbf{k}) = k_j k_l c_{ijkl}^0$ as the inverse of Green's function where $G_{ik}(\mathbf{0}) = 0$, it can be shown that the displacement field is

$$u_i(\mathbf{r}) = -\frac{i}{(2\pi)^3} \int k_k c_{jklm}^0 \varepsilon_{lm}^0(\mathbf{k}) G_{ij}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} d^3\mathbf{k} \quad (2.87)$$

by rearranging Eq. (2.86) and taking the inverse Fourier transform. The variation in strain is then given by

$$\delta \varepsilon_{ij}(\mathbf{r}) = \frac{1}{2(2\pi)^3} \int k_l c_{klmn}^0 \varepsilon_{mn}^0(\mathbf{k}) [k_i G_{jk}(\mathbf{k}) + k_j G_{ik}(\mathbf{k})] e^{i\mathbf{k} \cdot \mathbf{r}} d^3\mathbf{k} \quad (2.88)$$

using Eq. (2.79). The elastic strain energy U in the homogeneous system [112] is expressed as a functional

$$U = \frac{1}{2} \int_{\Omega} c_{ijkl}^0 (\bar{\varepsilon}_{ij} + \delta\varepsilon_{ij} - \varepsilon_{ij}^0) (\bar{\varepsilon}_{kl} + \delta\varepsilon_{kl} - \varepsilon_{kl}^0) d^3\mathbf{r} \quad (2.89)$$

where its functional derivative with respect to the eigenstrain is the negative of the stress

$$\frac{\delta U}{\delta \varepsilon_{ij}^0(\mathbf{r})} = -\sigma_{ij}(\mathbf{r}). \quad (2.90)$$

If body forces are present, mechanical equilibrium is expressed by Eq. (2.81). The procedure can be repeated with the body force present substituting the stress from the homogeneous system. The divergence can be taken and the expression rearranged to give

$$c_{ijkl}^0 \frac{\partial^2 u_k}{\partial x_j \partial x_l} = c_{ijkl}^0 \frac{\partial \varepsilon_{kl}^0}{\partial x_j} - F_i. \quad (2.91)$$

Taking the Fourier transform, it is found that

$$-k_j k_l c_{ijkl}^0 u_k(\mathbf{k}) = i k_j c_{ijkl}^0 \varepsilon_{kl}^0(\mathbf{k}) - F_i(\mathbf{k}). \quad (2.92)$$

The solution of the elastic fields accounting for the body forces gives

$$u_i(\mathbf{r}) = -\frac{i}{(2\pi)^3} \int k_k c_{jklm}^0 \varepsilon_{lm}^0(\mathbf{k}) G_{ij}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} d^3\mathbf{k} + \frac{1}{(2\pi)^3} \int G_{ij}(\mathbf{k}) F_j(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} d^3\mathbf{k} \quad (2.93)$$

for the displacement field and

$$\begin{aligned} \delta \varepsilon_{ij}(\mathbf{r}) = & \frac{1}{2(2\pi)^3} \int k_l c_{klmn}^0 \varepsilon_{mn}^0(\mathbf{k}) [k_i G_{jk}(\mathbf{k}) + k_j G_{ik}(\mathbf{k})] e^{i\mathbf{k} \cdot \mathbf{r}} d^3 \mathbf{k} \\ & + \frac{i}{2(2\pi)^3} \int [k_i G_{jk}(\mathbf{k}) + k_j G_{ik}(\mathbf{k})] F_k(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} d^3 \mathbf{k} \end{aligned} \quad (2.94)$$

for the variation in strain field.

2.5 Conduction revisited

The equivalent inclusion method that forms the basis of microelasticity modeling can be extended to steady-state conduction problems [113]. In much the same way, microscopic Ohm's law and Fourier's law can be solved using the concept of eigenelectric fields, and eigenthermal driving forces, respectively. One advantage of this approach is that the external field is no longer limited to applied electric fields or thermal driving forces. This approach allows current densities and heat fluxes to be applied, as well.

2.5.1 Steady state charge conduction

The electrical conductivity can be decomposed into two parts: a positive definite, invertible reference conductivity tensor σ_{ij}^0 with inverse resistivity $\rho_{ij}^0 = (\sigma_{ij}^0)^{-1}$ and a remaining

inhomogeneous part $\delta\sigma_{ij}(\mathbf{r})$ which sum to

$$\sigma_{ij}(\mathbf{r}) = \sigma_{ij}^0 + \delta\sigma_{ij}(\mathbf{r}). \quad (2.95)$$

In the context of steady-state conduction, the transient term $\partial\rho/\partial t$ goes to zero; [Eq. \(2.62\)](#) simplifies to

$$\nabla \cdot \mathbf{j} = 0. \quad (2.96)$$

The reference conductivity tensor forms the equivalent homogeneous system. The current density in the inhomogeneous system can be equivalently represented in the homogeneous system by

$$j_i = \sigma_{ij}^0(\bar{E}_j + \delta E_j - E_j^0) \quad (2.97)$$

where the eigenelectric field $\mathbf{E}^0$ is introduced to account for the inhomogeneous problem. The average eigenelectric field accounts for either external current or electric fields using

$$\bar{E}_i = \begin{cases} \bar{E}_i^0 + \rho_{ik}^0 j_k^\infty & \text{current-controlled} \\ \bar{E}_i^0 + E_i^\infty & \text{electric field-controlled} \end{cases} \quad \bar{E}_i^0 = \frac{1}{V} \int_{\Omega} E_i^0(\mathbf{r}) d^3\mathbf{r} \quad (2.98)$$

where the remote current density is j^∞ and electric field is $\mathbf{E}^\infty$. The divergence of the current density in [Eq. \(2.97\)](#) is equal to zero from [Eq. \(2.96\)](#) in the equilibrium case such that

$$-\sigma_{ij}^0 \frac{\partial^2 \phi}{\partial x_i \partial x_j} = \sigma_{ij}^0 \frac{\partial E_j^0}{\partial x_i} \quad (2.99)$$

where the eigencurrent density is $j_i^0 = \sigma_{ij}^0 E_j^0$. Taking the Fourier transform of Eq. (2.99) results in

$$k_i k_j \sigma_{ij}^0 \phi(\mathbf{k}) = i k_i \sigma_{ij}^0 E_j^0(\mathbf{k}). \quad (2.100)$$

Denoting $G^{-1}(\mathbf{k}) = k_i k_j \sigma_{ij}^0$ as the inverse of Green's function where $G(\mathbf{0}) = 0$, it can be shown that the electrostatic field is

$$\phi(\mathbf{r}) = \frac{i}{(2\pi)^3} \int k_i \sigma_{ij}^0 E_j^0(\mathbf{k}) G(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} d^3 \mathbf{k} \quad (2.101)$$

by rearranging Eq. (2.100) and taking the inverse Fourier transform. The variation in electric field is then given by

$$\delta E_i(\mathbf{r}) = \frac{1}{(2\pi)^3} \int k_i k_j \sigma_{jk}^0 E_k^0(\mathbf{k}) G(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} d^3 \mathbf{k} \quad (2.102)$$

using Eq. (2.58). The energy dissipated P in the homogeneous system is expressed as a functional

$$P = \frac{1}{2} \int_{\Omega} \sigma_{ij}^0 (\bar{E}_i + \delta E_i - E_i^0) (\bar{E}_j + \delta E_j - E_j^0) d^3 \mathbf{r} \quad (2.103)$$

where its functional derivative with respect to the eigenelectric field is the negative of the current density

$$\frac{\delta P}{\delta E^0(\mathbf{r})} = -\mathbf{j}(\mathbf{r}). \quad (2.104)$$

2.5.2 Steady state heat conduction

The thermal conductivity can be decomposed into two parts: a positive definite, invertible reference conductivity tensor κ_{ij}^0 with inverse resistivity $\rho_{ij}^0 = (\kappa_{ij}^0)^{-1}$ and a remaining inhomogeneous part $\delta\kappa_{ij}(\mathbf{r})$ which sum to

$$\kappa_{ij}(\mathbf{r}) = \kappa_{ij}^0 + \delta\kappa_{ij}(\mathbf{r}). \quad (2.105)$$

In the context of steady-state conduction, the transient term $\partial T / \partial t$ goes to zero; [Eq. \(2.72\)](#) simplifies to

$$-\nabla \cdot \mathbf{q} + \varphi = 0. \quad (2.106)$$

Heat sources and sinks are often negligible such that the steady state equation simplifies to

$$\nabla \cdot \mathbf{q} = 0. \quad (2.107)$$

The reference conductivity tensor forms the equivalent homogeneous system. The heat flux in the inhomogeneous system can be equivalently represented in the homogeneous system by

$$q_i = \kappa_{ij}^0(\bar{X}_j + \delta X_j - X_j^0) \quad (2.108)$$

where the eigothermal driving force X^0 is introduced to account for the inhomogeneous problem. The average eigothermal driving force accounts for either external heat or

temperature gradient fields using

$$\bar{X}_i = \begin{cases} \bar{X}_i^0 + \rho_{ik}^0 q_k^\infty & \text{heat-controlled} \\ \bar{X}_i^0 + X_i^\infty & \text{temperature gradient-controlled} \end{cases} \quad \bar{X}_i^0 = \frac{1}{V} \int_{\Omega} X_i^0(\mathbf{r}) d^3 \mathbf{r} \quad (2.109)$$

where the remote heat flux is $\mathbf{q}^\infty$ and thermal driving force is X^∞ . The divergence of the heat flux in Eq. (2.108) is equal to zero from Eq. (2.107) in the equilibrium case such that

$$-\kappa_{ij}^0 \frac{\partial^2 T}{\partial x_i \partial x_j} = \kappa_{ij}^0 \frac{\partial X_j^0}{\partial x_i} \quad (2.110)$$

where the eigenheat flux is $q_i^0 = \kappa_{ij}^0 X_j^0$. Taking the Fourier transform of Eq. (2.110) results in

$$k_i k_j \kappa_{ij}^0 T(\mathbf{k}) = i k_i \kappa_{ij}^0 X_j^0(\mathbf{k}) \quad (2.111)$$

Denoting $G^{-1}(\mathbf{k}) = k_i k_j \kappa_{ij}^0$ as the inverse of Green's function where $G(0) = 0$, it can be shown that the temperature field is

$$T(\mathbf{r}) = \frac{i}{(2\pi)^3} \int k_i \kappa_{ij}^0 X_j^0(\mathbf{k}) G(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} d^3 \mathbf{k} \quad (2.112)$$

by rearranging Eq. (2.111) and taking the inverse Fourier transform. The variation in thermal driving force is then given by

$$\delta X_i(\mathbf{r}) = \frac{1}{(2\pi)^3} \int k_i k_j \kappa_{jk}^0 X_k^0(\mathbf{k}) G(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} d^3 \mathbf{k}(\mathbf{r}) \quad (2.113)$$

using Eq. (2.66). The energy dissipated P in the homogeneous system is expressed as a functional

$$P = \frac{1}{2} \int_{\Omega} \kappa_{ij}^0 (\bar{X}_i + \delta X_i - X_i^0) (\bar{X}_j + \delta X_j - X_j^0) d^3 \mathbf{r} \quad (2.114)$$

where its functional derivative with respect to the eigenthal driving force is the negative of the heat flux

$$\frac{\delta P}{\delta X^0(\mathbf{r})} = -\mathbf{q}(\mathbf{r}). \quad (2.115)$$

If heat sources and/or sinks are present, steady state conduction is expressed by Eq. (2.106).

The procedure can be repeated with the heat generation term present substituting the current density from the homogeneous system. The divergence can be taken and the expression rearranged to give

$$-\kappa_{ij}^0 \frac{\partial^2 T}{\partial x_i \partial x_j} = \kappa_{ij}^0 \frac{\partial X_j^0}{\partial x_i} - \varphi. \quad (2.116)$$

Taking the Fourier transform, it is found that

$$k_i k_j \kappa_{ij}^0 T(\mathbf{k}) = i k_i \kappa_{ij}^0 X_j^0(\mathbf{k}) - \varphi(\mathbf{k}) \quad (2.117)$$

The solution of the thermal fields accounting for the heat sources and sinks gives

$$T(\mathbf{r}) = \frac{i}{(2\pi)^3} \int k_i \kappa_{ij}^0 X_j^0(\mathbf{k}) G(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} d^3 \mathbf{k} - \frac{1}{(2\pi)^3} \int \varphi(\mathbf{k}) G(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} d^3 \mathbf{k} \quad (2.118)$$

for the temperature field and

$$\delta X_i(\mathbf{r}) = \frac{1}{(2\pi)^3} \int k_i k_j \kappa_{jk}^0 X_k^0(\mathbf{k}) G(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} d^3 \mathbf{k} + \frac{i}{(2\pi)^3} \int k_i G(\mathbf{k}) \varphi(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} d^3 \mathbf{k} \quad (2.119)$$

for the variation in thermal driving force.

2.6 Elasticity revisited

So far, only uniform remote stresses (and strains) are considered: tension, compression, and shear. These represent loads that are acting far from the region where the elastic fields are calculated. These are appropriate representations based on Saint-Venant's principle which states that the distribution of forces in a region is generally independent of the loading if it is sufficiently far away [114]. This means different but statically equivalent loads produce negligible changes in the stress state far from the loading. Far field tensile and shear stresses can therefore represent remote force loading. There is another important class of external loads overlooked, however. They include bending and twisting moments. A moment does not generally induce a uniform stress field. Instead, it produces a *stress gradient*. The issue of stress (and strain) gradients is now considered.

The gradient of stress is a third rank tensor defined by $\gamma_{ijk} \equiv \partial \sigma_{ij} / \partial x_k$. Based on the symmetry of the stress tensor, the first two indices of the tensor can be exchanged $\gamma_{ijk} =$

γ_{jik} meaning there are 18 independent coefficients. Considering a state of stress due to external uniform stress and stress gradients only without internal stresses generated by microstructure, the stress tensor is written as

$$\sigma_{ij} = \sigma_{ij}^{\infty} + \gamma_{ijk}^{\infty} x_k. \quad (2.120)$$

Enforcing mechanical equilibrium which requires the divergence of stress to be zero $\partial\sigma_{ij}/\partial x_j = 0$, the following constraints on the stress gradient components are required:

$$\frac{\partial\sigma_{11}}{\partial x_1} + \frac{\partial\sigma_{12}}{\partial x_2} + \frac{\partial\sigma_{13}}{\partial x_3} = \gamma_{111}^{\infty} + \gamma_{122}^{\infty} + \gamma_{133}^{\infty} = 0 \quad (2.121)$$

$$\frac{\partial\sigma_{21}}{\partial x_1} + \frac{\partial\sigma_{22}}{\partial x_2} + \frac{\partial\sigma_{23}}{\partial x_3} = \gamma_{211}^{\infty} + \gamma_{222}^{\infty} + \gamma_{233}^{\infty} = 0 \quad (2.122)$$

$$\frac{\partial\sigma_{31}}{\partial x_1} + \frac{\partial\sigma_{32}}{\partial x_2} + \frac{\partial\sigma_{33}}{\partial x_3} = \gamma_{311}^{\infty} + \gamma_{322}^{\infty} + \gamma_{333}^{\infty} = 0 \quad (2.123)$$

For simplicity, all six of these components can be ignored since they are not generally meaningful. These components represent a gradient in a particular direction with index that has at least one common index of the stress component it represents. For example, γ_{111} represents a gradient of σ_{11} in the x_1 -direction. From an equilibrium point of view, this stress gradient is not physically meaningful. The alternative case where the third index is not repeated within the stress gradient component is indeed meaningful, however. In these cases, there are no restrictions based on mechanical equilibrium. Consider γ_{112} as an example; a gradient of σ_{11} in the x_2 -direction represents a bending moment about the x_3 -axis acting far along the x_1 -direction. The bending moments are all components where

the first two indices are repeated but not the third. The twisting moments arise from the components where all three indices are different. However, they by themselves do not give rise to the standard form of twisting moments leading to torsion. Instead a combination must be used. For instance, $\gamma_{231} = -\gamma_{312}$ gives a state of anti-plane shear stress (in cylindrical coordinates) that varies radially from the origin in the reference plane.

It is also possible to define a remote external strain gradient $\eta_{ijk} \equiv \partial \varepsilon_{ij} / \partial x_k$ which also has 18 independent components based on the symmetry of the infinitesimal strain tensor $\eta_{ijk} = \eta_{jik}$. Using similar reasoning, the six components, which are generally not meaningful, can be ignored. The case of a uniform strain state in a homogeneous material is given by

$$\varepsilon_{ij} = \varepsilon_{ij}^{\infty} + \eta_{ijk}^{\infty} x_k. \quad (2.124)$$

From the point of view of microelasticity modeling, the external strain and stress fields are related through the compliance tensor $\varepsilon_{ij}^{\infty} = s_{ijkl}^0 \sigma_{kl}^{\infty}$. Similarly, the relation between the external stress and strain gradients is $\eta_{ijm}^{\infty} = s_{ijkl}^0 \gamma_{klm}^{\infty}$. The total strain, therefore, is given by

$$\varepsilon_{ij} = \begin{cases} \bar{\varepsilon}_{ij}^0 + s_{ijkl}^0 (\sigma_{kl}^{\infty} + \gamma_{klm}^{\infty} x_m) + \delta \varepsilon_{ij}(\mathbf{r}) & \text{stress-controlled} \\ \bar{\varepsilon}_{ij}^0 + \varepsilon_{ij}^{\infty} + \eta_{ijm}^{\infty} x_m + \delta \varepsilon_{ij}(\mathbf{r}) & \text{strain-controlled} \end{cases} \quad (2.125)$$

which can be easily incorporated into the microelasticity framework.

2.7 Material properties

It is necessary to describe the transformation of the material properties in different coordinate systems. Measurements of the standard component tensor properties in a reference coordinate system (with respect to crystallographic directions) will be different when measured in a new coordinate system if the property is anisotropic. The standard symmetric chemical diffusivity D_{ij}^0 transforms as

$$D_{ij}(\mathbf{r}) = Q_{ik}(\mathbf{r})Q_{jl}(\mathbf{r})D_{kl}^0 \quad (2.126)$$

where the tensor $Q_{ij}(\mathbf{r})$ is the transformation tensor. Similarly, the standard electrical conductivity σ_{ij}^0 transforms according to

$$\sigma_{ij}(\mathbf{r}) = Q_{ik}(\mathbf{r})Q_{jl}(\mathbf{r})\sigma_{kl}^0, \quad (2.127)$$

and the standard thermal conductivity κ_{ij}^0 analogously transforms as

$$\kappa_{ij}(\mathbf{r}) = Q_{ik}(\mathbf{r})Q_{jl}(\mathbf{r})\kappa_{kl}^0. \quad (2.128)$$

Finally, the elastic stiffness transformation is given by

$$c_{ijkl}(\mathbf{r}) = Q_{im}(\mathbf{r})Q_{jn}(\mathbf{r})Q_{kp}(\mathbf{r})Q_{lq}(\mathbf{r})c_{mnpq}^0 \quad (2.129)$$

where c_{mnpq}^0 is the reference stiffness. All of the above properties can be represented in Voigt notation since they are symmetric tensors. The transformation tensor can be represented by a 3×3 matrix that is not required to be symmetric

$$Q = \begin{bmatrix} q_{11} & q_{12} & q_{13} \\ q_{21} & q_{22} & q_{23} \\ q_{31} & q_{32} & q_{33} \end{bmatrix} \quad (2.130)$$

which has the orthogonal property that its inverse is its transpose $Q^{-1} = Q^T$. In summary, the transformations as matrix multiplications are

$$D = QD_0Q^T \quad \sigma = Q\sigma_0Q^T \quad \kappa = Q\kappa_0Q^T \quad c = \alpha c_0\alpha^T \quad (2.131)$$

where the 3×3 matrices are denoted as D_0 , σ_0 , and κ_0 and the 6×6 matrix is c_0 . Here, the matrix α is used [27] to transform the fourth rank properties which is defined by the 6×6 matrix:

$$\alpha = \begin{bmatrix} q_{11}^2 & q_{12}^2 & q_{13}^2 & 2q_{12}q_{13} & 2q_{13}q_{11} & 2q_{11}q_{12} \\ q_{21}^2 & q_{22}^2 & q_{23}^2 & 2q_{22}q_{23} & 2q_{23}q_{21} & 2q_{21}q_{22} \\ q_{31}^2 & q_{32}^2 & q_{33}^2 & 2q_{32}q_{33} & 2q_{33}q_{31} & 2q_{31}q_{32} \\ q_{21}q_{31} & q_{22}q_{32} & q_{23}q_{33} & q_{22}q_{33} + q_{23}q_{32} & q_{21}q_{33} + q_{23}q_{31} & q_{22}q_{31} + q_{21}q_{32} \\ q_{31}q_{11} & q_{32}q_{12} & q_{33}q_{13} & q_{12}q_{33} + q_{13}q_{32} & q_{11}q_{33} + q_{13}q_{31} & q_{11}q_{32} + q_{12}q_{31} \\ q_{11}q_{21} & q_{12}q_{22} & q_{13}q_{23} & q_{12}q_{23} + q_{13}q_{22} & q_{13}q_{21} + q_{11}q_{23} & q_{11}q_{22} + q_{12}q_{21} \end{bmatrix} \quad (2.132)$$

A summary of the material properties is given in Table 2.1. It lists the property relationship between response and stimuli for each of the phenomena discussed. Furthermore, the transformation matrices can be constructed using the three Euler angles [115] to reduce

the number of parameters needed to describe the orientation of a coordinate system from nine to three.

Table 2.1
Summary of properties and fields for diffusion, conduction, and elasticity

Phenomena	Law	Response		Property		Stimuli	
Mass diffusion	Fick	Mass flux	J_i	Chemical mobility	M_{ij}	Chemical driving force	F_j
Charge conduction	Ohm	Current density	j_i	Electrical conductivity	σ_{ij}	Electric field	E_j
Heat conduction	Fourier	Heat flux	q_i	Thermal conductivity	κ_{ij}	Thermal driving force	X_j
Elastic deformation	Hooke	Stress	σ_{ij}	Elastic stiffness	c_{ijkl}	Strain	ε_{kl}

Chapter 3

Methods

The numerical approach chosen for implementation of the solvers is the Fourier spectral method [116, 117]. The basic idea is to use the discrete Fourier transform (DFT) which accommodates periodic boundary conditions and allows for efficient calculation of derivatives and harmonic functions in Fourier space facilitated by the fast Fourier transform (FFT) algorithm. In addition, it lends itself to parallel programming using either distributed or shared parallelism. Numerical differentiation and integration is discussed and their implementation into a solver framework is described. Special focus on Fourier space filters and semi-implicit time integration are highlighted. Finally, the programming languages used and other software tools that are built into the framework are explained. The result is a fast and reliable program for simulating materials processes including diffusion, conduction, and deformation.

3.1 Numerical differentiation and integration in space

The gradient, divergence, and curl are all efficiently calculated in Fourier space where the vector del operator becomes $\nabla \rightarrow i\mathbf{k}$ where i is the imaginary unit and $\mathbf{k}$ is the spatial frequency vector. The harmonic Newtonian potential integral with Green's function becomes $(4\pi)^{-1}|\mathbf{r} - \mathbf{r}'|^{-1} \rightarrow k^{-2}$ which corresponds to Poisson's function found in long-range interaction formulas. Similarly, the biharmonic potential integral with Green's function becomes $-(8\pi)^{-1}|\mathbf{r} - \mathbf{r}'| \rightarrow k^{-4}$ which is used along with the harmonic potential by Eshelby in the solution of the elastic fields in terms of the eigenstrain. In general, for any polyharmonic potential $(2\pi^2)^{-1}\Gamma(2-2p)\sin(\pi p)|\mathbf{r} - \mathbf{r}'|^{2p-3} \rightarrow k^{-2p}$ [118]. Using these relations and vector calculus identities, more complicated transforms can be constructed when needed.

3.1.1 Discrete Fourier transform

The discrete Fourier transform [119] of function $u(\mathbf{r})$ in real space corresponds to a new function $u(\mathbf{k})$ in frequency space. The DFT is the digital version of the Fourier transform which gives a complex-valued function that contains information about the amplitude and phase of sinusoidal functions. These new functions are a function of the frequency of the sinusoid. The DFT operates on discrete data sampled from an analog signal. The discrete

real-space data is denoted as $u_{\mathbf{n}}$ with corresponding frequency-space data $U_{\mathbf{k}}$. The DFT is defined by

$$U_{\mathbf{k}} = \sum_{\mathbf{n}=0}^{N-1} u_{\mathbf{n}} e^{-i\mathbf{k} \cdot (\mathbf{n}/N)} \quad (3.1)$$

where the real space vector $\mathbf{r}$ of discrete points have size $\mathbf{N} = (N_1, N_2, N_3)$ maps to integer vector $\mathbf{n} = (n_1, n_2, n_3)$ with $n_i = 0, 1, \dots, N_i - 1$. The summation operator is the triple sum over all $\mathbf{n}$ from $(0, 0, 0)$ to $(N_1 - 1, N_2 - 1, N_3 - 1)$ and the quantity $(\mathbf{n}/N) = (n_1/N_1, n_2/N_2, n_3/N_3)$. The discrete spatial frequency vector is given by

$$\frac{k_i}{2\pi} = \begin{cases} 0, 1, \dots, N_i/2 - 1, & -N_i/2, \dots, -1 & N_i \text{ is even} \\ 0, 1, \dots, (N_i - 1)/2, & -(N_i - 1)/2, \dots, -1 & N_i \text{ is odd} \end{cases} \quad (3.2)$$

which is nondimensional like the integer vector $\mathbf{n}$. Shown in Fig. 3.1a are an example of the Fourier frequencies for a one-dimensional transform with even sample size. The spatial frequencies do not include the positive Nyquist frequency at $N_i/2$ which is the highest frequency that can be resolved by the Nyquist–Shannon sampling theorem. Shown in Fig. 3.1b is an example of two sinusoids that fit the same set of data exactly; they are aliases of one another. Shown in Fig. 3.1c is a sinusoid that is sampled at exactly twice its frequency. The frequency of the sinusoid corresponds to the Nyquist frequency. The inverse discrete Fourier transform (IDFT) recovers the original digital signal from the Fourier components

$$u_{\mathbf{n}} = \frac{1}{N} \sum_{\mathbf{k}=0}^{N-1} U_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{n}/N)} \quad (3.3)$$

where $N = N_1 N_2 N_3$.

Figure 3.1: Illustration of discrete sampling

3.1.2 Low-pass filtering

In representing any signal by a Fourier series, the issue of Gibbs phenomenon responsible for the overshoot and undershoot at jump discontinuities becomes an issue. These Gibbs oscillations can be reduced in spectral methods using filters [120]. Fourier space low-pass filters operate on signals in the spatial frequency domain [121] simply multiplying the Fourier components by a filter function $\sigma(\mathbf{k}/N) = \sigma(k_1/N_1)\sigma(k_2/N_2)\sigma(k_3/N_3)$ which corresponds to convolution. A low-pass filter allows only the low frequencies and attenuates high ones. The Fourier space filter is one that operates on its components to enhance the decay rate of the Gibbs oscillations without reducing accuracy: these include the Lanczos filter $\sigma_0(k/N) = \text{sinc}(k/N)$, the raised cosine filter $\sigma_1(k/N) = [1 + \cos(k/N)]/2$, and

Figure 3.2: Illustration of a sawtooth wave using $N = 8$ harmonics

sharpened raised cosine filter $\sigma_2(k/N) = \sigma_1^4(35 - 84\sigma_1 + 70\sigma_1^2 - 20\sigma_1^3)$ [121]. The sinc function is the Fourier transform of the rectangular function. Shown in Fig. 3.2 is an example of a sawtooth function which has a jump discontinuity and both nonzero amplitudes of even and odd harmonics except for the zeroth frequency. Figure 3.2a shows the Fourier approximation of the sawtooth wave using the first 8 harmonics which shows the Gibbs oscillations. In Fig. 3.2b, the reconstructed signal after applying the Lanczos low-pass filter is shown. The resampling reduces the oscillations and improves the fit. The Lanczos sinc filter is implemented in the spectral solver and used as needed to reduce oscillations in simulations with sharp boundaries. For mass diffusion, the chemical potential is optionally filtered. In conduction problems, the electrostatic potential and temperature fields are filtered as needed in charge and heat problems, respectively. Finally in elastic deformation problems, the displacement field is filtered when required. This improves the stability of the simulations when there are boundaries with narrow widths while preserving the solution accuracy.

3.2 Numerical integration in time

It is necessary to devise a time integration scheme for each solver. There is a trade-off between accuracy, efficiency, and stability of various methods. A good compromise between all three allows for fast and reliable solutions. Analyzing a simpler model problem, the scheme can be utilized for mass diffusion, charge and heat conduction, and elastic deformation.

3.2.1 Model problem

The one-dimensional advection-diffusion equation is used as a model problem for investigating stability. The partial differential equation (PDE) is given by

$$\frac{\partial u}{\partial t} = \mu \frac{\partial^2 u}{\partial x^2} - v \frac{\partial u}{\partial x} \quad (3.4)$$

where μ is the diffusion coefficient and v is the advection coefficient corresponding to velocity. In the context of PDEs, the advection-diffusion equation is a combination of a parabolic PDE owing to the second order diffusion term and a hyperbolic PDE owing to the first order advection term [122]. In the limit of long time, the transient term of the left hand side goes to zero and the PDE becomes elliptic. In physical terms, a

parabolic PDE is one that represents an irreversible process like the heat equation and a hyperbolic PDE is one that represents a reversible process like the wave equation. An elliptic PDE generally represents a steady-state process. For these reasons, it is a good candidate for analyzing numerical methods like time integration in addition to having well known analytical solutions for various boundary conditions [123]. For example, the real space solution assuming periodic boundary conditions is found by transforming [124] the spatial coordinate according to $x' = x - vt$ and $t' = t$ which transform the advection-diffusion equation to the standard diffusion (heat) equation which has solution $u(x, t) = u(x' + vt, t') = u'(x', t') = u'(x - vt, t)$ given by

$$u'(x', t') = a_0 + \sum_{n=1}^{\infty} a_n \cos(n\pi x') e^{-\mu(n\pi)^2 t'} + \sum_{n=1}^{\infty} b_n \sin(n\pi x') e^{-\mu(n\pi)^2 t'}. \quad (3.5)$$

Here, the domain is on the interval $-1 \leq x \leq 1$ with eigenvalues $\lambda_n = (n\pi)^2$, eigenfunctions $\phi_n(x') = \cos(n\pi x')$ and $\sin(n\pi x')$, and coefficients

$$a_0 = \frac{1}{2} \int_{-1}^1 u_0(x') dx' \quad a_n = \int_{-1}^1 u_0(x') \cos(n\pi x') dx' \quad b_n = \int_{-1}^1 u_0(x') \sin(n\pi x') dx'. \quad (3.6)$$

The Fourier series solution lends itself to analysis with the Fourier transform. In Fourier space, the PDE becomes an ordinary differential equation (ODE)

$$\frac{dU}{dt} = -\mu k^2 U - vikU \quad (3.7)$$

where k is the spatial frequency and i is the imaginary unit. The variable $U(k)$ is the Fourier transform of $u(x)$:

$$U(k) = \int_{-\infty}^{\infty} u(x) e^{-ikx} dx. \quad (3.8)$$

The ODE can be rewritten as

$$\frac{dU}{dt} = \lambda U. \quad (3.9)$$

where $\lambda = -\mu k^2 - \nu ik$. The Fourier space solution of the ODE is

$$U(k, t) = U_0(k) e^{\lambda t} \quad (3.10)$$

where $U_0(k)$ is the Fourier transform of the initial condition $U_0(k) = \mathcal{F}[u_0(x)]$ and $u_0(x) = u(x, t = 0)$. The solution can be approximated by one of several linear multi-step integration methods either explicitly or implicitly by rewriting the ODE as

$$\frac{dU}{dt} = f(U) \quad (3.11)$$

where time is discretized according to $t^{n+1} = t^n + h$. Shown in [Fig. 3.3](#) is an overview of this Fourier spectral technique used to find the solution of the PDE by converting it into an ODE. Once the solution is obtained in the frequency domain, the inverse Fourier transform is used to convert it back to the real space solution. The linear multistep methods [[124](#)] are one method to numerically solve the initial value problem of the ODE. The basic idea is to save previous results of U and $f(U)$ evaluated at prior time step iterations and use them

Figure 3.3: Overview of the Fourier spectral method: obtaining solution of $u(x, t)$ from initial condition $u_0(x)$ using Fourier transform to convert the PDE to a simpler ODE

to predict future values. They differ from other methods like the Runge–Kutta or Crank–Nicolson methods where the right-hand side of the ODE can be evaluated at intermediate or future times. For example, it is not simple or straightforward to evaluate the diffusive derivative terms at a future time. Linear multistep methods overcome this obstacle by advancing the solution forward using previous results obtained.

The linear multistep methods include the Adams family of methods where the left hand side of Eq. (3.11) is approximated by a simple forward difference and the right-hand side uses a linear combination of $f(U)$. The first, second, and third order explicit Adams–Bashforth methods are

$$\frac{U^{n+1} - U^n}{h} = f(U^n) \quad (3.12)$$

$$\frac{U^{n+1} - U^n}{h} = \frac{3}{2}f(U^n) - \frac{1}{2}f(U^{n-1}) \quad (3.13)$$

$$\frac{U^{n+1} - U^n}{h} = \frac{23}{12}f(U^n) - \frac{4}{3}f(U^{n-1}) + \frac{5}{12}f(U^{n-2}) \quad (3.14)$$

which includes the forward Euler (first order Adams–Bashforth) method. Explicit Adams–Bashforth methods are generally best when the transient solution is desired. Future U^{n+1} depends on the past $f(U^{n-1}), f(U^{n-2}), \dots$ and present $U^n, f(U^n)$. These methods are more efficient than implicit methods but less stable. Shown in Fig. 3.4a are the stability regions of the Adams–Bashforth methods. With higher each order method, the stability region becomes smaller. The stability regions are outside the enclosed curve rather than inside. In general, higher order methods improve accuracy but are less stable and efficient. The first three implicit Adams–Moulton methods are given by

$$\frac{U^{n+1} - U^n}{h} = f(U^{n+1}) \quad (3.15)$$

$$\frac{U^{n+1} - U^n}{h} = \frac{1}{2}f(U^{n+1}) + \frac{1}{2}f(U^n) \quad (3.16)$$

$$\frac{U^{n+1} - U^n}{h} = \frac{5}{12}f(U^{n+1}) + \frac{2}{3}f(U^n) - \frac{1}{12}f(U^{n-1}) \quad (3.17)$$

which includes the backward Euler (first order Adams–Moulton) method. Implicit Adams–Moulton methods are generally best when the steady-state solution is desired. Future U^{n+1} depends on the future $f(U^{n+1})$, past $f(U^{n-1}), f(U^{n-2}), \dots$ and present $U^n, f(U^n)$. These methods are more stable than explicit methods but less efficient. Shown in Fig. 3.4b are the stability regions of the Adams–Moulton methods. An alternative implicit multistep method can be employed where the left hand side of Eq. (3.11) is approximated by higher order differences and the right-hand side is simply evaluated at future $f(U^{n+1})$.

These are the implicit backwards differentiation formulae given by

$$\frac{U^{n+1} - U^n}{h} = f(U^{n+1}) \quad (3.18)$$

$$\frac{3U^{n+1} - 4U^n + U^{n-1}}{2h} = f(U^{n+1}) \quad (3.19)$$

$$\frac{11U^{n+1} - 18U^n + 9U^{n-1} - 2U^{n-2}}{6h} = f(U^{n+1}) \quad (3.20)$$

which also includes the backward Euler (first order backwards differentiation formula) method. Shown in Fig. 3.4c are the stability regions of the backwards differentiation formula. Future U^{n+1} depends on the future $f(U^{n+1})$, past U^{n-1} , U^{n-2} , ... and present U^n .

Explicit and implicit methods are chosen for desirable accuracy and stability. For many problems, implicit methods are difficult to implement so explicit methods are usually employed out of convenience. The problem is that for many problems, they become prohibitively unstable for stiff problems. Therefore, a compromise can be reached by using semi-implicit methods which combines both explicit and implicit methods. One example is semi-implicit stiffly stable methods [125] which combines explicit Adams–Bashforth with implicit Adams–Moulton methods. The basic idea is to treat the two terms differently on right-hand side of Eq. (3.7). For example, the diffusion term can be treated implicitly and the advective term explicitly. Although both terms are linear, this splitting approach allows for cases where there are nonlinear terms. That is, linear terms are treated *implicitly* and nonlinear terms are treated *explicitly*. The first three orders of the stiffly stable

splitting methods are

$$\frac{U^{n+1} - U^n}{h} = f(U^{n+1}) + g(U^n) \quad (3.21)$$

$$\frac{3U^{n+1} - 4U^n + U^{n-1}}{2h} = f(U^{n+1}) + 2g(U^n) - g(U^{n-1}) \quad (3.22)$$

$$\frac{11U^{n+1} - 18U^n + 9U^{n-1} - 2U^{n-2}}{6h} = f(U^{n+1}) + 3g(U^n) - 3g(U^{n-1}) + g(U^{n-2}) \quad (3.23)$$

where the linear terms are $f(U)$ and nonlinear terms are $g(U)$. A nice feature of this approach is that the linear implicit terms do not require any additional treatment. For example, constant coefficient derivatives in real space become a simple multiplication in Fourier space allowing the term to be algebraically rearranged. Shown in [Fig. 3.4d](#) is the stability region of the stiffly stable splitting method. The regions are larger and more robust than the Adams–Bashforth methods while maintaining better accuracy than the backward differentiation formulae.

Using von Neumann stability analysis [[126](#)], the stability of the linear multistep methods can be investigated. The basic assumption is that the error between the numerical and analytical solution has the same form as the analytical solution, that is,

$$\epsilon(k, t) = \epsilon_0(k)e^{\lambda t}, \quad (3.24)$$

and the error can be discretized with the same form as the numerical solution for the chosen method. For the error to decay and not propagate with each time step requires

(a) Explicit Adams–Bashforth methods

(b) Implicit Adams–Moulton methods

(c) Implicit backwards differentiation formulae

(d) Semi-implicit stiffly stable splitting methods

Figure 3.4: Stability regions for the first three orders of the linear multistep methods: if the complex coefficients of the ODE multiplied by the time step fall within the region, the method is stable

that the error diminish for each subsequent step $n + 1$. If the magnitude of the error becomes smaller, the ratio

$$\left| \frac{\epsilon^{n+1}}{\epsilon^n} \right| \leq 1 \quad (3.25)$$

gives the condition of stability. Considering the first order explicit (forward Euler) method discretization of Eq. (3.7)

$$\frac{U^{n+1} - U^n}{h} = -\mu k^2 U^n - vik U^n, \quad (3.26)$$

the error should propagate according to the discretization and have the same form

$$\frac{\epsilon^{n+1} - \epsilon^n}{h} = -\mu k^2 \epsilon^n - vik \epsilon^n. \quad (3.27)$$

Rearranging the error discretization and substituting into the inequality of Eq. (3.25) gives a time constraint of

$$h < \frac{2\mu}{v^2 + \mu^2 k^2} \quad (3.28)$$

which means the method is *conditionally* stable. There is an upper limit to the time step, but as long as Eq. (3.28) is satisfied, the numerical solution is stable. Similarly, the first order implicit (backward Euler) method can be analyzed in the same way. The discretization of Eq. (3.7) follows

$$\frac{U^{n+1} - U^n}{h} = -\mu k^2 U^{n+1} - vik U^{n+1}, \quad (3.29)$$

and the error has the same form

$$\frac{\epsilon^{n+1} - \epsilon^n}{h} = -\mu k^2 \epsilon^{n+1} - vik \epsilon^{n+1}. \quad (3.30)$$

Rearranging the error discretization and substituting into the inequality of Eq. (3.25) gives

a time constraint of

$$\boxed{h > 0} \quad (3.31)$$

which means the method is *unconditionally* stable. Any time step can be used as long as it is greater than zero and the method will be stable. Of course, a negative or zero time step is not physically meaningful. For the first order semi-implicit method, the discretization of Eq. (3.7) follows

$$\frac{U^{n+1} - U^n}{h} = -\mu k^2 U^{n+1} - vik U^n \quad (3.32)$$

with error

$$\frac{\epsilon^{n+1} - \epsilon^n}{h} = -\mu k^2 \epsilon^{n+1} - vik \epsilon^n. \quad (3.33)$$

Following the same procedure, the time step constraint is

$$\boxed{h < \frac{2\mu}{v^2 - \mu^2 k^2}} \quad \text{or} \quad \boxed{h > 0} \quad (3.34)$$

if $v^2 > \mu^2 k^2$ or $v^2 < \mu^2 k^2$ giving both *conditional* and *unconditional* stability, respectively.

If diffusion dominates, there is no time constraint. However, if advection dominates, the time constraint is determined by the parameters.

The semi-implicit method is attractive for its improvement of stability while maintaining accuracy. However, there is a disadvantage of the stiffly stable splitting method. Many

PDEs have only nonlinear terms. For example, the heat equation with nonlinear temperature dependent conductivity and heat capacity

$$\frac{\partial T}{\partial t} = \frac{1}{\rho(T)c_p(T)} \frac{\partial}{\partial x} \left(\kappa(T) \frac{\partial T}{\partial x} \right) \quad (3.35)$$

does not have any linear terms. One approach employed by [116, 117] is to linearize the PDE and incorporate it into the integration scheme. Starting by rewriting Eq. (3.11) as a nonlinear ODE

$$\frac{dU}{dt} = g(U) \quad (3.36)$$

where $g(U)$ is the nonlinear term. The first order Taylor expansion of the function is $g(U) \approx g(\bar{U}) + (dg/dU)(U - \bar{U})$ which can be rewritten as $g(U) \approx C + f(U)$. Adding and subtracting a weighted linearization, the semi-implicit method becomes

$$\frac{U^{n+1} - U^n}{h} = \frac{g(U^n)}{1 + \alpha h L} \quad (3.37)$$

$$\frac{3U^{n+1} - 4U^n + U^{n-1}}{2h} = \frac{2g(U^n) - g(U^{n-1})}{1 + \alpha h L} \quad (3.38)$$

$$\frac{11U^{n+1} - 18U^n + 9U^{n-1} - 2U^{n-2}}{6h} = \frac{3g(U^n) - 3g(U^{n-1}) + g(U^{n-2})}{1 + \alpha h L} \quad (3.39)$$

where α is the weight of $f(U) = -LU$. These methods are tested for the heat equation, Eq. (3.35), which has analytical solution using the Kirchhoff transformation [127, 128] given by

$$u(T) = \frac{1}{\kappa_0} \int_0^T \kappa(T) dT \quad (3.40)$$

which converts Eq. (3.35) to a simple linear heat diffusion equation

$$\frac{\partial u}{\partial t} = \alpha \frac{\partial^2 u}{\partial x^2}. \quad (3.41)$$

Here, α is the thermal diffusivity which must be approximately constant $\alpha = \kappa/\rho c_p =$ constant. A thermal conductivity that can be integrated in Eq. (3.40) and resolved for $T = T(u)$ is chosen. One simple option is $\kappa = \kappa_0 e^{\sigma T}$ [128] where $\kappa_0 = 1$ and $\sigma = 0.5 \ln 2$ are arbitrary. Finally, the initial condition chosen is a sawtooth function which has both odd (sine) and even (cosine)

harmonics $T(x, t = 0) = T_0(x) = 1 - (2/\pi) \arctan[\cot(x\pi/2)]$.

Comparison of the first, second, and third order methods with various time steps are shown in Tables 3.1–3.3. In general, the addition of the weighted linearization improves the stability while maintaining reasonable stability. In addition, the third order method doesn't offer a significant accuracy improvement to justify

Table 3.1

Error for the first order semi-implicit method

	$h = 1 \times 10^{-5}$	$h = 1 \times 10^{-4}$	$h = 1 \times 10^{-3}$
$\alpha = 0.0^*$	0.0619%	unstable	unstable
$\alpha = 0.5$	0.0752%	0.833%	13.0%
$\alpha = 1.0$	0.102%	1.23%	17.9%

Table 3.2

Error for the second order semi-implicit method

	$h = 1 \times 10^{-5}$	$h = 1 \times 10^{-4}$	$h = 1 \times 10^{-3}$
$\alpha = 0.0^*$	unstable	unstable	unstable
$\alpha = 0.5$	0.0635%	0.520%	7.26%
$\alpha = 1.0$	0.0829%	0.919%	12.1%

Table 3.3

Error for the third order semi-implicit method

	$h = 1 \times 10^{-5}$	$h = 1 \times 10^{-4}$	$h = 1 \times 10^{-3}$
$\alpha = 0.0^*$	unstable	unstable	unstable
$\alpha = 0.5$	0.0732%	0.811%	12.0%
$\alpha = 1.0$	0.0984%	1.19%	17.0%

*Explicit method

the added memory and efficiency cost with lower stability. The second order method offers an improvement in accuracy while maintaining stability. The first order method, however, offers reasonable accuracy and good stability properties. From von Neumann stability analysis of the first order method, a linearization weight of $\alpha > 1/2$ gives *unconditional* stability $h > 0$.

This semi-implicit approach is employed for each solver which are, in general, nonlinear due to inhomogeneous properties. In addition, the anisotropic material properties are accounted for in this approach. The previous works [116, 117] ignored anisotropic properties and only applied to the Cahn–Hilliard and Ginzburg–Landau (Allen–Cahn) equations.

3.2.2 Mass diffusion

Conservation of mass with Fick’s law of diffusion is an especially stiff problem considering inhomogeneous mobility with external fields. At each time step, solutions of the electric, thermal, and elastic fields are solved and incorporated into the driving force for diffusion. Therefore, the rate limiting step of the numerical procedure is mass diffusion. A good implementation of the semi-implicit method allows for accurate solutions achieved in a reasonable amount of time while allowing for coupling to nonlinear external fields including conduction and deformation. As implemented in previous works [116, 117] for

diffusion only, the method is extended to account for anisotropic mobility and offers flexibility in the chosen linearization at runtime. Defining a nonzero symmetric reference mobility M_{ij}^0 which can be chosen in the diffusivity input file, it is used to split the total mobility $M_{ij}(\mathbf{r})$ into a homogeneous part and inhomogeneous part $\delta M_{ij}(\mathbf{r})$ such that

$$M_{ij}(\mathbf{r}) = M_{ij}^0 + \delta M_{ij}(\mathbf{r}). \quad (3.42)$$

An operator of the constant reference mobility can be defined in Fourier space where $k_i k_j M_{ij}^0$. Since the homogeneous mobility is constant everywhere, the gradient operator from the chemical potential becomes ik_j and the negative divergence becomes $-ik_i$ that when multiplied by the chemical potential or other potentials that contribute to external driving forces, it approximates the time rate of change of concentration. Linearizing the chemical potential about phase fraction $x = 1/2$ and utilizing the fourth order expansion and the gradient term, a linear operator can be defined

$$L(\mathbf{k}) = [16f_0(X_0) + \kappa k^2]k_i k_j M_{ij}^0 \quad (3.43)$$

The operator can be multiplied by the concentration to approximate the convergence of the flux. That is, it approximates the time rate of change of the concentration itself. This linearity can be used as the implicit part of the semi-implicit scheme in frequency space and help improve the stability. Again, the choice of the reference mobility must be chosen carefully on a per problem basis to produce the desired stability for a given time step with

reasonable accuracy. The first, second, and third order time integration methods for the Fourier spectral method of diffusion are

$$\frac{c(\mathbf{k})^{n+1} - c(\mathbf{k})^n}{h} = -\frac{i\mathbf{k} \cdot \mathbf{J}(\mathbf{k})^n}{1 + \alpha h L(\mathbf{k})} \quad (3.44)$$

$$\frac{3c(\mathbf{k})^{n+1} - 4c(\mathbf{k})^n + c(\mathbf{k})^{n-1}}{2h} = -\frac{i\mathbf{k} \cdot [2\mathbf{J}(\mathbf{k})^n - \mathbf{J}(\mathbf{k})^{n-1}]}{1 + \alpha h L(\mathbf{k})} \quad (3.45)$$

$$\frac{11c(\mathbf{k})^{n+1} - 18c(\mathbf{k})^n + 9c(\mathbf{k})^{n-1} - 2c(\mathbf{k})^{n-2}}{6h} = -\frac{i\mathbf{k} \cdot [3\mathbf{J}(\mathbf{k})^n - 3\mathbf{J}(\mathbf{k})^{n-1} + \mathbf{J}(\mathbf{k})^{n-2}]}{1 + \alpha h L(\mathbf{k})} \quad (3.46)$$

where α is the weight of the linearization and h is the time step. Higher order methods tend to be more accurate but sacrifice stability. Listed in [Appendix A.1](#) include verification of the mass diffusion solver both in time integration schemes and concentration profiles.

3.2.3 Charge conduction

To solve the transient problem, a semi-implicit scheme can be devised by splitting the conductivity into a spatially homogeneous and inhomogeneous part just like that used in the steady state approach:

$$\sigma_{ij}(\mathbf{r}) = \sigma_{ij}^0 + \delta\sigma_{ij}(\mathbf{r}) \quad (3.47)$$

where the inverse of Green's function with respect to the defined homogeneous conductivity can be reused

$$G^{-1}(\mathbf{k}) = k_i k_j \sigma_{ij}^0 \quad (3.48)$$

in defining a new linear operator approximation. The Fourier transform of the electrostatic potential is related to the charge density field given by

$$\phi(\mathbf{k}) = \frac{\rho(\mathbf{k})}{\varepsilon_0 k^2}. \quad (3.49)$$

Using the Green's function and the Fourier transform result, a new linear operator can be defined

$$L(\mathbf{k}) = \frac{k_i k_j \sigma_{ij}^0}{\varepsilon_0 k^2} \quad (3.50)$$

which by multiplying the Fourier transform of the charge distribution gives a linearized approximation in Fourier space of the current density *convergence*, that is, negative divergence. Treating the linear approximation implicitly and the correct nonlinear term explicitly, the first, second, and third order methods are

$$\frac{\rho(\mathbf{k})^{n+1} - \rho(\mathbf{k})^n}{h} = -\frac{i\mathbf{k} \cdot \mathbf{j}(\mathbf{k})^n}{1 + \alpha h L(\mathbf{k})} \quad (3.51)$$

$$\frac{3\rho(\mathbf{k})^{n+1} - 4\rho(\mathbf{k})^n + \rho(\mathbf{k})^{n-1}}{2h} = -\frac{i\mathbf{k} \cdot [2\mathbf{j}(\mathbf{k})^n - \mathbf{j}(\mathbf{k})^{n-1}]}{1 + \alpha h L(\mathbf{k})} \quad (3.52)$$

$$\frac{11\rho(\mathbf{k})^{n+1} - 18\rho(\mathbf{k})^n + 9\rho(\mathbf{k})^{n-1} - 2\rho(\mathbf{k})^{n-2}}{6h} = -\frac{i\mathbf{k} \cdot [3\mathbf{j}(\mathbf{k})^n - 3\mathbf{j}(\mathbf{k})^{n-1} + \mathbf{j}(\mathbf{k})^{n-2}]}{1 + \alpha h L(\mathbf{k})} \quad (3.53)$$

where α is the weight of the linearization. Listed in [Appendix A.2](#) are several examples illustrating the time integration of the charge conduction module. In addition, several steady state problems are verified in the long time limit of the transient problems.

3.2.4 Heat conduction

A similar approach for charge conduction is applied to heat conduction except that electrostatic potential is replaced by the temperature field which acts locally. To solve the transient problem, a semi-implicit scheme can be devised by splitting the conductivity into a spatially homogeneous and inhomogeneous part

$$\kappa_{ij}(\mathbf{r}) = \kappa_{ij}^0 + \delta\kappa_{ij}(\mathbf{r}) \quad (3.54)$$

which is used to define the inverse of Green's function with respect to the defined homogeneous conductivity and is the same function used in the steady state problem

$$G^{-1}(\mathbf{k}) = k_i k_j \kappa_{ij}^0. \quad (3.55)$$

The Fourier transform of the temperature $T(\mathbf{k})$ by the inverse Green's function gives an approximation of the time rate of change of the temperature. The linear operator is simply equal to the inverse Green's function

$$L(\mathbf{k}) = k_i k_j \kappa_{ij}^0 \quad (3.56)$$

which by multiplying the Fourier transform of the heat distribution gives a linearized approximation in Fourier space of the heat flux *convergence*, that is, negative divergence.

Treating the linear approximation implicitly and the correct nonlinear term explicitly, the first, second, and third order methods are

$$\frac{T(\mathbf{k})^{n+1} - T(\mathbf{k})^n}{h} = -\frac{i\mathbf{k} \cdot \mathbf{q}(\mathbf{k})^n}{\rho c_p + \alpha h L(\mathbf{k})} \quad (3.57)$$

$$\frac{3T(\mathbf{k})^{n+1} - 4T(\mathbf{k})^n + T(\mathbf{k})^{n-1}}{2h} = -\frac{i\mathbf{k} \cdot [2\mathbf{q}(\mathbf{k})^n - \mathbf{q}(\mathbf{k})^{n-1}]}{\rho c_p + \alpha h L(\mathbf{k})} \quad (3.58)$$

$$\frac{11T(\mathbf{k})^{n+1} - 18T(\mathbf{k})^n + 9T(\mathbf{k})^{n-1} - 2T(\mathbf{k})^{n-2}}{6h} = -\frac{i\mathbf{k} \cdot [3\mathbf{q}(\mathbf{k})^n - 3\mathbf{q}(\mathbf{k})^{n-1} + \mathbf{q}(\mathbf{k})^{n-2}]}{\rho c_p + \alpha h L(\mathbf{k})} \quad (3.59)$$

where α is the weight of the linearization. Examples of heat conduction problems are verified using known solutions shown in [Appendix A.3](#).

3.2.5 Elastic deformation

Mechanical equilibrium is solved using microelasticity modeling where equivalency of the stress in both the homogeneous and inhomogeneous system requires that

$$\sigma_{ij} = c_{ijkl}(\bar{\varepsilon}_{kl} + \delta\varepsilon_{kl}) = c_{ijkl}^0(\bar{\varepsilon}_{kl} + \delta\varepsilon_{kl} - \varepsilon_{kl}^0). \quad (3.60)$$

Here, the difference between homogeneous and inhomogeneous system, denoted as

$$\delta\sigma_{ij}(\mathbf{r}) = -\delta c_{ijkl}(\bar{\varepsilon}_{kl} + \delta\varepsilon_{kl}) - c_{ijkl}^0\varepsilon_{kl}^0, \quad (3.61)$$

can be solved using the method of false transients. Here, a fictitious time derivative is introduced to drive the difference in stress between both systems toward zero $\delta\sigma_{ij}(\mathbf{r}) = 0$ by evolving the eigenstrain with Ginzburg–Landau form. Because the time derivative is only a numerical approach, there is no need for accuracy in time, only stability. Therefore, only the first order method is needed. The semi-implicit approach can be used by treating the two terms in Eq. (3.61). The first nonlinear term is treated explicitly and the second linear term is treated implicitly. The first order semi-implicit scheme in Fourier space is

$$\varepsilon_{ij}^0(\mathbf{k})^{n+1} = \varepsilon_{ij}^0(\mathbf{k})^n + \frac{\delta\sigma_{ij}(\mathbf{k})^n}{1 + hc_{ijkl}^0\delta_{ki}\delta_{lj}} \quad (3.62)$$

where the false time step h advances the time forward according to $t^{n+1} = t^n + h$. The choice to implement in Fourier space eliminates the need to transform the eigenstrain from real space which is necessary to compute the displacement integral of the next step. Many examples verifying the stress solution are given in Appendix A.4 which include classic examples of defects including holes, inclusions, cracks, dislocations, and point defects.

3.2.6 Conduction revisited

In an analogous way that the equilibrium elastic fields are solved using the semi-implicit method, the alternative approach using eigenelectric field and eigenthermal driving force

to obtain the steady state solution for conduction utilize the semi-implicit method. Equivalency of the current density in both the homogeneous and inhomogeneous system is

$$j_i = \sigma_{ij}(\bar{E}_j + \delta E_j) = \sigma_{ij}^0(\bar{E}_j + \delta E_j - E_j^0) \quad (3.63)$$

where the difference between the two systems is

$$\delta j_i(\mathbf{r}) = -\delta \sigma_{ij}(\bar{E}_j + \delta E_j) - \sigma_{ij}^0 E_j^0. \quad (3.64)$$

Using the method of false transients, the first order semi-implicit scheme of the eigenelectric field in Fourier space is

$$E_i^0(\mathbf{k})^{n+1} = E_i^0(\mathbf{k})^n + \frac{h \delta j_i(\mathbf{k})^n}{1 + h \sigma_{ij}^0 \delta_{ji}} \quad (3.65)$$

which drives the difference in current density between the two systems toward zero $\delta \mathbf{j}(\mathbf{r}) = \mathbf{0}$. Similarly, equivalency of the heat flux in both the homogeneous and inhomogeneous system is

$$q_i = \kappa_{ij}(\bar{X}_j + \delta X_j) = \kappa_{ij}^0(\bar{X}_j + \delta X_j - X_j^0) \quad (3.66)$$

where the difference between the two systems is

$$\delta q_i(\mathbf{r}) = -\delta \kappa_{ij}(\bar{X}_j + \delta X_j) - \kappa_{ij}^0 X_j^0. \quad (3.67)$$

Using the method of false transients, the first order semi-implicit scheme of the eigen-thermal driving force in Fourier space is

$$X_i^0(\mathbf{k})^{n+1} = X_i^0(\mathbf{k})^n + \frac{h \delta q_i(\mathbf{k})^n}{1 + h \kappa_{ij}^0 \delta_{ji}} \quad (3.68)$$

which drives the difference in heat flux between the two systems toward zero $\delta \mathbf{q}(\mathbf{r}) = \mathbf{0}$.

Using this steady-state approach over the corresponding transient case allows either the current density of heat flux far-field to be specified.

3.3 Implementation and programming

The solver is mainly written in C and Fortran. The low-level C functions invoke the parallel environment, fast Fourier transform, and random number generator. Fortran is used to modularize each solver. This makes it possible to combine any number of solvers at any time by simply loading its corresponding module. Additional tools are written in C++, Python, and Bash. C++ is used to create visualization files and other operations on large datasets. Python is used to create input data arrays. Finally, Bash is used to launch jobs on high-performance supercomputers and transfer data across networks. The solver is compiled using a Makefile which has platform specific variables for compilation on various computer platforms.

The four solvers are each wrapped into their own modules each with their own object file and program binary. Shown in Table 3.4 are each of the files corresponding to a solver environment. Here, each Fortran module has an underlying C object file: `fick.mod` corresponds to `mass.diffusion.o`, `ohm.mod` corresponds to `charge.conduction.o`, `fourier.mod` corresponds to `heat.conduction.o`, and `hooke.mod` corresponds to `elastic.deformation.o`. The module files are compiled from Fortran code while the corresponding object files are written in C. The binary executables can each be run independently or combined into a single executable and run simultaneously.

Table 3.4
Program binary, module, and object files

Program bin/	Module mod/	Object obj/
evolution	<code>fick.mod</code>	<code>mass.diffusion.o</code>
revolution	<code>ohm.mod</code>	<code>charge.conduction.o</code>
devolution	<code>fourier.mod</code>	<code>heat.conduction.o</code>
deconvolution	<code>hooke.mod</code>	<code>elastic.deformation.o</code>

Table 3.5
C/Fortran interface modules and common algorithm object files

Module mod/	Object obj/
<code>interaction.mod</code>	<code>discrete.fourier.transform.o</code> <code>standard.functions.o</code>
<code>interfacial.mod</code>	<code>random.number.generator.o</code> <code>auxiliary.functions.o</code>
	<code>input.output.o</code>

main framework

functions. The modules `interaction.mod` and `interface.mod` are used to initialize the C/Fortran environment including the allocation of arrays. The object files are for the main parallel functions including the fast Fourier transform, random number generator, and read-write file subroutines. The C object `standard.functions.o` has all routines to initialize the parallel environments and general data function such as computing

the gradient, divergence, and curl. Similarly, `auxiliary.functions.o` has all optional routines that map the material properties to the microstructure variables. Shown in [Appendix B](#) are several source codes and input files for the solvers.

3.3.1 Software libraries

Many of the core algorithms of the program use available software libraries including fast Fourier transform (FFT), random number generator (RNG), linear algebra operations, and parallel programming environments. Some of the software and compilers are interchangeable depending on availability in various computer resources. Not all possible combinations are highlighted, just the basic ones. Those libraries and compilers listed that are optional are denoted. All of these libraries can be utilized with C.

The fast Fourier transform library FFTW <http://www.fftw.org/> is a portable and typically the fastest freely available implementation of the FFT which computes the DFT in $O(N \log_2 N)$ operations. It supports both distributed and shared memory parallel programming. The name FFTW stands for “Fastest Fourier Transform in the West.” The GNU Scientific Library (GSL) <https://www.gnu.org/software/gsl/> is a general purpose and free numerical C library. It is used for the generation of random numbers and also as an interface to the BLAS (Basic Linear Algebra Subprograms) <http://www.netlib.org/blas/> subroutines including matrix multiplication and inversion.

The CBLAS library can be optionally replaced using the Automatically Tuned Linear Algebra Software (ATLAS) <http://math-atlas.sourceforge.net/> free library that is self-optimizing. The main solver can be compiled using GCC, the GNU Compiler Collection <https://gcc.gnu.org/> that interfaces with parallel programming implementations.

Message Passing Interface (MPI) is a portable standard for distributed memory parallel computing. One common implementation is Open MPI <https://www.open-mpi.org/>, a free library available on many supercomputers. Another is MPICH <https://www.mpich.org/>. The interface OpenMP (Open Multi-Processing) <https://www.openmp.org/> supports shared memory processing instructions for the parallelization of programs. The main program is built to allow for a combination of both MPI and OpenMP parallelism; this hybrid scheme gives flexibility on different platforms.

3.3.2 Key algorithms

In all simulations, the real-space data is real-valued, not complex-valued. For these reasons the DFT of real input data gives output data with complex conjugate symmetry. Mathematically, this is expressed as $U_{k_1, k_2, k_3} = U_{N_1 - k_1, N_2 - k_2, N_3 - k_3}^*$ where $*$ indicates the complex conjugate. For these reasons, only about half of the outputs need be computed and the missing data are simply the conjugate. Using the real-to-complex transform from

FFTW, the real data array is padded by one or two extra values along its last dimension if it is odd or even, respectively. The real data corresponds to the complex output data half its size plus one to account for the Nyquist frequency. Shown in [Fig. 3.5](#) is an illustration of this correspondence in two dimensions where the two arrays have equivalent sizes in bytes. This gives an improvement in speed of nearly two with just the small difficulty in allocating and managing arrays.

Another significant improvement using FFTW is utilizing transposed distributions. In performing the FFT on multidimensional input data using MPI, the `MPI_Alltoall(...)` routine can be used which transposes the order of the first two dimensions of the output array. This is illustrated in [Fig. 3.6](#) for a two-dimensional array using four MPI tasks. By working with the transposed distribution, there is no reason to swap the axes back to their correct order. Although additional care must be taken in iterating through the output array, the routine can be used again performing the inverse FFT (IFFT) which converts the complex output back to the real input in the correct order. The OpenMP parallelism mainly utilizes the `#pragma omp parallel for` directive to make the for loops parallel. This is illustrated in [Fig. 3.7](#) for four OpenMP threads where each thread operates on the array on a “first come, first served” basis. Many other operations like reduction using both approaches are done in parallel. MPI gather and scatter routines are used as needed. Finally, arrays are read and written in parallel using MPI read write operations and OpenMP for loops.

	0	1	2	3		n1-4	n1-3	n1-2	n1-1	n1	n1+1
0	0	1	2	3		n1-4	n1-3	n1-2	n1-1	n1	n1+1
1	n1+2	n1+3	...	...		...	...	...	...	...	...
2	...	...	...	...		...	...	...	...	...	...
n0-2	...	...	...	...		...	...	...	...	...	...
n0-1	...	...	...	...		...	...	...	...	...	n0(n1+2)

(a) Real data array n_0 by n_1 padded to n_0 by $2(n_1/2+1)$ along the last dimension

	0	1		n1/2-2	n1/2-1	n1/2
0	0	1		n1/2-2	n1/2-1	n1/2
1	n1/2+1	...	...	...	...	...
2	...	...	...	...	...	...
n0-2	...	...	...	...	...	...
n0-1	...	...	...	...	...	n0(n1/2+1)

(b) Complex data array n_0 by $n_1/2+1$ with identical size to real array

Figure 3.5: Illustration of real and complex data in two dimensions (adapted from <http://www.fftw.org/> documentation)

Figure 3.6: Diagram depicting all-to-all message passing of an array with 4 tasks

Figure 3.7: Diagram depicting multiprocessing of an array with 4 threads

3.3.3 Performance

The overall performance of the solver is benchmarked using the Stampede2 supercomputer at Texas Advanced Computing Center, an Extreme Science and Engineering Discovery Environment (XSEDE) resource. The speedup of the mass diffusion solver is showcased in Fig. 3.8. The results of the distributed MPI, shared OpenMP, and hybrid memory parallelization is fitted to Amdahl's law which states that the speedup s is related to the number of cores used n which act to speed up the fraction p of the code that benefits from the parallelism [129]. Here it is assumed the number of cores n speeds up the parallel portion by n itself. This law is $s = 1/(1 - p + p/n)$. For MPI tasks only, the percentage benefiting from the parallelism is $p = 93.6\%$. Conversely, for OpenMP threads only, the percentage is $p = 63.2\%$. Finally, the hybrid cases with equal tasks and threads is $p = 76.9\%$. In general, MPI only produces the best speedup since it can take advantage of the `MPI_Alltoall(...)` routine. The main point here is to emphasize the *flexibility* of the parallelization schemes. Depending on the particular problem size being simulated and the architecture it is run on, the optimal scheme may be different. Shown in Fig. 3.9 is a comparison in complexity between the DFT and FFT. In terms of two to three-dimensional problems, the complexity at best is multiplied by the size of the additional dimension for the operations outside of the FFT and at worse its square if using the DFT. The FFT computes the DFT on the order of $N_1 N_2 N_3 \log_2 N_1 N_2 N_3$ operations.

Figure 3.8: Speedup using distributed MPI ($p = 93.6\%$), shared OpenMP ($p = 63.2\%$), and hybrid ($p = 76.9\%$) memory parallelization

Figure 3.9: Comparison of quadratic and linearithmic time complexity for the discrete and fast Fourier transforms, respectively, given input size N

Chapter 4

Conduction

Volume and surface diffusion mechanisms are verified for circular cylindrical inclusions and pores and inclusions without assuming rigid circle shape. Two-dimensional pores and inclusions are chosen since they behave similar to spherical ones while being simpler to analyze and faster to simulate. Although the solvers work in three dimensions, the complexity of the problem at best case is on the order of $O(N_1 N_2 N_3)$ and worst case $O(N_1 N_2 N_3 \log_2 N_1 N_2 N_3)$ using the FFT. Electric field and temperature gradient induced migration are then analyzed. In general, ellipsoidal pore/inclusion shapes result in uniform fields at the surface between the pore/inclusion and the matrix. Therefore, migration follows rigid body translations since uniform driving forces do not tend to change its shape. Finally, the migration of pores accounting for the anisotropic properties of tin is studied.

4.1 Pore and inclusion migration

The velocity v_n of the outward normal $\mathbf{n}$ at the surface of a pore or inclusion describes its motion: for volume and surface diffusion [130], it is given by

$$v_n = \mathbf{v} \cdot \mathbf{n} = v \cos \theta = \begin{cases} \Omega J_n & \text{volume} \\ -\Gamma(\nabla_s \cdot \mathbf{J}_s) & \text{surface} \end{cases} \quad (4.1)$$

where J_n is the normal component of the flux, $\nabla_s \cdot \mathbf{J}_s$ is the surface divergence of the surface flux $\mathbf{J}_s$ or tangential component of the flux, $\Omega = 1/c$ is the molar volume of the component (V_m for a solution), $\Gamma = \delta/c$ is the moles per unit area (A_m for a solution), and δ is the interface thickness. Recall that the dot product between any two vectors is a product of their magnitudes and the cosine of the angle between them. The surface del operator ∇_s is related to the del operator ∇ and the normal vector $\mathbf{n}$ of the surface

$$\nabla_s = \nabla - (\mathbf{n} \cdot \nabla)\mathbf{n} \quad (4.2)$$

which can be applied to gradient, divergence and curl operators. Any vector at a surface defined by normal vector $\mathbf{n}$ can be decomposed into a normal and tangential component $\mathbf{A} = \mathbf{A}_n + \mathbf{A}_s$ which are both perpendicular vector to one another such that $A^2 = A_n^2 + A_s^2$.

Given a normal vector $\mathbf{n}$, the decomposed components are

$$\mathbf{A}_n = (\mathbf{n} \cdot \mathbf{A})\mathbf{n} = (\mathbf{A} \cdot \mathbf{n})\mathbf{n} \quad A_n = \mathbf{A} \cdot \mathbf{n} \quad \text{normal} \quad (4.3)$$

$$\mathbf{A}_s = (\mathbf{n} \times \mathbf{A}) \times \mathbf{n} = \mathbf{A} - (\mathbf{A} \cdot \mathbf{n})\mathbf{n} \quad A_s = \sqrt{\mathbf{A} \cdot \mathbf{A} - (\mathbf{A} \cdot \mathbf{n})^2} \quad \text{tangential} \quad (4.4)$$

where the identities are given to highlight the surface del operator in Eq. (4.2). The surface normal in Cartesian coordinates for a cylindrical surface is illustrated in Fig. 4.1.

The tangential component lies in the tangent plane, but its direction is not unique for general two-dimensional surfaces. That is, the tangential unit direction vector depends on both

Figure 4.1: Normal vector for a cylinder

the normal vector and the vector being decom-

posed. In the case of one-dimensional “perimeter surfaces” like the circular cylinder in Fig. 4.1 with $\mathbf{n} = (n_x, n_y, 0)$, it is $\mathbf{s} = (n_y, -n_x, 0)$. Therefore, two-dimensional inclusions are simpler to analyze for volume and surface diffusion problems. Given a uniform driving force $\mathbf{F} = (F, 0, 0)$ in the x -direction, the normal and tangential components of the driving force at the interface of the pore/inclusion and matrix are

$$F_n = F \cos \theta \quad \text{volume} \quad (4.5)$$

$$F_s = F \sin \theta \quad \text{surface} \quad (4.6)$$

The corresponding components of the flux are found by multiplying the components of

the force with the isotropic mobility according to

$$J_n = MF \cos \theta \quad \text{volume} \quad (4.7)$$

$$J_s = MF \sin \theta \quad \text{surface} \quad (4.8)$$

where the mobility for volume and surface diffusion are different. Considering volume diffusion, the description of the mobility follows that of a dilute solution with low concentrations. In realistic cases, the diffusion is dominated by surface diffusion which is confined to the interface. The mobility is

$$M = \begin{cases} \frac{Dc_0}{RT} X & \text{volume} \\ \frac{Dc_0}{RT} X(1 - X) & \text{surface} \end{cases} \quad (4.9)$$

for both mechanisms [80]. In the surface diffusion case, the diffusivity between both phases is assumed to be the identical. This need not be the case; for example, assuming the inclusion is a pore with zero diffusion coefficient gives the same result. Substituting Eq. (4.9) into Eqs. (4.7) and (4.8), Eq. (4.1) gives corresponding surface normal velocity

$$v_n = \begin{cases} \frac{DF}{RT} \cos \theta & \text{volume} \\ \frac{DF\delta}{RT\tau} \cos \theta & \text{surface} \end{cases} \quad (4.10)$$

expanding about $X = 0$. Comparing Eq. (4.10) to Eq. (4.1), the constant horizontal velocity magnitude of the pore/inclusion is found by recognizing that the dot product of the vector

field with the circular cylinder normal is simply $v \cos \theta$; it is

$$v = \begin{cases} \frac{DF}{RT} & \text{volume} \\ \frac{DF\delta}{RT r} & \text{surface} \end{cases} \quad (4.11)$$

for both mechanisms. The velocity of the pore or inclusion is directly proportional to the driving force. Imposing a uniform driving force everywhere, the velocity of the pore/inclusion is verified using a grid size of 512×512 and $\kappa/f_0 a_0^2 = 5 \times 10^{-4}$. The velocity is verified in Fig. 4.2 for both mechanisms which shows good agreement with Eq. (4.11). Here, Fig. 4.2a shows the volume and Fig. 4.2b shows the surface diffusion mechanism. With respect to the size of the pore/inclusion, Eq. (4.11) indicates the velocity is independent of its radius for the volume diffusion mechanism while is inversely proportional to its radius for the surface diffusion mechanism. This is verified in Fig. 4.3 and Fig. 4.4, respectively. The illustrations in Fig. 4.3a and Fig. 4.4a show the distribution of both the normal and

Figure 4.2: Velocity of a cylindrical pore/inclusion as a function of driving force

tangential flux at the interface. The velocity of the volume mechanism in Fig. 4.3b is generally constant. In addition, the velocity in Fig. 4.3b for the surface diffusion mechanism shows good agreement with inverse radial dependence where smaller pores migrate faster than larger ones. The ratio of pore sizes considered is 2.4 from largest to smallest.

Figure 4.3: Migration of a circular cylindrical pore/inclusion with volume diffusion mechanism

Figure 4.4: Migration of a circular cylindrical pore/inclusion with surface diffusion mechanism

Considering two pores/inclusions of unequal size separated by some distance, a uniform external driving force will result in different evolution. Shown in Fig. 4.5 is an example of this scenario comparing the two cases. The smaller pore is offset below and behind a larger pore. Subjecting it to a uniform external driving force, the pores will move to the right. In the volume diffusion case shown in Fig. 4.5a, the two pores migrate at the same velocity and the distance between them remains rigid. In other words, they do not catch up or drive apart from one another due to uniform fields. Shown in Fig. 4.5b is the surface diffusion case. Here, the smaller pore migrates at a faster rate than the larger pore. The smaller one eventually catches up and collides with the larger pore. The two coalesce and form a single and larger pore that reestablishes a circular cross-section shape. Indeed, the migration driven by an external field does not account for pore-pore interactions since there is no internal field which is microstructure-dependent. To account for this, the electric and temperature gradient fields need be solved for the inhomogeneous problem.

Figure 4.5: Migration of two pores/inclusions with different radii

4.2 Migration by thermal and electric fields

So far, only uniform external driving forces are considered. In reality, the driving forces are due to internal and external fields. The internal electric field and thermal driving force are established due to conductivity inhomogeneities. Considering a single pore (with zero conductivity) in an isotropic matrix, both charge and heat conduction are verified for the volume and surface diffusion mechanisms. Shown in Fig. 4.6 is verification for electric field driven pore migration. The circular cylindrical pore has zero conductivity $\sigma_{ij} = 0$ and matrix has isotropic electrical conductivity $\sigma_{ij} = \sigma_0 \delta_{ij}$. Application of a uniform external field, the total field is also uniform with magnitude that is twice as large inside and at the surface of the pore. In addition, isotropic effective charge $Z_{ij}^* = Z_0^* \delta_{ij}$ is considered. Both the volume diffusion and surface diffusion mechanisms in Figs. 4.6a and 4.6b follow the same general behavior with respect to pore size. That is, the velocity is invariant with respect to radius under the volume diffusion mechanism and inversely proportional to radius under the surface diffusion mechanism. The same trend is followed in Fig. 4.7 for heat conduction. In this case, the thermal conductivity of the pore and matrix are $\kappa_{ij} = 0$ and $\kappa_{ij} = \kappa_0 \delta_{ij}$, respectively, with heat of transport $Q_{ij}^* = Q_0^* \delta_{ij}$. Recall that in steady state conduction, heat and charge behave analogously. Hence, why Figs. 4.7a and 4.7b look virtually identical to Figs. 4.6a and 4.6b despite being driven by a uniform temperature gradient.

Figure 4.6: Velocity of a cylindrical pore as a function of radius subject to electric field

Figure 4.7: Velocity of a cylindrical pore as a function of radius subjected to thermal driving force

If the circular cylindrical pore is replaced by an inclusion with identical size but finite conductivity, the total field inside is a function of the inclusion and matrix conductivity. For charge conduction, the isotropic electrical conductivity of the inclusion is $\sigma_{ij} = \sigma_1 \delta_{ij}$; application of an external electric field gives total field inside proportional to $1 + (\sigma_0 - \sigma_1)/(\sigma_0 + \sigma_1)$. The inclusion velocity is proportional to the total field, so it is possible

to verify the speed with respect to the conductivity ratio σ_1/σ_0 for the two mechanisms shown in Figs. 4.8a and 4.8b. Analogously, Figs. 4.9a and 4.9b show the verification for heat conduction with κ_1/κ_0 and $\kappa_{ij} = \kappa_1\delta_{ij}$. The negative temperature gradient inside the inclusion is proportional to $1 + (\kappa_0 - \kappa_1)/(\kappa_0 + \kappa_1)$. For the volume diffusion examples, the lattice velocity is subtracted to obtain the velocity relative the lattice. This means an inclusion with conductivity identical to the matrix migrates along with the lattice [130].

Figure 4.8: Velocity of a cylindrical inclusion as a function of electrical conductivity

Figure 4.9: Velocity of a cylindrical inclusion as a function of thermal conductivity

4.3 Pore electromigration in tin polycrystals

Considering electromigration of voids in tin polycrystals, the role of anisotropic conductivity is pronounced. These voids or pores are assumed to follow the surface diffusion mechanism since the operating temperatures of tin solders are high relative to its melting temperature. Verification of pore velocity as a function of crystallographic direction in tin single crystals shows good agreement. Its velocity is examined with respect to the magnitude of applied electric field and its radius for two different crystal orientations: parallel to the principal c -axis and perpendicular in the basal plane. The effective charge is taken to be isotropic $Z_{ij}^* = Z_0^* \delta_{ij}$ with $Z_0^* < 0$ [90]. Measurements of the single crystal effective charge coefficients are known to be anisotropic with parallel to perpendicular ratio of 0.61 [131]. Similarly, the diffusion coefficient is also assumed to be isotropic $D_{ij} = D \delta_{ij}$. Although the self-diffusion volume coefficient of tin is known to be anisotropic [132], surface diffusion is considerably higher [133]. Without knowledge of the surface anisotropy, assuming isotropic diffusion properties emphasizes the role of electrical conductivity anisotropy. The conductivity components of tin are $\sigma_{11}^0 = \sigma_{22}^0 = 1.01 \times 10^7 \text{ S m}^{-1}$ and $\sigma_{33}^0 = 6.99 \times 10^6 \text{ S m}^{-1}$ [27]. In Fig. 4.10 is the dependence of pore velocity on crystallographic direction of the applied field: pores migrate at a velocity that varies directly with the applied field magnitude in Fig. 4.10a and inversely with pore radius in Fig. 4.10b agreeing with analytical solutions [60, 130]. The transformation tensor components in the first case where the c -axis is perpendicular to the applied

Figure 4.10: Velocity of a cylindrical pore in a tin grain subjected to external electric field oriented parallel and perpendicular to the principal c -axis

field direction are $Q_{12} = Q_{23} = Q_{31} = 1$ and all other are zero. For the second case where the c -axis is parallel to the applied field direction, the transformation tensor components are $Q_{13} = Q_{21} = Q_{32} = 1$ and all other are zero. The ratio of pore velocities in the two cases of the c -axis parallel and perpendicular to the applied field direction is verified to be $\sqrt{\sigma_{33}^0/\sigma_{11}^0}$. This is explained by the ratio of electric field inside the pore in the two cases; the electric field is uniform inside the pore all the way out to its boundary where surface diffusion occurs. It is derived from the analytical solution for steady state conduction with ellipsoidal inhomogeneities [113] that the electric field at the pore boundary is proportional $1 + \sqrt{\sigma_{33}^0/\sigma_{11}^0}$ for the c -axis parallel to the applied field and $1 + \sqrt{\sigma_{11}^0/\sigma_{33}^0}$ for the c -axis perpendicular to the applied field. Dividing these two expressions results in the ratio $\sqrt{\sigma_{33}^0/\sigma_{11}^0}$; this is the proportionality constant between the two curves in Figs. 4.10a and 4.10b. The pore migrates faster when the external field is applied in the basal plane compared to that along the principal axis.

Having verified migration in single crystals, pore electromigration is investigated in tin polycrystals. To study the electromigration behavior, a tin polycrystal must be generated. Recalling that the size of solders is such that only several grains are present, it is necessary to construct grain structures with realistic grain boundaries. Using Allen–Cahn (Ginzburg–Landau) kinetic equations [134], the boundaries of a simple Voronoi tessellation can be relaxed to obtain realistic curvatures. A periodic polycrystal with three grains is constructed and different grain orientations can be mapped to each grain. For example, the grain structure in Fig. 4.11 shows the orientation map of a tin polycrystal which has central grain with its c -axis in the specimen y -direction. The remaining outer grains have c -axis oriented in the x -direction. The specimen x -, y -, and z -direction are shown in Figs. 4.11a–4.11c where the red color indicates the $[001]$ c -axis direction.

Figure 4.11: Orientation map for a tin polycrystal with c -axis of the central grain in the specimen y -direction and outer grains in the specimen x -direction

Application of an external electric field in the x -direction results in an homogeneous distribution of charges along the grain boundaries. Since the magnitude of electrical conductivity is smaller in the direction of the c -axis, the central grain in Fig. 4.11 will accumulate along its boundaries positive charges to the right and negative charges to the left. Its

higher conductivity in the x -direction enhances the current density while diminishing the total electric field. This is shown in Fig. 4.12a which gives the total electric field magnitude in color and internal electric field as vectors. Figure 4.12b shows the current density magnitude in color with streamlines. Its elongated shape which is oriented roughly 45° from the horizontal and conductivity mismatch with the surrounding grains distorts the electric field. The internal field points upward and to the left which diminishes the total field in the central grain.

Figure 4.12: A tin polycrystal subjected to remote electric field with c -axis of the central grain in the specimen y -direction

Although the total field is diminished by the central grain, the total field still points generally in the direction of the applied field. A pore present in the central grain in Fig. 4.12 will migrate upwards and to the right driven by the total field; this is shown in Fig. 4.13a. Compared to its initial starting position which is aligned with the triple junction to the right,

the pore will migrate away from the triple junction toward the upper-right grain. [Figure 4.13b](#) shows the pore at the boundary between the central grain and upper-right grain above the triple junction. Included is the distribution of charge density and internal field streamlines at the grain boundary. Negative charges accumulated along the right edge of the pore initially interacts with the positive charges along the grain boundary which tends to hasten its attraction to the boundary. As it is crossing the boundary, positive and negative charges along the left and right edge of the pore interact with the positive charges at the boundary. Under a small external electric field, the pore may become stuck at the boundary due to the competing interactions.

Figure 4.13: Migration of a pore in a tin polycrystal with c -axis of the central grain in the specimen y -direction

A contrasting case to investigate the migration of pores in polycrystals can be constructed choosing different grain orientations for the grain structure. Instead, the central grain has c -axis in the specimen x -direction and the surrounding grains have their c -axes in the specimen y -direction. The orientation map of these directions corresponding to

this case is given in Fig. 4.14. The specimen x - and y -directions in Figs. 4.14a and 4.14b are essentially swapped from Fig. 4.11 while Fig. 4.14c is the same. With respect to the specimen x -direction, the conductivity is less than the surrounding grains.

Figure 4.14: Orientation map for a tin polycrystal with c -axis of the central grain in the specimen x -direction and outer grains in the specimen y -direction

An applied electric field in the x -direction results in Fig. 4.15. The central grain acts as a capacitor where positive and negative charges accumulate along the left and right edges of the grain boundary, respectively. The electric field shown in Fig. 4.15a is enhanced by the central grain where the internal field points downward and to the right. The color represents the magnitude of the electric field while the vectors represent the internal field. The corresponding current density is reduced as displayed in Fig. 4.15b which shows the streamlines of current. The central grain has reduced current density compared to the surrounding grains. The resulting fields in Fig. 4.12 and Fig. 4.15 subjected to the same external field are extremes of one another: in the first case, the electric field is reduced and the current density is enhanced; in the second case, the opposite is observed. This illustrates the role of conductivity mismatch has on the developed fields inside polycrystals.

Figure 4.15: A tin polycrystal subjected to remote electric field with c -axis of the central grain in the specimen x -direction

As before, a pore present inside the central grain will migrate to the right. However, its path now has a downward component. Starting from the same position, the pore will migrate toward the lower-right grain below the triple junction. This is summarized in [Fig. 4.16a](#). As the pore approaches the grain boundary, the negative charges along the right edge of the grain boundary interacts with the negative charges along the right side of the pore. These interactions tend to slow the velocity of the pore. If the field is large enough, the pore will migrate to begin to cross the grain boundary as shown in [Fig. 4.16b](#). The complicated interactions of the pore with the grain boundary are revealed by the internal electric field streamlines. As it crosses the grain, the positive charges on left side and negative charges on the right edge of the pore interact with the negative charges at the boundary. Beyond a certain threshold distance, the pore speed may increase as it migrates away from the boundary.

Figure 4.16: Migration of a pore in a tin polycrystal with c -axis of the central grain in the specimen x -direction

Considering anisotropic conductivity, the crystallographic direction of the applied field is responsible for different pore migration speeds. Comparing Fig. 4.13 with Fig. 4.16, conductivity mismatch plays an important role on pore migration path and pore-grain boundary interactions. The inhomogeneous charge distribution is responsible for the development of internal electric field which either tends to enhance or diminish the total electric field and current density.

Pores will also interact with each other where conductivity anisotropy plays an important role in their interactions. This is illustrated in the following example. Two pores with unequal sizes are positioned next to each other inside a large tin grain with out-of-plane c -axis. In-plane, the grain is effectively isotropic with respect to conductivity. An external field is applied such that the smaller pore is behind the larger pore as they migrate to the right. Figures 4.17a–4.17e show the evolution of the two pores: the initial configuration is given in Fig. 4.17a; the distance between the pores begins to lessen in Fig. 4.17b; the pores

Figure 4.17: Pore annihilation and the effects of orientation on charge density and internal electric field

collide and begin to impinge on one another in Fig. 4.17c; the pores begin to grow into a single pore in Fig. 4.17d; finally, the single pore reestablish a circular configuration in Fig. 4.17e. Just prior to the collision in Fig. 4.17b, the interaction of the pores is shown in Fig. 4.17f with the internal electric field streamlines and charge density. The negative charges along the right side of the smaller pore interact with the positive charges along the left side of the larger pore. The charge density distribution of both pores is rotated clockwise from a single pore which is shown in Fig. 4.17g. Comparing Figs. 4.17f and 4.17g, the distortion of the internal field due to the presence of both pores is clearer. The electric field near the pores is generally oriented downward and to the right. Just below the pores, the field is distorted in such a way indicating the electrostatic potential is zero between the

pores. If the pores are instead present in a grain with the c -axis is in-plane, the anisotropic conductivity plays a role in their interaction. Shown in Fig. 4.17h are the charge density and internal electric field for the two pores with in-plane anisotropy where the c -axis points 45° clockwise from the horizontal direction of the applied field. The charge density and internal field are now rotated counterclockwise compared to Fig. 4.17f. These fields now more closely resemble that of the single pore in Fig. 4.17g. Indeed, the electrostatic potential between the pores no longer goes to zero as in Fig. 4.17f.

Two pores separated by distance r and at angle θ to an externally applied field interact as two point dipoles if they are sufficiently far apart. The force components acting on two parallel dipole moments [97] are given by

$$F_x = -\frac{3pp'}{16\pi\epsilon_0 r^4}(5 \cos 3\theta + 3 \cos \theta) \quad (4.12)$$

$$F_y = -\frac{3pp'}{16\pi\epsilon_0 r^4}(5 \sin 3\theta + \sin \theta) \quad (4.13)$$

where p and p' are the strengths of the dipole moments. A uniformly polarized cylinder with polarization density $\mathbf{P}$ has uniform electric field $\mathbf{E} = -(1/2\epsilon_0)\mathbf{P}$ [97]. Indeed, the field inside a remote circular cylindrical pore is also uniform being twice the magnitude of the externally applied field for an isotropic material. Taking this as the polarization density and multiplying by the volume of the cylinder results in the dipole moment $p = -4\pi\epsilon_0 a^2 E_\infty$ (per unit length). If the two pores are far apart such that size effects can be ignored, the radii of both pores only affects the relative strength of the interaction. Taking

the pores as equal size of radius $a = a'$, an illustration of the two pores separated by distance r at angle θ is given in Fig. 4.18a. The total force is traced out at a fixed distance and varying angles in Fig. 4.18b. The horizontal and vertical components of force are shown in Figs. 4.18c and 4.18d, respectively. If the pores are positioned such that one is behind each

Figure 4.18: Two circular cylindrical pores of equivalent size interacting at distance r apart and angle θ to an applied field showing the force and force components as a function of angle to the applied field direction

other with respect to the applied field, there is an attractive force that tends to decrease the distance between them. Conversely, the pores stacked on top of one another generally repel each other as they migrate with the external field. As previously mentioned, pores (or inclusions) of different radii following the volume diffusion mechanism move at the same rate under a *constant* field. Considering the electrostatic interactions, this statement will no longer be generally true due to the inhomogeneous charge density distribution and internal electric fields developed. Inspecting Fig. 4.18b, it is clear that the total force never goes completely to zero. However, the components Figs. 4.18c and 4.18d each go to zero at various angles. The horizontal component of the force vanishes at $\theta = \pm 39.23 \dots^\circ, \pm 90^\circ$, and $\pm(180 - 39.23 \dots)^\circ$. Similarly, at angles $\theta = 0^\circ, \pm 63.43 \dots^\circ, \pm(180 - 63.43 \dots)^\circ$, and

$\pm 180^\circ$, the vertical component of the force goes to zero. Clearly, at no angle does the total force become zero. Instead, at $\theta = 39.23^\circ$ and $\theta = 63.43^\circ$, the pores exert a torque on one another tending to decrease the angle between them.

To demonstrate the pore interactions in Fig. 4.18, two equally sized pores are positioned next to each other at various angles relative to the applied field in a large tin grain (single crystal) with c -axis out of plane. Again, the in-plane conductivity is isotropic. The two pores are separated by distance $r/r_0 = 0.375$ at angles $\theta = 90^\circ$, 63.43° , and 39.23° with a horizontally applied electric field. This is shown in Figs. 4.19a–4.19c, respectively. In terms of vertical component of force, the pores are repelling, neutral, or attracting. Although the

(d) Horizontal distance between two pores

(e) Vertical distance between two pores

Figure 4.19: Migration of two circular cylindrical pores separated by $r/r_0 = 0.375$ interacting due to electric field

pores are large relative to their distance apart, the general behavior still holds. In each, the path of both pores is traced and the charge density internal field sometime after is shown to highlight their interaction. At $\theta = 90^\circ$, the repulsion is greatest and the paths begin to diverge. However, the force scales inversely with the fourth power of the distance between them such that at sufficiently far distances the force is so small that their interaction is negligible. The configuration initially at $\theta = 63.43^\circ$ shows paths that are roughly parallel. In this case, the vertical force is zero but the horizontal force is positive which tends to decrease the angle between them by repulsion. The large size of the pores relative to the distance is also responsible for their general downward motion. Over the course of their interaction, the distance will increase while the angle decreases. At a certain angle $\theta = 39.23^\circ$, the force will transition to attraction as the horizontal force transitions from positive to negative. In addition, the vertical force component is attractive. The pores will migrate toward each other and eventually collide. [Figures 4.19d](#) and [4.19e](#) show the

horizontal distance r_x and vertical distance r_y between pores which clearly demonstrates that pores repelling in Fig. 4.19a and attracting in Fig. 4.19c.

If the c -axis is in-plane, the situation changes since the crystal is no longer effectively isotropic. Application of an external field in the x_1 -direction, the electric field inside a circular pore with an anisotropic conducting matrix is given by

$$\frac{E_1}{E_\infty} = 1 + \sqrt{\frac{\sigma_{11}}{\sigma_{22}} - \left(\frac{\sigma_{12}}{\sigma_{22}}\right)^2} \quad \text{and} \quad \frac{E_2}{E_\infty} = \frac{\sigma_{12}}{\sigma_{22}}. \quad (4.14)$$

Notice that the square root for the first term has a subtraction term related to the off-diagonal conductivity component σ_{12} . Aside from being a symmetric tensor by Onsager's reciprocal relations, the conductivity is positive semi-definite. In other words, all of its principal conductivity components (eigenvalues) are non-negative. For the thermal conductivity tensor, this statement is required by the second law of thermodynamics which can be shown through the Clausius–Duhem inequality [135]. The same requirement should also hold for the electrical conductivity tensor. Considering transversely isotropic conductivity in two dimensions, the positive semi-definite requires that $\sigma_{11} \geq 0$, $\sigma_{22} \geq 0$, and $\sigma_{11}\sigma_{22} \geq \sigma_{12}^2$. This ensures that the quantity inside the square root is never negative which would give rise to imaginary electric field values. However, there is no restriction on the sign of the off-diagonal component. The maximum and minimum off-diagonal component σ_{12} occurs where the principal axes are at $\theta = \pm 45^\circ$. In particular, this corresponds to the case $\sigma_{11} = \sigma_{22}$. The principal values σ_1, σ_2 and principal axis angle θ are

given by

$$\sigma_1, \sigma_2 = \frac{\sigma_{11} + \sigma_{22}}{2} \pm \sqrt{\left(\frac{\sigma_{11} - \sigma_{22}}{2}\right)^2 + \sigma_{12}^2} \quad \text{and} \quad \tan 2\theta = \frac{2\sigma_{12}}{\sigma_{11} - \sigma_{22}}. \quad (4.15)$$

The minimum and maximum angle the field makes relative to the applied field is $\alpha = \arctan(E_2/E_1)$. Substituting the solutions, the angle as expressed in terms of the components is

$$\alpha = \arctan \left[\frac{\sigma_{12}}{\sigma_{22} + \sqrt{\sigma_{11}\sigma_{22} - \sigma_{12}^2}} \right]. \quad (4.16)$$

Taking the conductivity values of tin, the maximum and minimum angles are $\alpha = \pm 5.24 \dots^\circ$ when the c -axis makes an angle of $\theta = \pm 45^\circ$ referenced from the applied field direction. This result can be used to illustrate the role of in-plane anisotropy on pore interactions. Two unequal pores separated at angle that corresponds to vertically neutral pores in the isotropic cases will result in two different results if they are present in single crystals with c -axis at orientations $\pm 45^\circ$ from the applied field direction. In these cases, if the pores are significantly far apart such that their size is small relative to the distance between them, the in-plane anisotropy only affects the angle the dipoles make relative to the applied field. In other words, the dipoles remain parallel to one another, but they are just rotated by some amount. The force between parallel dipoles may still be used by rotating the coordinate system to correspond with the rotated total field. Shown in [Fig. 4.5](#) is the case described above. Here, the two pores are brought close together. Although they are close, the major interaction effects due to in-plane anisotropy still influence the migration

Figure 4.20: Two unequally sized pores migrating in a tin single crystal with c -axis in-plane

path compared to the surface charge interaction effects. The case where the c -axis is 45° pointing roughly in line with the separation vector is shown in Fig. 4.20a. Effectively, the two pores tend to repel each other as shown. The internal field between the pores illustrates this repulsion. The pores are shown to tend to move away from each other. In addition, few field lines emanate from the left side of the larger pore with positive charges that terminate on the right side of the smaller pore with negative charges. Conversely, the alternative case where the c -axis is 45° roughly perpendicular to the separation vector tends to cause the pores to attract one another as shown in Fig. 4.20b. Indeed, the pores are shown to actually coalesce and form a single pore. The internal field between the pores just prior to combination show the strong interactions. The internal field from the left edge of the larger pore are shown to terminate on the right edge of the smaller pore

which indicates attraction. In these two cases, the pores are shown to distort slightly. This is due to the effects of the surface charge interactions causing the charges to redistribute along its edge and establish electrostatic equilibrium. The field inside is no longer uniform. Generally uniform electric fields do not tend to cause distortions which is always the case for single remote pores. Accounting for pore interactions, there are distortion effects. Another important source of pore and inclusion migrations is mechanical stress.

Chapter 5

Elasticity

Arguably one of the most important but overlooked materials process, elastic deformation plays a dominant role in the evolution and morphology of microstructure. The computation of stress and strain fields accounting for material properties that are both inhomogeneous and anisotropic is especially difficult since elastic interactions are transferred directly by the medium. This contrasts with electric and magnetic fields which exist in spite of the medium they reside in: they depend solely on the charges, currents, and dipoles that create them and persist even in a vacuum. Elastic fields can only exist and be transferred by matter. Despite their difficulty, many important solutions exist for stress, strain, and displacement fields. In addition, microelasticity modeling allows for efficient computation of elastic field for complicate microstructures.

In general, stress, unlike electric and thermal fields, affect the shape of remote pores and inclusions through distortion. The equilibrium aspect ratio of elastic inclusions and pores under stress is analyzed. It is demonstrated that pores grow into unstable cracks beyond a maximum aspect ratio and critical tensile stress. Stress gradients are well established to induce migration of matter. Internal stress fields are generated by microstructural features including point defects, dislocations, cracks, pores, inclusions, and polycrystals which influence the chemical potential and ultimately driving force for diffusion. The application of a remote stress gradient is somewhat difficult to visualize but can be incorporated into diffusional studies of pores and inclusions. Both volume and surface diffusion mechanisms are verified for elliptical inhomogeneities under uniform driving forces and for circular pores and inclusions by stress gradient.

5.1 Pore and inclusion deformation

So far, only the movement of pores under constant volume have been discussed. In addition to migration, pores and inclusions may deform especially by stress. The equilibrium shape of pores may be analyzed through free energy considerations since deformation alone does not involve the net movement of the pore/inclusion. Under the assumption of constant volume, the shape is determined by the competition between surface energy and elastic strain energy. In the absence of external stress (or strain), an elastic inclusion or inhomogeneity with isotropic expansivity has circular equilibrium

shape in two-dimensions. Conversely, an anisotropic inhomogeneity is no longer circular. Shown in Fig. 5.1 are some equilibrium shapes of elastic inclusions with isotropic elastic stiffness identical to the surrounding matrix. Here, the elastic stiffness is given by $c_{ijkl} = \lambda\delta_{ij}\delta_{kl} + \mu(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$ where λ and μ are Lamé's parameters. Although this is not generally a realistic case, it is an illustrative example to examine equilibrium shapes considering deformation. In Fig. 5.1a, the equilibrium shape is an elliptical cylinder where the anisotropic expansivity has principal strain only $\eta_{11} > 0$ and $\eta_{22} = \eta_{33} = \eta_{23} = \eta_{13} = \eta_{12} = 0$. The ellipse is elongated in the direction perpendicular to the principal strain component. Transforming the expansivity tensor by 45° such that $\eta_{11} = \eta_{22} = \eta_{12} > 0$ and $\eta_{33} = \eta_{23} = \eta_{13} = 0$, the equilibrium shape is another elliptical cylinder that is oriented 45° relative to Fig. 5.1a as shown in Fig. 5.1b. Finally, the equilibrium shape is cuboidal for $\eta_{12} > 0$ and $\eta_{11} = \eta_{22} = \eta_{33} = \eta_{23} = \eta_{13} = 0$ and is shown in Fig. 5.1c. In this case, the principal strain components are $\eta_1 = -\eta_2$ which indicate the signs of the principal components do not affect the shape. Instead, it is their magnitude only. If the alternative is the case, it would be expected that the shape would

Figure 5.1: Distortion of a cylindrical inhomogeneity by stress-free strain

be an elliptical cylinder oriented 45° like it is shown in Fig. 5.1b. This is confirmed for Fig. 5.1a by specifying an equal but opposite value of the principal strain component such that $\eta_{11} < 0$. The resulting elliptical aspect ratio is identical.

The non-circular equilibrium shape of a pore due to some internal stimuli is determined from minimum free energy. Assuming an elliptical shape, the free energy as a function of its semi-major and semi-minor axes is

$$F(a, b) = T(a, b) + U(a, b) \quad (5.1)$$

where $T(a, b)$ is the change in surface energy and $U(a, b)$ is the change in elastic strain energy [136]. The surface energy T is related to the surface energy density γ and circumference C according to $T = \gamma C$. As a function of the semi-minor axis a and semi-major axis b , the surface free energy $T(a, b)$ is given by

$$T(a, b) = 4\gamma b E\left(\sqrt{1 - \frac{a^2}{b^2}}\right) \quad (5.2)$$

where the function $E(\sqrt{1 - a^2/b^2})$ is the complete elliptic integral of the second kind. The eccentricity of the ellipse is the parameter $e = \sqrt{1 - a^2/b^2}$. The elastic strain energy of an elliptical inhomogeneity [100] where $\eta_{11} \neq 0$ and $\eta_{22} = \eta_{33} = \eta_{23} = \eta_{13} = \eta_{12} = 0$ is

$$U(a, b) = \frac{\pi \mu a^2 b (2a + b) \eta_{11}^2}{2(1 - \nu)(a + b)^2} \quad (5.3)$$

where μ is the shear modulus and ν is Poisson's ratio are related to the first Lamé parameter $\lambda = 2\mu\nu/(1 - 2\nu)$. Notice that the elastic strain energy depends on the square of the principal strain component η_{11} . This is consistent with the result displayed in Fig. 5.1 where the deformation is independent of the sign of the component. Minimizing the free energy with respect to aspect ratio gives the equilibrium elliptical shape as a function of principal strain component. The derivative of the free energy with respect to aspect ratio is

$$\frac{\partial F}{\partial(b/a)} = \frac{\partial F}{\partial b} \frac{\partial b}{\partial(b/a)} = \frac{\partial F}{\partial b} \left/ \frac{\partial(b/a)}{\partial b} \right. = \frac{V}{2\pi b} \frac{\partial F}{\partial b} \quad (5.4)$$

where the constant volume per unit length of the elliptical cylinder is $V = \pi ab$. An illustration of this minimization is shown in Fig. 5.2a. Verification of the equilibrium aspect ratio as a function of the expansion coefficient is shown in Fig. 5.2 which agrees well with the derived analytical solution ($\nu = 0.3$). Again, this case is not realistic physically as a

Figure 5.2: Elliptical cylindrical inhomogeneity due to nonzero principal expansion coefficient

highly anisotropic expansion coefficient is generally not expected, but it provides a simple approach to analyzing deformation. More importantly, it provides a way to investigate the migration of elliptical inclusions and pores. The equilibrium shapes of inclusion with cubic symmetry have been analyzed in some detail in cubic matrices [137]. They give rise to cuboidal precipitate shapes.

5.2 Pore and inclusion migration

Using anisotropic expansivity, it is possible to investigate the migration of elliptical pores.

An elliptical cylindrical pore has radius from its center

$$r = \frac{ab}{\sqrt{b^2 \cos^2 \theta + a^2 \sin^2 \theta}} \quad (5.5)$$

where θ is the polar angle (which should not be confused with the eccentric anomaly typically used to parameterize an ellipse). Revisiting the normal velocity for volume and surface diffusion mechanisms, the normal flux and surface divergence of the tangential flux give rise to the movement of an interface:

$$v_n = \begin{cases} \Omega J_n & \text{volume} \\ -\Gamma(\nabla_s \cdot J_s) & \text{surface} \end{cases} \quad (5.6)$$

For simplicity, a uniform driving force is used again that has horizontal component only $F = (F, 0, 0)$. In addition, the semi-major and semi-minor axes are aligned with the horizontal and vertical directions. In particular, a lies along the horizontal and b in the vertical.

The normal and tangential vector for an ellipse

is illustrated in Fig. 5.3 which show the horizontal

and vertical components. Again, the normal

vector and tangential vector for this surface is

simply $\mathbf{n} = (n_x, n_y, 0)$ and $\mathbf{s} = (n_y, -n_x, 0)$,

respectively. Assuming the elliptical inclusion

moves rigidly along the horizontal with velocity v , the dot product of the velocity vector

$\mathbf{v} = (v, 0, 0)$ with the normal vector gives normal velocity as a function of the angle and

semi-major and semi-minor axes

Figure 5.3: Normal vector for an elliptical cylinder

$$v_n = \mathbf{v} \cdot \mathbf{n} = v \frac{b \cos \theta}{\sqrt{b^2 \cos^2 \theta + a^2 \sin^2 \theta}}. \quad (5.7)$$

Evaluating Eq. (5.6) for both the volume and surface diffusion mechanisms with isotropic

mobility and linearizing about $X = 0$ results in normal velocity

$$v_n = \begin{cases} \frac{DF}{RT} \frac{b \cos \theta}{\sqrt{b^2 \cos^2 \theta + a^2 \sin^2 \theta}} & \text{volume} \\ \frac{DF\delta}{RTb} \frac{b \cos \theta}{\sqrt{b^2 \cos^2 \theta + a^2 \sin^2 \theta}} \left[1 + \frac{2a(b-a) \sin^2 \theta}{b^2 \cos^2 \theta + a^2 \sin^2 \theta} \right] & \text{surface} \end{cases} \quad (5.8)$$

Comparing Eq. (5.7) to Eq. (5.8) for the volume diffusion mechanism, it is clear that the

velocity of the elliptical cylinder is simply

$$v = \frac{DF}{RT} \quad \text{volume} \quad (5.9)$$

which is identical to the result for the circular cylinder. In other words, the velocity is independent of the size and aspect ratio. For the surface diffusion mechanism, the normal velocity contains two terms in Eq. (5.8). The first term is a migration term and the second is a deformation term. The second term can be safely ignored. Integrating the term as with respect to the first moment of the horizontal normal component n_x gives zero average velocity in the horizontal direction. Assuming the elliptical cylinder remains rigid, the velocity is approximately

$$v \approx \frac{DF\delta}{RTb} \quad \text{surface} \quad (5.10)$$

by neglecting the higher order term. The velocity is inversely proportional to b , that is, the semi-axis perpendicular to the uniform driving force. In the limit of a circular cylinder, $a = b = r$ making the velocity consistent with the result for a circle. It is interesting that the velocity is dependent on only one of the axes. Under the volume diffusion mechanism, the aspect ratio does *not* affect the velocity, whereas for the surface diffusion mechanism, the aspect ratio does affect the velocity through the semi-axis perpendicular to the applied field. In addition, neither depend directly on aspect ratio.

The velocity of elliptical pores and/or inclusions are verified for both volume and surface diffusion mechanisms. In these cases, various aspect ratios are considered under fixed volume which are established by the anisotropic expansivity as verified in Fig. 5.2. The results of the volume diffusion mechanism are shown in Fig. 5.4 while those of the surface diffusion mechanism are given in Fig. 5.5 both agreeing with the analytical derivation.

Figure 5.4: Migration of elliptical pore/inclusion with volume diffusion mechanism and constant volume

Figure 5.5: Migration of elliptical pore/inclusion with surface diffusion mechanism and constant volume

Illustrations of the normal and tangential flux for an ellipse are given in Figs. 5.4a and 5.5a, respectively. The results are summarized for the volume and surface diffusion mechanisms in Figs. 5.4b and 5.5b. In each, the aspect ratios verified include $b/a = 0.125, 0.25, 0.5, 1.0, 2.0, 4.0,$ and 8.0 . For the volume diffusion mechanism, there is no clear dependence on aspect ratio. Whereas for surface diffusion, the velocity is proportional to $\sqrt{a/b}$ under constant volume.

A uniform external field is not generally going to generate the same field inside a pore/inclusion if the properties are different than the surrounding matrix. In particular, the solutions [113] assuming isotropic conductivity for the negative temperature gradient (matrix κ_0 , inclusion κ_1) inside is

$$\frac{X_1}{X_\infty} = 1 + \frac{b(\kappa_0 - \kappa_1)}{a\kappa_0 + b\kappa_1} \quad \text{and} \quad \frac{X_2}{X_\infty} = 0, \quad (5.11)$$

while for the electric field (matrix σ_0 , inclusion σ_1) inside is

$$\frac{E_1}{E_\infty} = 1 + \frac{b(\sigma_0 - \sigma_1)}{a\sigma_0 + b\sigma_1} \quad \text{and} \quad \frac{E_2}{E_\infty} = 0. \quad (5.12)$$

For both heat and charge conduction, the application of external field gives total field inside a nonconducting inclusion or pore proportional to $1 + b/a$. Assuming isotropic interference coefficients, its velocity under the same external field is proportional to b/a (less the lattice) for the volume mechanism and $(a + b)/\sqrt{ab}$ for the surface mechanism.

5.3 Deformation by stress

Stress itself tends to cause distortion. A pore or inclusion will change shape in accordance with an externally applied stress, for example. Considering a cavity in an isotropic matrix with lattice parameter that varies as Vegard's law $a = a_0 X$ ($a = 0$ in the pore and $a = a_0$ in the matrix), the isotropic expansion coefficient follows $\eta_0 = \partial \ln a / \partial X = 1/X$ such that $\epsilon_{ij}^0 = \eta_{ij} X = \delta_{ij}$. For a homogeneous material with only one phase, the component k chemical potential $\mu_k = G_k^0 + RT \ln \gamma_k X - \eta_{ij} \sigma_{ij} / c_0$ simplifies to $\mu_k = G_k^0 + RT \ln \gamma_k X - \Omega \sigma_{kk}$ consistent for single component systems [87]. Shown in Fig. 5.6 are examples of a pore distorted by external stresses. As expected [2, 64, 65, 138], an initially circular cylindrical pore deforms into an elliptical pore under uniaxial tension as shown in Fig. 5.6a. Similarly, under shear stress as shown in Fig. 5.6b the shape is elliptical but rotated 45° from the horizontal compared to Fig. 5.6a. Finally, Fig. 5.6c shows the pore subjected to compression. The pore is elliptical in shape but oblate rather than oblong as in Fig. 5.6a. The equilibrium shape can be estimated by considering the elastic strain energy contribution.

Figure 5.6: Distortion of a cylindrical pore by stress

For a uniaxially stressed elliptical pore where, the elastic strain energy is determined from the equivalent inclusion method [100]; it is given by

$$U(a, b) = \frac{\pi b[a + 2b(1 - \nu^2)]\sigma_\infty^2}{4\mu(1 + \nu)} \quad (5.13)$$

where σ_∞ is the applied field. Other expressions exist for elastic strain energy [139] that consider an initially uniform system as a reference point. Both are equivalent in terms of the energy change with respect to aspect ratio. However, the free energy in Eq. (5.1) needs an additional term to account for the work due to the presence of external stress. The work W is the negative of the potential energy change V . From Clapeyron's theorem [140], the potential energy change is twice the magnitude of the elastic strain energy $V = 2U$. The Gibbs free energy of the ellipse subjected to remote external stress field [100] is

$$G(a, b) = T(a, b) - U(a, b). \quad (5.14)$$

Following the minimization procedure of Eq. (5.14) with Eq. (5.13) as the elastic strain energy function, a critical aspect ratio can be determined [64, 65] by minimizing the free energy function twice. In Fig. 5.7a is an illustration of the free energy minimization showing the competing surface and elastic strain energy terms. Plotting the curves of $\partial G / \partial(b/a) = 0$ and $\partial^2 G / \partial(b/a)^2 = 0$, the simultaneous solution gives the critical aspect ratio as shown in Fig. 5.7b. Using a Poisson's ratio of $\nu = 0.3$, the critical aspect ratio is $(b/a)^* = 2.817$. This means that above a critical stress, initially circular pores deform

Figure 5.7: Instability of an elliptical pore due to uniaxial stress

into elliptical pores; upon reaching its critical aspect ratio, pore distortion is unstable. Free energy is minimized for higher and higher aspect ratios without bound. The pore maintains its volume and tending to become an infinitely long crack ultimately leading to failure of the material. This is illustrated in Fig. 5.8 for various stresses above the critical stress which is determined to be $\sigma_\infty^*/\sigma_0 = 0.2$. In each, an outline of the elliptical pore with critical aspect ratio is shown. For higher values of stress, deformation occurs more rapidly. Catastrophic crack growth is faster than equilibrium shape change distortions.

Figure 5.8: Unstable growth of an initially circular cylindrical pore into a crack due to uniaxial tension

This preceding approach gives a simple picture of microscopic creep rupture. It was developed mainly with assumptions used in analysis of Griffith crack propagation explaining brittle failure but instead propagating by diffusion [138]. An important critique of this analysis is needed considering the equilibrium shape of pores below the critical uniaxial stress. Recalling that the elastic strain energy in Eq. (5.13) depends on the square of the uniaxial stress, it effectively predicts that a compression stress with equal magnitude will initiate the same catastrophic cavity growth in the exact configuration as Figs. 5.7 and 5.8. More disconcerting, the equilibrium shape for the case of a biaxial stress state corresponding to shear (at 45° by Mohr's circle) comprised of equal but opposite stresses in tension and compression is a circular pore, not elliptical. The elastic strain energy [100] is

$$U(a, b) = \frac{\pi(1 - \nu)(a + b)^2 \sigma_\infty^2}{2\mu}. \quad (5.15)$$

Obviously, this seems unreasonable. The discrepancy can be resolved by realizing that assumptions of these Griffith type cracks assume the elastic contribution to the chemical potential is simply proportional to the elastic strain energy density [139] as opposed to the hydrostatic stress for isotropic materials [89, 93]. Shown in Appendix C is a derivation of the latter. For the case of this analysis, there is a term missing that has a dependence on the external stress alone instead of its square as in the elastic strain energy term. It is from the interaction of the external stress with the stress-free strain that accounts for this discrepancy. From the equivalent inclusion method [100], it is possible to obtain an estimate of this term assuming the stress free strain is everywhere constant throughout

the homogeneous system. The elastic strain energy in this case is given by

$$U(a, b) = \frac{\pi b[a + 2b(1 - \nu^2)]\sigma_\infty^2}{4\mu(1 + \nu)} + \frac{\pi(1 + \nu)b[a(1 - 2\nu) - 2b(1 - \nu)]\eta_0\sigma_\infty}{2(1 - 2\nu)} \quad (5.16)$$

The former analysis of unstable pore shape is still valid. It provides a relative simple analysis of the critical stress and aspect ratio of elliptical pores. Shown in Fig. 5.9a is an example of an initially circular pore subjected to stress above the critical uniaxial stress magnitude. At constant volume, the pore aspect ratio changes at constant rate until it reaches its critical aspect ratio. After which, it changes at faster rate still at constant volume which agrees with the analytical analysis [64, 65]. Using the estimate for the eigenstrain contribution, the equilibrium pore shape aspect ratio is fitted and agrees reasonably well to the simulation results shown in Fig. 5.9b. Accounting for this additional term, compressive stresses are now predicted to cause the elliptical pore to become oblate rather than oblong.

Figure 5.9: Elliptical cylindrical pore due to uniaxial stress

5.4 Migration by stress gradient

Unlike the driving force for diffusion by an applied electric field or temperature gradient, it is somewhat difficult to visualize the driving force due to an externally applied stress gradient. Eshelby gives an approximate result for the total force on a spherical inclusion including a cavity and rigid (incompressible) inclusion due to applied pressure gradient [141]. Other work incorporates the effects of a pressurized spherical bubble with surface tension on its migration under the influence of uniaxial compressive and tensile stress gradients [142, 143]. However, the results disagree on the migration direction of the bubble into regions of stress in compression, tension, or neither. Additional work for the application of an external tensile stress gradient and pressure gradient on a spherical cavity show that it is expected to move towards a region of higher stress intensity [62]. In all of these analyses, it is not generally physically meaningful to consider a far-field applied pressure gradient or pure uniaxial stress gradient. For example, a remote pressure gradient makes more sense in terms of fluids flowing in viscous media (Newton's law of viscosity) and porous media (Darcy's law of permeability). From the point of view of mechanical equilibrium, it is difficult to justify a pure uniaxial stress gradient which varies linearly in the direction it is applied in. *If a remote uniform stress represents an external load, what does an external moment correspond to?* Perhaps the simplest moment to visualize is a bending moment. Analyzing the internal stresses of an Euler–Bernoulli beam subjected to bending moment, for example, the normal stress varies *linearly* such that above and below the

neutral axis, the beam is in a state of tension and compression. In this sense, a remote uniaxial stress gradient that varies in any direction other than the direction it is applied in corresponds to a bending moment. For instance, a uniaxial stress in the horizontal that varies with the vertical direction corresponds to a bending moment about the out-of-plane axis.

In the case of this stress gradient above, the velocity of a cylindrical pore or inclusion will be in the vertical direction $\mathbf{v} = (0, v, 0)$ such that the motion is towards a higher stress intensity. The normal velocity along the interface varies as

$$v_n = \mathbf{v} \cdot \mathbf{n} = v \sin \theta. \quad (5.17)$$

The solution for stress around an isotropic circular inclusion is known at the interface in the isotropic matrix phase [144]. In addition, the complete elastic field solution (stress, strain, and displacement) in an isotropic material away from a circular hole is known [145]. These solutions can be used to construct the driving force for diffusion due to stress gradient corresponding to bending. Before analyzing each of these cases, it is useful to first look at the driving force due to stress gradient only where no internal stresses are generated by inhomogeneities. In other words, an inclusion with identical elastic properties as the matrix. For isotropic phases, the driving force is $F_i = - \partial(\mu_0 - \Omega \sigma_{kk}) / \partial x_i$. The hydrostatic stress (or mean stress) is one-third of the first invariant of the stress tensor σ_{kk} . It is useful to define a “stress gradient vector” that corresponds to the gradient of this

invariant (stress trace) defined by $G_i \equiv \partial \sigma_{kk} / \partial x_i$. In addition, plane strain conditions are considered where the out-of-plane stress component is $\sigma_{33} = \nu(\sigma_{11} + \sigma_{22})$. This gradient evaluated for the case of stress gradient only without hole or inclusion is $G_1 = 0$ and $G_2 = (1 + \nu)\gamma_\infty$ where γ_∞ is the slope of the far field stress gradient. This result is identical to the gradient evaluated far from a hole or inclusion by boundary condition. Evaluating the driving force using these gradient components and assuming constant molar volume gives normal and tangential forces

$$F_n = \Omega(1 + \nu)(\sin \theta)\gamma_\infty \quad \text{volume} \quad (5.18)$$

$$F_s = \Omega(1 + \nu)(\cos \theta)\gamma_\infty \quad \text{surface} \quad (5.19)$$

which correspond to the volume and surface diffusion mechanisms. Multiplying the forces by the mobility gives the normal and tangential flux which can be substituted into [Eq. \(5.6\)](#) to obtain

$$v_n = \begin{cases} \frac{D\Omega(1 + \nu)\gamma_\infty}{RT} \sin \theta & \text{volume} \\ \frac{D\Omega(1 + \nu)\delta\gamma_\infty}{RT\tau} \sin \theta & \text{surface} \end{cases} \quad (5.20)$$

This is identical in form to the uniform driving force cases. In other words, the magnitude of the driving force is $F = \Omega(1 + \nu)\gamma_\infty$. Comparing [Eq. \(5.20\)](#) to [Eq. \(5.17\)](#), it is clear that for the volume diffusion mechanism

$$v = \frac{D\Omega(1 + \nu)\gamma_\infty}{RT} \quad \text{volume} \quad (5.21)$$

where the velocity is proportional to the magnitude of the stress gradient and independent of size. Similarly, for the surface diffusion mechanism, the velocity is

$$v = \frac{D\Omega(1 + \nu)\delta\gamma_\infty}{RT r} \quad \text{surface} \quad (5.22)$$

which varies inversely with the radius of the inclusion (with identical properties to that of the matrix). Clearly, a remote stress gradient contributes to rigid motion of a cylindrical inclusion without the generation of internal stresses. The result for the volume diffusion mechanism indicates the velocity of the lattice. This procedure can be utilized for the analysis of the hole and inclusion. Shown in Figs. 5.10 and 5.11 is verification of the volume and surface diffusion mechanisms without generation of internal stresses due to property mismatches. Illustrations of these mechanisms showing the vertical velocity of the pore/inclusion are given in Figs. 5.10a and 5.11a while the migration velocity as a function of radius is shown in Figs. 5.10b and 5.11b.

Figure 5.10: Migration of a circular cylindrical pore/inclusion with volume diffusion mechanism

Figure 5.11: Migration of a circular cylindrical pore/inclusion with surface diffusion mechanism

Due to property mismatches between the inclusion or pore with the matrix, additional internal stresses will be generated which also contributes to the driving force for diffusion through their gradients. For the case of the hole [145], the stress gradient vector evaluated at the outside boundary of the hole is

$$\frac{G_1}{\gamma_\infty} = 3(1 + \nu) \sin 4\theta \quad \text{and} \quad \frac{G_2}{\gamma_\infty} = (1 + \nu)(1 - 3 \cos 4\theta). \quad (5.23)$$

It is interesting to note that the result does not depend on the magnitude of the elastic modulus in any way. This observation is similar to that of the stresses around a hole due to externally applied uniform tensile stress. At $\theta = \pm 45$ and ± 135 , the vector is at a maximum at $4(1 + \nu)$. At the top and bottom of the hole, the vector is at a minimum at $-2(1 + \nu)$. In both cases, the horizontal component is the only nonzero component. The incorporation of Poisson's ratio is due to the plane strain condition in two dimensions.

On the outside of the cavity, the driving force is

$$F_n = \Omega(1 + \nu)(\sin \theta + 3 \sin 3\theta)\gamma_\infty \quad \text{volume} \quad (5.24)$$

$$F_s = \Omega(1 + \nu)(\cos \theta - 3 \cos 3\theta)\gamma_\infty \quad \text{surface} \quad (5.25)$$

while inside $F_n = 0$ and $F_s = 0$. Because the driving force is related to the stress, and the stress itself is not required continuous across the hole, there is a jump discontinuity in the flux across its surface. This is contrasted with the conduction driving forces where it is often assumed there is no jump continuity. In general, both the electrostatic potential and temperature are required to be continuous across any inhomogeneity. This means the electric field and temperature gradient will also be continuous. If the coupling coefficients are identical across the interface, the driving force will be continuous, too. However, if these properties are significantly different across the interface, a jump discontinuity will also develop. One approach is to average the two fluxes together to obtain the normal velocities

$$v_n = \begin{cases} \frac{D\Omega(1 + \nu)\gamma_\infty}{2RT}(\sin \theta + 3 \sin 3\theta) & \text{volume} \\ \frac{D\Omega(1 + \nu)\delta\gamma_\infty}{2RT r}(\sin \theta - 9 \sin 3\theta) & \text{surface} \end{cases} \quad (5.26)$$

Notice that the normal velocities contain two terms: $\sin \theta$ which represents migration and $\sin 3\theta$ which corresponds to distortion. The distortion term can generally be ignored if the applied gradient is small such that the stress magnitude is not large enough to cause significant distortion. In this case, the surface gradient term will help maintain the rigid circular shape. The velocity of a pore in the laboratory reference frame for the volume

diffusion mechanism is approximately

$$v \approx \frac{D\Omega(1+\nu)\gamma_\infty}{2RT} \quad \text{volume} \quad (5.27)$$

which is half the magnitude of the lattice reference frame. The approximate velocity for the surface diffusion mechanism is

$$v \approx \frac{D\Omega(1+\nu)\delta\gamma_\infty}{2RT r} \quad \text{surface} \quad (5.28)$$

which also is half the result for stress gradient only migration. The general behavior observed in both of these results is generally the same with respect to size for conduction driven migration. Shown in Fig. 5.12 are results for a pore driven by a small stress gradient that tends to cause migration but not distortion. Too large of an applied stress will induce shape change. For volume diffusion mechanism, the velocity of the pore is shown in

Figure 5.12: Velocity of a cylindrical pore as a function of radius subject to stress gradient

Fig. 5.12a to be independent of its size. The velocity of the pore under surface diffusion mechanism is shown in Fig. 5.12b. The velocity varies inversely with the radius of the circular cylinder. The numerical results agree well with the derived solutions.

Next, the case of an inclusion is considered. Unfortunately, the complete solution for the stress in and around an elastic inclusion is not known. The stress in the matrix at the hole is known [144] and can be used to construct the complete solution using the Airy stress function approach in [145]. Putting coefficients in the excess Airy function that account for the disturbance due to the inhomogeneity from the homogeneous stress gradient, it is possible to solve for the unknown coefficients using the known solution at the inclusion. To do this, an additional Airy stress function is constructed with unknown coefficients that give the solution inside the inclusion. The form of the function is assumed to be of the same form as the homogeneous function which gives rise to linear stress field inside. The boundary condition at the interface between the inclusion and matrix requires that both the stress traction vector $\sigma_{ij}n_j$ and displacement vector u_i be continuous. The form of the displacement vector is determined from the Michell solution [146]. To further simplify the analysis, Poisson's ratio is assumed to be identical between the two phases, but the moduli may be different. Using the derived elastic field solution, the stress gradient vector evaluated in the matrix at the interface is determined to be

$$\frac{G_1}{\gamma_\infty} = \frac{3(1+\nu)^2(\mu_0 - \mu_1) \sin 4\theta}{(1+\nu)\mu_0 + (3-\nu)\mu_1} \quad \text{and} \quad \frac{G_2}{\gamma_\infty} = (1+\nu) - \frac{3(1+\nu)^2(\mu_0 - \mu_1) \cos 4\theta}{(1+\nu)\mu_0 + (3-\nu)\mu_1}. \quad (5.29)$$

Here, the shear modulus of the matrix and inclusion are denoted as μ_0 and μ_1 , respectively.

Checking the case of the hole where $\mu_1 = 0$, the gradient components reduce to the case of the hole where $G_1 = 3(1 + \nu)(\sin 4\theta)\gamma_\infty$ and $G_2 = (1 + \nu)(1 - \cos 3\theta)\gamma_\infty$. The gradient evaluated at the interface within the inclusion is determined to be

$$\frac{G_1}{\gamma_\infty} = 0 \quad \text{and} \quad \frac{G_2}{\gamma_\infty} = \frac{4\mu_1(1 + \nu)}{(3 - \nu)\mu_0 + (1 + \nu)\mu_1}. \quad (5.30)$$

In the limit of a hole, $\mu_1 = 0$ and the gradient components simplify to $G_1 = G_2 = 0$ as expected. When there is no hole present and the moduli are equivalent such that $\mu_0 = \mu_1$, the gradient components are $G_1 = 0$ and $G_2 = (1 + \nu)\gamma_\infty$. This is true whether starting from the result for the gradient evaluated in the matrix or inclusion. The normal and tangential components of the driving force for diffusion at the interface evaluated in the matrix is

$$F_n = \Omega(1 + \nu) \left[\sin \theta + \frac{3(1 + \nu)(\mu_0 - \mu_1) \sin 3\theta}{(1 + \nu)\mu_0 + (3 - \nu)\mu_1} \right] \gamma_\infty \quad \text{volume} \quad (5.31)$$

$$F_s = \Omega(1 + \nu) \left[\cos \theta - \frac{3(1 + \nu)(\mu_0 - \mu_1) \sin 3\theta}{(1 + \nu)\mu_0 + (3 - \nu)\mu_1} \right] \gamma_\infty \quad \text{surface} \quad (5.32)$$

Evaluating at the interface within the inclusion, the driving force components are

$$F_n = \Omega(1 + \nu) \frac{4\mu_1(1 + \nu) \sin \theta}{(3 - \nu)\mu_0 + (1 + \nu)\mu_1} \gamma_\infty \quad \text{volume} \quad (5.33)$$

$$F_s = \Omega(1 + \nu) \frac{4\mu_1(1 + \nu) \cos \theta}{(3 - \nu)\mu_0 + (1 + \nu)\mu_1} \gamma_\infty \quad \text{surface} \quad (5.34)$$

Averaging the two driving forces within the inclusion and matrix together results in normal velocity at the interface given by

$$v_n = \begin{cases} \frac{D\Omega(1+\nu)\gamma_\infty}{2RT} \left[\sin \theta + \frac{4\mu_1 \sin \theta}{(3-\nu)\mu_0 + (1+\nu)\mu_1} + \frac{3(1+\nu)(\mu_0 - \mu_1) \sin 3\theta}{(1+\nu)\mu_0 + (3-\nu)\mu_1} \right] & \text{volume} \\ \frac{D\Omega(1+\nu)\delta\gamma_\infty}{2RT r} \left[\sin \theta + \frac{4\mu_1 \sin \theta}{(3-\nu)\mu_0 + (1+\nu)\mu_1} + \frac{9(1+\nu)(\mu_0 - \mu_1) \sin 3\theta}{(1+\nu)\mu_0 + (3-\nu)\mu_1} \right] & \text{surface} \end{cases} \quad (5.35)$$

Again, the volume and surface diffusion mechanisms both contain a $\sin 3\theta$ term which can be ignored. The velocity of the inclusion is approximately

$$v \approx \frac{D\Omega(1+\nu)\gamma_\infty}{2RT} \left[1 + \frac{4\mu_1}{(3-\nu)\mu_0 + (1+\nu)\mu_1} \right] \quad \text{volume} \quad (5.36)$$

for the volume diffusion mechanism where the lattice velocity has to be subtracted to obtain its velocity relative the lattice. The lattice term corresponds to the first term in brackets which does not contain any elastic property variables. That is, the relative velocity of the inclusion as a function of the two elastic moduli is $4\mu_1/[(3-\nu)\mu_0 + (1+\nu)\mu_1]$.

The approximate velocity for the surface diffusion mechanism is

$$v \approx \frac{D\Omega(1+\nu)\delta\gamma_\infty}{2RT r} \left[1 + \frac{4\mu_1}{(3-\nu)\mu_0 + (1+\nu)\mu_1} \right] \quad \text{surface} \quad (5.37)$$

Shown in [Fig. 5.13](#) are the verification of these two results. For the volume diffusion mechanism given in [Fig. 5.13a](#), the velocity relative the lattice is plotted after subtracting [Eq. \(5.21\)](#). As observed above, the case of a hole migrates at a speed half that of the

lattice. It is interesting that unlike conduction where a pore migrates faster than the lattice driven by temperature gradient or electric field, the pore migrates slower than the lattice driven by stress gradient. In addition, as the modulus of the inclusion increases relative to the matrix, the migration velocity also increases. This is also observed in Fig. 5.13b for surface diffusion. This contrasts the increasing conductivity of the inclusion which tends to decrease its migration velocity. The reason for this is explained recognizing that stress is analogous to heat flux and electric current. The driving force for diffusion is related to the temperature gradient or electric field in conduction but stress gradient in elasticity. In general, the greatest temperature gradient or electric field is observed when conductivity of the inclusion tends to become insulative such that the heat flux or current density goes towards zero. Conversely, the greatest stress observed is where the inclusion becomes more incompressible such that the strain is less. This permits a higher stress gradient to be transmitted across the inclusion.

Figure 5.13: Velocity of a cylindrical inclusion as a function of elastic modulus

5.5 Internal stress concentrations

Using the microelasticity model, it is possible to solve a wide range of elastic problems subjected to external loading. This includes microstructures with both inhomogeneous and anisotropic properties. Some particular examples of structural inhomogeneities include cracks, pores, and inclusions which have misfitting elastic moduli. Polycrystals of a particular material have orientation misfit through its anisotropy which contribute to its inhomogeneous structure. In addition, the model accounts for defects that contribute to stress-free strains that includes dilation misfit, for example, point defects and includes distortion misfit such as edge and screw dislocations. Listed in [Appendix A](#) are several examples of these kinds of defects and problems verified. Shown in [Fig. 5.14](#) is an overview of this modeling approach. [Figure 5.14a](#) summarizes all the types of problems the model is suited for. Solving for the elastic fields presents a new problem for visualizing the results. This is especially true for stress and strain which are second rank tensors. There are many ways to visualize the six independent components. For example, the result of stress in an isotropic acrylic model [\[147\]](#) is visualized in [Fig. 5.14b](#) using isochromatic (maximum shear stress) contours. This particular model, despite being isotropic and of homogeneous material, demonstrates the complexity of the stress state even at a larger scale compared to that of a microstructure. Thinking about the role stress and its gradient (which has 18-independent components) on diffusional processes, it even becomes more challenging to visualize and understand their role on migration behaviors.

(a) Solving for arbitrary anisotropic and inhomogeneous material systems

(b) Example visualizing isochromatic fringes of a photoelastic model

Figure 5.14: Microelasticity modeling

One way to graphically visualize stress in three-dimensions is using Lamé's stress ellipsoid which represents the principal stress magnitudes and directions in physical space [114]. However, it is generally difficult to visualize these as they vary across a microstructure, for example. Despite these difficulties, some simplification are achieved in two-dimensions using Mohr's circle where the two principal stress components and principal angle are

$$\sigma_1, \sigma_2 = \frac{\sigma_{11} + \sigma_{22}}{2} \pm \sqrt{\left(\frac{\sigma_{11} - \sigma_{22}}{2}\right)^2 + \sigma_{12}^2} \quad \text{and} \quad \tan 2\theta = \frac{2\sigma_{12}}{\sigma_{11} - \sigma_{22}}. \quad (5.38)$$

Other stress visualization includes von Mises stress [148]

$$\sigma = \frac{\sqrt{2}}{2} \sqrt{(\sigma_{11} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{11})^2 + 6(\sigma_{12}^2 + \sigma_{23}^2 + \sigma_{31}^2)}. \quad (5.39)$$

5.6 Elastic fields in tin polycrystals

Considering the two tin polycrystals from [Chapter 4](#), the stress and strain fields can be calculated under different loads. The elastic stiffness components for tin are given by $c_{11} = c_{22} = 7.35 \times 10^{10}$ Pa, $c_{33} = 8.7 \times 10^{10}$ Pa, $c_{44} = c_{55} = 2.2 \times 10^{10}$ Pa, $c_{66} = 2.265 \times 10^{10}$ Pa, $c_{12} = 2.34 \times 10^{10}$ Pa, and $c_{13} = c_{23} = 2.8 \times 10^{10}$ Pa [[149](#)]. The tin crystal is stiffest along its c -axis. In addition, the $[100]$ -direction is stiffer than along the $[110]$ -direction. The first case of the 3-grain polycrystal has central grain c -axis along the vertical direction and the surrounding grains in the horizontal direction. Conversely, the second case is the opposite where the central grain has its c -axis in the horizontal direction and the remaining grains perpendicular in the vertical direction. In the following examples, the internal von Mises stress and strain are in color and the internal principal stresses and strains are drawn at various locations similar to a vector field. The first case under tension and compression are shown in [Figs. 5.15](#) and [5.16](#). Similarly, the second case under tensile and compressive stresses are given in [Figs. 5.17](#) and [5.18](#). From the perspective of stress and strain magnitude, the case where the c -axis is perpendicular with the applied load gives the highest strain ([Figs. 5.15a](#) and [5.16a](#)) but lowest stress ([Figs. 5.15b](#) and [5.16b](#)) in the central grain. When it is parallel, the opposite is observed where the strain is lowest ([Figs. 5.17a](#) and [5.18a](#)) and stress is highest ([Figs. 5.17b](#) and [5.18b](#)). From tension to compression, the principal axis rotates by approximately 90° in each grain.

Figure 5.15: A tin polycrystal subjected to remote tensile stress with c -axis of the central grain in the specimen y -direction

Figure 5.16: A tin polycrystal subjected to remote compressive stress with c -axis of the central grain in the specimen y -direction

Figure 5.17: A tin polycrystal subjected to remote tensile stress with c -axis of the central grain in the specimen x -direction

Figure 5.18: A tin polycrystal subjected to remote compressive stress with c -axis of the central grain in the specimen x -direction

In the above examples, it is clear that the central grain experiences different states of stress that would lead to distortion of a pore or inclusion present within it. The stress and strains are highest at triple junctions, and, in particular, they are highest where the c -axis of the grains meet since they stiffer along that corresponding crystallographic direction. It is likely a migrating pore driven by migration will be affected greatly not only by the stresses at triple junctions but also across grain boundaries. Here, a pore at a grain boundary may become stuck and tend to deform along the boundary leading to intergranular fracture. In addition to tensile and compressive stress states given above, in-plane and out-of-plane shear stresses may be applied. In-plane shear is not shown since the particular arrangement of grains is effectively isotropic to in-plane shear loading. In other words, no internal stresses develop for these particular misfitting grains. The case of stress gradient by bending moment can also be considered. Shown in Figs. 5.19 and 5.20 are the two grain structures with gradient applied. In these examples, the color now corresponds to internal maximum shear strain (Figs. 5.19a and 5.20a) and stress (Figs. 5.19b and 5.20b) less the average gradient part. The streamlines also illustrate this type of internal distribution of strain and stress. They are the strain and stress trajectories [150]. The thicker lines correspond to the major principal plane axis while the thinner lines correspond to the minor principal plane axis. For the two different cases, it is clear an additional internal stress gradient develops inside the central grain. However, the direction of these internal stress gradients are in opposite directions across the grain. This will likely influence the migration behavior of pores across the grain driven by stress gradient.

Figure 5.19: A tin polycrystal subjected to remote stress gradient with c -axis of the central grain in the specimen y -direction

Figure 5.20: A tin polycrystal subjected to remote stress gradient with c -axis of the central grain in the specimen x -direction

Chapter 6

Conclusion

A multiphysics phase field model is developed to investigate electromigration behaviors in solder interconnect microstructures. In particular, the effects of thermal, electrical, and mechanical fields on the driving force for diffusion have been accounted for and investigated through simulation. The computer program has been developed to run on high-performance supercomputers and also has been extensively verified. Semi-implicit methods have also been developed to facilitate efficient solution of these fields that couple to the microstructure evolution equation through chemical diffusion. Appropriate analytical solutions have been utilized or derived to demonstrate fundamental migration behaviors related to heat and charge conduction and elastic deformation. Finally, the role of conductivity anisotropy has been investigated which is relevant to tin solder alloys.

6.1 Modeling

Mass diffusion is modeled through Fick's law of diffusion which relates the mass flux to the driving forces acting on each species by their mobility. In particular, binary systems are emphasized accounting both for the internal chemical potential describing their solution behavior and the driving forces due to multiphysical gradient fields including that of temperature, electrostatic potential, and stress. The evolution of microstructures follows conservation of chemical species. Both volume and surface diffusion mechanisms have been accounted for. The model is also capable of describing anisotropic mobility coefficients, if necessary.

Both heat and charge conduction have been appropriately modeled using microscopic Fourier's law of conduction and microscopic Ohm's law of conduction, respectively. The transient equations describing conservation of energy and charge have also been implemented using semi-implicit methods. In addition, the modeling of steady state conduction using a microelasticity-like approach has also been developed and verified allowing for new boundary conditions that include remote far-field heat fluxes and current densities in addition to remote far-field negative temperature gradients and electric fields. Their contributions for the driving force for diffusion have also been accounted for. This approach also allows for efficient incorporation of heat sources and sinks through Joule heating, for example.

Finally, elastic deformation under mechanical equilibrium has been implemented using microelasticity modeling making it possible to solve for the elastic fields in microstructures with inhomogeneous and anisotropic properties. In particular, it is possible to solve for microstructures subjected to external stress and strain fields. The incorporation of stress-free strains generated by misfitting defects is also accounted for. Semi-implicit methods have been implemented to improve the stability of the relaxation equations used to obtain the equilibrium fields. The microelasticity method has also been extended to account for body forces and external stress (and strain) gradients. The latter is used to demonstrate stress gradient driven migration behavior of pores and inclusions.

All of these models are combined into a computer program package developed to run on high-performance supercomputers. It is optimized and implemented with parallel programming support including OpenMP and MPI. It is also modular allowing for the concurrent solution of different fields together. The semi-implicit methods are applied to each solver module to speedup calculations by improving stability. The program has many tools to facilitate across-network simulations and transfers of data. This also includes tools for visualization. The program is built using a Makefile and can be run on many different machines including personal computer. An optional low-pass filter has also been incorporated to overcome difficulties associated with sharp boundaries to reduce Gibbs oscillations in computing the Discrete Fourier Transform. The program also utilizes GSL, FFTW, and other libraries for random number generator, linear algebra routines, and Fast Fourier transform algorithms.

6.2 Simulation

Pore and inclusion migration is extensively verified for conduction driven electromigration and temperature gradient driven migration. The velocity is verified for both volume and surface diffusion mechanisms. In addition, stress deformation and stress gradient migration is derived and simulated. Detailed simulations are carried out studying the role of electrical conductivity anisotropy in pore migration through tin polycrystals. Simulations detailing the migration path of pores across grain boundaries are shown along with their interactions near grain boundaries. These electrostatic interactions are revealed through the internal electric field which develops in response to property mismatches across phases in microstructure. Pore-pore interactions that tend to cause attraction or repulsion are also studied and analyzed in terms of distortion of the internal electric field between them. Their general interaction is compared to that of and explained by the forces between point dipoles. Finally, the role of grain orientation on their interactions is showcased.

This work is a significant extension of previous work on pore migration that focuses only on heat conduction in isotropic nuclear fuel materials. The incorporation of electric field effects offers new insights into the multiphysical processes that complicate the degradation behavior and performance of solder interconnects. Specifically, the incorporation of conductivity anisotropy. Anisotropic conductivity plays a larger role in electromigration

behavior due to the miniaturization trend of microelectronics where solder bumps contain only a few grains. This multiphysics modeling allows for the study of complicated interactions that arise from crystalline defects especially with polycrystalline β -tin solder alloys. The incorporation of elastic fields using microelasticity modeling is also another important development. Arguably one of the most important affecting microstructure evolution and morphology, stress is complicated whether considering the loading of microstructures by external fields by forces and moments or considering internal stresses generated by defects like edge and screw dislocations and point defects. All fit within the microelasticity framework. Simulations of stress fields in tin polycrystals are shown to demonstrate the complicated stress state inside polycrystals.

6.3 Analysis

Some new solutions for migration velocities of pores and inclusions have been developed both dealing with volume and surface diffusion mechanisms. Although being discussed in some detail, they are all listed here for completeness and summary. For the volume diffusion mechanism, the lattice velocity has been subtracted to obtain the relative velocity of the pore or inclusion. Without loss of generality, the migration velocity of a circular pore in an anisotropic conducting matrix due to externally applied field in the x_1 -direction

is given by the following. For heat conduction, the velocity is

$$v = \frac{N_A}{RT^2} \begin{bmatrix} D_{11} & D_{12} \\ D_{12} & D_{22} \end{bmatrix} \begin{bmatrix} Q_{11}^* & Q_{12}^* \\ Q_{12}^* & Q_{22}^* \end{bmatrix} \begin{bmatrix} \sqrt{\kappa_{11}/\kappa_{22} - \kappa_{12}^2/\kappa_{22}^2} \\ \kappa_{12}/\kappa_{22} \end{bmatrix} X_\infty \quad \text{volume} \quad (6.1)$$

$$v = \frac{N_A \delta}{RT^2 r} \begin{bmatrix} D_{11} & D_{12} \\ D_{12} & D_{22} \end{bmatrix} \begin{bmatrix} Q_{11}^* & Q_{12}^* \\ Q_{12}^* & Q_{22}^* \end{bmatrix} \begin{bmatrix} 1 + \sqrt{\kappa_{11}/\kappa_{22} - \kappa_{12}^2/\kappa_{22}^2} \\ \kappa_{12}/\kappa_{22} \end{bmatrix} X_\infty \quad \text{surface} \quad (6.2)$$

while for charge conduction it is given by

$$v = \frac{N_A e}{RT} \begin{bmatrix} D_{11} & D_{12} \\ D_{12} & D_{22} \end{bmatrix} \begin{bmatrix} Z_{11}^* & Z_{12}^* \\ Z_{12}^* & Z_{22}^* \end{bmatrix} \begin{bmatrix} \sqrt{\sigma_{11}/\sigma_{22} - \sigma_{12}^2/\sigma_{22}^2} \\ \sigma_{12}/\sigma_{22} \end{bmatrix} E_\infty \quad \text{volume} \quad (6.3)$$

$$v = \frac{N_A e \delta}{RT r} \begin{bmatrix} D_{11} & D_{12} \\ D_{12} & D_{22} \end{bmatrix} \begin{bmatrix} Z_{11}^* & Z_{12}^* \\ Z_{12}^* & Z_{22}^* \end{bmatrix} \begin{bmatrix} 1 + \sqrt{\sigma_{11}/\sigma_{22} - \sigma_{12}^2/\sigma_{22}^2} \\ \sigma_{12}/\sigma_{22} \end{bmatrix} E_\infty \quad \text{surface} \quad (6.4)$$

Here, both anisotropic diffusion and coupling coefficients have been provided. Additional analytical solutions derived for the migration velocity of an isotropic elliptical inclusion driven by heat and charge conduction have also been derived. They are given in the following where the external field is applied along the x_1 -direction which coincides with one of the semi-axes. For temperature gradients, the velocity is

$$v = \frac{DN_A Q^*}{RT^2} \left[\frac{b(\sigma_0 - \sigma_1)}{a\sigma_0 + b\sigma_1} \right] X_\infty \quad \text{volume} \quad (6.5)$$

$$v \approx \frac{DN_A Q^* \delta}{RT^2} \left[\frac{(a+b)\kappa_1}{b(a\kappa_0 + b\kappa_1)} \right] X_\infty \quad \text{surface} \quad (6.6)$$

while for electric fields it is

$$v = \frac{DN_A e Z^*}{RT} \left[\frac{b(\kappa_0 - \kappa_1)}{a\kappa_0 + b\kappa_1} \right] E_\infty \quad \text{volume} \quad (6.7)$$

$$v \approx \frac{DN_A e Z^* \delta}{RT} \left[\frac{(a+b)\sigma_0}{b(a\sigma_0 + b\sigma_1)} \right] E_\infty \quad \text{surface} \quad (6.8)$$

For these cases, although the external field is applied in the direction of one of the semi-axes, it can be further generalized for off-axis applied fields using superposition. That is, each component of velocity are independent in the isotropic case where each component of the external field tends to cause migration of the pore along that particular direction. Finally, the solution for an isotropic circular inclusion driven by stress gradient induced by a bending-like moment has been approximated for the volume and surface diffusion mechanism. It is given by

$$v \approx \frac{D\Omega(1+\nu)}{2RT} \left[\frac{4\mu_1}{(3-\nu)\mu_0 + (1+\nu)\mu_1} \right] \gamma_\infty \quad \text{volume} \quad (6.9)$$

$$v \approx \frac{D\Omega(1+\nu)\delta}{2RT r} \left[1 + \frac{4\mu_1}{(3-\nu)\mu_0 + (1+\nu)\mu_1} \right] \gamma_\infty \quad \text{surface} \quad (6.10)$$

This solution assumes that the inclusion has identical Poisson's ratio to that of the matrix. It also neglects any distortion behavior which is valid for small external stress gradients such that the distortion effects are not able to overcome surface energy effects tending to preserve its shape.

6.4 Outlook

Using the solutions derived for pores subjected to stress gradient, additional work is underway to analyze the migration velocities of pores in tin subjected to remote stress gradients taking into account the two grain structure cases. A similar approach deriving the analytical solutions for electric field inside pores present in anisotropic conducting matrices may be used to obtain the stress gradient at pore interfaces taking into account elastic stiffness anisotropy. Some work using this approach adapted to elasticity and stiffness anisotropy has shown to agree for the case of circular hole subjected to remote tensile stress using known solutions for anisotropic plates in the book by Lekhnitskii referenced in this work. A similar adaptation may prove to be useful for the stress gradient. In this derivation (not presented in this work), there are certain simplifying assumptions made about the extent of the anisotropic stiffness to make the analogy to electrical conductivity.

Aside from pores, other investigations focusing on inclusion electromigration may also be studied. For instance, the bismuth-tin system has recently attracted some attention. Due to its much simpler phase diagram than copper-tin, it may be a good system to investigate both in the available physical and thermodynamic properties for the two phase system. The basic idea is to simplify the systems studied to investigate fundamental electromigration behaviors. Other work for the vacancy-tin system can be investigated considering the migration behaviors with other defects present. For example, edge dislocations generate

hydrostatic stress gradients and may contribute to certain migration behaviors of pores and inclusions. As only elliptical and circular inclusion shapes have been considered, it is also possible to investigate more complicated shapes due to misfitting elastic constants. Finally, for both conduction and elasticity driven migration, the interactions defects like pores and free surfaces can also be considered.

As all the appropriate models have been developed into a complete and efficient computer program, there are many additional works and investigations that can be undertaken to study these fundamental electromigration behaviors. All of this work also fits into the larger picture of phase field modeling of microstructure evolution.

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Appendix A

Verification

Each solver is verified using known analytical solutions and shown below. There are two verification types: (1) lines across the domain to emphasize accuracy near and away from disturbances due to inclusions or inhomogeneities; and (2) points near interfaces or within these inclusions or inhomogeneities to verify relationships as function of parameters such as aspect ratio. For the former case, a grid size of 1024×1024 is used. The far-field analytical solution is resolved for the periodic boundary conditions by using the method of images where neighbors are constructed of tiled remote domain solutions out to 16 grids in both the positive and negative x_1 and x_2 directions. For the latter case, a grid size of 512×512 is used and only the single domain solution is used since the local features are negligibly affected by nearest image neighbors.

A.1 Mass diffusion

For diffusional processes, it is important to verify correct static interface shapes which are related to surface energy of at interfaces and volume energy within the bulk material. In addition, time rate of change of these interfaces are verified for accuracy using the semi-implicit method. There is always a trade-off between accuracy, efficiency, and stability. It is important to resolve the underlying microstructural processes, so accuracy is important. However, to achieve realistic and timely simulations a compromise must be made to efficiently solve the diffusion equation while maintaining stability.

The concentration profile of a cylindrical pore or inclusion is shown in Fig. A.1. The diffuse interface thickness is proportional to the square root of the gradient coefficient-barrier

Figure A.1: A cylindrical pore or inclusion

(a) Illustration of diffuse planar interface

(b) Comparison between analytical and numerical solution for diffuse planar interface thickness

Figure A.2: A planar interface

height ratio [151]. Shown in Fig. A.2 is the thickness of a planar interface as a function of this ratio which shows good agreement. For a remote pore or inclusion without any elasticity effects, the equilibrium shape is circular. Allowing a pore to take on a non-equilibrium elliptical pore shape, surface energy reduction drives the pore shape back to its equilibrium circular shape. Considering the two extreme cases of volume and surface diffusion mechanisms, both follow an exponential decay rate of the aspect ratio. In Fig. A.3 is a comparison of the analytical and numerical solutions for the time rate of change of the aspect ratio using the first order semi-implicit method using time step $h = 1 \times 10^{-5}$, weight $\alpha = 1.0$, and ratio $\kappa/f_0 a_0^2 = 5 \times 10^{-4}$. The numerical solution agrees well with the analytical solution.

Similarly, a sinusoidal interface representing a disturbance from a planar interface with amplitude decays exponentially at a rate related to its wavelength and the surface energy

Figure A.3: Comparison between analytical and numerical solution for aspect ratio of an elliptical pore using first order semi-implicit method

[80, 90, 152]. This analytical solution is an approximation and is not exact but serves as a good test for the time integration scheme. Comparisons of the first, second, and third order methods with time step $h = 1 \times 10^{-4}$ and weight $\alpha = 1.0$ are shown in Fig. A.4. Here, the mobility is everywhere constant. Each method shows good agreement so no additional accuracy is achieved with the second and third order methods. Thus, the first order method can be used which gives the best stability and efficiency. To establish the accuracy of the first order method, the decay of the sinusoidal interface is tracked for different weights and time steps. Shown in Fig. A.5a is the decay of the amplitude for weights $\alpha = 0.5$, $\alpha = 1.0$, and $\alpha = 1.5$ with time step $h = 1 \times 10^{-5}$. For larger values of α , the method is more stable but loses accuracy. In Fig. A.5b is the comparison of the numerical and analytical solution for time steps $h = 1 \times 10^{-4}$, $h = 1 \times 10^{-5}$, and $h = 1 \times 10^{-6}$ with weight $\alpha = 1.0$. For time step $h = 1 \times 10^{-4}$, the accuracy is not sufficient. However for $h = 1 \times 10^{-5}$, good agreement is achieved giving a speed-up of 10 over $h =$

1×10^{-6} which is required for the explicit first order method $\alpha = 0.0$. The sinusoidal interface also decays at an exponential rate for both the volume and surface diffusion mechanisms. Shown in Fig. A.6 are the numerical solutions compared to known analytical solution using the first order method. In both cases, the time step is $h = 1 \times 10^{-4}$, weight is $\alpha = 1.0$, and energy ratio is $\kappa/f_0 a_0^2 = 5 \times 10^{-4}$. For the surface diffusion mechanism, thickness of the interface comes into play.

Figure A.4: Comparison between analytical and numerical solution for a sinusoidal interface decaying amplitude

(a) Different weights

(b) Different steps

Figure A.5: Comparison between analytical and numerical solution for a sinusoidal interface decaying amplitude using first order semi-implicit method

(a) Volume diffusion mechanism

(b) Surface diffusion mechanism

Figure A.6: Comparison between analytical and numerical solution for a sinusoidal interface decaying amplitude using first order semi-implicit method

A.2 Charge conduction

For the motion of charges in an electrical conductors, charge-charge interactions are long-range. It is therefore helpful to verify the electric field in steady and transient problems due to the presence of charges and far-field uniform electric fields. In addition, the steady-state solutions of current density due to the presence of holes, inclusions, and cracks are also illustrated. Many solutions of charge conduction are shared by heat conduction problems.

The simplest case to verify the electric field is due to the presence of charge-charge interactions without conduction. Shown in Fig. A.7 is a uniformly charged circular cylinder. Inside the cylinder, the electric field varies linearly with the distance from its center. Outside the cylinder, the electric field is inversely proportional to the distance away from its center. Another case is to verify the electric field around a conducting cylinder which is initially uniform [56]. The verification is shown in Fig. A.8. The opposite case is a conducting matrix with a nonconducting cylinder [55] given in Fig. A.9. Inside the nonconducting cylinder, the magnitude of the electric field is twice that of the applied field. If the nonconducting cylinder takes on an elliptical cross section, the electric field inside is a function of the aspect ratio proportional to $1 + b/a$ [153] where the aspect ratio is b/a ; this is shown in Fig. A.10.

(a) Electric field emanating from a uniformly charged cylinder

(b) Comparison between analytical and numerical solution for electric field emanating from a uniformly charged cylinder

Figure A.7: A uniformly charged cylinder

(a) Electric field around a conducting cylinder

(b) Comparison between analytical and numerical solution for electric field across a conducting cylinder

Figure A.8: A conducting cylinder subjected to an initially uniform electric field

(a) Illustration of a nonconducting cylinder

(b) Comparison between analytical and numerical solution for electric field across a nonconducting elliptic cylinder

Figure A.9: A nonconducting cylinder subjected to a uniform electric field

(a) Electric field around a nonconducting elliptic cylinder

(b) Comparison between analytical and numerical solution for electric field inside a nonconducting elliptic cylinder

Figure A.10: A nonconducting elliptic cylinder subjected to a uniform electric field

Verifying the semi-implicit method is accomplished using the transient solution of the electric field inside a conducting cylinder due to an initially uniform field [56]. The electric field decays exponentially toward zero with decay rate proportional to the conductivity of the cylinder. Verification of the first, second, and third order methods is shown in Fig. A.11 where a time step of $h = 1 \times 10^{-3}$ with weight of $\alpha = 1.0$ is used. In general, the first order method is sufficient giving good accuracy with the best stability and efficiency properties.

Figure A.11: Comparison between analytical and numerical solution for electric field inside a conducting cylinder

To verify the electric field with respect to anisotropic electrical conductivity, a solution is derived mapping the anisotropic conductivity tensor to the solution of the electric field inside a nonconducting ellipse. Shown in Fig. A.12 are examples of the electric field dependence inside a nonconducting cylinder embedded inside a transversely isotropic matrix. The example includes various ratios of the principal conductivity coefficients where the field inside is proportional to $1 + \sqrt{\sigma_1/\sigma_2}$ when one of the principal axes is aligned with the applied field. Rotating the principal axes away from the applied field, the electric field is a function of the angle the principal axis makes with the external field direction. The two components of the electric field are proportional to $1 + \sqrt{\sigma_{11}/\sigma_{22} - \sigma_{12}^2/\sigma_{22}^2}$ in the direction of the applied field and σ_{12}/σ_{22} in the direction perpendicular to the applied field. The principal axes are at angle defined by $\tan 2\theta = 2\sigma_{12}/(\sigma_{11} - \sigma_{22})$. In this example, the principal components are held fixed using arbitrarily $\sigma_1/\sigma_2 = 2.0$.

Figure A.12: Comparison between analytical and numerical solution for electric field inside a nonconducting cylinder with a transversely isotropic matrix

The steady state module is verified for current density where an external far-field is applied. Cases verified include a circular cylindrical hole Fig. A.13, insulative inclusion Fig. A.14, conductive inclusion Fig. A.15, perfectly conducting inclusion Fig. A.16. Finally, streamlines of current density around a crack are shown in Fig. A.17. All show good agreement with the analytical solutions obtained from the analogous [113] micromechanics solutions [100]. For the first case, the maximum current density outside the hole is twice the magnitude of the applied field. Inside the perfectly conducting cylindrical inclusion, it is twice the magnitude of the applied field. In general, for a matrix of conductivity σ_0 and inclusion σ_1 , the current density inside is proportional to $1 - (\sigma_0 - \sigma_1)/(\sigma_0 + \sigma_1)$ and maximum outside is $1 + (\sigma_0 - \sigma_1)/(\sigma_0 + \sigma_1)$. In the case of the current density near a crack, the magnitude of the field tends toward infinity in linear conduction.

Figure A.13: A cylindrical hole subjected to remote far-field current density

(a) Streamlines of current density around a cylindrical inclusion

(b) Comparison between analytical and numerical solution for current density across a cylindrical inclusion

Figure A.14: An insulative cylindrical inclusion subjected to remote far-field current density

(a) Streamlines of current density around a cylindrical inclusion

(b) Comparison between analytical and numerical solution for current density across a cylindrical inclusion

Figure A.15: A conductive cylindrical inclusion subjected to remote far-field current density

(a) Streamlines of current density around a cylindrical inclusion

(b) Comparison between analytical and numerical solution for current density across a cylindrical hole

Figure A.16: A perfectly conducting cylindrical inclusion subjected to remote far-field current density

(a) Streamlines of current density around a crack

(b) Comparison between analytical and numerical solution for current density near a crack tip

Figure A.17: A crack subjected to remote far-field current density

A.3 Heat conduction

Many classic solutions are available for heat conduction problems due to its simplicity. Unlike electrical charge conduction where interactions are long range, the thermal interactions act locally are short range. Both steady and transient problems are verified due to uniform far-field thermal driving forces (negative temperature gradients) and heat fluxes which are verified for temperature, thermal driving force, and heat flux fields. For the steady problems, the solutions are similar to that of electrical conduction.

Under a uniform far-field temperature gradient, the isotherms are known around a circular cylinder in an isotropic conducting matrix [55]; this is shown in Fig. A.18. Inside the cylinder, the temperature varies linearly with the distance from the center. Outside the nonconducting cylinder in the direction of the applied temperature gradient field, the temperature varies inversely with the distance away from the edge of the cylinder. Considering a nonconducting elliptical cylinder, the negative temperature gradient inside in the direction of the applied field is related to the aspect ratio b/a and is proportional to $1 + b/a$ [153]. The perpendicular component of the negative temperature gradient is zero. This verification is displayed in Fig. A.19 and shows good agreement.

(a) Isotherms around a nonconducting cylinder

(b) Comparison between analytical and numerical solution for temperature across a nonconducting elliptic cylinder

Figure A.18: A nonconducting cylinder subjected to a uniform thermal driving force

(a) Illustration of a nonconducting elliptic cylinder

(b) Comparison between analytical and numerical solution for thermal driving force inside a nonconducting elliptic cylinder

Figure A.19: A nonconducting elliptic cylinder subjected to a uniform thermal driving force

To verify the numerical methods, the known transient solution of the temperature due to heat initially concentrated at a point flowing outward decays at an exponential rate [154]. For the first, second, and third order methods using a time step of $h = 1 \times 10^{-4}$, weight $\alpha = 1$, and thermal diffusivity $\kappa/\rho c_p = 0.2$ gives good accuracy. The first order method is typically sufficient and provides the best stability properties.

(a) Heat flow away from heat concentrated initially at a point

(b) First order semi-implicit method

(c) Second order semi-implicit method

(d) Third order semi-implicit method

Figure A.20: Comparison between analytical and numerical solution of decaying maximum temperature from heat concentrated initially at a point

To verify the thermal driving force with respect to anisotropic thermal conductivity, the solution derived for anisotropic electrical conductivity tensor is reused. Shown in Fig. A.21 are examples of the thermal driving force dependence inside a nonconducting cylinder embedded inside a transversely isotropic matrix. The example includes various ratios of the principal conductivity coefficients where the field inside is proportional to $1 + \sqrt{\kappa_1/\kappa_2}$ when one of the principal axes is aligned with the applied field. Rotating the principal axes away from the applied field, the thermal driving force is a function of the angle the principal axis makes with the external field direction. The two components of the thermal driving force are proportional to $1 + \sqrt{\kappa_{11}/\kappa_{22} - \kappa_{12}^2/\kappa_{22}^2}$ in the direction of the applied field and κ_{11}/κ_{22} in the direction perpendicular to the applied field. The principal axes are at angle defined by $\tan 2\theta = 2\kappa_{12}/(\kappa_{11} - \kappa_{22})$. In this example, the principal components are held fixed using arbitrarily $\kappa_1/\kappa_2 = 2.0$.

Figure A.21: Comparison between analytical and numerical solution for thermal driving force inside a nonconducting cylinder with a transversely isotropic matrix

Following the charge conduction cases for current density, the steady state module is verified for heat flux where an external far-field is applied. Cases verified include the same cases including a circular cylindrical hole [Fig. A.22](#), insulative inclusion [Fig. A.23](#), conductive inclusion [Fig. A.24](#), perfectly conducting inclusion [Fig. A.25](#). In addition, streamlines of heat flux around a crack are shown in [Fig. A.26](#). All show good agreement with the analytical solutions obtained from the analogous micromechanics solutions [113] which were first derived for heat conduction but equivalent to the charge conduction cases. For the first case, the maximum heat flux outside the hole is twice the magnitude of the applied field. Inside the perfectly conducting cylindrical inclusion, it is twice the magnitude of the applied field. In general, for a matrix of conductivity κ_0 and inclusion κ_1 , the heat flux inside is proportional to $1 - (\kappa_0 - \kappa_1)/(\kappa_0 + \kappa_1)$ and maximum outside is $1 + (\kappa_0 - \kappa_1)/(\kappa_0 + \kappa_1)$. In the case of the heat flux near a crack, the magnitude of the field tends toward infinity in linear conduction. Finally, the case of heat sources and sinks is verified in [Fig. A.27](#) which shows a cylinder generating heat uniformly; the cylinder has conductivity identical to that of the matrix. The solution is identical in form to the electric field outside a uniformly charged cylinder. Instead of the electric field, the heat flux emanates radially from the heat source/sink. Inside the cylinder, the heat flux varies linearly with distance from center. Outside in the matrix where there is no heat generation, the heat flux decays inversely with distance from the edge of the heat source/sink. The analogy of steady state conduction to electrostatics has the same equation form: $\nabla \cdot \mathbf{q} = \varphi$ for conduction and $\nabla \cdot \mathbf{E} = \rho/\epsilon_0$ for electrostatics.

(a) Streamlines of heat flux around a cylindrical hole

(b) Comparison between analytical and numerical solution for heat flux across a cylindrical hole

Figure A.22: A cylindrical hole subjected to remote far-field heat flux

(a) Streamlines of heat flux around a cylindrical inclusion

(b) Comparison between analytical and numerical solution for heat flux across a cylindrical inclusion

Figure A.23: An insulative cylindrical inclusion subjected to remote far-field heat flux

(a) Streamlines of heat flux around a cylindrical inclusion

(b) Comparison between analytical and numerical solution for heat flux across a cylindrical inclusion

Figure A.24: A conductive cylindrical inclusion subjected to remote far-field heat flux

(a) Streamlines of heat flux around a cylindrical inclusion

(b) Comparison between analytical and numerical solution for heat flux across a cylindrical inclusion

Figure A.25: A perfectly conducting cylindrical inclusion subjected to remote far-field heat flux

(a) Streamlines of heat flux around a crack

(b) Comparison between analytical and numerical solution for heat flux near a crack tip

Figure A.26: A crack subjected to remote far-field heat flux

(a) Streamlines of heat flux due to a cylinder generating uniform heat

(b) Comparison between analytical and numerical solution for heat flux across a cylinder generating uniform heat

Figure A.27: A cylinder generating uniform heat

A.4 Elastic deformation

Many solutions are known for inclusions or holes in a matrix with isotropic properties. The classical Kirsch solution first reported in 1898 for stress around a cylindrical hole subjected to uniaxial tension [155] is verified in Fig. A.28. The hoop stress is three times that of the applied uniaxial stress. Considering an inclusion embedded in the matrix, the equivalent inclusion method can be used to obtain the stress field solution [156]. A soft inclusion is shown in Fig. A.29 and a hard inclusion is shown in Fig. A.30. Considering the isotropic parameters, there are no simple expressions for the constant stress inside and maximum stress outside at the surface of hole; however, assuming $\nu = 1/4$ [157] for both phases, the stress inside is proportional to $1 - (\mu_0 - \mu_1)/(\mu_0 + 2\mu_1)$ where μ_0 and μ_1 are the shear modulus of the matrix and inclusion, respectively. Given Poisson's ratio, the other moduli (Young's modulus and the bulk modulus) of the two phases may also be substituted directly. Outside, the maximum stress is proportional to $1 + (\mu_0 - \mu_1)/(\mu_0 + 2\mu_1)$ using the same assumption. Shown in Fig. A.31 is a rigid inclusion embedded in a matrix under tension. Not only can uniaxial tensile stress be specified but also shear. Superimposing the solution for uniaxial tension and compression is equivalent to applied shear stress. These results are shown in Fig. A.32 for shear and Fig. A.33 for biaxial stress. Subjecting the hole to far-field pressure results in Fig. A.34. Conversely, pressurizing the hole gives Fig. A.35. Adding these two solutions gives uniform pressure in both the matrix and hole.

Figure A.28: A cylindrical hole subjected to remote far-field tensile stress

Figure A.29: A soft cylindrical inclusion subjected to remote far-field tensile stress

(a) Distribution of hoop stress around a cylindrical inclusion

(b) Comparison between analytical and numerical solution for stress across a cylindrical inclusion

Figure A.30: A hard cylindrical inclusion subjected to remote far-field tensile stress

(a) Distribution of hoop stress around a cylindrical inclusion

(b) Comparison between analytical and numerical solution for stress near a cylindrical inclusion

Figure A.31: A rigid cylindrical inclusion subjected to remote far-field tensile stress

(a) Distribution of hoop stress around a cylindrical hole

(b) Comparison between analytical and numerical solution for stress across a cylindrical hole

Figure A.32: A cylindrical hole subjected to remote far-field shear stress

(a) Distribution of hoop stress around a cylindrical hole

(b) Comparison between analytical and numerical solution for stress across a cylindrical hole

Figure A.33: A cylindrical hole subjected to remote far-field biaxial stress

(a) A cylindrical hole subjected to uniform pressure

(b) Comparison between analytical and numerical solution for stress across a cylindrical hole

Figure A.34: A cylindrical hole subjected to uniform pressure

(a) A pressurized cylindrical hole

(b) Comparison between analytical and numerical solution for stress across a cylindrical hole

Figure A.35: A pressurized cylindrical hole

Additional solutions for stress around holes and inclusions due to far-field tensile stress gradients are shown below. Lekhnitskii presents a solution for stress near a circular inclusion (or hole) at the interface corresponding to a bending moment [144]. The exact solution for the elastic fields due to a bending moment (or linear stress gradient) is known [145] and verified in Fig. A.36. The distribution of the hoop stress around the hole is illustrated. Its maximum tensile stress is at the top of the hole and is also equal and opposite to the maximum compression at the bottom of the hole. There are six places where the stress is zero around the hole. Every multiple of 45° from the horizontal gives maximum, minimum or zero hoop stress. Using the Airy stress function approach [146] to solve for the elastic fields for the hole subjected to linear stress gradient [145], unknown coefficients of the Airy stress function are found for the case of an inclusion in a matrix by equating the stress terms in the Lekhnitskii solution at the interface [144]. The solution of the stress inside the inclusion is determined by continuity of the stress traction vector and displacement vector field at the interface. It is assumed the stress inside the inclusion has the same form as the solution of stress in a uniform material due to linear stress gradient without inclusion or hole. This assumption is valid considering linear elasticity and that the inclusion is an ellipsoid (cylinder in plane strain or disk in plane stress). Ellipsoids have uniform fields inside when subjected to uniform fields [55, 56, 100]. Consider Curie's principle where the symmetry of stimuli are observed in the response [69]; it is reasonable to assume the same for linear fields. Figures A.37–A.39 show verification of the numerical solution with the derived analytical solution for a soft, hard, and rigid

(a) Distribution of hoop stress around a cylindrical hole

(b) Comparison between analytical and numerical solution for stress across a cylindrical inclusion

Figure A.36: A cylindrical hole subjected to remote far-field tensile stress gradient

(a) Distribution of hoop stress around a cylindrical inclusion

(b) Comparison between analytical and numerical solution for stress across a cylindrical inclusion

Figure A.37: A soft cylindrical inclusion subjected to remote far-field tensile stress gradient

inclusion, respectively.

(a) Distribution of hoop stress around a cylindrical inclusion

(b) Comparison between analytical and numerical solution for stress across a cylindrical inclusion

Figure A.38: A hard cylindrical inclusion subjected to remote far-field tensile stress gradient

(a) Distribution of hoop stress around a cylindrical inclusion

(b) Comparison between analytical and numerical solution for stress near a cylindrical inclusion

Figure A.39: A rigid cylindrical inclusion subjected to remote far-field tensile stress gradient

The next major advancement in stress analysis around holes is given by Inglis in 1913 [158]. The stress state around an elliptical hole in an isotropic matrix is mapped to the circular hole using elliptical coordinates. Figure A.40 shows the classical solution with biaxial stress state with both components equal in tension. This analysis allows any elliptical shape to be considered. In the limit of large or small aspect ratios, the ellipse becomes a crack. A mode I crack which is subjected to tensile stress is displayed in Fig. A.41. Similarly, a mode II crack which is subjected to in-plane shear stress is shown in Fig. A.42. Finally, a mode III crack which is subjected to anti-plane shear stress is given in Fig. A.43. These cracks correspond to opening, sliding, and tearing modes, respectively. In each of the crack solutions, the plastic zones are plotted each using von Mises yield criterion. Under uniaxial tension, the maximum hoop stress of the ellipse varies with $1 + 2b/a$ at the tip which is verified in Fig. A.44. Under shear stress, the maximum hoop stress is proportional to $(a + b)^2/ab$ [159] which is shown to agree in Fig. A.44. Here, the maximum stress is not necessarily at the ellipse tip; it is at an angle away defined by $\sin 2\beta = 2ab/(a^2 + b^2)$. In addition to the specification of remote external stress, a constant stress gradient can be applied which corresponds to a moment. An elliptical hole subject to far-field moment (stress gradient) has maximum hoop stress proportional to $1 + b/a$ at the vertex of the ellipse [144]. This verification is shown in Fig. A.46 for both ends of the ellipse. In general, the six unique stress or strain components can be applied. Similarly, there are 18 unique stress (or strain) gradient components that can be specified of which 12 are physically meaningful in the context of mechanical equilibrium.

(a) Distribution of hoop stress around an elliptical cylindrical hole

(b) Comparison between analytical and numerical solution for stress across an elliptical cylindrical hole

Figure A.40: An elliptical cylindrical hole subjected to remote far-field biaxial stress

(a) Plastic stress zones near a crack tip

(b) Comparison between analytical and numerical solution for stress near a crack tip

Figure A.41: A mode I crack subjected to tensile stress

(a) Plastic stress zones near a crack tip

(b) Comparison between analytical and numerical solution for stress near a crack tip

Figure A.42: A mode II crack subjected to in-plane shear stress

(a) Plastic stress zones near a crack tip

(b) Comparison between analytical and numerical solution for stress near a crack tip

Figure A.43: A mode III crack subjected to anti-plane shear stress

(a) Illustration of an elliptical cylindrical hole

(b) Comparison between analytical and numerical solution for stress across an elliptic cylindrical hole

Figure A.44: An elliptical cylindrical hole subjected to remote far-field tensile stress

(a) Illustration of an elliptical cylindrical hole

(b) Comparison between analytical and numerical solution for stress across an elliptic cylindrical hole

Figure A.45: An elliptical cylindrical hole subjected to remote far-field shear stress

Figure A.46: An elliptical cylindrical hole subjected to stress gradient moment

So far, only structural inhomogeneities have been verified. Another important class of problems involves elastic inhomogeneities corresponding to misfit strains. In these cases, the material everywhere is isotropic and there is some volume that has uniform inelastic strain. If this volume of strain takes on an elliptical shape, the stress inside is uniform and the stress outside can be found using Eshelby's methods. The stress solution of a cylindrical inhomogeneity with only in-plane normal strain is verified in Fig. A.47. Similarly, the case for a cylindrical inhomogeneity with out-of-plane normal strain is shown in Fig. A.48. The case for a cylindrical inhomogeneity with in-plane shear strain is shown in Fig. A.49 which is the rotated equivalent to a biaxial stress state with equal but opposite normal strain components given in Fig. A.50. A more realistic case corresponds to Fig. A.51 which has uniform dilation strain; this is typical for isotropic materials experiencing thermal expansion where the inclusion has identical properties of the matrix.

(a) Displacement around a cylindrical inhomogeneity

(b) Comparison between analytical and numerical solution for stress across a cylindrical inhomogeneity

Figure A.47: A cylindrical inhomogeneity with in-plane normal strain

(a) Displacement around a cylindrical inhomogeneity

(b) Comparison between analytical and numerical solution for stress across a cylindrical inhomogeneity

Figure A.48: A cylindrical inhomogeneity with out-of-plane normal strain

(a) Displacement around a cylindrical inhomogeneity

(b) Comparison between analytical and numerical solution for stress across a cylindrical inhomogeneity

Figure A.49: A cylindrical inhomogeneity with in-plane shear strain

(a) Displacement around a cylindrical inhomogeneity

(b) Comparison between analytical and numerical solution for stress across a cylindrical inhomogeneity

Figure A.50: A cylindrical inhomogeneity with biaxial shear strain, or equivalently in-plane shear strain at 45°

(a) Displacement around a cylindrical inhomogeneity

(b) Comparison between analytical and numerical solution for stress across a cylindrical inhomogeneity

Figure A.51: A cylindrical inhomogeneity with dilation strain

Other types of defects which can be modeled by the stress-free strains include dislocations [100] and point defects [160]. Two straight edge dislocation can either be attracting or repelling depending on whether they are on the same or different slip planes and direction of the Burgers vector $\mathbf{b}$. Cases are considered for an edge dislocation pair with anti-parallel Burgers vectors both with parallel slip planes. An attracting case with nonzero burgers vector component b_1 is shown in Fig. A.52 where the two dislocations lie on the same slip plane. A repelling case with nonzero burgers vector component b_2 is shown in Fig. A.53 where the two dislocations lie on different slip planes. Similarly, two straight screw dislocations attract each other with anti-parallel Burgers vector component b_3 shown in Fig. A.54. A point defect can be thought of as infinitesimal point where this a misfit of volume; the defect can be considered an elastic inclusion or rigid non-deforming inclusion. Both behave similarly and only affect the magnitude of the stress emanating away from the defect. Shown in Fig. A.55 are the stress components away from a point defect.

(a) Hydrostatic stress near an edge dislocation

(b) Comparison between analytical and numerical solution for stress near an edge dislocation

Figure A.52: An attracting edge dislocation pair on the same slip plane

(a) Hydrostatic stress near an edge dislocation

(b) Comparison between analytical and numerical solution for stress near an edge dislocation

Figure A.53: A repelling edge dislocation pair on different slip planes

(a) Shear stress near a screw dislocation

(b) Comparison between analytical and numerical solution for stress near a screw dislocation

Figure A.54: An attracting screw dislocation pair

(a) Illustration of a point defect

(b) Comparison between analytical and numerical solution for stress near a point defect

Figure A.55: A point defect

The solutions for stress inside an elliptical inhomogeneity in an anisotropic matrix is known [161, 162]. For simplicity, only two general cases are considered: elliptical inhomogeneities in an isotropic matrix and circular inhomogeneities in an anisotropic matrix. The strain components considered include in-plane normal, in-plane shear, and anti-plane shear strains. Shown in Fig. A.56 are the stress components inside an elliptical inclusion as a function of aspect ratio b/a . The anisotropic cases are verified both for a cubic crystal and transversely isotropic material.

Figure A.56: Comparison between analytical and numerical solution for stress inside an elliptical inhomogeneity

For the cubic crystal, in-plane normal and shear strains are verified for different Zener ratios $\alpha = 2c_{44}/(c_{11}-c_{12})$ and orientations of the matrix with respect to the strain component where $\alpha = 2.0$; results are summarized in Fig. A.57. For the transversely isotropic material, the anti-plane strain is verified for different ratios of c_{44}/c_{55} and orientations with ratio 2.0 which is displayed in Fig. A.58. A cylindrical inclusion with identical isotropic properties of the matrix subjected to uniform body force [163] is shown in Fig. A.58.

Figure A.57: Comparison between analytical and numerical solution for stress inside a cylindrical inhomogeneity with a cubic matrix

Figure A.58: Comparison between analytical and numerical solution for stress inside a cylindrical inhomogeneity with a transversely isotropic matrix

Figure A.59: A cylindrical body force

Appendix B

Programs

Each solver is built as a module and can be run independently or combined together. The number of threads are specified with an environment variable and tasks are specified at runtime. For example, 10 iterations using two threads and two tasks is run by

```
export OMP_NUM_THREADS=2  
mpirun -np 2 ./bin/volution 10
```

where the binary files are stored in the `bin/` directory. The `get/` directory has all input files while the folder `put/` contains the output files. Several hidden directories are used to save temporary files necessary for doing a transient restart. This means the simulation can be rerun with the same parameters and conditions at the end of a previous run.

Shown in [Fig. B.1](#) is the main parameter file where the variables for the simulation are specified. These parameters include the spatial size, temporal restart, material mapping, discrete Fourier transform filtering and performance, random number generator noise, and input/output variables.

```
# spatial variables

size-0 | (integer)
size-1 | (integer)
size-2 | (integer)

# temporal variables

restart      | (boolean)
restart-state | (boolean)
restart-time  | (integer)

# material variables

rotate | (boolean)
map    | (boolean)

# discrete fourier transform variables

filter  | (boolean)
wisdom  | (boolean)
patience | (boolean)

# random number generator variables

noise          | (boolean)
noise-period    | (integer)
noise-amplitude | (float)

# input/output variables

silent | (boolean)
text   | (boolean)
```

Figure B.1: Parameter input file

B.1 Mass diffusion

The solver input file and main program for mass diffusion is shown Fig. B.2 which requires the module `mod/fick.mod`.

initial conditions

```
steady-state      | (boolean)
steady-state-tolerance | (float)
```

temporal variables

```
time-step | (float)
time-period | (integer)
```

boundary conditions

```
external-0 | (float)
external-1 | (float)
external-2 | (float)
```

spatial variables

```
interactive-parameter | (float)
interface-parameter   | (float)
```

material variables

```
mobility | (integer)
constant | (float)
```

transient parameters

```
order | (integer)
weight | (float)
```

(a) Input file

program evolution

use fick

implicit none

integer(c_int) :: i

call solver_initialize()

call fick_initialize()

call fick_preprocess()

do i = 1, solver_steps()

call fick_solve()

call fick_postprocess()

end do

call fick_finalize()

call solver_finalize()

end program

(b) Main program

Figure B.2: Mass diffusion solver

B.2 Charge conduction

The solver input file and main program for mass diffusion is shown [Fig. B.3](#) which requires the module `mod/ohm.mod`.

```
# initial conditions
```

```
    steady-state      | (boolean)
    steady-state-tolerance | (float)
```

```
# temporal variables
```

```
    time-step | (float)
    time-period | (integer)
```

```
# boundary conditions
```

```
    external-0 | (float)
    external-1 | (float)
    external-2 | (float)
```

```
# transient parameters
```

```
    order | (integer)
    weight | (float)
```

```
# steady parameters
```

```
    penalty | (boolean)
    constant | (float)
```

(a) Input file

```
program revolution
```

```
    use ohm
```

```
    implicit none
```

```
    integer(c_int) :: i
```

```
    call solver_initialize()
```

```
    call ohm_initialize()
```

```
    call ohm_preprocess()
```

```
    do i = 1, solver_steps()
```

```
        call ohm_solve()
```

```
        call ohm_postprocess()
```

```
    end do
```

```
    call ohm_finalize()
```

```
    call solver_finalize()
```

```
end program
```

(b) Main program

Figure B.3: Charge conduction solver

B.3 Heat conduction

The solver input file and main program for mass diffusion is shown Fig. B.4 which requires the module `mod/fourier.mod`.

```
# initial conditions

    steady-state          | (boolean)
    steady-state-tolerance | (float)

# temporal variables

    time-step   | (float)
    time-period | (integer)

# boundary conditions

    external-0 | (float)
    external-1 | (float)
    external-2 | (float)

# transient parameters

    order | (integer)
    weight | (float)

# steady parameters

    penalty | (boolean)
    constant | (float)
```

(a) Input file

```
program devolution

    use fourier

    implicit none

    integer(c_int) :: i

    call solver_initialize()

    call fourier_initialize()

    call fourier_preprocess()

    do i = 1, solver_steps()

        call fourier_solve()

        call fourier_postprocess()

    end do

    call fourier_finalize()

    call solver_finalize()

end program
```

(b) Main program

Figure B.4: Heat conduction solver

B.4 Elastic deformation

The solver input file and main program for mass diffusion is shown Fig. B.5 which requires the module `mod/hooke.mod`.

<pre># initial conditions steady-state (boolean) steady-state-tolerance (float) # temporal variables time-step (float) time-period (integer) # boundary conditions external-0 (float) external-1 (float) external-2 (float) external-3 (float) external-4 (float) external-5 (float) external-00 (float) external-10 (float) external-20 (float) external-01 (float) external-11 (float) : external-25 (float)</pre>	<pre>program deconvolution use hooke implicit none integer(c_int) :: i call solver_initialize() call hooke_initialize() call hooke_preprocess() do i = 1, solver_steps() call hooke_solve() call hooke_postprocess() end do call hooke_finalize() call solver_finalize() end program</pre>
(a) Input file	(b) Main program

Figure B.5: Elastic deformation solver

Appendix C

Miscellanea

Some additional details are provided for clarification and completeness. This includes the derivation of the elastic strain energy contribution to the chemical potential which ultimately affects the driving force for diffusion. This involves taking the variational derivative of the energy functional. In addition, the details concerning the system subjected to external stress and strains are also discussed. This includes the macroscopic enthalpy and free energies. A brief description of the thermodynamic terms used throughout this work are summarized for clarity. Finally, derivations of solutions obtained for this work are discussed in some detail. This includes electric field inside a pore in an anisotropic conducting matrix and stress in and around an inclusion with isotropic elastic stiffness due to stress gradient. Some analysis of migration behavior is also discussed

C.1 Microelasticity

The elastic strain energy U for the equivalent system is identical to the original system.

For the equivalent system, it is given by the functional

$$U = \frac{1}{2} \int_{\Omega} c_{ijkl}^0 (\bar{\varepsilon}_{ij} + \delta\varepsilon_{ij} - \varepsilon_{ij}^0) (\bar{\varepsilon}_{kl} + \delta\varepsilon_{kl} - \varepsilon_{kl}^0) d^3\mathbf{r} \quad (\text{C.1})$$

where c_{ijkl}^0 is the reference stiffness tensor, $\bar{\varepsilon}_{ij}$ is the average strain given by the integral of the infinitesimal strain field ε_{ij} ; that is

$$\bar{\varepsilon}_{ij} = \frac{1}{V} \int_{\Omega} \varepsilon_{ij} d^3\mathbf{r}. \quad (\text{C.2})$$

Subtracting the average strain from the total field gives the spatially inhomogeneous field

$\delta\varepsilon_{ij} = \varepsilon_{ij} - \bar{\varepsilon}_{ij}$. Finally, ε_{ij}^0 is the stress-free eigenstrain. The elastic strain energy can be expanded out to

$$\begin{aligned} U = & \frac{V}{2} c_{ijkl}^0 \bar{\varepsilon}_{ij} \bar{\varepsilon}_{kl} + \frac{1}{2} \int_{\Omega} c_{ijkl}^0 \delta\varepsilon_{ij} \delta\varepsilon_{kl} d^3\mathbf{r} \\ & + \frac{1}{2} \int_{\Omega} c_{ijkl}^0 \varepsilon_{ij}^0 \varepsilon_{kl}^0 d^3\mathbf{r} - \int_{\Omega} c_{ijkl}^0 \bar{\varepsilon}_{ij} \varepsilon_{kl}^0 d^3\mathbf{r} - \int_{\Omega} c_{ijkl}^0 \varepsilon_{ij}^0 \delta\varepsilon_{kl} d^3\mathbf{r} \end{aligned} \quad (\text{C.3})$$

where V is the system volume. From the expansion, the term

$$\int_{\Omega} c_{ijkl}^0 \bar{\varepsilon}_{ij} \delta\varepsilon_{kl} d^3\mathbf{r} = 0 \quad (\text{C.4})$$

is omitted since the volume integral of inhomogeneous part of the strain field is zero by definition. From Parseval's formula, the two terms that depend on the infinitesimal part of the strain field can be represented in Fourier space according to

$$\int_{\Omega} c_{ijkl}^0 \delta \varepsilon_{ij} \delta \varepsilon_{kl} d^3 \mathbf{r} = \frac{1}{(2\pi)^3} \int_{\Omega} c_{ijkl}^0 \delta \varepsilon_{ij} \delta \varepsilon_{kl}^* d^3 \mathbf{k} \quad (\text{C.5})$$

$$\int_{\Omega} c_{ijkl}^0 \varepsilon_{ij}^0 \delta \varepsilon_{kl} d^3 \mathbf{r} = \frac{1}{(2\pi)^3} \int_{\Omega} c_{ijkl}^0 \varepsilon_{ij}^0 \delta \varepsilon_{kl}^* d^3 \mathbf{k} \quad (\text{C.6})$$

where the asterisk $*$ represents the complex conjugate and the vector $\mathbf{k}$ is the spatial frequency. Using the identity for infinitesimal strain field

$$\delta \varepsilon_{ij}(\mathbf{r}) \delta \varepsilon_{kl}(\mathbf{r}) = \frac{\partial u_i}{\partial x_j} \frac{\partial u_k}{\partial x_l}, \quad (\text{C.7})$$

it can be shown in Fourier space that the term in Eq. (C.5) is

$$\delta \varepsilon_{ij}(\mathbf{k}) \delta \varepsilon_{kl}^*(\mathbf{k}) = k_j k_n c_{mnpq}^0 \varepsilon_{pq}^0(\mathbf{k}) G_{jm}(\mathbf{k}) k_k k_s c_{rstu}^0 \varepsilon_{tu}^{0*}(\mathbf{k}) G_{lr}(\mathbf{k}) \quad (\text{C.8})$$

where G_{ij} is Green's tensor. It is recalled that the inverse Green's tensor is defined according to $G_{ij}^{-1}(\mathbf{k}) = k_k k_l c_{ikjl}^0$. In addition, the term in Eq. (C.6) is expressed as

$$\varepsilon_{ij}^0(\mathbf{k}) \delta \varepsilon_{kl}^*(\mathbf{k}) = \varepsilon_{ij}^0(\mathbf{k}) k_n c_{mnpq}^0 \varepsilon_{pq}^{0*}(\mathbf{k}) [k_k G_{lm}(\mathbf{k}) + k_l G_{km}(\mathbf{k})]. \quad (\text{C.9})$$

Using the inverse Green's tensor, it can be shown that two terms expressed in Eqs. (C.5) and (C.6) are actually equivalent such that

$$\int_{\Omega} c_{ijkl}^0 \delta \varepsilon_{ij} \delta \varepsilon_{kl} d^3 \mathbf{r} = \int_{\Omega} c_{ijkl}^0 \varepsilon_{ij}^0 \delta \varepsilon_{kl} d^3 \mathbf{r} = \frac{1}{(2\pi)^3} \int_{\Omega} k_i c_{ijkl}^0 \varepsilon_{kl}^0 G_{jm} c_{mnpq}^0 k_n \varepsilon_{pq}^{0*} d^3 \mathbf{k}. \quad (\text{C.10})$$

This simplification reduces the number of terms in the strain energy functional from five to four terms. The strain energy functional simplifies to

$$U = \frac{V}{2} c_{ijkl}^0 \bar{\varepsilon}_{ij} \bar{\varepsilon}_{kl} - \frac{1}{16\pi^3} \int_{\Omega} k_i c_{ijkl}^0 \varepsilon_{kl}^0 G_{jm} c_{mnpq}^0 k_n \varepsilon_{pq}^{0*} d^3 \mathbf{k} + \frac{1}{2} \int_{\Omega} c_{ijkl}^0 \varepsilon_{ij}^0 \varepsilon_{kl}^0 d^3 \mathbf{r} - \int_{\Omega} c_{ijkl}^0 \bar{\varepsilon}_{ij} \varepsilon_{kl}^0 d^3 \mathbf{r} \quad (\text{C.11})$$

which now depends only on the stress-free strain and the average strain. The stress free strain is a function describing the misfit strain which is material dependent. It can be due to thermal, chemical, magnetic, or electrical effects. In the context of diffusion, it is often written as $\varepsilon_{ij}^0 = \eta_{ij}(X - X_0)$ where X is the mole fraction and X_0 is a reference equilibrium composition. Recalling for externally applied fields, the average strain is represented as either

$$\bar{\varepsilon}_{ij} = \begin{cases} \bar{\varepsilon}_{ij}^0 + s_{ijkl}^0 \sigma_{kl}^{\infty} & \text{stress-controlled} \\ \bar{\varepsilon}_{ij}^0 + \varepsilon_{ij}^{\infty} & \text{strain-controlled} \end{cases} \quad (\text{C.12})$$

where σ_{ij}^{∞} and $\varepsilon_{ij}^{\infty}$ are the external stress and strain, respectively. Taking the functional derivative of the elastic strain energy, it can be shown that

$$\boxed{\frac{\delta U}{\delta \varepsilon_{ij}^0} = -\sigma_{ij}}. \quad (\text{C.13})$$

This important identity is useful in describing the role of elastic strain energy in microstructural processes. Supposing that the stress-free strain depends on some parameter η where $\varepsilon_{ij}^0 = \varepsilon_{ij}^0(\eta)$, the chain rule identity

$$\frac{\delta U}{\delta \eta} = \frac{\delta U}{\delta \varepsilon_{ij}^0} \frac{\delta \varepsilon_{ij}^0}{\delta \eta} \quad (\text{C.14})$$

can be used to evaluate the functional derivative with respect to the order parameter. For diffusional processes, the order parameter is the composition c such that

$$\frac{\delta U}{\delta c} = \frac{1}{c_0} \frac{\delta U}{\delta X} = -\frac{1}{c_0} \eta_{ij} \sigma_{ij}. \quad (\text{C.15})$$

The chemical potential can be defined by any of the thermodynamic potentials including internal strain energy U , enthalpy H , Helmholtz free energy F , or Gibbs free energy G . In particular, it is given by the partial differentials molar amount of component n

$$\mu_k = \left(\frac{\partial U}{\partial n_k} \right)_{S, \varepsilon_{\infty}, n_{j \neq k}} \quad \mu_k = \left(\frac{\partial F}{\partial n_k} \right)_{T, \varepsilon_{\infty}, n_{j \neq k}} \quad \text{strain-controlled} \quad (\text{C.16})$$

$$\mu_k = \left(\frac{\partial H}{\partial n_k} \right)_{S, \sigma_{\infty}, n_{j \neq k}} \quad \mu_k = \left(\frac{\partial G}{\partial n_k} \right)_{T, \sigma_{\infty}, n_{j \neq k}} \quad \text{stress-controlled} \quad (\text{C.17})$$

where T and S are the temperature and entropy, respectively. For a stress-controlled system, the enthalpy includes internal energy and work required to achieve its macroscopic strain under constant load $H = U - V \sigma_{ij}^{\infty} \bar{\varepsilon}_{ij}$. In this case, the average strain is $\bar{\varepsilon}_{ij}^0 + s_{ijkl}^0 \sigma_{kl}^{\infty}$,

specifically

$$\bar{\varepsilon}_{ij}^0 = \frac{1}{V} \int_{\Omega} \varepsilon_{ij}^0 d^3\mathbf{r} = \frac{1}{V} \int_{\Omega} \eta_{ij} (X - X_0) d^3\mathbf{r}. \quad (\text{C.18})$$

The enthalpy can be expanded according to $H = U - V\sigma_{ij}^{\infty}\bar{\varepsilon}_{ij}^0 - Vs_{ijkl}^0\sigma_{ij}^{\infty}\sigma_{kl}^{\infty}$; taking the variational derivative gives

$$\frac{\delta H}{\delta c} = \frac{1}{c_0} \frac{\delta H}{\delta X} = -\frac{1}{c_0} \eta_{ij} \sigma_{ij} - \frac{1}{c_0} \eta_{ij} \sigma_{ij}^{\infty}. \quad (\text{C.19})$$

Although there is an additional term, its gradient is zero if η_{ij} is everywhere constant. This term is often neglected or overlooked. The above two results for internal energy and enthalpy hold in the case of isentropic (adiabatic) conditions. Considering the Helmholtz free energy $F = U - TS$ and Gibbs free energy $G = H - TS$, the same respective results are obtained under isothermal conditions. For a binary system at constant temperature and stress, the Gibbs free energy is $G = \mu_j n_j + \mu_k n_k$ where n_j and n_k are the molar amount of component j and k , respectively. Similarly, the volumetric Gibbs free energy is $G_v = \mu_j c_j + \mu_k c_k$. Using the typically defined parameters for a binary system including potential $\mu \equiv \mu_k - \mu_j$, reference amount $n \equiv n_k$ and composition $c \equiv c_k$, the chemical potential is given by

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{T, \sigma_{\infty}} = \left(\frac{\partial G_v}{\partial c} \right)_{T, \sigma_{\infty}} = \frac{1}{c_0} \left(\frac{\partial G_v}{\partial X} \right)_{T, \sigma_{\infty}}. \quad (\text{C.20})$$

This suggests that for a binary system, the chemical potential is indeed the functional derivative

$$\mu = \frac{1}{c_0} \frac{\delta G}{\delta X}. \quad (\text{C.21})$$

C.2 Thermodynamics

In dealing with both microscopic and macroscopic thermodynamics, there are several terms introduced and used that should not be confused. In particular, the thermodynamics of microscopic crystals often involves volumetric terms that are used to describe variations of that particular term throughout the material that may be integrated to obtain the standard macroscopic form. Similarly, specific (per unit mass) quantities are often used to describe microscopic transport processes while molar (per unit mole) are used in chemistry. All of these terms are briefly summarized below in [Table C.1](#). It is noted that the specific volume is the reciprocal of the mass density $v = 1/\rho$, and there is no dimensionless “volumetric volume” term generally defined or used. It is, therefore, omitted from [Table C.1](#).

Table C.1
Summary of thermodynamic quantities

Quantity	Macroscopic	Molar	Volumetric	Specific
Internal energy	U	U_m	U_v	u
Enthalpy	H	H_m	H_v	h
Helmholtz free energy	F	F_m	F_v	f
Gibbs free energy	G	G_m	G_v	g
Work	W	W_m	W_v	w
Heat	Q	Q_m	Q_v	q
Entropy	S	S_m	S_v	s
Heat capacity	C	C_m	C_v	c
Volume	V	V_m		v

C.3 Solutions

The problem of finding the electric field inside a circular pore or hole in an anisotropic conducting matrix can be found using the solution of an elliptical hole in an isotropic matrix and coordinate transformation. This is illustrated in Fig. C.1. The electric field inside an elliptical cylindrical hole in an isotropic matrix [113] is given by

$$\frac{E_1}{E_\infty} = \left(1 + \frac{b}{a}\right) \cos \alpha \quad \text{and} \quad \frac{E_2}{E_\infty} = \left(1 + \frac{a}{b}\right) \sin \alpha \quad (\text{C.22})$$

where the applied field is along the x_1 -axis. Figure C.1a shows an illustration of this. Here, the angle α represents misorientation of the major and minor axes of the ellipse which is equivalent to applying a field along both axes where

$$(E_1^\infty)' = E_\infty \cos \alpha, \quad (E_2^\infty)' = E_\infty \sin \alpha, \quad \text{and} \quad \tan \alpha = \frac{(E_2^\infty)'}{(E_1^\infty)'}. \quad (\text{C.23})$$

For the anisotropic case shown in Fig. C.1b, steady state charge conduction follows

$$\frac{\partial}{\partial x_i} \left(\sigma_{ij} \frac{\partial \phi}{\partial x_j} \right) = 0 \quad (\text{C.24})$$

where σ_{ij} is the electrical conductivity tensor and ϕ is the electrostatic potential. The conductivity in the anisotropic space can be written as a transformation of the isotropic

Figure C.1: The solution of the electric field inside an elliptical hole in an isotropic matrix can be transformed into a circular hole in an anisotropic matrix

conductivity according to

$$\sigma'_{kl} = L_{ki} \sigma_{ij} L_{lj}. \quad (\text{C.25})$$

Here, L_{ij} is the transformation tensor. Explicitly, the conductivity matrices for the isotropic and anisotropic case can be written, respectively, as

$$\sigma'_{ij} = \begin{bmatrix} 1 & 0 & 0 \\ & 1 & 0 \\ & & 1 \end{bmatrix} \quad \text{and} \quad \sigma_{ij} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & 0 \\ & \sigma_{22} & 0 \\ & & \sigma_{33} \end{bmatrix}. \quad (\text{C.26})$$

The anisotropic case considered has in-plane off-diagonal components, only. The transformation can be decomposed into two parts: a circle into ellipse with semi axis lengths $a = 1/\sqrt{\sigma_1}$ and $b = 1/\sqrt{\sigma_2}$ related to the principal conductivity values; and a rotation by principal angle θ . This is illustrated in Fig. C.2 and is represented by the transformation matrix given by

$$L_{ij} = \begin{bmatrix} 1/\sqrt{\sigma_1} & 0 & 0 \\ 0 & 1/\sqrt{\sigma_2} & 0 \\ 0 & 0 & 1/\sqrt{\sigma_3} \end{bmatrix} \begin{bmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (\text{C.27})$$

Figure C.2: Transformation of a circular cylinder into an elliptical cylinder

Using the electric field inside an elliptical cylinder, the angle of misorientation is related to the principal angle by the relation

$$\alpha = -\arctan\left(\frac{b}{a} \tan \theta\right). \quad (\text{C.28})$$

Putting all this together, the electric field inside a circular cylindrical pore in an anisotropic matrix is found to be after simplification

$$\frac{E_1}{E_\infty} = 1 + \sqrt{\frac{\sigma_{11}}{\sigma_{22}} - \left(\frac{\sigma_{12}}{\sigma_{22}}\right)^2} \quad \text{and} \quad \frac{E_2}{E_\infty} = \frac{\sigma_{12}}{\sigma_{22}}. \quad (\text{C.29})$$

By analogy, the thermal driving force (negative temperature gradient) has identical solution form; that is,

$$\frac{X_1}{X_\infty} = 1 + \sqrt{\frac{\kappa_{11}}{\kappa_{22}} - \left(\frac{\kappa_{12}}{\kappa_{22}}\right)^2} \quad \text{and} \quad \frac{X_2}{X_\infty} = \frac{\kappa_{12}}{\kappa_{22}}. \quad (\text{C.30})$$

The problem of the stress near an inclusion in an isotropic matrix due to stress gradient is solved using the Airy stress function [146]. The function expresses the equations of mechanical equilibrium in two-dimensions according to the biharmonic equation given

in Cartesian coordinates by

$$\frac{\partial^4 \phi}{\partial x^4} + \frac{\partial^4 \phi}{\partial x^2 \partial y^2} + \frac{\partial^4 \phi}{\partial y^4} = 0. \quad (\text{C.31})$$

The stresses can be obtained by differentiating the Airy stress function

$$\sigma_{xx} = \frac{\partial^2 \phi}{\partial y^2} \quad \sigma_{yy} = \frac{\partial^2 \phi}{\partial x^2} \quad \sigma_{xy} = -\frac{\partial^2 \phi}{\partial x \partial y} \quad (\text{C.32})$$

The form [145] of the Airy stress function in the matrix is taken as the Michell solution which is the general solution in polar coordinates

$$\phi = \frac{\gamma_\infty}{24} \left[3r^3 \sin \theta - r^3 \sin 3\theta + \frac{Aa^4 \sin \theta}{r} + \frac{Ba^6 \sin 3\theta}{r^3} + \frac{Ca^4 \sin 3\theta}{r} \right] \quad (\text{C.33})$$

where the coefficients A , B , and C are unknown and represent the disturbance of the inclusion. These three terms all go toward zero in the limit of large distances away from the inclusion as they contain $1/r$ terms such that only the first two terms of the uniform stress gradient remain. The corresponding polar stress components can be found according to

$$\sigma_{rr} = \frac{1}{r} \frac{\partial \phi}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \phi}{\partial \theta^2} \quad \sigma_{\theta\theta} = \frac{\partial^2 \phi}{\partial r^2} \quad \sigma_{r\theta} = \frac{1}{r^2} \frac{\partial \phi}{\partial \theta} - \frac{1}{r} \frac{\partial^2 \phi}{\partial r \partial \theta} \quad (\text{C.34})$$

after coordinate transformation. Similarly, the corresponding polar strain components are found by differentiating the displacement vector. In this case, the displacement vector

is also in polar coordinates. The strain components are

$$\varepsilon_{rr} = \frac{\partial u_r}{\partial r} \quad \varepsilon_{\theta\theta} = \frac{1}{r} \frac{\partial u_\theta}{\partial \theta} + \frac{u_r}{r} \quad \varepsilon_{r\theta} = \frac{1}{2} \left(\frac{1}{r} \frac{\partial u_r}{\partial \theta} + \frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r} \right) \quad (\text{C.35})$$

The polar displacement vector is given by

$$u_r = \frac{\gamma_\infty}{48\mu_0} \left[3r^2 \sin 3\theta + 3(\kappa_0 - 2)r^2 \sin \theta + \frac{Aa^4 \sin \theta}{r^2} + \frac{3Ba^6 \sin 3\theta}{r^4} + \frac{Ca^4(\kappa_0 + 2) \sin 3\theta}{r^2} \right] \quad (\text{C.36})$$

$$u_\theta = \frac{\gamma_\infty}{48\mu_0} \left[3r^2 \cos 3\theta - 3(\kappa_0 + 2)r^2 \cos \theta - \frac{Aa^4 \cos \theta}{r^2} - \frac{3Ba^6 \cos 3\theta}{r^4} + \frac{Ca^4(\kappa_0 + 2) \cos 3\theta}{r^2} \right] \quad (\text{C.37})$$

where the parameter κ is Muskhelishvili's coefficient [157] which is $\kappa = 3 - 4\nu$ in plane strain and $\kappa = (3 - \nu)/(1 + \nu)$ in plane stress. From the solution at the edge of the inclusion in the matrix [144], the parameters are found to be

$$A = \frac{3[\mu_1(\kappa_1 - 7)(\kappa_0 + 9) - \mu_0(\kappa_1 + 9)(\kappa_0 - 7)]}{(\kappa_0 - 7)[\mu_1(\kappa_1 - 7) - \mu_0(\kappa_1 + 9)]} \quad (\text{C.38})$$

$$B = -\frac{2(\kappa_0 - 7)(\mu_1 - \mu_0)}{\mu_1(\kappa_0 + 9) - \mu_0(\kappa_0 - 7)} \quad (\text{C.39})$$

$$C = \frac{3(\kappa_0 - 7)(\mu_1 - \mu_0)}{\mu_1(\kappa_0 + 9) - \mu_0(\kappa_0 - 7)} \quad (\text{C.40})$$

which reduce to $A = 3$, $B = -2$, and $C = 3$ in the limit of a hole ($\mu_1 = 0$) and $A = 0$, $B = 0$, and $C = 0$ in the limit of no inclusion ($\mu_0 = \mu_1$ and $\kappa_0 = \kappa_1$). To find the stress inside the inclusion, it is recognized that the stress traction vector must be continuous across

the inclusion. For a circular inclusion, this means only the radial and shear stress are continuous across the inclusion. Assuming the Airy stress function inside the inclusion has the same form as the remote gradient, it can be written according to

$$\phi = \frac{Y_\infty}{24}(3Ur^3 \sin \theta - Vr^3 \sin 3\theta) \quad (\text{C.41})$$

where U and V are unknown coefficients. The corresponding displacement components are given by

$$u_r = \frac{Y_\infty}{48\mu_0}(3Vr^2 \sin 3\theta + 3U(\kappa_0 - 2)r^2 \sin \theta) \quad (\text{C.42})$$

$$u_\theta = \frac{Y_\infty}{48\mu_0}(3Vr^2 \cos 3\theta - 3U(\kappa_0 + 2)r^2 \cos \theta) \quad (\text{C.43})$$

Equating the stress between the inclusion and matrix for the radial and shear components, the unknown coefficients are found to be

$$U = -\frac{16\mu_1(\kappa_1 - 7)}{(\kappa_0 - 7)[\mu_1(\kappa_1 - 7) - \mu_0(\kappa_1 + 9)]} \quad (\text{C.44})$$

$$V = \frac{16\mu_1}{\mu_1(\kappa_0 + 9) - \mu_0(\kappa_0 - 7)} \quad (\text{C.45})$$

which reduce to $U = 0$ and $V = 0$ in the case of a hole ($\mu_1 = 0$) and $U = 1$ and $V = 1$ in the case of no inclusion ($\mu_0 = \mu_1$ and $\kappa_0 = \kappa_1$). These solutions agree in the two limiting cases [145] and that of [144]. This new solution can be used to obtain the stress gradient at the inclusion interface.

The analysis of pore or inclusion behavior can be analyzed in terms of its interface velocity. These velocities can be decomposed into three modes: volume changes under constant shape and position (dilations); center shift under constant shape and volume (translations), and shape changes under constant volume and position (distortions). This is illustrated in Fig. C.3 which show the expansion of the horizontal surface normal component of an ellipse into Chebyshev polynomials. For circular shapes, these modes for the

Figure C.3: Evolution of a pore/inclusion due to interface normal velocity expanded in terms of Chebyshev polynomials (adapted from Olander [2])

horizontal component expansion correspond to $\cos n\theta$ where n is any nonnegative integer. Here $n = 0$ corresponds to dilation, $n = 1$ to translation, and $n \geq 2$ to distortion modes. As an expression, the normal velocity is

$$v_n = A_0 + \sum_{n=1}^{\infty} A_n \cos n\theta \quad (\text{C.46})$$

which takes the form of a Fourier cosine series. As mentioned above, this is really the expansion of the components in terms of Chebyshev polynomials. The first few Chebyshev

polynomials of the first kind [63] are given by

$$T_0(x) = 1 \quad \text{dilation} \quad (\text{C.47})$$

$$T_1(x) = x \quad \text{translation} \quad (\text{C.48})$$

$$T_2(x) = 2x^2 - 1 \quad \text{distortion} \quad (\text{C.49})$$

$$T_3(x) = 4x^3 - 3x \quad \text{distortion} \quad (\text{C.50})$$

$$\vdots \quad \text{distortion} \quad (\text{C.51})$$

where the next polynomial is given by the recurrence relation $T_{n+1} = 2xT_n(x) - T_{n-1}(x)$. Substituting $x = n_x = \cos \theta$ gives $T_n(\cos \theta) = \cos n\theta$. For an elliptical inclusion with semi-axes a and b , the normal components are $n_x = (b \cos \theta) / \sqrt{b^2 \cos^2 \theta + a^2 \sin^2 \theta}$ and $n_y = (a \sin \theta) / \sqrt{b^2 \cos^2 \theta + a^2 \sin^2 \theta}$ which reduce to $n_x = \cos \theta$ and $n_y = \sin \theta$ in the limit of a circle ($a = b$). Letting $x = n_x$ as before, the velocity of the normal component in terms of the polynomials can be written as

$$v_n = A_0 + \sum_{n=1}^{\infty} A_n T_n(n_x). \quad (\text{C.52})$$

For example, the rigid horizontal translation component is given by $T_1(n_x) = (b \cos \theta) / \sqrt{b^2 \cos^2 \theta + a^2 \sin^2 \theta}$. Similarly, the first horizontal distortion component for the ellipse is $T_2(n_x) = (b^2 \cos^2 \theta - a^2 \sin^2 \theta) / (b^2 \cos^2 \theta + a^2 \sin^2 \theta)$. Because the Chebyshev polynomials are orthogonal [63], the only term that contributes to the average velocity of

the inclusion or pore is the $n = 1$ term. The orthogonality can be expressed by the integral

$$\int_{-1}^1 \frac{T_m(x)T_n(x)}{\sqrt{1-x^2}} dx = \begin{cases} 0 & \text{if } n \neq m \\ \frac{\pi}{2} & \text{if } n = m \neq 0 \\ \pi & \text{if } n = m = 0 \end{cases} \quad (\text{C.53})$$

which can be transformed to polar angle coordinates using the transformation $\theta = \varphi(x) = 2 \arcsin x$ such that $\varphi'(x) = 2/\sqrt{1-x^2}$ and $d\theta = 2/\sqrt{1-x^2} dx$. In addition, evaluating the original limits of integration gives new interval from $\theta = \varphi(x = -1) = -\pi$ to $\theta = \varphi(x = 1) = \pi$. This transformation is chosen to correspond integration around the entire edge of the pore/inclusion. Recalling that the vector normal velocity is found from $\mathbf{v}_n = v_n \mathbf{n}$, the average velocity in the horizontal direction can be found by integrating around the edge of the pore/inclusion. Using this transformation results in

$$\bar{v}_x^n = \frac{1}{2\pi} \int_{-\pi}^{\pi} v_n n_x d\theta = A_1 \frac{b}{a+b} T_1(n_x). \quad (\text{C.54})$$

The division by 2π is since the average is around the entire pore/inclusion. This means only the $n = 1$ term of the normal velocity expansion contributes to the average velocity. In other words, normal velocities that contain $(b \cos \theta)/\sqrt{b^2 \cos^2 \theta + a^2 \sin^2 \theta}$ terms are related to the average horizontal velocity. All others are negligible. So far, only the normal velocity has only been expanded using the horizontal component. The vertical component can also be used using similar procedures. For a circle, $\sin n\theta$ results in translations in the

vertical direction ($n = 1$) and distortions $n \geq 2$. Of course, $n = 0$ results in no changes (the volume part in the $n = 0$ cosine term). In this case, the expansion is now in terms of a Fourier series with even (cosine) and odd (sine) modes. The extension to an elliptical pore can also be considered with some additional care.