# Contents

Acknowledgements .......................................................... i

Abstract ............................................................................. iii

List of Tables ...................................................................... viii

List of Figures ..................................................................... xiii

1 Introduction ....................................................................... 1
   1.1 Phase separation and coarsening ........................................ 2
   1.2 Cahn-Hilliard and Phase Field Modelling ............................ 3
   1.3 CH model with elasticity .................................................. 6
   1.4 Variable mobility owing to grain boundaries ....................... 9

2 Derivation of governing equations ....................................... 12
   2.1 Problem formulation ..................................................... 12
   2.2 Cahn-Hilliard equation with elasticity ............................... 14
   2.3 Role of elasticity .......................................................... 16
   2.4 Elasticity equations ........................................................ 17
      2.4.1 Two-dimensional case for isotropic materials ............... 17
      2.4.2 Two-dimensional case for materials with cubic symmetry 18
      2.4.3 Three-dimensional case for materials with orthotropic symmetry . 19

3 Compositional elastic field in two dimensions — isotropic case 20
   3.1 Introduction ............................................................... 20
   3.2 Preliminaries ............................................................... 21
   3.3 Free-standing film — periodic solution ............................ 23
      3.3.1 Taking Laplace transform ....................................... 23
      3.3.2 Pole analysis ........................................................ 26
      3.3.3 Airy stress function $U$ .......................................... 26
      3.3.4 Stress field in the film .......................................... 27
   3.4 Free-standing film — exact closed form solution ................ 29
      3.4.1 Finite Laplace transform ....................................... 29
      3.4.2 Formulation of the exact solution ......................... 29

iv
3.4.3 Determination of the unknown constants .......................... 36
3.5 Film-substrate system ..................................................... 38
3.5.1 Misfit strain and local coordinate systems ......................... 38
3.5.2 Boundary conditions on the interface ............................... 39
3.5.3 Stress field in the substrate ............................................ 42
3.5.4 Solving the unknown constants ....................................... 42
3.5.5 Stress field in the film ................................................. 44
3.6 Summary and discussion .................................................. 46

4 Compositional elastic field in two dimensions — anisotropic case 49
4.1 Effect of anisotropy ......................................................... 49
4.2 Free-standing film — periodic solution .................................. 51
4.3 Free-standing film — exact closed form solution ..................... 53
4.4 Film-substrate system ...................................................... 55
4.4.1 Boundary conditions on the interface ............................... 56
4.4.2 Airy stress functions in the film and substrate .................... 57
4.4.3 Solving the unknown constants ....................................... 58
4.4.4 Stress field in the film ................................................. 59
4.5 Summary and discussion .................................................. 60

5 Compositional elastic field in three dimensions for anisotropic materials 61
5.1 Introduction ................................................................. 61
5.2 Governing equations ...................................................... 62
5.2.1 Governing equation and boundary conditions ..................... 62
5.2.2 Double Laplace transform ............................................. 65
5.3 Displacement potential $\phi$ ............................................. 68
5.4 Strain and stress fields in the film ..................................... 71
5.4.1 Strains in terms of $\tilde{\phi}$ .......................................... 71
5.4.2 Inverse transform preliminaries ..................................... 73
5.4.3 Evaluation of $R_i^f (z) (i = 0..3)$ ................................... 75
5.5 Strain and stress fields in the substrate ............................... 77
5.6 Determination of the unknown coefficients ............................ 79
5.6.1 Modes M$^{2d}$ and M$^{3d}$ ............................................. 79
5.6.2 Mode M$^{1d}$ — first order bending analysis ....................... 80
5.6.3 Remark on in-plane and twisting moments ....................... 83
5.7 Numerical verification with FEM ...................................... 84
5.8 Extension to orthotropic materials .................................... 86
6 Diffusional phase transformations in self-stressed solid films with constant mobility

6.1 Perturbation analysis on the role of elasticity

6.2 Numerical analysis

6.2.1 Nondimensionalization

6.2.2 Choice of system parameters

6.2.3 Numerical scheme

6.2.4 Convergence analysis

6.3 Simulation results in 2D

6.3.1 Results for isotropic free-standing films

6.3.2 Results for isotropic film-substrate systems

6.3.3 Results for cubic anisotropic free-standing films

6.3.4 Results for cubic anisotropic film-substrate systems

6.3.5 Results for layered structures

6.4 Simulation results in 3D CFS system

6.4.1 Results for random initial composition profiles

6.4.2 Results for layered structures

6.5 Summary and discussion

7 Grain boundary effect in the coarsening of polycrystalline solid films

7.1 Introduction

7.2 Governing equations

7.2.1 Grain boundary migration

7.2.2 Contribution of elasticity

7.3 Numerical analysis

7.3.1 Nondimensionalization

7.3.2 Determination of $R_\tau$

7.3.3 Numerical scheme

7.4 Simulation results

7.4.1 Results in two dimensions with fixed grain boundaries

7.4.2 Results in three dimensions with fixed grain boundaries

7.4.3 Results in two dimensions with migrating grain boundaries

7.5 Summary and discussion
8 Summary and future work 133

8.1 Summary . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 133
8.2 Future work . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 134

Appendices 135

A $\tilde{U}^A, \tilde{U}^F, \tilde{U}^B$ and $M_{ag}^{O}(p_k^I)$ etc. for exact closed form solution for isotropic free-standing film case 135
B Exact closed form solution for isotropic free-standing film case 138
C Eigenfunctions for isotropic film-substrate system case 140
D Eigenfunctions for free-standing film case for cubic symmetry 142
E Eigenfunctions for film-substrate system for cubic symmetry 143
F Property of related matrices when $p_1 \to 0$ or $p_2 \to 0$ 146
G Linear systems for unknown coefficients $\xi_{[m,n]}^{[n,b]}$ and $\xi_{[m,0,0n]}^{[x,y,z]}$ 147
H Evaluation for $R_z^f (z)[\epsilon_S]$ for shear strains 148

References 149
List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>The first 25 roots of $\sin 2z \pm 2z = 0$</td>
<td>33</td>
</tr>
<tr>
<td>6.1</td>
<td>Parameters used in numerical convergence analysis</td>
<td>99</td>
</tr>
<tr>
<td>C.1</td>
<td>Some limit properties of the eigenfunctions for the film in Eqn. (C-1a) –</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>Eqn. (C-1d) and those for the substrate in Eqn. (3.74c)</td>
<td></td>
</tr>
</tbody>
</table>
## List of Figures

1.1 Free energy versus composition plot indicating different phase separation behaviors. ......................................................... 3
1.2 Binodal and spinodal. ................................................................. 4
1.3 Two types of interfaces. ............................................................. 5
1.4 Micrograph No. 21 from DoITPoMS Micrograph Library, University of Cambridge (http://www.doitpoms.ac.uk/). This is a two-dimensional section of a hypereutectoid polycrystalline alloy showing grain structure. It has a composition of Fe, C 1.0 (wt%). ................................................................. 9
1.5 A typical grain boundary migration by numerical simulation using a model given in Section 7.2.1. .............................................................. 10

2.1 Geometry of the film (and substrate). For a free-standing film, the external loading is applied to the film; while for a film-substrate system, it is applied to the whole system. If a substrate is present, the film-substrate interface is coherent. ................................................................. 13

3.1 Pole distribution and integral contours used for the piece-by-piece inverse transform of $\tilde{U}$ (Eqn. (3.40b)). ......................................................... 32
3.2 The film-substrate system and their local coordinate systems are shown. The film is isotropic with elastic constants $E, \nu, \mu$; the substrate is also isotropic with elastic constants $E^*, \nu^*, \mu^*$. The composition of the film is $C(x, y)$ and in the substrate a fixed constant. The interface between the film and the substrate is assumed to be coherent. ................................................................. 39
3.3 The nondimensional stress components are shown along $y = 0$ from both FEM and our analytical solution for an isotropic material. ................................................................. 48

4.1 The bifurcation pattern of the distribution of $r/p$ of the characteristic equation $r^4 + 2(1 + \kappa)p^2r^2 + p^4 = 0$ is shown. ................................................................. 50
4.2 The film-substrate system and their local coordinate systems are shown. The film is cubic anisotropic with elastic constants $C_{11}, C_{12}, C_{44}$; the substrate is also cubic anisotropic with elastic constants $C_{11}^*, C_{12}^*, C_{44}^*$. The composition in the film is $C(x, y)$ and in the substrate a fixed constant. The interface between the film and the substrate is assumed to be coherent. ................................................................. 56
5.1 The film-substrate system and their local coordinate systems are shown. The film and substrate both are made of materials with cubic symmetry. The elastic constants are $C_{11}$, $C_{12}$, $C_{44}$ and $C_{11}^r$, $C_{12}^r$, $C_{44}^r$ in the film and substrate respectively. The composition in the film is $C(x, y, z)$ and uniform in the substrate. The interface between the film and the substrate is assumed to be coherent.

5.2 The composition/temperature profile used to compare the analytical and FEM (Ansys®) solution is shown. The value ($C$ or $T$) decreases gradually from the center of the spheres to the outer region with a uniform reference value.

5.3 The stress components along axis ($y = 3, z = 0$) in a comparison of the analytical method and FEM for a 3D cubic anisotropic modeling problem are shown. The temperature/composition field is shown in Figure 5.2.

5.4 The stress components along axis ($x = 4, z = 0$) are shown for the temperature/composition field in Figure 5.2.

5.5 The stress components along axis ($x = 4, y = 3$) are shown for the temperature/composition field in Figure 5.2. The analytical results show very good agreement of boundary conditions on the top traction free surface. Note the FEM results near the interface are suspect owing to a transition layer caused by the discretization.

6.1 Numerical convergence test for 2D and 3D codes.

6.2 Initial composition in 2D simulations. (a) Perturbed bilayer system with magnitude 0.05, $\Gamma_0 = 0$; (b) Particle system with $\Gamma_0 = 0$; (c) Perturbed bilayer system with magnitude 0.5, $\Gamma_0 = 0$; (d) Perturbed bilayer system with magnitude 0.9, $\Gamma_0 = 0$; (e) Perturbed multilayered system with phase $\Gamma \approx +1$ on bottom, $\Gamma_0 = 0.1087$; (f) Perturbed multilayered system with phase $\Gamma \approx -1$ on bottom, $\Gamma_0 = -0.1087$.

6.3 Effect of strength of elasticity. Higher strength of compositional misfit accelerates the evolution. (a) $\kappa^{el} = 0$; (b) $\kappa^{el} = 0.4$. The initial profile is in Figure 6.2(b).

6.4 Externally applied bending ($f_x^{ex} / (Y \eta) = s \zeta$) changes the composition evolution dramatically. (a) $s = 0.5$; (b) $s = 1$. For both systems, $\kappa^{el} = 0.4$ and the initial composition profile is in Figure 6.2(a).

6.5 The nondimensional moment provided by the substrate with units of $T^2$ as function of thickness ratio $r = \mathcal{H}^s / \mathcal{H}^f$ and elastic modulus ratio $\gamma$. . . . . 103
6.6 The variation of metastable composition structures for a particle system with different \( r (= \mathcal{H}^s / \mathcal{H}^f) \) and \( \gamma \). For all cases, the initial composition profile is in Figure 6.2(b). A frame box is added to make the computation domain distinct from the white background.

6.7 Evolution for an initial profile in Figure 6.2(b) for 2D CTR cases. (a) \( A = 1.83 \ (C_{11} = 2.0, C_{12} = 0.91, C_{44} = 1.0) \); (b) \( A = 0.72 \ (C_{11} = 7.78, C_{12} = 2.71, C_{44} = 1.83) \). For both cases, the composition aligns in the elastically soft directions at early time, but at long enough times, a columnar structure forms.

6.8 Composition evolution for an initial profile in Figure 6.2(b) for 2D CFS cases with \( \Delta T = \varepsilon = -1 \). (a) \( A_f = 2.85, A_s = 1.83 \); (b) \( A_f = 0.72, A_s = 1.83 \). A wetting behavior occurs in (a), while in (b) a columnar structure with varying thickness is formed.

6.9 Bilayer 2D IFS cases. \( \epsilon = 0.1, \epsilon^T/\eta = -1, r = 1 \) and \( \gamma = 1 \). The initial composition profiles is Figure 6.2(c). (a) \( K^{cl} = 0.4, \xi_0 = 16, \zeta_0 = 4 \); (b) \( K^{cl} = 0.2, \xi_0 = 8, \zeta_0 = 2 \). Note (a) has relatively strong elasticity while (b) has relatively strong interfacial energy.

6.10 Multilayer 2D IFS cases. \( \epsilon^T/\eta = 1, \epsilon = 0.1, r = 1 \) and \( \gamma = 1 \). The initial composition profile is Figure 6.2(e). (a) \( K^{cl} = 0.4, \xi_0 = 16, \zeta_0 = 4 \); (b) \( K^{cl} = 0.2, \xi_0 = 8, \zeta_0 = 2 \). Note (a) has relatively strong elasticity while (b) has relatively strong interfacial energy.

6.11 Bilayer 2D CFS cases for initial composition profile in Figure 6.2(d). (a) \( A_f = 2.85, A_s = 1.83 \); (b) \( A_f = 0.72, A_s = 1.83 \). For both cases, \( \epsilon^T/\eta = -1, r = 1 \). Large perturbation develops: for (a), a bilayer structure is formed; while for (b), a columnar structure with varying thickness is formed.

6.12 Multilayer 2D CFS cases. The initial composition profile for both cases is in Figure 6.2(e). \( \epsilon^T/\eta = -1, r = 1 \). (a) \( A_f = 2.85, A_s = 1.83 \); (b) \( A_f = 0.72, A_s = 1.83 \). Both cases degrade to a bilayer structure.

6.13 Initial composition profiles for 3D simulations. (a) and (b) have smoothed random composition and (c) is randomly perturbed multilayered structure. Composition in (a) ranges in \([-0.0018, 0.0018]\) while in (b) and (c) it is broader and ranges in \((-1, 1]\). Composition profiles in (a)-(b) have an average \( \Gamma_0 = 0 \), in (c), \( \Gamma_0 = -0.0035 \).

6.14 Evolution of an initial profile in Figure 6.13(a) with \( A_f = 2.67, A_s = 1.55 \) and \( \epsilon^T/\eta = -0.5 \). A multilayer structure forms at very early times due to the spinodal decomposition, and evolves to a bilayer structure at later times.
6.15 Evolution of an initial profile in Figure 6.13(b) with $A^f = 0.72$, $A^s = 1.55$ and $\varepsilon^T/\eta = -0.5$. The composition is aligned in the film plane along (11). A columnar structure with varying thicknesses forms due to the constraint of film geometry, and also due to the relative tension on the bottom of the film to the top of the film. ......................................................... 113

6.16 Evolution of an initial profile in Figure 6.13(b) with $A^f = 2.67$, $A^s = 1.55$ and $\varepsilon^T/\eta = -0.5$. The composition is aligned in the film plane along (01). A columnar structure with varying thicknesses forms due to the constraint of film geometry, and also due to the relative tension on the bottom of the film to the top of the film. ......................................................... 114

6.17 Evolution of an initial profile in Figure 6.13(b) with $A^f = 2.67$, $A^s = 1.55$ and $\varepsilon^T/\eta = -2$. The enhanced epitaxial misfit strain leads to a bilayer structure. 115

6.18 Evolution of a layered initial composition profile in Figure 6.13(c) with $A^f = 2.67$, $A^s = 1.55$, $\varepsilon = 0.12$ and $\varepsilon^T/\eta = -0.5$. The layer structure evolves very slowly. The structure may be very close to a metastable state. ................. 116

6.19 Evolution of a layered initial composition profile in Figure 6.13(c) with $A^f = 2.67$, $A^s = 1.55$, $\varepsilon = 0.12$ and $\varepsilon^T/\eta = -2$. The enhanced epitaxial misfit strain leads to a bilayer structure. ......................................................... 116

7.1 An initial composition profile for 2D simulation. The two phases are distributed in such a way that one of the phases ($\Gamma \approx +1$) is on the grain boundaries, while the other ($\Gamma \approx -1$) resides in the grains. The gray-scale scheme is shown in Figure 7.2. ......................................................... 126

7.2 Composition evolution for a 2D case with initial profile in Figure 7.1. (a) The relative mobility ratio $\mathcal{M}_{GB}/\mathcal{M}_L = 1000$. The $\Gamma \approx +1$ phase diffuses immediately toward the triple junctions and coarsens. (b) The mobility ratio $\mathcal{M}_{GB}/\mathcal{M}_L = 1$. Standard coarsening occurs. ......................................................... 126

7.3 Two grain structures with the same initial composition profile for a simulation with $R_\tau = 1$. (a) A relative large grain structure; (b) A very large grain structure. The gray-scale scheme is shown in Figure 7.4. ......................... 127

7.4 The evolution of a particle system in a polycrystalline solid film with large grains. $\mathcal{M}_{GB}/\mathcal{M}_L = 1000$. The grain boundary migration is very slow, with $R_\tau = 1$, thus emulating a ‘fixed’ grain boundary. Coarsening occurs with preference on the grain boundary. Note the shaded color indicates channels with fast diffusion rate. (a) A relative large grain structure; (b) A very large grain structure. ......................................................... 127
7.5 A three-dimensional initial profile with small range random composition around $\Gamma = 0$. The average composition is $\Gamma_0 = 0$. The plot is overlapped with a three-dimensional fixed grain boundary. The grain boundary structure is extended from a two-dimensional grain boundary profile. On the left is a top view, on the right a side view.

7.6 Composition evolution in a free-standing film with a fixed columnar grain structure in three dimensions. $M_{GB}/M_L = 1000$. Spinodal decomposition occurs in the plane and along the thickness direction on the grain boundary. The initial composition profile is in Figure 7.5. On the left is a top view, on the right a side view.

7.7 A particle initial composition profile in a polycrystalline solid film. The gray-scale scheme is shown in Figure 7.8.

7.8 The evolution of a particle system in a polycrystalline solid film. For both cases, $M_{GB}/M_L = 1000$. (a) $R_T = 1K$. Noticeable change of the grain boundary structure occurs. (b) $R_T = 10K$. Grain boundaries move faster. The fast growing grains freeze some of the composition when the grain boundary moves away quickly.