Morphology and Topology of Interfaces During Coarsening Via Nonconserved and Conserved Dynamics

A DISSERTATION

SUBMITTED TO THE GRADUATE SCHOOL
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

for the degree

DOCTOR OF PHILOSOPHY

Field of Materials Science and Engineering

By

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EVANSTON, ILLINOIS

December 2007
ABSTRACT

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Large-scale simulations in three-dimensions were performed with the phase-field method on a parallel computing platform to model coarsening of two-phase mixtures. Simulations included symmetric mixtures evolving via nonconserved dynamics (model A) governed by the Allen-Cahn equation and symmetric and asymmetric mixtures with volume fractions of 22%, 30%, 36%, and 40% evolving via conserved dynamics (model B) governed by the Cahn-Hilliard equation. Symmetric mixtures with the two different dynamics were compared. The volume fraction dependency was investigated in mixtures evolving via conserved dynamics.

The scaled morphology and topology were studied using the interfacial shape distribution and the genus, respectively. The interfacial shape distribution and the genus were scaled by a characteristic length. For symmetric mixtures evolving via both dynamics and 36% and 40% mixtures evolving via conserved dynamics, time-invariant scaled morphologies were found. Each bicontinuous mixture has a unique scaled interfacial shape
distribution. The probability flux that governs the interfacial shape distributions was calculated for the two symmetric mixtures to investigate the time-evolution of interfacial patches. However, all these mixtures have similar topology, yielding a universal value in the scaled genus. Additionally, these bicontinuous mixtures are different from the topology of Schoen’s G surface that has been considered previously as a good model for such bicontinuous mixtures.

The presence of a range of volume fractions where interfacial structures remain bicontinuous in the late-stage coarsening is of great interest. It has been assumed that symmetric mixtures have a bicontinuous structure and asymmetric mixtures have a droplet or clustered structure in the late-stage coarsening regardless of the dimensionality. This assumption is based upon experimental results from thick films that can be considered as two-dimensions and 2D simulations. We find that mixtures can remain bicontinuous down to volume fraction of 36%. The differences between the behavior of 2D and 3D systems are attributed to different percolation limits in different dimensions and the presence of Rayleigh instability that exists only in three-dimensions.
Acknowledgements
Contents

ABSTRACT 3

Acknowledgements 5

List of Figures 9

List of Tables 21

Chapter 1. Introduction 22

Chapter 2. Methods 28

2.1. Phase-field model of nonconserved and conserved dynamics 28

2.2. Implementation of simulations - parallel computing with a finite difference method 34

2.3. Determination of the grid spacing, $\Delta x$ 38

2.3.1. Calculation of surface area per volume, $S_V$ 45

2.4. Structure Function 46

2.5. Morphology and Topology 48

2.5.1. 3D curvatures 48

2.5.2. Morphology 52

2.5.3. Topology 55

Chapter 3. Three-Dimensional Mixtures Evolving via Nonconserved Dynamics 60
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Structure Function</td>
<td>61</td>
</tr>
<tr>
<td>3.2</td>
<td>Morphology - Interfacial shape distribution</td>
<td>69</td>
</tr>
<tr>
<td>3.3</td>
<td>Topology</td>
<td>81</td>
</tr>
<tr>
<td>3.4</td>
<td>Dynamics of the interfacial shape distribution</td>
<td>83</td>
</tr>
<tr>
<td>4.1</td>
<td>Three-Dimensional Mixtures Evolving via Conserved Dynamics</td>
<td>91</td>
</tr>
<tr>
<td>4.1.1</td>
<td>Symmetric mixtures</td>
<td>92</td>
</tr>
<tr>
<td>4.1.1.1</td>
<td>Structure function</td>
<td>93</td>
</tr>
<tr>
<td>4.1.2</td>
<td>Morphology</td>
<td>101</td>
</tr>
<tr>
<td>4.1.3</td>
<td>Topology</td>
<td>113</td>
</tr>
<tr>
<td>4.2</td>
<td>Asymmetric mixtures</td>
<td>115</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Structure functions</td>
<td>126</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Morphology</td>
<td>127</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Topology</td>
<td>149</td>
</tr>
<tr>
<td>5.1</td>
<td>Two-Dimensional Mixtures</td>
<td>152</td>
</tr>
<tr>
<td>5.1</td>
<td>Nonconserved dynamics</td>
<td>153</td>
</tr>
<tr>
<td>5.2</td>
<td>Conserved dynamics</td>
<td>154</td>
</tr>
<tr>
<td>6.1</td>
<td>Discussion</td>
<td>166</td>
</tr>
<tr>
<td>6.1.1</td>
<td>Comparison of symmetric mixtures evolving via nonconserved and conserved dynamics</td>
<td>166</td>
</tr>
<tr>
<td>6.2</td>
<td>The effects of volume fraction and dimensionality</td>
<td>173</td>
</tr>
<tr>
<td>7.1</td>
<td>Conclusions</td>
<td>182</td>
</tr>
</tbody>
</table>
List of Figures

2.1 Landau-Ginsburg potential having two minima at $X = 0$ and 1. 33

2.2 A planar interface at equilibrium located at $x = 0$. The order parameter profile is marked at two different resolutions. $n$: the number of grid points across interface. 39

2.3 3D tests with different mesh size. 41

2.4 ISDs from 36% mixtures having computational box dimension of $L = 256\sqrt{2}$ at $t = 64000$ ($t^{1/3} = 40$). 42

2.5 Domains of 22% mixtures at $t = 153600$ ($t^{1/3} = 53.6$). Interfaces are colored with scaled Gauss curvature ($K/S_V^2$). The Gauss curvature $K$ is defined as $K = \kappa_1\kappa_2$ where $\kappa_1$ and $\kappa_2$ are the principal curvatures as a function of position on the interfaces. An edge length is $4(1/S_V)$. These are portions of the entire computational domain. Note that there are many flat interfaces in (b). 45

2.6 Illustration of 3D curvatures at an interfacial patch, $p$. $\hat{n}$: interfacial normal, $R_1$ and $R_2$: principal radii of curvatures, $\kappa_1$: minimum principal curvature, and $\kappa_2$: maximum principal curvature 49

2.7 Interfacial profiles of a conserved order parameter $\phi$ along the line from $(200, 0, 0)$ to $(300, 0, 0)$ before and after smoothing at $t = 409600$. 51
2.8 Interfacial morphology before and after smoothing. These are \((128\sqrt{2})^3\) portions taken from a conserved order parameter \(\phi\) with 512\(^3\) grid points at \(t = 409600\).

2.9 A map for interfacial shapes in the interfacial shape distribution.

3.1 A symmetric \(\eta\) at \(t = 480\) \((1/S_V = 56.8)\). Transparent regions denote the phase with \(\eta = 0\), and gray regions denote the phase with \(\eta = 1\).

3.2 A symmetric \(\eta\) at \(t = 1600\) \((1/S_V = 101.4)\). Transparent regions denote the phase with \(\eta = 0\), and gray regions denote the phase with \(\eta = 1\).

3.3 A symmetric \(\eta\) at \(t = 4000\) \((1/S_V = 158.9)\). Transparent regions denote the phase with \(\eta = 0\), and gray regions denote the phase with \(\eta = 1\).

3.4 A symmetric \(\eta\) at \(t = 9600\) \((1/S_V = 245.4)\). Transparent regions denote the phase with \(\eta = 0\), and gray regions denote the phase with \(\eta = 1\).

3.5 Self-similar evolution of 3D domains in a 50\% mixture with a nonconserved order parameter. These are portions taken from the computational domains. An edge length is \(6(1/S_V)\).

3.6 Square of the characteristic length \(l = S_V^{-1}\) vs time. The line is the best fit \(l^2 = 6.2147t + 414.93\) \((R^2 = 0.9999)\).

3.7 Growth rate vs. wave number in the initial stage of phase separation when \(W = 1\), \(\epsilon = 1\), and \(L_\eta = 1\).

3.8 Evolution of structure functions in a symmetric mixture with a nonconserved order parameter.
### 3.9 The interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter $\eta$ at $t = 480$ ($1/S_V = 56.8$).

### 3.10 The interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter $\eta$ at $t = 1600$ ($1/S_V = 101.4$).

### 3.11 The interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter $\eta$ at $t = 4000$ ($1/S_V = 158.9$).

### 3.12 The interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter $\eta$ at $t = 9600$ ($1/S_V = 245.4$).

### 3.13 The scaled interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter $\eta$ at $t = 480$ ($1/S_V = 56.8$).

### 3.14 The scaled interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter $\eta$ at $t = 1600$ ($1/S_V = 101.4$).

### 3.15 The scaled interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter $\eta$ at $t = 4000$ ($1/S_V = 158.9$).

### 3.16 The scaled interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter $\eta$ at $t = 9600$ ($1/S_V = 245.4$).

### 3.17 Fraction of elliptic interfacial area (FE) in a system with a nonconserved order parameter $\eta$ at different times.
3.18 A log-log plot of genus density vs time. The fitting equation is
\[
\log \left( \frac{g}{V} \right) = -1.4 \log t - 1.1946.
\]

3.19 Scaled genus vs. characteristic length of mixtures with a nonconserved order parameter.

4.1 A symmetric \( \phi \) at \( t = 64000 \ (1/S_V = 35.6) \). Transparent regions denote the phase with \( \phi = 0 \), and grey regions denote the phase with \( \phi = 1 \).

4.2 A symmetric \( \phi \) at \( t = 281600 \ (1/S_V = 57.0) \). Transparent regions denote the phase with \( \phi = 0 \), and grey regions denote the phase with \( \phi = 1 \).

4.3 A symmetric \( \phi \) at \( t = 755200 \ (1/S_V = 77.9) \). Transparent regions denote the phase with \( \phi = 0 \), and grey regions denote the phase with \( \phi = 1 \).

4.4 A symmetric \( \phi \) at \( t = 1113600 \ (1/S_V = 88.6) \). Transparent regions denote the phase with \( \phi = 0 \), and grey regions denote the phase with \( \phi = 1 \).

4.5 Self-similar evolution of 3D domains in a 50% mixture with a conserved order parameter. These are portions taken from the computational domains. An edge length is \( 6(1/S_V) \).

4.6 Cube of the characteristic length, \( l = 1/S_V \), vs time. The line is the best fit \( l^3(t) = 0.6122t + 10179 \ (R^2 = 0.9998) \).

4.7 Growth rate vs. wave numbers in the initial stage of phase separation when \( W = 1, \epsilon = 1, \) and \( L_\phi = 1 \).
4.8 Evolution of structure functions in a symmetric mixture with a conserved order parameter.

4.9 The interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 64000 \ (1/S_V = 35.6)$. 

4.10 The interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 281600 \ (1/S_V = 57.0)$. 

4.11 The interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 755200 \ (1/S_V = 77.9)$. 

4.12 The interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 1113600 \ (1/S_V = 88.6)$. 

4.13 The scaled interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 64000 \ (1/S_V = 35.6)$. 

4.14 The scaled interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 281600 \ (1/S_V = 57.0)$. 

4.15 The scaled interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 755200 \ (1/S_V = 77.9)$. 

4.16 The scaled interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 1113600 \ (1/S_V = 88.6)$. 

4.17 The fraction of elliptic interfacial area (FE) present in symmetric mixtures with a conserved order parameter.

4.18 A log-log plot of genus density vs time. The fitting equation is $
\log (g/V) = -0.95 \log t - 0.6695 \ (R^2 = 0.9999)$.
4.19 Scaled genus vs. time in symmetric mixtures with a conserved order parameter.

4.20 Self-similar evolution of 3D domains in the 36% and 40% mixtures with a conserved order parameter. These are portions taken from the computational domains. An edge length is $6(1/S_V)$.  

4.21 An asymmetric $\phi$ with volume fraction of 22% at $t = 102400$ ($1/S_V = 72.0$). Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(256\sqrt{2})^3$.  

4.22 An asymmetric $\phi$ with volume fraction of 22% at $t = 307200$ ($1/S_V = 102.2$). Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(256\sqrt{2})^3$.  

4.23 An asymmetric $\phi$ with volume fraction of 30% at $t = 102400$ ($1/S_V = 72.0$). Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(256\sqrt{2})^3$.  

4.24 An asymmetric $\phi$ with volume fraction of 30% at $t = 307200$ ($1/S_V = 82.6$). Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(256\sqrt{2})^3$.  

4.25 An asymmetric $\phi$ with volume fraction of 36% at $t = 25600$

$(1/S_V = 32.0)$. Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(1024\sqrt{2})^3$.

4.26 An asymmetric $\phi$ with volume fraction of 36% at $t = 64000$

$(1/S_V = 84.9)$. Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(1024\sqrt{2})^3$.

4.27 An asymmetric $\phi$ with volume fraction of 40% at $t = 25600$

$(1/S_V = 36.0)$. Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(1024\sqrt{2})^3$.

4.28 An asymmetric $\phi$ with volume fraction of 40% at $t = 76800$

$(1/S_V = 36.0)$. Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(1024\sqrt{2})^3$.

4.29 (Characteristic length, $1/S_V = l^3$) vs time. The fitting equations are $S_V^{-3}(t) = 3.4474t + 29661$ ($R^2 = 0.9969$) for 22% mixture,

$S_V^{-3}(t) = 1.8652t - 10196$ ($R^2 = 0.9991$) for 30% mixtures,

$S_V^{-3}(t) = 0.9297t + 23295$ ($R^2 = 0.9992$) for 36% mixtures,

$S_V^{-3}(t) = 0.7194t + 14087$ ($R^2 = 0.9998$) for 40% mixtures, and

$S_V^{-3}(t) = 0.6122t + 10179$ ($R^2 = 0.9998$) for 50% mixtures.
4.30 Evolution of structure functions in 36% and 40% asymmetric mixtures with a conserved order parameter.

4.31 Evolution of structure functions in 22% and 30% asymmetric mixtures with a conserved order parameter.

4.32 The scaled interfacial shape distribution of the 36% mixture with a conserved order parameter $\phi$ at $t = 25600$ ($1/S_V = 32.0$). The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{\text{avg}}/S_V$ ($H = H_{\text{avg}}$).

4.33 The scaled interfacial shape distribution of the 36% mixture with a conserved order parameter $\phi$ at $t = 179200$ ($1/S_V = 57.8$). The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{\text{avg}}/S_V$ ($H = H_{\text{avg}}$).

4.34 The scaled interfacial shape distribution of the 36% mixture with a conserved order parameter $\phi$ at $t = 460800$ ($1/S_V = 76.8$). The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{\text{avg}}/S_V$ ($H = H_{\text{avg}}$).

4.35 The scaled interfacial shape distribution of the 36% mixture with a conserved order parameter $\phi$ at $t = 640000$ ($1/S_V = 84.9$). The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{\text{avg}}/S_V$ ($H = H_{\text{avg}}$).

4.36 The scaled interfacial shape distribution of the 40% mixture with a conserved order parameter $\phi$ at $t = 51200$ ($1/S_V = 36.0$). The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{\text{avg}}/S_V$ ($H = H_{\text{avg}}$).

4.37 The scaled interfacial shape distribution of the 40% mixture with a conserved order parameter $\phi$ at $t = 153600$ ($1/S_V = 50.0$). The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{\text{avg}}/S_V$ ($H = H_{\text{avg}}$).
4.38 The scaled interfacial shape distribution of the 40% mixture with a conserved order parameter $\phi$ at $t = 332800 \ (1/S_V = 63.5)$. The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{\text{avg}}/S_V \ (H = H_{\text{avg}})$. 137

4.39 The scaled interfacial shape distribution of the 40% mixture with a conserved order parameter $\phi$ at $t = 768000 \ (1/S_V = 82.7)$. The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{\text{avg}}/S_V \ (H = H_{\text{avg}})$. 138

4.40 The fraction of elliptic interfacial area (FE) present in the 36% and 40% mixtures with a conserved order parameter at different times. 139

4.41 The scaled interfacial shape distribution of the 22% mixture with a conserved order parameter $\phi$ at $t = 102400 \ (1/S_V = 72.0)$. 141

4.42 The scaled interfacial shape distribution of the 22% mixture with a conserved order parameter $\phi$ at $t = 153600 \ (1/S_V = 82.4)$. 142

4.43 The scaled interfacial shape distribution of the 22% mixture with a conserved order parameter $\phi$ at $t = 204800 \ (1/S_V = 91.0)$. 143

4.44 The scaled interfacial shape distribution of the 22% mixture with a conserved order parameter $\phi$ at $t = 307200 \ (1/S_V = 102.0)$. 144

4.45 The scaled interfacial shape distribution of the 30% mixture with a conserved order parameter $\phi$ at $t = 25600 \ (1/S_V = 35.8)$. 145

4.46 The scaled interfacial shape distribution of the 30% mixture with a conserved order parameter $\phi$ at $t = 51200 \ (1/S_V = 44.6)$. 146

4.47 The scaled interfacial shape distribution of the 30% mixture with a conserved order parameter $\phi$ at $t = 179200 \ (1/S_V = 68.1)$. 147
4.48 The scaled interfacial shape distribution of the 30% mixture with a conserved order parameter $\phi$ at $t = 307200 \ (1/S_V = 82.6)$.

4.49 The fraction of elliptic interfacial area (FE) presented in the 30% mixture with a conserved order parameter.

4.50 The time-evolution of the scaled genus of mixtures with a conserved order parameter.

5.1 Evolution of domains in a 50% mixture with a nonconserved order parameter.

5.2 Characteristic length vs. time during coarsening of mixtures with a nonconserved order parameter. The fitting equation is $l^2(t) = 8.9782t^2 - 122.9 \ (R^2 = 0.9997)$.

5.3 Distributions of the scaled curvature $\tilde{\kappa} = \kappa \cdot l$ in mixtures with a nonconserved order parameter.

5.4 (Characteristic length)$^3$ vs. time during coarsening of mixtures with a conserved order parameter. The fitting equation of $l^3(t) = At + B$ was used.

5.5 Evolution of domains in a 40% mixture with a conserved order parameter.

5.6 Evolution of domains in a 44% mixture with a conserved order parameter.

5.7 Evolution of domains in a 48% mixture with a conserved order parameter.
5.8 Evolution of domains in a 50% mixture with a conserved order parameter.

5.9 Distributions of the scaled curvature $\tilde{\kappa} = \kappa \cdot l$ in mixtures with a conserved order parameter.

5.10 Distributions of the scaled curvature $\tilde{\kappa} = \kappa \cdot l$ in mixtures with a conserved order parameter.

6.1 Scaled interfacial morphologies of symmetric mixtures unique to nonconserved ((a) and (c)) and conserved dynamics ((b) and (d)), respectively. These are portions of the interfaces colored with scaled Gaussian curvature $K/S_V^2$ ((a) and (b)) and scaled mean curvature $H/S_V$ ((c) and (d)). All portions are cubic domains with edge lengths of $6(1/S_V)$. In (b), the pair of red regions marked with a red arrow is a remnant of a pinched tube. More red regions are observed in (a) than (b).

6.2 Comparison of the scaled ISDs of symmetric mixtures unique to the nonconserved and the conserved dynamics, respectively.

6.3 Genus per characteristic volume ($g_V S_V^{-3}$) versus characteristic length $(1/S_V)$.

6.4 Schoen’s G surface that has been considered as a good model for the final structure when a two-phase mixture evolves via conserved dynamics. Two unit cells are repeated in each direction (eight unit cells).
Scaled genus per characteristic volume \(g_V S_V^{-3}\) versus characteristic length \((1/S_V)\) of all three-dimensional mixtures that were modeled.

Portions of interfaces presented in the 36%, 40%, and 50% mixtures with a conserved order parameter at \(t = 384,000\) \((1/S_V = 72.69)\), \(t = 512,000\) \((1/S_V = 72.69)\), and \(t = 588,800\) \((1/S_V = 71.96)\), respectively. An edge length is scaled to be \(4(1/S_V)\).

Evolution of domains in a 40% mixture with a rectangular computational box of \(512 \times 512 \times 32\) grids with \(\Delta x = \sqrt{2}\) evolving via conserved dynamics. Transparent regions denote the \(\phi = 0\) phase and grey regions denote the \(\phi = 1\) phase.

Corresponding scaled ISDs of mixtures present in Figure 6.7.

Cube of characteristic length vs. time during coarsening of domains in a rectangular system with \(512 \times 512 \times 32\) grids with \(\Delta x = \sqrt{2}\). The poorer statistics indicated by the \(R^2\) value smaller than other simulations in this study is because only one set of simulation was performed for the PTD.
List of Tables

2.1 Parameters for simulations. AC=nonconserved dynamics (model A), CH=conserved dynamics (model B), \(V_f\) =volume fraction of minority phase, \(N\) =the number of array elements along one direction, \(\Delta x\) =mesh size, \(n\) =the number of meshes at interfaces, and \(\Delta t\) =time step. 43

2.2 List of vertices and vertex areas 46

2.3 List of vertices and vertex areas 53

5.1 List of fitting parameters (A and B) and correlation coefficient \((R^2)\) for the fitting equation \(l(t) = At^{1/3} + B\) in conserved dynamics. 157

6.1 Area-averaged scaled curvatures in symmetric mixtures. AC=nonconserved dynamics (model A), CH=conserved dynamics (model B) 170
CHAPTER 1

Introduction

Phase separation followed by coarsening occurs in a wide range of two-phase mixtures from ferromagnetic materials to binary mixtures of metals or polymers, where a homogeneous single phase above its critical temperature ($T_C$) separates into two different phases when cooled below $T_C$. This is usually driven by nonconserved dynamics, named model A, or conserved dynamics, named model B.

A typical example for conserved dynamics is spinodal decomposition in a binary A-B alloy having positive heat of mixing, where A-A or B-B bonding is favorable than A-B bonding, resulting in a miscibility gap in its phase diagram. Above $T_C$, their concentration is spatially uniform due to the entropy contribution ($TS$) dominating the internal energy contribution ($U$) in Helmholtz free energy ($F = U - TS$). When quenched below $T_C$, the energy effect dominates. As a result, unmixing occurs to form two kinds of phase domains, one of which is A-rich and the other B-rich. This process occurs by diffusion. Initial domain sizes are related to the diffusion length of A and B species. In most cases, the initial domain sizes are very small because of rapid quenching preventing the species from having enough time to travel for a long distance. Macroscopically, the small fluctuations of an initially uniform concentration grow until their minimum and maximum values reach their saturated values, each corresponding to the equilibrium concentrations of each phase. Subsequent to this phase separation, coarsening of the domains follows to
reduce total free energy of system by reducing the extra energy associated with interfaces between the two phases.

A typical example for nonconserved dynamics is the most simplified model of paramagnetic-ferromagnetic transition. Above $T_C$, magnetic dipoles are randomly oriented or completely disordered, so the net magnetization is zero. When the system is quenched below $T_C$, two kinds of magnetic domains, (+) and (-), form spontaneously. In each domain, magnetic dipoles align in the same direction. Like the binary alloy case, then, domains having small sizes undergo coarsening. In both cases, late-stage coarsening is driven by interfacial curvature.

In certain cases of the late-stage coarsening after a sufficient coarsening time, the interfacial morphology becomes self-similar, i.e., time-independent when scaled by a time-dependent characteristic length of the system. This self-similar evolution has been investigated extensively for systems with a polydisperse array of particles embedded in a matrix. In this case, Lifshitz, Slyozov, and Wagner (LSW) determined the particle size distribution and proved that it assumed a time-independent shape when scaled with average particle size for highly asymmetric mixtures containing precipitates. They assumed that the volume of precipitates is negligible (no overlapping of the diffusion fields established by precipitates) and that interfacial free energy is isotropic (spherical particles) $[1,2]$. The other limiting case is symmetric or moderately asymmetric mixtures with comparable amounts of two phases, where the two phases are intricately interpenetrating or *bicontinuous*. In these systems, other measures of the interfacial structure are used such as the structure function, the distribution of interfacial curvatures (morphology), and the connectivity of domains (topology), instead of a particle size distribution.
The LSW theory predicted the well-known power growth law for the coarsening of spherical particles, assuming that the volume fraction of particles is close to zero. The assumption is called the zero-volume-fraction limit where the diffusion fields established by particles do not overlap because distances between particles are sufficiently large.

\[(1.1) \quad \bar{R}^m(t) - \bar{R}^m(0) = kt\]

where \(\bar{R}\) is the average particle radius; \(m\) is the growth exponent, 2 for nonconserved dynamics and 3 for conserved dynamics; \(k\) is the kinetic constant. However, a particle size cannot be defined in systems having topologically complex phase domains. Hence, a different measure related to domain spacing, such as characteristic length, is needed. We use \(1/S_V\), the reciprocal of interfacial area per volume, as the characteristic length, \(l\), of a given system. The method for calculating \(S_V\) is described in Section [2.3.1]. The characteristic length increases with time as the mixture undergoes coarsening by reducing interfacial area. By replacing \(\bar{R}\) by \(l\) in Equation \((1.1)\), the growth law for the mixtures having interconnected domains is obtained.

\[(1.2) \quad l^m(t) - l^m(0) = kt\]

where \(l\) is the characteristic length, \(S_V^{-1}\), and \(m\) is the growth exponent that depends upon the coarsening mechanism. The systems with other effects, for example, hydraulic fluid flow or elastic stress yield different exponents. Therefore, experimentalists measure the exponent to decide the coarsening mechanism. In the late-stage where \(l(t) \gg l(0)\),
Equation 1.2 becomes

\begin{equation}
I(t) = S_V^{-1}(t) \sim kt^{1/m}
\end{equation}

Although a coarsening system obeys this growth law, it is not necessarily true that the system undergoes the self-similar coarsening because the systems that do not undergo the self-similar coarsening can still obey the growth law [3, 4].

The bicontinuous domain structures are frequently observed in many fluid-fluid interfaces [5–7], microemulsions [8], and block copolymers [9–12] as well as phase-separating [13–15] and phase-ordering systems [16–19]. It has been known that the bicontinuous structures in block-copolymers are related to those of periodic surfaces with zero mean curvature, so called minimal surfaces [9–12]. It has also been speculated that Schoen’s G surface, one of minimal surface with genus of 5 per unit cell, is a good model for coarsening bicontinuous structures. However, it was mathematically predicted that those minimal surfaces cannot be present in coarsening systems because the minimal surfaces are unstable to small morphological perturbations in the case of surface-tension driven dynamics [20].

Bicontinuous structures are usually characterized with indirect measures such as two-point correlation function or its Fourier transform, structure function. Although it has been known that those measures scale with characteristic length [21], corresponding with average particle size in the LSW theory, it is still controversial if the interfacial structures attain self-similarity or how they may differ from that of minimal surfaces. For example, Aksimentiev et al characterized distribution of interfacial curvature for systems coarsening via conserved dynamics and did not observe self-similarity [22]. While Fialkowski et al
did observe scaling of the interfacial curvature distribution for systems coarsening via nonconserved dynamics [23], Brown and Rikvold claim that these are transient states [24].

To settle these controversies, it is necessary to characterize quantitatively the bicontinuous structures in the very late-stage coarsening regime where scaling may exist. We use curvature distribution related to interfacial shapes, morphology, and genus related to connectivity of domains, topology, because one cannot explicitly understand the detailed shapes of interfaces with such indirect measures as structure function in Fourier space. Thus the geometry of bicontinuous domains can be fully understood by the combination of morphology and topology both of which are direct measures in real space. If these structures could be characterized accurately and if the measures used to quantify the structures exhibit scaling, then the counterpart for these bicontinuous structures to the well known scaled particle-size distribution found many years ago by LSW would finally be known. Furthermore, if such unique structures exist, one could determine whether the interfacial structures and their evolution in experiment or simulation depend on the mechanism of coarsening. These unique structures would also form the basis of comparison for the future work on systems in which other effects, such as anisotropic interfacial energy, external fields, and hydrodynamic flows, play a role in the interfacial evolution.

We investigate symmetric mixtures evolving via nonconserved (model A) and conserved dynamics (model B) to identify such unique scaled structures. In addition, we also investigate asymmetric mixtures with different volume fractions evolving via conserved dynamics. It has been believed that moderately asymmetric mixtures (volume fraction close to but not equal to 50%) have interconnected structures in the initial stage which, then, transform to droplets or clustered structures in the late-stage while both systems
with small particles in a matrix and symmetric bicontinuous mixtures coarsen in the self-similar manners [25–29]. In other words, no self-similarity exists in coarsening of asymmetric mixtures. However, most systems that have been investigated so far are 2D systems where the characteristic length is larger compared to the thickness of rectangular systems one of whose dimensions is much smaller than the others. No large-scale 3D work simulations have been done for asymmetric mixtures.

One may expect that asymmetric mixtures with more than \( \sim 30\% \) volume fraction of minor phase could have bicontinuous domains because the percolation limits (\( P_C \)) in 3D are \( \sim 30\% \) [30–32]. On the other hand, the \( P_C \) in 2D is \( \sim 60\% \) [30], meaning that both phases cannot be bicontinuous simultaneously below 60%. It is also of great interest investigating whether asymmetric mixtures actually have bicontinuous domains and whether they evolve self-similarly during coarsening.

In this work, we model large-scale two-phase mixtures with phase-field modeling, which is a great tool for modeling systems with a lot of atoms or molecules for which other atomistic or molecular scale modeling techniques cannot be used. We use the morphological and topological measures mention previously, the ISD or genus, to investigate whether the modeled mixtures attain the self-similarity during coarsening.
CHAPTER 2

Methods

2.1. Phase-field model of nonconserved and conserved dynamics

Phase-field model based on diffuse interface theory \cite{33} has been known as a great tool for modeling the evolution of microstructures during as solidification and coarsening \cite{34}. Such systems involve many atoms or molecules such that even the most advanced computing technology cannot handle. Thus modeling such phenomena is usually performed in the continuum limit. Among techniques dealing with this continuum limit, the phase-field method has proven most useful because explicit tracking of interfaces between phases that is mathematically hard is not required. However, despite of the mathematical simplicity, the phase-field method is a computationally expensive technique that requires a massive amount of calculations and a large memory size because the method performs calculations not only in the interfacial region but also on the whole mixture system.

The total Helmholtz free energy ($F$) of a given heterogeneous system comprises two contributions, bulk (phase 1 and 2) and interfacial free energy.

\begin{equation}
F = F_{\text{phase 1}} + F_{\text{interface}} + F_{\text{phase 2}}
\end{equation}

The first and the third terms in the right-hand side are fixed if the volume fraction is fixed. Therefore, the second term, the interfacial free energy, has to decrease continuously during coarsening. The phase at a given location, $(x, y, z)$, is described by the order
parameter, $X'$. For example, $X'(x, y, z) = X_1$ when the location belongs to phase 1, and
$X'(x, y, z) = X_2$ when the location belongs to phase 2. Assuming that the variation of $X'$
is continuous across interfaces, all three terms in the right hand side are combined into
one integral term.

$$F = \int_V \left\{ f(X') + \frac{1}{2} \epsilon^2 |\nabla X'|^2 \right\} dV \tag{2.2}$$

Within the volume of $V$, $f$ is the free energy density and $\epsilon'$ is the gradient energy coefficient. The free energy density, $f(X')$, is assumed to have a Landau-Ginzburg form, a
double-well potential, having minima at $X' = X_1$ and $X' = X_2$.

$$f(X') = \frac{1}{4} W'(X' - X_1)^2(X' - X_2)^2 \tag{2.3}$$

where $f((X'_1 + X'_2)/2) = (W'/64)(X_2 - X_1)^4$ is the well height. We scale the order
parameter by $X = (X' - X_1)/(X_2 - X_1)$. Then, we obtain the energy density having
minima at $X = 0$ and 1. Using $X$, a scaled order parameter, Equation (2.2) and (2.3)
become Equation (2.4) and (2.5).

$$F = \int_V \left\{ f(X) + \frac{1}{2} \epsilon^2 |\nabla X|^2 \right\} dV \tag{2.4}$$

$$f(X) = \frac{1}{4} WX^2(1 - X)^2 \tag{2.5}$$
where $\epsilon^2 = (X_2 - X_1)^2 \epsilon^2$ and $W = W'(X_2 - X_1)^4$. The chemical potential, $(\delta F/\delta X)$, is obtained as a variational derivative of the free energy functional given by Equation (2.4).

\begin{equation}
\frac{\delta F}{\delta X} = \frac{df}{dX} - \epsilon^2 \nabla^2 X
\end{equation}

\begin{equation}
\frac{df}{dX} = \frac{W}{2} X(1 - X)(1 - 2X)
\end{equation}

The Allen-Cahn (AC) equation governs nonconserved dynamics (model A) while the Cahn-Hilliard (CH) equation governs conserved dynamics (model B) \[18,35,36\]. Nonconserved dynamics without long-range diffusion describes the evolution of a nonconserved order parameter such as magnetic dipole or crystalline order. Equation (2.8), the AC equation, is obtained by postulating that the time rate of change in the order parameter is proportional to the chemical potential, Equation (2.6). The chemical potential always changes toward minima of the double well potential. Thus a negative sign is appearing in Equation (2.8). On the other hand, conserved dynamics requiring long-range diffusion describes the evolution of conserved order parameters such as concentration. The CH equation is obtained by plugging Equation (2.6) into Fick’s second law. Here, the $\eta$ for the AC equation and the $\phi$ for the CH equation represent a nonconserved and a conserved order parameter, respectively.

\begin{equation}
\text{AC equation: } \frac{\partial \eta}{\partial t} = -L_\eta \left( \frac{df}{d\eta} - \epsilon^2 \nabla^2 \eta \right)
\end{equation}

\begin{equation}
\text{CH equation: } \frac{\partial \phi}{\partial t} = L_\phi \nabla^2 \left( \frac{df}{d\phi} - \epsilon^2 \nabla^2 \phi \right)
\end{equation}
where $L_\eta$ and $L_\phi$ are mobilities of nonconserved and conserved order parameter, respectively. We have assumed the $L_\eta$ and $L_\phi$ are independent of $\eta$ and $\phi$, or $\gamma$. These equations yield the following order parameter profile for a planar interface located at $x = 0$.

\begin{equation}
\phi(x) = \frac{1}{2} \left[ 1 + \tanh \left( \frac{2x}{\delta} \right) \right]
\end{equation}

\begin{equation}
\delta = 4\epsilon \sqrt{\frac{2}{W}}
\end{equation}

where $\delta$, the interfacial thickness, is a result of a balance between two opposing effects. The interface tends to be sharp in order to minimize the contribution by the first term in the integrand in Equation (2.6). This term is nonzero only at the interfacial region where $\phi$ varies between 0 and 1. Contrarily, the interface tends to be diffuse in order to minimize the contribution by the second term in the integrand in Equation 2.6, the excess free energy caused by the gradient of $\phi$. The phase-field $\phi$ varies from 0.1 to 0.9 over a distance of about $\delta$. The excess free energy of the interface, $\gamma$, is related to the gradient energy coefficient and the order parameter profile through the interface.

\begin{equation}
\gamma = \int_{-\infty}^{+\infty} \epsilon^2 \left( \frac{\partial \phi}{\partial x} \right)^2 dx
\end{equation}

Equation 2.12 is simplified to Equation 2.13 after a change of variables [18].

\begin{equation}
\gamma = \int_{0}^{1} \sqrt{2\epsilon^2 f(\phi)} d\phi
\end{equation}
By substituting Equation 2.5 into Equation 2.13, the interfacial free energy is given by constant parameters.

\begin{equation}
\gamma = \frac{\epsilon}{6} \sqrt{\frac{W}{2}} \tag{2.14}
\end{equation}

Equation (2.8) and (2.9) were nondimensionalized to investigate universal behaviors of two-phase mixtures having different values of parameters like gradient energy coefficient, potential well height, and mobilities for different mixtures. Different coefficients result in different rates of change in characteristic length, different size and time scales. Different mixtures with different size and time scales can be treated in a universal way by defining the dimensionless lengths and times.

For the AC equation, by setting \( \tilde{t} = (L_\eta W)t \), \( \tilde{\nabla} = (\frac{\epsilon}{\sqrt{W}})\nabla \), and \( \tilde{f}(\phi) = f/W \), Equation (2.15) is obtained where the tilde denotes dimensionless quantities.

\begin{equation}
\frac{\partial \eta}{\partial \tilde{t}} = - \left[ \frac{d \tilde{f}}{d \eta} - \tilde{\nabla}^2 \eta \right] \tag{2.15}
\end{equation}

For the CH equation, the length and energy scales are the same with the AC equation while the dimensionless time should be \( \tilde{t} = tL_\phi W^2/\epsilon^2 \).

\begin{equation}
\frac{\partial \phi}{\partial \tilde{t}} = \tilde{\nabla}^2 \left[ \frac{d \tilde{f}}{d \phi} - \tilde{\nabla}^2 \phi \right] \tag{2.16}
\end{equation}

The only difference between Equation (2.15) and (2.16) is the presence of a Laplacian and a negative sign. However, these two dynamics result in very different kinetics and morphology. The difference will be discussed in the Chapter 6. These equations were numerically solved using periodic boundary conditions and a finite-difference algorithm with
spatially centered, temporally forward-Euler scheme implemented on a multiple processor parallel computing platform. Hereafter, $f$, $x$, and $t$ are used as dimensionless quantities without using tilde. Then these nondimensional equations are equivalent to original equations with all constants assumed to be 1.
2.2. Implementation of simulations - parallel computing with a finite difference method

The AC and CH equations are nonlinear and thus must be solved numerically in most cases. A simple, accurate technique that can be used to solve a wide variety of nonlinear partial differential equations (PDEs) is the finite difference method. Although this technique is simple to implement, it is not easy to obtain stable solutions. Much skill and insight are required to use the FMD (Finite Difference Method) properly. It has said, "this technique is an art as much as a science" [37].

The PDEs (Equation 2.15 and 2.16) given in the previous section will be solved numerically by the use of an explicit finite difference technique. This method will be accomplished using FORTRAN 90 combined with Message Passing Interface (MPI) using AMD Opteron 64-bit cluster. Time evolution of Equation 2.15 and 2.16 will be solved on a three-dimensional (3D) or two-dimensional (2D) uniform grid depending upon the dimensionality of modeled mixture systems. From this point to the end of this section, three-dimensions will be discussed because in this study more interest is put on the three-dimensional mixtures.

The finite difference grid is a simple mesh of points in the $xyz$-space that are used to represent any function, $u(x_i, y_j, z_k)$, by its values at a discrete set of points. For a uniform 3D mesh,

$$
x_i = x_0 \pm i\Delta x, \quad i = 0, 1, 2, ... \\
y_j = y_0 \pm j\Delta y, \quad j = 0, 1, 2, ... \\
z_k = z_0 \pm k\Delta z, \quad k = 0, 1, 2, ...
$$

(2.17)
where $\Delta x$, $\Delta y$, and $\Delta z$ are grid spacings in the $x$, $y$, and $z$ direction, respectively. For a uniform grid, grid spacings in different directions are the same, $\Delta x = \Delta y = \Delta z$. From now on, $u(x_i, y_j, z_k)$ will be denoted as $u(i, j, k)$. The value of $u(i \pm l \Delta x, j \pm m \Delta x, k \pm n \Delta x)$ at a small distance from $u(i, j, k)$ can be expressed in terms of the function $u$ and its derivatives at the original mesh point, $(x_i, y_j, z_k)$, by means of Taylor series expansion about the $(x_i, y_j, z_k)$. The Taylor series expansion of the function (Equation 2.18) can be used to obtain the approximate expressions for the derivatives of $u(i, j, k)$ at $(x_i, y_j, z_k)$ in terms of the values of $u$ at adjoining mesh points.

\begin{align}
\frac{\partial u(i, j, k)}{\partial x} &= \frac{u(i + 1, j, k) - u(i - 1, j, k)}{2 \Delta x} - \left[ \frac{(\Delta x)^2}{6} \frac{\partial^3 u(i, j, k)}{\partial x^3} + \ldots \right]
\end{align}

For example, subtracting the Taylor expansion for $u(i - 1, j, k)$ from that of $u(i + 1, j, k)$ gives the exact expression.

\begin{align}
\frac{\partial u(i, j, k)}{\partial x} &= \frac{u(i + 1, j, k) - u(i - 1, j, k)}{2 \Delta x} - \left[ \frac{(\Delta x)^2}{6} \frac{\partial^3 u(i, j, k)}{\partial x^3} + \ldots \right]
\end{align}

Neglecting the terms in square brackets, the approximate expression for the derivative having an error of order $(\Delta x)^2$ is obtained.

\begin{align}
\frac{\partial u(i, j, k)}{\partial x} &= \frac{u(i + 1, j, k) - u(i - 1, j, k)}{2 \Delta x}
\end{align}

Thus this centered finite difference of the first derivative of $u(i, j, k)$ with respect to $x$ is regarded as a second order approximation.
Other derivatives and their approximations can be derived in a similar manner; this includes the temporal derivatives of the function $u$ which is also a function of time $u = u(t, x_i, y_j, z_k)$. As indexed $x$, $y$, and $z$ variables with $i$, $j$, and $k$, respectively, $p$ is used to index time such as $t_p = t_0 + p\Delta t$ where $t_0$ is the initial time, usually zero. The value of function at a given time ($t_p$) and position ($x_i, y_j, z_k$) is denoted as $u_{ijk}^p$. The forward Euler differencing in time is used.

(2.21) \[
\frac{\partial u_{ijk}^p}{\partial t} = \frac{u_{ijk}^{p+1} - u_{ijk}^p}{\Delta t} + O(\Delta t)
\]

While forward Euler is only first-order accurate in $\Delta t$, it has the advantage that the functions are defined at time step of $p+1$ only in terms of quantities known at the previous time step of $p$. This implies that the forward Euler is an explicit method.

The combination of a forward Euler for the temporal derivatives and second-order centered spatial derivatives is called the FTCS (Forward Time Centered Space) method. Substituting these finite difference approximations into the evolution equations yields the following discretized equations for nonconserved and conserved dynamics.

(2.22) \[
\phi_{ijk}^{p+1} = \phi_{ijk}^p + \Delta t \cdot \nabla^2 \left[ \frac{1}{2} (2(\phi_{ijk}^p)^3 - 3(\phi_{ijk}^p)^2 + \phi_{ijk}^p) - \nabla^2(\phi_{ijk}^p) \right]
\]

(2.23) \[
\eta_{ijk}^{p+1} = \eta_{ijk}^p + \Delta t \cdot \nabla^2 \left[ \frac{1}{2} (2(\eta_{ijk}^p)^3 - 3(\eta_{ijk}^p)^2 + \eta_{ijk}^p) - \nabla^2(\eta_{ijk}^p) \right]
\]

The laplacians are calculated with the following equation.

(2.24) \[
\nabla^2 X_{ijk} = \frac{X_{i+1,j,k}^p + X_{i-1,j,k}^p + X_{i,j+1,k}^p + X_{i,j-1,k}^p + X_{i,j,k+1}^p + X_{i,j,k-1}^p - 6X_{i,j,k}^p}{\Delta x^2}
\]
The order parameters ($\phi$ and $\eta$) at $t_{p+1}$ are computed from data at $t_p$. This single-level FTCS algorithm is the most efficient for large-scale simulations using a parallel computing technique. In our simulations, a large array of $\phi$ or $\eta$ is divided into small pieces, each of which is dispatched to a computing node having its own CPU (Central Processing Unit) and RAM (Random Access Memory). The FFT (Fast Fourier Transform) method can adopt 100 times larger time step than the FDM. However, the parallel FFT requires communications between all computing nodes while the parallel FDM requires communications only between adjacent nodes. As the number of nodes increases, the computing speed in the parallel FFT does not increase effectively due to the heavier load for data transfer between nodes. In the parallel FDM, more computing nodes results in better speed enhancement than the parallel FFT. In both cases, however, the computing speed starts to decrease when the number of nodes exceeds a certain limit depending upon the array size. Thus the optimum number of nodes should be selected by a series of testing. In this study, 8 CPUs are used for the evolution of $\phi$ whose array is $512^3$ and 32 CPUs are used for the evolution of $\eta$ whose array is $1024^3$.

Initial conditions for an order parameter ($\eta$ or $\phi$) are random noise whose average corresponds with the alloy composition. For 30% mixtures, random noise of $0.25 \sim 0.35$ are assigned to an order parameter array having the average of 0.3. The fluctuation of 0.05 is not small. However, we confirmed that the systems with the same average composition and different magnitudes of fluctuation attain statistically the same domain structure in late-stage. The noises are created by subtract-and-borrow random number generator proposed by Marsaglia and Zaman, implemented by James with the name RCARRY in
1991, and later improved by Luscher in 1993 to produce "Luxury Pseudorandom Numbers" [38,39]. These initial conditions represent a homogeneous phase of binary mixtures above $T_C$. When this system is quenched below $T_C$, phase separation processes ensue via nonconserved or conserved dynamics depending upon the nature of order parameter. The phase separation followed by coarsening was modeled by obtaining the time-evolution of the order parameter as described in this section with periodic boundary conditions.

$$X(x, y, z) = X(x + L, y, z)$$

$$X(x, y, z) = X(x, y + L, z)$$

$$X(x, y, z) = X(x, y, z + L)$$

(2.25)

2.3. Determination of the grid spacing, $\Delta x$

Large-scale simulations are required for following three reasons: to obtain large interfacial areas that allow for accurate statistical treatment of local curvatures along interfaces, to avoid the finite size effects, and to be closer to the sharp interface limit where the interface thickness is small enough compared to the radius of curvature of an interface or domain spacing. Due to the limitations of computer memory, modeling mixture systems larger than a certain size is impossible. Another important requirement is that the time duration of simulations should be reasonable. The largest arrays with $N^3$ elements should be chosen so that simulations may take affordable memory space. The array sizes for nonconserved and conserved dynamics are $N = 512$ and $N = 1024$, respectively. With the numbers of grids fixed, then the mesh size ($\Delta x$) and the time step ($\Delta t$) remain to be determined. The dimension of mixture systems is $L = N \Delta x$. Smaller values of $\Delta x$ and $\Delta t$ yield better accuracy with poorer computational economy while larger values of them
Figure 2.2. A planar interface at equilibrium located at \( x = 0 \). The order parameter profile is marked at two different resolutions. \( n \): the number of grid points across interface.

yield poorer accuracy with better computational economy. Thus it is very important in modeling to find the optimum values from trade-offs between accuracy and economy.

The mesh size is determined by examining interfacial region where the order parameter changes smoothly. During the numerical iterations using Equation (2.8) and (2.9), nonzero gradients occur only in the interfacial region. Therefore, the accuracy of gradients depends upon the number of grid points within the interfaces. Equation (2.8) and (2.9) yield a time-independent solution for a planar interface in equilibrium located at \( x = 0 \) as if
$W = 1$ and $\epsilon = 1$ in Equation 2.10.

\[
\phi(x) = \frac{1}{2} \left[ 1 + \tanh\left( \frac{x}{2\sqrt{2}} \right) \right]
\]

(2.26)

The order parameter, $\phi(x)$, changes smoothly from 0 to 1 across the interface located at $x = 0$ as shown in Figure 2.26. The interfacial thickness is defined as the width of the smooth transition region where $0.1 \leq \phi(x) \leq 0.9$. The interfacial thickness is $\delta = 4\sqrt{2} \approx 6.2146$ for the dimensionless equations, Equation (2.8) and (2.9). Numerically, by putting $n$ grids in an interface, the mesh size becomes $\Delta x = \delta/(n-1)$. Better accuracy results from a larger value in $n$ (higher resolution with a smaller mesh size) such that the interfacial energy ($\sigma = \int_{-\infty}^{\infty} (\partial \phi / \partial x)^2 dx$) is more accurately estimated. However, a larger $n$ decreases $L/\delta$ which should be large enough to reach the sharp interface limit. In addition, valid curvature data used to obtain morphological statistics must be obtained from systems where the interfacial thickness is much smaller than the characteristic length related to the average radius of curvature ($\delta \ll l$) that should be in turn much smaller than the computational box dimension ($l \ll L$) to avoid the finite size effects. Therefore, the $n$ value should be minimized as long as it does not cause the numerical instability.

A series of test runs are implemented with $(n, N)$ values of $(5, 256)$, and $(3, 128)$ in three-dimensions where $n = 5$, and $3$ correspond with $\Delta x = \sqrt{2}$, and $2\sqrt{2}$, respectively. The test runs have the same computational box dimension ($L = 256\sqrt{2}$) that is a quarter of the box dimension used in the actual simulations. The statistics may be poor because the $L = 256\sqrt{2}$ is not sufficiently large, or the finite size effects may occur. However, the purpose of these test runs is to determine the resolution, which can be selected by measuring statistical difference between microstructures resulting from two resolutions.
(a) Characteristic length ($S^{-1}_{V}$) vs. time.

(b) Difference in $S^{-1}_{V}$ defined as $\text{diff.} = \frac{(S^{-1}_{V})_{n=3} - (S^{-1}_{V})_{n=5}}{(S^{-1}_{V})_{n=5}}$.

Figure 2.3. 3D tests with different mesh size.
Tests are performed for asymmetric mixture systems with different volume fractions (36% and 40%) evolving via conserved dynamics, using the CH equation. Hence, four sets of simulations for two volume fractions and two resolutions are examined.

Different time steps must be used for two resolutions. The time steps should be sufficiently small to maintain the stability during numerical iterations such that $\Delta t \ll (\Delta x)^4$ for the CH equation. The largest possible time steps were taken to be 0.032 and 0.512 for $n = 3$ and $n = 5$, respectively. It was confirmed that they do not cause the numerical instability by testing a series of different time steps and different stable time steps produce identical results. Then we compare the two resolutions by plotting the characteristic lengths in Fig. 2.3(a) and difference in the characteristic lengths between
the two resolutions in Fig. 2.3(b) as functions of time. Hereafter, the characteristic length \( l \) is defined as the reciprocal of the interfacial area per volume, \( S_V^{-1} \), that has the dimension of length. The results indicate that the growth trends approximately match with the LSW growth law \( (1/S_V \sim t^{1/3}) \). Two resolutions yield very little difference in the characteristic length for the two mixture systems. The differences are within 2.5%. More importantly, the difference decreases with time.

The interfacial shape distributions (ISD) were calculated for more rigorous comparisons. The ISD is a probability density contour plot of interfacial curvatures, whose details are explained in the following section, for 36% mixtures with different resolutions. The ISDs were calculated to establish that the mesh size and the time step do not cause the significant morphological difference for the 36% mixtures with two resolutions. We select the simulation time of \( t = 64000 \) \( (t^{1/3} = 40) \). The ISDs are presented in Figure 2.4. The two resolutions yield similar ISDs although they are not exactly identical. However, these

<table>
<thead>
<tr>
<th>dimensions</th>
<th>dynamics</th>
<th>( V_f )</th>
<th>( N )</th>
<th>No. of simulation sets</th>
<th>( \Delta x ) (n)</th>
<th>( \Delta t )</th>
</tr>
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<tr>
<td>3D</td>
<td>AC</td>
<td>50%</td>
<td>1024</td>
<td>2</td>
<td>( 2\sqrt{2} ) (3)</td>
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<tr>
<td>3D</td>
<td>CH</td>
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<td>512</td>
<td>2</td>
<td>( 2\sqrt{2} ) (3)</td>
<td>0.512</td>
</tr>
<tr>
<td>3D</td>
<td>CH</td>
<td>40%</td>
<td>512</td>
<td>2</td>
<td>( 2\sqrt{2} ) (3)</td>
<td>0.512</td>
</tr>
<tr>
<td>3D</td>
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<td>( 2\sqrt{2} ) (3)</td>
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</tr>
<tr>
<td>3D</td>
<td>CH</td>
<td>30%</td>
<td>256</td>
<td>2</td>
<td>( \sqrt{2} ) (5)</td>
<td>0.032</td>
</tr>
<tr>
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<td>CH</td>
<td>22%</td>
<td>256</td>
<td>2</td>
<td>( \sqrt{2} ) (5)</td>
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</tr>
<tr>
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<td>2048</td>
<td>4</td>
<td>( \sqrt{2} ) (5)</td>
<td>0.4</td>
</tr>
<tr>
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<td>CH</td>
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<td>1024</td>
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<tr>
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<tr>
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<td>4</td>
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<td>0.032</td>
</tr>
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</table>

Table 2.1. Parameters for simulations. AC=nonconserved dynamics (model A), CH=conserved dynamics (model B), \( V_f \) =volume fraction of minority phase, \( N \) =the number of array elements along one direction, \( \Delta x \) =mesh size, \( n \) =the number of meshes at interfaces, and \( \Delta t \) =time step.
test runs use small computational box dimensions where the interfacial areas are not sufficiently large for good statistics. Nevertheless, the pairs of principal curvatures with the highest probability are similar, located at \((\kappa_1/S_V, \kappa_2/S_V) \simeq (-0.4, 1.5)\). In addition, the values of the maximum probability (0.35 for \(n = 5\) and 0.36 for \(n = 3\)) are also similar. The overall shapes of probability contours are approximately similar as well. Based on results in Fig. 2.3 and 2.4, the resolution of \(n = 3\) (the mesh size of \(\Delta x = 2\sqrt{2}\)) was selected for the modeling of 36\% mixtures with a conserved order parameter. Three mesh points at an interface was also used by Badalassi et al [5].

In the same manners, the mesh size and the time step were determined for other volume fractions or dynamics. They are listed in Table 2.1. Note that a mesh size of \(\Delta x = \sqrt{2}\) was used for 22\% and 30\% mixtures in which droplet-shaped domains of the minority phase form. It is well-known that a spherical domain becomes a cuboidal domain when the mesh size is too large, which is called grid anisotropy (See Figure 2.5). When the anisotropy presents, the ISD has nonzero probability at the origin representing a planar interfacial patch \((\kappa_1 = \kappa_2 = 0)\). The \(\kappa\)'s denote the principal curvatures. There are clear planar interfacial patches on the domains in Figure 2.5(b), there is no probability at the origin. Other 3D mixtures with higher volume fractions than 36\% do not produce such planar interfacial patches when \(\Delta x = 2\sqrt{2}\) is used. However, when \(\Delta x = 2\sqrt{2}\) is used, the grid anisotropy appears in all mixture systems having spherical (3D) or circular (2D) domains including three-dimensional 22\% and 30\% mixtures and all asymmetric two-dimensional mixtures. Therefore, \(\Delta x = \sqrt{2}\) was adopted for such mixtures with droplets.
Figure 2.5. Domains of 22% mixtures at $t = 153600$ ($t^{1/3} = 53.6$). Interfaces are colored with scaled Gauss curvature ($K/S_V^2$). The Gauss curvature $K$ is defined as $K = \kappa_1 \kappa_2$ where $\kappa_1$ and $\kappa_2$ are the principal curvatures as a function of position on the interfaces. An edge length is $4(1/S_V)$. These are portions of the entire computational domain. Note that there are many flat interfaces in (b).

2.3.1. Calculation of surface area per volume, $S_V$

With a given 3D array of order parameter having values of 0 to 1, a three-dimensional surface representing interfaces between two phases was determined as a set of $(x, y, z)$-locations where the order parameter values are 0.5 by means of the shade volume method [40]. This method is similar to the marching cubes algorithms described by Lorenson and Cline [41]. Each individual element in the set is called vertex. The shade volume method using a built-in function SHADE_VOLUME in IDL (Interactive Data Language),
a commercial package, was implemented to produce a list of N vertices constituting the interfaces present in the mixture and their vertex areas that the vertices occupy as shown in Table 2.2. This is the level surface of $\phi = 0.5$. Each vertex area serves as a weighting factor of each vertex. The sum of all vertex areas is the total interface area, $S$. Then, $S_V$ is obtained by dividing $S$ by the volume of the system, $V$.

\[
S = \sum_{i=1}^{N} S_i
\]

\[
S_V = \frac{S}{V}
\]

where $S_i$ is the vertex area of the $i$th vertex and $V$ is the system volume. The list of vertices and vertex areas will be used again for morphological and topological calculations described in Section 2.5.2 and 2.5.3.

### 2.4. Structure Function

The most common method for characterizing complicatedly shaped domains is structure function (SF), $F(\vec{q}, t)$. The SF is a Fourier transform of spatial correlation function between two points in a mixture. It is very useful for analyzing patterned structures,

<table>
<thead>
<tr>
<th>vertex, $i$</th>
<th>location, $(x_i, y_i, z_i)$</th>
<th>vertex area, $S_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$(x_1, y_1, z_1)$</td>
<td>$S_1$</td>
</tr>
<tr>
<td>2</td>
<td>$(x_2, y_2, z_2)$</td>
<td>$S_2$</td>
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<td>.</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td>$N$</td>
<td>$(x_N, y_N, z_N)$</td>
<td>$S_N$</td>
</tr>
</tbody>
</table>
showing how a given patterned structure scatters incident radiation. To analyze experimental domain structures, light scattering is used for polymer blends [25, 42, 43] and neutron scattering [44–46] or small-angle X-ray scattering [47, 48] is used for metallic alloys or glass systems. Mathematically, the SF is defined as a norm of Fourier transform of order parameter $\phi$.

\begin{equation}
\hat{\phi}(\vec{q}, t) = \frac{1}{V} \int_V \phi(\vec{r}, t) e^{-2\pi i \vec{q} \cdot \vec{r}} dV
\end{equation}

\begin{equation}
F(\vec{q}, t) = \hat{\phi}(\vec{q}, t) \hat{\phi}^*(\vec{q}, t)
\end{equation}

\begin{equation}
\vec{q} = \vec{r}/L
\end{equation}

where the hat denotes Fourier transform and the asterisk denotes complex conjugate. The discrete Fourier transforms were obtained using the FFT function in IDL. The SFs are averaged spherically as follows since the structures are isotropic.

\begin{equation}
F(q_u, t) = \frac{1}{N_q} \sum_{q_u \leq q \leq q_u + \Delta q} F(q, t)
\end{equation}

where $q = \sqrt{q_x^2 + q_y^2 + q_z^2}$; $\Delta q = \Delta x/L = 1/N$; $u = 0, 1, 2, 3, ..., N$. The Fourier intensity of the $u$th mode is denoted by $F(q_u, t)$. The SFs obtained from mixtures undergoing late-stage coarsening are well known to satisfy the scaling hypothesis [49].

\begin{equation}
F(q) = l^d F_{sc}(ql)
\end{equation}

where $d$ is the dimensionality of the given order parameter; $l$ is the characteristic length.
2.5. Morphology and Topology

Unlike the systems with precipitates embedded in a matrix where the particle size distribution can be measured, interfacial curvatures are used to quantify morphology and topology of complex three-dimensional domains. The morphology is quantified by the statistics of 3D curvatures that represent interfacial shapes, and the topology is quantified by the genus related to the area averaged Gaussian curvature, a kind of three-dimensional curvatures. This section includes the basics of the three-dimensional curvatures, the calculation of curvature statistics for morphology and genus for topology. The techniques used in this study are described in many literatures [22, 50–58]. All the curvature calculations were done for the mixtures in the late-stage where their characteristic lengths are at least five times greater than the interfacial thickness ($\delta = 4\sqrt{2} \simeq 5.66$).

2.5.1. 3D curvatures

An interfacial patch has two principal directions along which two principal curvatures are defined. One is the minimum principal curvature denoted by $\kappa_1$ and the other is the maximum principal curvature denoted by $\kappa_2$. Both principal curvatures have the dimension of $[1/\text{length}]$. These are illustrated in Figure 2.6. Another pair of 3D curvatures is mean curvature ($H$) having the dimension of $[1/\text{length}]$ and Gaussian curvature ($K$) having the dimension of $[1/\text{length}^2]$ that are related to the principal curvatures by the following equations.

$$H = \frac{\kappa_1 + \kappa_2}{2}$$
Figure 2.6. Illustration of 3D curvatures at an interfacial patch, $p$. $\vec{n}$: interfacial normal, $R_1$ and $R_2$: principal radii of curvatures, $\kappa_1$: minimum principal curvature, and $\kappa_2$: maximum principal curvature

\begin{equation}
K = \kappa_1 \kappa_2
\end{equation}

The pair of two principal curvatures determines the shape of the patch. If both $\kappa_1$ and $\kappa_2$ have the same sign ($K > 0$), the interface patch is elliptic (convex or concave). If $\kappa_1$ is negative and $\kappa_2$ is positive ($K < 0$), the patch is hyperbolic (saddle-shaped). If one of principal curvatures is zero ($K = 0$), the patch is parabolic (cylindrical). On the other hand, the mean curvature is related to the evolution kinetics of the patch and the Gaussian curvature area-averaged over all the interfaces present in a mixture is related to the genus of domains, which will be explained in the last part of this section.

Owing to Equations 2.34 and 2.35, one can obtain one pair of 3D curvatures by knowing the other pair of them. First, mean and Gaussian curvatures were calculated because they
can be easily obtained from the interfacial normal, $\vec{n}$, using the following equations [59].

\begin{equation}
H = \frac{1}{2} (\nabla \cdot \vec{n})
\end{equation}

\begin{equation}
K = \frac{1}{2} \left[ (\nabla \cdot \vec{n})^2 - \sum_{i=1}^{3} \sum_{j=1}^{3} \left( \frac{\partial n_j}{\partial x_i} \right)^2 \right]
\end{equation}

\begin{equation}
\vec{n} = -\frac{\nabla \phi}{|\nabla \phi|}
\end{equation}

where $\phi$ is the order parameter as a function of position, $\phi = \phi(x_1, x_2, x_3)$. However, these calculations require high order derivatives of $\phi$. As discussed in the previous section, only three points are placed at interfacial regions. Although the resolution is sufficient for evolving the order parameter, it is not sufficient for obtaining accurate curvature data. Hence the smoothing technique is used to put more grid points at interfacial regions with a minimal change of the interfacial locations or the locations of the level surface $\phi = 0.5$.

Two steps of smoothing operations were performed for systems with $\Delta x = 2\sqrt{2}$ ($n = 3$). First, the system is evolved with the lower potential barrier until its characteristic length increases by 0.075%. Equation 2.5 is modified yielding a quarter of the well height.

\begin{equation}
f(\phi) = \frac{1}{16} \phi^2 (1 - \phi)^2
\end{equation}
Figure 2.7. Interfacial profiles of a conserved order parameter $\phi$ along the line from $(200, 0, 0)$ to $(300, 0, 0)$ before and after smoothing at $t = 409600$.

which doubles the interfacial thickness. At this point, there are five points across an interface. Then a $5 \times 5 \times 5$ boxcar smoothing is operated on the $\phi$ using Equation (2.40)

$$\phi(i, j, k) = \frac{1}{125} \sum_{I=i-2}^{i+2} \sum_{J=j-2}^{j+2} \sum_{K=k-2}^{k+2} \phi(I, J, K)$$

Interfacial profiles of $\phi$ are shown in Figure 2.7. It is noticed that the location of $\phi = 0.5$ slightly moved to the left. However, more grid points in interfacial regions provide the SHADE VOLUME function better resolution for determining interfacial locations. Figure
2.8 shows the three-dimensionally rendered surface of $\phi = 0.5$. Many wiggles are observed in Figure 2.8(a) while the surface is very smooth in Figure 2.8(b). After the smoothing operations, the $\phi$ arrays are ready for curvature calculations.

Knowing all the curvatures of all interfacial patches existing in mixtures, we are ready to quantify the morphology related to the statistics of local interfacial shapes and the topology related to the global connectivity of interconnected structures.

2.5.2. Morphology

Interfacial shape distribution (ISD), $P(\kappa_1, \kappa_2)$, is defined as a probability density of finding a patch of interface with principal curvatures of $\kappa_1$ and $\kappa_2$. It is very useful for quantifying interfacial shapes present in a mixture. In Figure 2.9 there are four possible regions marked 1 to 4, divided by four lines such as two axes ($\kappa_1 = 0$ and $\kappa_2 = 0$) where $K = 0$, $\kappa_1 = -\kappa_2$ where $H = 0$, and $\kappa_1 = \kappa_2$. The region below $\kappa_1 = \kappa_2$ is forbidden by the definition of minimum and maximum principle curvatures ($\kappa_1 \leq \kappa_2$). All parabolic (cylindrical) patches are on the $\kappa_1$– and $\kappa_2$–axes and all spherical patches are on $\kappa_1 = \kappa_2$. All zero mean curvature patches lie on $\kappa_1 = -\kappa_2$. All elliptic patches are on Region 1 or 4 while all hyperbolic (saddle-shaped) patches are on Region 2 or 3.

An ISD is obtained by the following procedures.

1. **Calculating** $(H, K)$ **on a given order parameter** ($\phi$ or $\eta$) **using Equation 2.36 and 2.37.** Now we have three-dimensional arrays of $H(x, y, z)$ and $K(x, y, z)$. However, the curvature values are meaningful only at interfaces where $\phi$ or $\eta = 0.5$.  


(2) **Interpolating** \((H, K)\) **values** on the vertices that is obtained when \(S_V\) is calculated (See Section 2.3.1).

(3) **Converting** \((H, K)\) **values** to \((\kappa_1, \kappa_2)\) **values** by using Equation 2.41 and 2.42 resulted from Equation 2.34 and 2.35.

\[
\begin{align*}
\kappa_1 &= H - \sqrt{H^2 - K} \\
\kappa_2 &= H + \sqrt{H^2 - K}
\end{align*}
\]

Then we have a complete list of vertex areas, \((H, K), (\kappa_1, \kappa_2)\) **values** on corresponding vertices as shown in Table 2.3.

<table>
<thead>
<tr>
<th>vertex, (i)</th>
<th>location, ((x_i, y_i, z_i))</th>
<th>vertex area, (S_i)</th>
<th>((H_i, K_i))</th>
<th>((\kappa_1, \kappa_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>((x_1, y_1, z_1))</td>
<td>(S_1)</td>
<td>((H_1, K_1))</td>
<td>((\kappa_1)_1, (\kappa_2)_1))</td>
</tr>
<tr>
<td>2</td>
<td>((x_2, y_2, z_2))</td>
<td>(S_2)</td>
<td>((H_2, K_2))</td>
<td>((\kappa_1)_2, (\kappa_2)_2))</td>
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</tr>
<tr>
<td>(N)</td>
<td>((x_N, y_N, z_N))</td>
<td>(S_N)</td>
<td>((H_N, K_N))</td>
<td>((\kappa_1)_N, (\kappa_2)_N))</td>
</tr>
</tbody>
</table>

(4) **Obtaining** the sum of vertex areas of interfacial patches whose principal curvatures belong to \(\kappa_1\) to \(\kappa_1 + \Delta \kappa\) and \(\kappa_2\) to \(\kappa_2 + \Delta \kappa\).

\[
A(\kappa_1, \kappa_2) = \text{The sum of areas } (S_i) \text{ of vertices}
\]

where \(\kappa_1 \leq (\kappa_1)_i < \kappa_1 + \Delta \kappa\) and \(\kappa_2 \leq (\kappa_2)_i < \kappa_2 + \Delta \kappa\)
Finally, $A(\kappa_1, \kappa_2)$ is divided by the total interfacial area, $S$, times $(\Delta \kappa)^2$.

\[ P(\kappa_1, \kappa_2) = \frac{A(\kappa_1, \kappa_2)}{S(\Delta \kappa)^2} \]

where selecting an adequate bin size for curvature data, $\Delta \kappa$, is important to get meaningful statistics. When $\Delta \kappa$ is too small, the ISD is very noisy (not a smooth function). When $\Delta \kappa$ is too large, an accurate probability contour shape cannot be obtained. In our calculation, we used $\Delta \kappa = 0.029 S_V$ for both dynamics. Note that $\Delta \kappa$ decreases with $S_V$. As coarsening proceeds, interfacial curvatures decrease to reduce total free energy of the system. Therefore, finer bin sizes are needed for the systems at the later stage of coarsening.

The ISD is normalized by integrating over the entire curvature space and setting this value to one.

\[ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P(\kappa_1, \kappa_2) d\kappa_1 d\kappa_2 = 1 \]

ISDs were scaled with characteristic length, satisfying the following relations.

\[ P_{scd}(\tilde{\kappa}_1, \tilde{\kappa}_2) = S_V^2 P(\kappa_1, \kappa_2) \]

\[ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P(\tilde{\kappa}_1, \tilde{\kappa}_2) d\tilde{\kappa}_1 d\tilde{\kappa}_2 = 1 \]

where $\tilde{\kappa}_1 = \kappa_1 / S_V$ and $\tilde{\kappa}_2 = \kappa_2 / S_V$. Unlike the scaling of SFs where the intensity of scaled SFs are obtained by multiplying $S_V^3$ to the intensity of original SFs, the probability density of scaled ISDs is obtained by multiplying $S_V^2$. Note that SFs are functions in
three-dimensional reciprocal space while ISDs are functions in two-dimensional curvature space.

2.5.3. Topology

Another measure to understand complex structures is topology. In this section, we investigate the topology of phase domains, the connectivity of interconnected domains. We use genus \( g \) defined as the number of cuts that can be made upon an enclosed surface without separating it into two disconnected bodies. By this definition, a cube, sphere, and pyramid are all topologically equivalent \( (g = 0) \) while a cup with a handle and a donut are also equivalent \( (g = 1) \). Conversely, a sphere and a donut are different because one cannot be deformed to the other by stretching and squeezing, without cutting or sticking together bodies that were previously separated. A cube within which \( n \) separate spheres exist has a genus of \( -n \). In addition, genus corresponds with the 1st Betti number \( (\beta_1) \) that Gameiro et al used [60] to their two-dimensional calculations, if the domains are bicontinuous. Genus per volume, \( g_V \), is interpreted as the handle or tunnel density. A higher genus object is more complicated in its structure such that a pretzel has a more complicated shape than a donut. In self-similar coarsening of bicontinuous domains, topology is modified by pinching, a genus-decreasing event. Thus it should be interesting to measure the genus as a function of time or the time-rate of genus reduction in coarsening systems.

Gauss-Bonnet theorem links the genus to the Gaussian curvature, a parameter that is related to morphology. This theorem offers us a precise method to calculate genus of
domains in mixtures satisfying the periodic boundary conditions.

\begin{equation}
\tag{2.48}
g = 1 - \frac{1}{4\pi} \int_S KdS
\end{equation}

where \( S \) denotes interfaces between domains. On an enclosed surface such as a sphere, the integration \( \int_S KdS \) yields \( 4\pi \) which yields the genus of zero. The numerical area integration with Equation \ref{2.48} was performed using the Gaussian curvature data at interfacial patches (vertices) and the areas of the patches (vertex areas) listed in Table \ref{2.3}.

\begin{equation}
\tag{2.49}
g = 1 - \frac{1}{4\pi} \sum_{i=1}^{N} K_i S_i
\end{equation}

The genus is related to the Euler characteristic, sometimes also known as the Euler-Poincaré characteristic, \( \chi \).

\begin{equation}
\tag{2.50}
\chi = 2(1 - g)
\end{equation}

For a polyhedron, the Euler characteristic is related to the number of faces (\( v \)), edges (\( e \)), and vertices (\( f \)).

\begin{equation}
\tag{2.51}
\chi = v - e + f
\end{equation}

Equation \ref{2.50} and \ref{2.51} provides another method to calculate the genus. When the SHADE VOLUME function is operated on a smooth enclosed surface, it divides the smooth surface into a large number of small polygons. The enclosed surface becomes a polyhedron having a large number of faces, edges, and vertices. Thus the genus can be obtained by counting the number of faces, edges, and vertices. However, we choose the
method that uses the GB theorem because the data from our other calculations can be re-used.
Figure 2.8. Interfacial morphology before and after smoothing. These are $(128\sqrt{2})^3$ portions taken from a conserved order parameter $\phi$ with $512^3$ grid points at $t = 409600$. 
Figure 2.9. A map for interfacial shapes in the interfacial shape distribution.
CHAPTER 3

Three-Dimensional Mixtures Evolving via Nonconserved Dynamics

The nonconserved dynamics, also called model A, describes the evolution of a non-conserved order parameter such as magnetization in an Ising magnet. In this dynamics, there is no exchange of mass between two different locations. Instead, an interfacial patch evolves depending upon its own curvature, \( v = -MH \) when \( v \) is the velocity normal to the interface and \( M \) is a mobility. Therefore, the evolution of an interfacial patch is local. The weak coupling between interfacial patches would be expected to yield a large deviation from zero mean curvature in the distributions of interfacial curvatures that will be investigated by the morphological calculations, the interfacial shape distributions.

Only symmetric mixtures were investigated. The order parameter is not conserved if the volume fraction is not 50\%. In asymmetric mixtures, one domain will quickly grow to the size of the system. In the symmetric mixtures, domains are interconnected rather than droplet-shaped. In this chapter, we focus on the evolution of morphology and topology in mixtures with a nonconserved order parameter. Four snapshots of the evolution of mixtures via nonconserved dynamics are presented in Figure 3.1 to 3.4. This system maintains its bicontinuous domain structures within our simulation time. Different types of interfacial shapes are observed in all the snapshots. In Figure 3.5 portions of the whole computational domains are presented. All the portions have the edge length of \( 6(1/S_V) \).
The evolution of the characteristic length is shown in Figure 3.6. The growth exponent is \( m = 2 \) for \( l^m(t) - l^m(0) = kt \) [18].

### 3.1. Structure Function

Much literature presents the structure functions (SFs) of two phase systems with a nonconserved order parameter. Prior to our morphological and topological investigations, it is good to check whether our results agree with past results. The SFs of a nonconserved order parameter have highest intensity at \( q \to 0 \) which reflects the nature of the non-conserved dynamics. We investigate the early phase separation stage and the late-stage domain coarsening.

Consider the evolution of \( \eta(r, t) \), a nonconserved order parameter at the very early stage of phase separation.

\[
\eta = \eta_0 + \delta \eta
\]

where \( \eta_0 = 0.5 \) and \( \delta \eta \ll 1 \). If a small fluctuation \( \delta \eta \) is expressed as a sinusoidal wave,

\[
\delta \eta = A_\eta(q, t)e^{2\pi i q \cdot r}
\]

where \( q \) is the wave vector whose element has a dimension of \([1/\text{length}]\). By substituting Equation 3.1 and 3.2 into the Allen-Cahn equation (Equation 2.15), we can obtain the growth rate of the Fourier amplitude, \( A(q, t) \).

\[
\frac{\partial \delta \eta}{\partial t} = - [g(\eta_0 + \delta \eta) - \nabla^2 \delta \eta]
\]
Figure 3.1. A symmetric $\eta$ at $t = 480$ ($1/S_V = 56.8$). Transparent regions denote the phase with $\eta = 0$, and gray regions denote the phase with $\eta = 1$. 
Figure 3.2. A symmetric $\eta$ at $t = 1600 (1/S_V = 101.4)$. Transparent regions denote the phase with $\eta = 0$, and gray regions denote the phase with $\eta = 1$. 
Figure 3.3. A symmetric $\eta$ at $t = 4000$ ($1/S_V = 158.9$). Transparent regions denote the phase with $\eta = 0$, and gray regions denote the phase with $\eta = 1$. 
Figure 3.4. A symmetric $\eta$ at $t = 9600$ ($1/S_V = 245.4$). Transparent regions denote the phase with $\eta = 0$, and gray regions denote the phase with $\eta = 1$. 
Figure 3.5. Self-similar evolution of 3D domains in a 50% mixture with a nonconserved order parameter. These are portions taken from the computational domains. An edge length is $6(1/S_V)$. 
where \( g(\eta) = df/d\eta \). The Taylor expansion of \( g(\eta) \) around \( \eta_0 \) is used to get approximate \( g(\eta_0 + \delta\eta) \).

\[
(3.4) \quad g(\eta_0 + \delta\eta) \approx g(\eta_0) + \left( \frac{dg}{d\eta} \right)_{\eta=\eta_0} \delta\eta
\]

For symmetric mixtures, \( g(\eta_0 = 0.5) \) is zero because of Equation 2.7. Thus Equation 3.3 becomes Equation 3.5.

\[
(3.5) \quad \frac{\partial\delta\eta}{\partial t} = - \left[ \left( \frac{dg}{d\eta} \right)_{\eta=\eta_0} \delta\eta - \nabla^2 \delta\eta \right]
\]
Finally, combining Equation 3.5 and Equation 3.2 yields Equation 3.7, the growth rate of the Fourier amplitude, $A_\eta(q, t)$.

\[
\frac{1}{A} \frac{\partial A}{\partial t} = - \left[ \left( \frac{dg}{d\eta} \right)_{\eta=\eta_0} + 4\pi^2 q^2 \right] A(q, t) e^{2\pi i q \cdot q}
\]
\[ \frac{\partial A_\eta(q,t)}{\partial t} = - \left[ -\frac{1}{4} + 4\pi^2 q^2 \right] \]

where

\[ \frac{\partial g}{\partial \eta} \bigg|_{\eta=\eta_0=1/2} = \frac{1}{2} (6\eta_0^2 - 6\eta_0 + 1) = -\frac{1}{4} \]

where \( q = |q| \). The growth rate is positive for \( q < (4\pi)^{-1} \approx 0.080 \) and negative for \( q > (4\pi)^{-1} \). More importantly, the growth rate does not have a nonzero maximum for \( q > 0 \). Thus fluctuations of wavenumber \( q < (4\pi)^{-1} \) grow.

SFs obtained in the late-stage are presented in Figure 3.8. Our results agree with calculations done by others [61–63]. Consistent with the linear stability theory; Equation 3.7 and Figure 3.7, as coarsening proceeds, longer wavelength modes grow faster than shorter wavelength modes. There is no peak intensity at a nonzero \( q \). SFs were scaled by the characteristic length \( (1/S_v) \) satisfying the scaling hypothesis expressed by Equation 2.33. All the scaled SFs at selected times are nearly identical, and thus the scaled SFs of a nonconserved order parameter are time-invariant in the late-stage where the linearized theory does not hold.

### 3.2. Morphology - Interfacial shape distribution

Interfacial shape distributions (ISDs) described in Section 2.5.2 were calculated for the mixtures with a nonconserved order parameter. The time-evolution of ISDs are presented in Figure 3.9 to 3.12. Since coarsening is driven by the reduction of interfacial curvature, the probability contours move toward the origin. The shape of contours is round and symmetric about the zero mean curvature line \( \kappa_2 = -\kappa_1 \) or \( H = 0 \) due to the equal
Figure 3.8. Evolution of structure functions in a symmetric mixture with a nonconserved order parameter.
volume fractions of the two phases. Although the majority of interfacial patches are hyperbolic (saddle-shaped), there are also elliptic interfacial patches. The boundaries between different colors are smooth at earlier times while those are not completely smooth in the latter ISD at $t = 9600$. This poorer statistics in the latest ISD is due to the fact that the number of interfacial patches where curvature data are obtained decreases as coarsening proceeds. Most importantly, the shapes of ISDs at different times are similar, which is verified by scaling the ISDs with the characteristic length ($l = 1/S_V$) shown in Figure 3.13 to 3.16. The scaled ISD at $t = 9600$ is a little bit asymmetric about the $H = 0$ line, translated to the down left from the $H = 0$ line. It is also due to the poor statistics.

These self-similar scaled ISDs are unique to the nonconserved dynamics. If a scaled ISD from an experiment of domain coarsening in a real sample is similar to this unique scaled ISD, then we may state that the system evolves with nonconserved dynamics. This serves as a counterpart for interconnected domain structures to the scaled particle-size distribution for spherical precipitates in a matrix.

The majority of interfacial area is hyperbolic (saddle-shaped) ($\kappa_1 \kappa_2 = K < 0$) although there is a small interfacial area with elliptic shapes ($\kappa_1 \kappa_2 = K > 0$). The peak is located at $\kappa_1/S_V \simeq -1$ and $\kappa_2/S_V \simeq 1$. The pair of interfacial curvatures with the highest probability represents the most probable interfacial shape existing in symmetric mixtures with a nonconserved order parameter. The highest probability at $\kappa_1/S_V = -1$ and $\kappa_2/S_V = 1$ implies that the interfacial area per volume is a good estimation of the length scale of curvature in the system. By integrating these scaled ISDs, the fractions of hyperbolic and elliptic interfacial areas in the mixtures with a nonconserved dynamics were calculated. The calculations yield the results that $(17.38 \pm 0.15)\%$ of the interfacial area
Figure 3.9. The interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter $\eta$ at $t = 480 (1/S_v = 56.8)$. 
Figure 3.10. The interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter $\eta$ at $t = 1600$ ($1/S_V = 101.4$).
Figure 3.11. The interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter $\eta$ at $t = 4000$ ($1/S_V = 158.9$).
Figure 3.12. The interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter \( \eta \) at \( t = 9600 \) \((1/S_V = 245.4)\).
Figure 3.13. The scaled interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter \( \eta \) at \( t = 480 \) (\( 1/S_V = 56.8 \)).
Figure 3.14. The scaled interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter $\eta$ at $t = 1600$ ($1/S_V = 101.4$).
Figure 3.15. The scaled interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter $\eta$ at $t = 4000$ ($1/S_V = 158.9$).
Figure 3.16. The scaled interfacial shape distribution of a system undergoing coarsening with a nonconserved order parameter $\eta$ at $t = 9600$ ($1/S_V = 245.4$).
in the system is composed of elliptic interfaces. This number was obtained by averaging results from different times. The time-evolution of the fraction of elliptic interfacial area is shown in Figure [3.17]. The average values of principal curvatures were calculated. They are \( \langle k_1/S_V \rangle \approx -1.39 \pm 0.02 \), \( \langle k_2/S_V \rangle \approx -1.36 \pm 0.01 \) and \( \langle K/S_V^2 \rangle \approx -1.77 \pm 0.03 \). For mean curvature whose average is zero in symmetric mixtures, the root-mean-squared value of \( \sqrt{\langle (H/S_V)^2 \rangle} \approx 0.94 \pm 0.01 \) was obtained.
3.3. Topology

The self-similar scaled morphology unique to the nonconserved dynamics was investigated using the scaled ISD in the previous section. In this section, the scaled structure is investigated from another point of view, topology. While the morphology is represented by the statistics of curvatures, the topology is represented by genus \( g \). As mentioned previously, \( g \) is related to the average Gaussian curvature according to the Gauss-Bonnet theorem given by Equation \( \text{2.48} \). The numerical area integration with Equation \( \text{2.49} \) is calculated using the list of the Gaussian curvatures at vertices of interfaces and the areas of the corresponding vertices given in Table \( \text{2.3} \).

Prior to the calculation of genus, the bicontinuity of domains in mixtures with a nonconserved order parameter were confirmed by visual inspection of interfaces shown in Figure \( \text{3.1} \) to \( \text{3.4} \) using a 3D rendering technique. The LABEL REGION function, a built-in function in Interactive Data Language, which indices separate domains by consecutive integers, was also used along with the 3D rendering to determine if the domains are interconnected.

The time evolution of genus per volume, interpreted as a handle or a tunnel density, is shown in Figure \( \text{3.18} \). The log-log plot shows that the genus density is approximately proportional to \( t^{3/2} \) which agrees with the topological scaling law proposed by Fialkowski et al \( \text{[23]} \), \( \chi(t) \sim l^{-d}(t) \) where \( \chi(t) \) is the Euler characteristic per volume; \( l(t) \) is the characteristic length; \( d \) is the dimensionality. Since \( l(t) \sim t^{1/2} \), \( d = 3 \), and \( g \sim -\chi/2 \) when \( g \gg 1 \), the genus also obeys the scaling hypothesis, \( g(t) \sim l^{-3}(t) \sim (t^{1/2})^{-3} \), in three-dimensions.
Figure 3.18. A log-log plot of genus density vs time. The fitting equation is \( \log(g/V) = -1.4 \log t - 1.1946 \).

We define the scaled genus, \( g_V S_V^{-3} \), where \( g_V \) is the genus density \((g/V)\) and \( S_V \) is the interfacial area per volume. The characteristic volume is \( S_V^{-3} \) since \( S_V^{-1} \) is the characteristic length. Thus the scaled genus represents the genus per characteristic volume, interpreted as the number of handles or tunnels within a characteristic volume. Because of the topological scaling hypothesis, the scaled genus is time-invariant. The time-evolution of the scaled genus of the mixtures with a nonconserved order parameter is shown in Figure 3.19. The scaled genus is approximately time-invariant. A the scaled genus of 0.13 corresponds to a system in which there are 13 handles or tunnels within a volume of \( 100S_V^{-3} \). The average and the standard deviation of scaled genii at different times is \( 0.139 \pm 0.003 \). This scaled genus will be compared with that from systems evolving during coarsening with conserved dynamics.
Figure 3.19. Scaled genus vs. characteristic length of mixtures with a non-conserved order parameter.

3.4. Dynamics of the interfacial shape distribution

The probability of finding a patch of interface with a given $\kappa_1, \kappa_2$ is defined as:

\[ P(\kappa_1, \kappa_2, t) = \frac{A(\kappa_1, \kappa_2, t)}{A_T(t)} \]

where $A$ is the total area of all patches with a given pair of principle curvatures, and $A_T$ is the total area of interface.
The area of interface, $A_\kappa$, in a given area with $(\kappa_1 \sim \kappa_1 + \Delta \kappa_1, \kappa_2 \sim \kappa_2 + \Delta \kappa_2)$ in $\kappa$-space, $\Omega$, is thus,

$$A_\kappa = \int_\Omega A_T(t)P(\kappa_1, \kappa_2, t)d\kappa_1d\kappa_2$$

(3.10)

The time rate of change of this area is,

$$\frac{\partial A_\kappa}{\partial t} = \int_\Omega \frac{\partial (A_T P)}{\partial t} d\kappa_1d\kappa_2$$

(3.11)

The change in interfacial area demarked in $\kappa$-space is given by the amount of interfacial area that flows into this demarked area in $\kappa$-space through the boundary of $\Omega$, $\partial \Omega$, and the amount of area that is created by topological singularities that cannot described by a flow through the boundary of $\Omega$,

$$\frac{\partial A_\kappa}{\partial t} = -\int_{\partial \Omega} (A_T P) \dot{\kappa} \cdot n dl + \int_\Omega Q d\kappa_1d\kappa_2$$

(3.12)

where $\dot{\kappa} = \dot{\kappa}_1 \hat{\kappa}_1 + \dot{\kappa}_2 \hat{\kappa}_2$, $\dot{\kappa} = d\kappa/dt$, $n$ is the normal to $\partial \Omega$ and $\hat{\kappa}_i$ are unit vectors and $Q = Q(\kappa_1, \kappa_2, t)$ is the creations of interfacial area due to topological singularities.

Here we are parameterizing the change in area using the principal curvatures and their time derivatives. This is possible since the time rate of change of a patch of area $A_\kappa$ is,

$$\frac{dA_\kappa}{dt} = 2A_\kappa Hv$$

(3.13)
where $H$ is the mean curvature and $V$ is the local normal velocity of the interfacial patch. From Drew’s formulation [64],

$$
\dot{R}_J = v + R^2_J v_{JJ}
$$

where $R_j$ is the principal radius of curvature, and the comma denotes partial differentiation with respect to the noted principal directions. The double subscript of $JJ$ following the comma denotes the second derivative along one of the principal directions. Multiplying both equations ($J = 1, 2$) by $1/2$ and adding,

$$
v = \frac{1}{2} \left( \dot{R}_1 + \dot{R}_2 \right) - \frac{1}{2} \left( R^2_1 v_{,11} + R^2_2 v_{,22} \right)
$$

Using Equation 3.15 in Equation 3.13 yields an expression for the change in area of a patch,

$$
\frac{dA_\kappa}{dt} = A_\kappa H \left( \dot{R}_1 + \dot{R}_2 \right) - A_\kappa H \left( R^2_1 v_{,11} + R^2_2 v_{,22} \right)
$$

Thus if $v_{,11}$ and $v_{,22}$ can be expressed in terms of $R_1$ and $R_2$, the $dA_\kappa/dt$ can be expressed as a function of $R_1$ and $R_2$.

Using the divergence theorem in the first term on the RHS of Equation 3.12 becomes,

$$
\frac{\partial A_\kappa}{\partial t} = - \int_\Omega \nabla \cdot (A_T P \kappa) \, d\kappa_1 d\kappa_2 + \int_\Omega Q \, d\kappa_1 d\kappa_2
$$

where

$$
\nabla = \frac{\partial}{\partial \kappa_1} \kappa_1 + \frac{\partial}{\partial \kappa_2} \kappa_2
$$
Equating Equation 3.17 to 3.11 yields,

\begin{equation}
\int_{\Omega} \left[ \frac{\partial (A_T P)}{\partial t} + \nabla \cdot (A_T P \dot{\kappa}) - Q \right] d\kappa_1 d\kappa_2 = 0
\end{equation}

For this to hold over all \( \Omega \) the term in the brackets must be zero,

\begin{equation}
\frac{\partial (A_T P)}{\partial t} + \nabla \cdot (A_T P \dot{\kappa}) = Q
\end{equation}

Dividing both sides by the volume of the system that is time independent yields,

\begin{equation}
\frac{\partial (S_v P)}{\partial t} + \nabla \cdot (S_v P \dot{\kappa}) = Q_v
\end{equation}

where \( Q_v = Q/(\text{the volume of the system}) \).

Defining \( \tilde{\kappa}_1 = \kappa_1/S_v, \tilde{\kappa}_2 = \kappa_2/S_v \) and \( P(\kappa_1, \kappa_2, t) = G(\tilde{\kappa}_1, \tilde{\kappa}_2, t) \) (which implies that both \( G \) and \( P \) have the same normalizations). Thus,

\begin{equation}
\frac{\partial (S_v P)}{\partial t} = \frac{\partial (S_v G)}{\partial t} + \frac{\partial (S_v G)}{\partial \tilde{\kappa}_1} \frac{\partial \tilde{\kappa}_1}{\partial t} + \frac{\partial (S_v G)}{\partial \tilde{\kappa}_2} \frac{\partial \tilde{\kappa}_2}{\partial t}
\end{equation}

The partial derivatives with respect to \( t \) on the RHS are taken at constant \( \kappa_1, \kappa_2 \) consistent with the definition of the partial derivative on the LHS. In addition,

\begin{equation}
\frac{\partial (S_v G)}{\partial \kappa_1} = \frac{\partial (S_v G)}{\partial \tilde{\kappa}_1} \frac{\partial \tilde{\kappa}_1}{\partial \kappa_1}
\end{equation}

and since the derivative is a constant \( t \),

\begin{equation}
\frac{\partial (S_v G)}{\partial \kappa_1} = \frac{\partial (S_v G)}{\partial \tilde{\kappa}_1} S_v^{-1}
\end{equation}
This allows us to transform the divergence operator ($\nabla = S_v \nabla$). Finally,

\begin{equation}
\dot{\kappa} = S_v \dot{\kappa} + \dot{S}_v \kappa \tag{3.25}
\end{equation}

Thus the continuity equation in scaled space is:

\begin{equation}
\frac{\partial (S_v G)}{\partial t} + \tilde{\nabla} (S_v G) \cdot \dot{\kappa} + \dot{\tilde{\nabla}} \left[ G S_v \dot{\kappa} + G \dot{S}_v \kappa \right] = \tilde{Q}_v \tag{3.26}
\end{equation}

The partial differential equation for the time independent ISD is found by assuming that in the scaling regime $G(\tilde{\kappa}_1, \tilde{\kappa}_2, t) = B(t) X(\tilde{\kappa}_1, \tilde{\kappa}_2, \tilde{\kappa}_1, \tilde{\kappa}_2, v, 11, v, 22)$ and substituting this into Equation 3.26, and similarity for $\tilde{Q}_v$, but we can start by taking this equal to zero.

\begin{equation}
X \frac{\partial (S_v B)}{\partial t} + B S_v \tilde{\nabla} X \cdot \dot{\kappa} + B S_v \nabla \cdot (X \dot{\kappa}) + B \dot{S}_v \tilde{\nabla} \cdot (X \kappa) = 0 \tag{3.27}
\end{equation}

Assuming that $\dot{\kappa} = S_v^m \xi(\tilde{\kappa}_1, \tilde{\kappa}_2, v, 11, v, 22)$ and inserting it to Equation 3.27 yields,

\begin{equation}
X \frac{\partial (S_v B)}{\partial t} + S_v^{m+1} B \tilde{\nabla} X \cdot \xi + S_v^{m+1} B \tilde{\nabla} \cdot (X \xi) + B \dot{S}_v \tilde{\nabla} \cdot (X \kappa) = 0 \tag{3.28}
\end{equation}

Dividing both sides by $X S_v^{m+1} B$,

\begin{equation}
- \frac{1}{S_v^{m+1} B} \frac{\partial (S_v B)}{\partial t} = \frac{1}{X} \tilde{\nabla} X \cdot \xi + \frac{1}{X} \tilde{\nabla} \cdot (X \xi) + \frac{1}{X} \frac{\dot{S}_v}{S_v^{m+1}} \tilde{\nabla} \cdot (X \kappa) = \lambda_1 \tag{3.29}
\end{equation}
To satisfy the independence of $X$ upon time,

$$(3.30) \quad \frac{\dot{S}_v}{S_{v+1}^m} = \text{constant}.$$  

From the power growth law for late-stage coarsening, we know $1/S_v \simeq at^n$ where $a$ is a constant; $n = 1/2$ for nonconserved dynamics given by the Allen-Cahn equation; $n = 1/3$ for conserved dynamics given by the Cahn-Hilliard equation. Thus,

$$(3.31) \quad \dot{S}_v = -\frac{n}{a} t^{-n-1} = -\frac{n}{a} (aS_v)^{\frac{n+1}{n}}$$

and thus,

$$(3.32) \quad \frac{\dot{S}_v}{S_{v+1}^m} = -\frac{a^n}{m} = \text{constant}$$

where $m = 1/n$.

Finally, we have two ordinary differential equations for the function $B(t)$ and $X(\kappa_1, \kappa_2, \dot{\kappa}_1, \dot{\kappa}_2, v_{11}, v_{22})$ for nonconserved dynamics where $m = 2$.

$$(3.33) \quad \frac{\partial}{\partial t} (S_v B) + \lambda_1 S_v^3 B = 0$$

$$(3.34) \quad \nabla X \cdot \xi + \nabla \cdot (X \xi) - \frac{a^2}{2} \nabla \cdot (X \kappa) - \lambda_1 X = 0$$

where $\lambda_1$ is an eigenvalue.
The assumption made in Equation 3.28, \( \dot{\tilde{\kappa}} = S_v^2 \xi \) where \( \xi = \xi_1 \tilde{\kappa}_1 + \xi_2 \tilde{\kappa}_2 \) can be quantitatively verified for AC. From the definition of scaled principle curvatures (\( \tilde{\kappa}_i = \kappa_i / S_v \)),

\[
\frac{d\tilde{\kappa}_J}{dt} = \dot{\tilde{\kappa}}_J = \frac{\kappa_J S_v - \kappa_J S_v}{S_v^2}
\]

Using Equation 3.14,

\[
\dot{\kappa}_J = \frac{\partial \kappa_J}{\partial t} = \frac{\partial}{\partial t} \left( \frac{1}{R_J} \right) = -\frac{1}{R_J^2} \dot{R}_J = -\frac{1}{R_J^2} (v + R_J^2 v_{JJ}) = -\kappa_J^2 v - v_{JJ}
\]

Using Equation 3.32 and 3.36 in Equation 3.35

\[
\dot{\tilde{\kappa}}_J = \frac{1}{S_v^2} \left[ (-\kappa_J^2 v - v_{JJ}) S_v + \frac{a^2}{2} S_v^3 \kappa_J \right]
\]

For a system evolving in the late-stage by nonconserved dynamics, \( v = -M H \) and thus,

\[
v = -\frac{M}{2} (\kappa_1 + \kappa_2) = -\frac{M}{2} S_v (\tilde{\kappa}_1 + \tilde{\kappa}_2)
\]

Choosing \( J = 1 \) for example, we obtain

\[
\dot{\tilde{\kappa}}_1 = \frac{1}{S_v^2} \left[ \frac{M}{2} S_v^4 \tilde{\kappa}_1^2 (\tilde{\kappa}_1 + \tilde{\kappa}_2) - S_v v_{,11} + \frac{a^2}{2} S_v^4 \tilde{\kappa}_1 \right]
\]

Here we assume

\[
v_{,11} = S_v^3 \chi_1 (\tilde{\kappa}_1, \tilde{\kappa}_2)
\]
Then, Equation 3.39 becomes

\[ \dot{\tilde{\kappa}}_1 = S_{\psi}^2 \left[ \frac{M}{2} \tilde{\kappa}_1^2 (\tilde{\kappa}_1 + \tilde{\kappa}_2) - \chi_1(\tilde{\kappa}_1, \tilde{\kappa}_2) + \frac{a^2}{2} \tilde{\kappa}_1 \right] = S_{\psi}^2 \xi_1 \]

In the same manner,

\[ \dot{\tilde{\kappa}}_2 = S_{\psi}^2 \left[ \frac{M}{2} \tilde{\kappa}_2^2 (\tilde{\kappa}_1 + \tilde{\kappa}_2) - \chi_2(\tilde{\kappa}_1, \tilde{\kappa}_2) + \frac{a^2}{2} \tilde{\kappa}_2 \right] = S_{\psi}^2 \xi_2 \]

Verifying the assumption given by Equation 3.40 remains for the future work.
CHAPTER 4

Three-Dimensional Mixtures Evolving via Conserved Dynamics

The conserved dynamics, also called model B, describes the evolution of a conserved order parameter such as composition in binary mixtures. In this dynamics, the evolution of domains is driven by diffusion of mass. The concentration of species such as atoms or molecules located near highly curved is higher than at lower curved interfaces. Thus atoms diffuse from regions of high curvatures to low curvatures depending upon the curvatures of other interfacial patches surrounding it. However, the exchange of mass between the patches over a long distance cannot occur. The stronger coupling of an interfacial patch with neighboring interfacial patches in the conserved dynamics than that in the nonconserved dynamics results in a smaller deviation from zero mean curvature in the distribution of interfacial curvatures, which will be shown in the interfacial shape distributions.

In this section, the evolution of symmetric mixtures having 50% volume fraction will be covered first. Then, we will move to asymmetric mixtures having volume fractions of 22%, 30%, 36%, and 40%. All the data were averaged over two simulations per volume fraction (See Table 2.1). It has been assumed that symmetric mixtures attain interconnected domains in the late-stage while asymmetric mixtures attain droplet-shaped domains of the minority phase. However, it will be shown that 36% and 40% mixtures also have interconnected domains in the late-stage. The domain structures of 36% and 40% mixtures are not only interconnected but also bicontinuous such that both domains are continuously
connected. Moreover, all the mixtures with bicontinuous domains undergo the self-similar coarsening. The self-similarity will be verified by means of structure function, interfacial shape distribution, and genus as was done in the previous chapter about mixtures with a nonconserved order parameter. The same characterization will be done for 22% and 30% mixtures. The 22% mixtures have droplet-shaped domains in the late-stage. The 30% mixtures have somewhat interconnected but do not have bicontinuous domains.

The volume fractions that were investigated were chosen within spinodal compositions ($\phi_{s1}$ and $\phi_{s2}$) where $\frac{d^2f}{d\phi^2} = 0$. With our energy density function $f(\phi) = (1/4)\phi^2(1 - \phi)^2$ at a temperature below $T_C$, the spinodal compositions are $\phi_{s1} \simeq 0.21$ and $\phi_{s2} \simeq 0.79$. At this temperature, volume fractions, $V_f$, in the range $21\% < V_f < 50\%$ are possible. The volume fractions above 50% need not to be studied because the two-phase mixtures have the phase-inversion symmetry.

### 4.1. Symmetric mixtures

As presented in the previous chapter for nonconserved dynamics, four snapshots of the evolution of a conserved order parameter in a symmetric mixture are presented in Figure 4.1 to 4.4. This system also maintains its bicontinuity throughout the coarsening process. The interfacial morphologies are clearly different from the interfacial morphologies shown in Figure 3.1 to 3.4. The difference is more clear from the cross sections of the $y = 0$ plane of the two symmetric mixtures evolving with different dynamics. In Figure 4.5 portions of the whole computational domains are presented. All the interfacial shapes are statistically similar to each other and clearly different from the interfacial shapes in Figure 3.5. The evolution of the characteristic length is shown in Figure 4.6. The growth
exponent is \( m = 3 \) for \( l^m(t) - l^m(0) = kt \). Our results confirm the growth law that is commonly known in this field.

### 4.1.1. Structure function

Here we start with the linear stability analysis of the very initial stage of the spinodal decomposition process in a conserved order parameter, \( \phi(r,t) \), as done with a nonconserved order parameter, \( \phi(r,t) \). Just after quenching a system below \( T_C \), small fluctuations, \( \delta \phi \), in the order parameter are introduced.

\[
\phi = \phi_0 + \delta \phi
\]

where \( \phi_0 = 0.5 \) and \( \delta \phi \ll 1 \). The small fluctuation \( \delta \phi \) is expressed as a sinusoidal wave.

\[
\delta \phi = A_\phi(q,t)e^{2\pi i q \cdot r}
\]

where \( q \) is the wave vector whose element has a dimension of [1/length]. By substituting Equation 4.1 and 4.2 into the Cahn-Hilliard equation (Equation 2.16), we can obtain the growth rate of the Fourier amplitude, \( A(q,t) \).

\[
\frac{\partial \delta \phi}{\partial t} = \nabla^2 [g(\phi_0 + \delta \phi) - \nabla^2 \delta \phi]
\]

where \( g(\phi) = df/d\phi \). The Taylor expansion of \( g(\phi) \) around \( \phi_0 \) is used to determine \( g(\phi_0 + \delta \phi) \).

\[
g(\phi_0 + \delta \phi) \simeq g(\phi_0) + \left( \frac{dg}{d\phi} \right)_{\phi=\phi_0} \delta \phi
\]
Figure 4.1. A symmetric $\phi$ at $t = 64000$ ($1/S_V = 35.6$). Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. 
Figure 4.2. A symmetric $\phi$ at $t = 281600$ ($1/S_V = 57.0$). Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. 
Figure 4.3. A symmetric $\phi$ at $t = 755200 \,(1/S_V = 77.9)$. Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. 
Figure 4.4. A symmetric $\phi$ at $t = 1113600 \ (1/S_V = 88.6)$. Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. 
Figure 4.5. Self-similar evolution of 3D domains in a 50% mixture with a conserved order parameter. These are portions taken from the computational domains. An edge length is $6(1/S_V)$. 

(a) $t = 64000 \ (1/S_V = 35.6)$  
(b) $t = 281600 \ (1/S_V = 57.0)$  
(c) $t = 755200 \ (1/S_V = 77.9)$  
(d) $t = 1113600 \ (1/S_V = 88.6)$
For symmetric mixtures, \( g(\phi_0 = 0.5) \) is zero because of Equation 2.7. Thus Equation 4.3 becomes,

\[
\frac{\partial \delta \phi}{\partial t} = \nabla^2 \left[ \left( \frac{dg}{d\phi} \right)_{\phi=\phi_0} \delta \phi - \epsilon^2 \nabla^2 \delta \phi \right]
\]

Finally, combining Equation 4.5 and Equation 4.2 yields the growth rate of the Fourier amplitude, \( A_\phi(q, t) \),

\[
e^{2\pi i q \cdot r} \frac{\partial A(q, t)}{\partial t} = -4\pi^2 q^2 \left[ \left( \frac{dg}{d\phi} \right)_{\phi=\phi_0} + 4\pi^2 q^2 \right] A(q, t) e^{2\pi i q \cdot r}
\]
Growth rate \( \frac{1}{A_{\phi}(q,t)} \frac{\partial A_{\phi}(q,t)}{\partial t} = -4\pi^2 q^2 \left[ -\frac{W}{4} + 4\pi^2 q^2 \right] \)

Since in our case, for symmetric mixtures

\[
(4.8) \quad \left( \frac{dg}{d\phi} \right)_{\phi=\phi_0=1/2} = \frac{1}{2} \left( 6\phi_0^2 - 6\phi_0 + 1 \right) = -\frac{1}{4}
\]

where \( q = |q| \). The growth rate is positive for \( q < (4\pi)^{-1} \approx 0.080 \) and negative for \( q > (4\pi)^{-1} \). More importantly, the growth rate has a maximum at \( q_{\text{max}} = (4\sqrt{2}\pi)^{-1} \approx 0.056 \) which corresponds with a wavelength of \( 4\sqrt{2}\pi \approx 17.77 \). For \( 0 \leq q \leq q_{\text{max}} \), the growth rate decreases as the \( q \) goes to zero. Thus long wavelength modes grow slower, which is due to the fact that the mass transport at longer distances is slower than at shorter distances. The presence of \( q_{\text{max}} \) implies that the most probable initial domain spacing is \( \sim 17.77 \) which is about six grid points.

SFs obtained in the late-stage are presented in Figure 4.8. Our results agree with calculations done by others \([61, 63, 65]\). There exist the dominant Fourier modes \((q_{\text{max}})\) in all the SFs. The \( q_{\text{max}} \) moves toward the zeroth mode \((q = 0)\). The intensity at \( q = q_{\text{max}} \) increases with time, implying that the most probable domain spacing increases with time. Sometimes, the reciprocal of the dominant wave number \((1/q_{\text{max}})\) is used as the characteristic length. SFs scaled by the characteristic length \((1/S_{\gamma})\) are shown in Figure 4.8(b). They also obey the scaling hypothesis expressed by Equation 2.33. All the scaled SFs at selected times are almost identical, and thus the scaled SFs of a conserved order parameter are time-invariant in the late-stage.
Figure 4.7. Growth rate vs. wave numbers in the initial stage of phase separation when $W = 1$, $\epsilon = 1$, and $L_{\phi} = 1$.

4.1.2. Morphology

The evolution of domains in a conserved order parameter was shown in Figure 4.1 to 4.5. In this section, the interfacial morphologies will be quantified by the interfacial shape distribution (ISD). ISDs of symmetric mixtures with a conserved order parameter are presented in Figure 4.9 to 4.12. All the ISDs are symmetric about the $H = 0$ ($\kappa_2 = -\kappa_1$) line because these are symmetric mixtures. Similarly to the ISDs in nonconserved dynamics, the probability contours in these ISDs become smaller and move toward the origin. However, the shape of the contours does not change, as is very clear when the ISDs are scaled by the characteristic length $(1/S_V)$ shown in Figure 4.13 to 4.16. The
Figure 4.8. Evolution of structure functions in a symmetric mixture with a conserved order parameter.
last scaled ISD at $t = 1113600$ has a slightly different shape, which may be due to poorer statistics or finite size effects. These self-similar scaled ISDs are unique to the conserved dynamics. If a scaled ISD from an experiment of domain coarsening in a real sample is similar to this unique scaled ISD, then we may state that the system evolves with conserved dynamics. Along with the scaled ISD for nonconserved dynamics, the scaled ISD for conserved dynamics serves as a counterpart for interconnected domain structures to the scaled particle-size distribution for spherical precipitates in a matrix.

The majority of the interfacial area is hyperbolic (saddle-shaped) ($\kappa_1\kappa_2 = K < 0$) and a small amount of interfacial area is elliptic ($\kappa_1\kappa_2 = K > 0$). The peak is located at $\kappa_1/S_V \simeq -1$ and $\kappa_2/S_V \simeq 1$. The pair of interfacial curvatures with the highest probability corresponds with the most probable interfacial shape existing in symmetric mixtures with a conserved order parameter. This implies that the interfacial area per volume is a good estimate of the most probable curvature in case of the symmetric mixtures. Using the scaled ISDs, the fraction of elliptic interfacial area (FE) present in the symmetric mixtures with a conserved order parameter was calculated. The data are shown in Figure 4.17. The FE does not change significantly throughout the evolution, as it should since the structure scales. The last data point at $t = 1113600$ ($1/S_V = 88.6$) is slightly higher than others, which is consistent with the fact that the peak of the scaled ISD at $t = 1113600$ (Figure 4.16) is slightly lower than that of the scaled ISDs at earlier times. The average of FE at different times is $(6.29 \pm 0.15)$% where 0.15 is a standard deviation.

Average curvatures were also calculated. All the average curvatures except $< K/S_V^2 >$ are different from those of nonconserved dynamics. The average of scaled principal curvatures are $< \kappa_1/S_V > \simeq -1.18 \pm 0.00$ < $\kappa_2/S_V > \simeq 1.18 \pm 0.00$ and $< K/S_V^2 > \simeq -1.70 \pm 0.01$. 
Figure 4.9. The interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 64000$ ($1/S_V = 35.6$).
Figure 4.10. The interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 281600$ ($1/S_V = 57.0$).
Figure 4.11. The interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 755200$ ($1/S_V = 77.9$).
Figure 4.12. The interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 1113600$ ($1/S_V = 88.6$).
Figure 4.13. The scaled interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 64000$ ($1/S_V = 35.6$).
Figure 4.14. The scaled interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 281600$ ($1/S_V = 57.0$).
Figure 4.15. The scaled interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 755200$ ($1/S_V = 77.9$).
Figure 4.16. The scaled interfacial shape distribution of a symmetric mixture with a conserved order parameter $\phi$ at $t = 1113600$ ($1/S_V = 88.6$).
Figure 4.17. The fraction of elliptic interfacial area (FE) present in symmetric mixtures with a conserved order parameter.

Since the average of mean curvature is zero in symmetric mixtures, the root-mean-squared (RMS) value of $\sqrt{\langle (H/S_V)^2 \rangle} \simeq 0.34 \pm 0.00$ was calculated. The RMS scaled mean curvature is actually the standard deviation in the scaled mean curvature which is larger in nonconserved dynamics by the factor of $\sim 3$. The larger deviation in nonconserved dynamics is due to the weaker coupling between interfacial patches. However, the average scaled Gaussian curvatures $\langle K/S_V^2 \rangle$ of nonconserved and conserved dynamics are $1.77 \pm 0.02$ and $1.70 \pm 0.01$, respectively, having a small difference of $\sim 4\%$. 
4.1.3. Topology

The self-similar scaled morphology unique to the conserved dynamics was investigated using the scaled ISD in the previous section. In this section, the scaled structure of conserved dynamics is investigated from another point of view, topology. While the morphology is represented by the statistics of curvatures, the ISD, the topology is represented by genus \( g \) is related to the average Gaussian curvature according to the Gauss-Bonnet theorem given by Equation 2.48. The numerical area integration with Equation 2.49 is calculated using the list of the Gaussian curvatures at vertices of interfaces and the areas of the corresponding vertices.

Prior to the calculation of genus, the bicontinuity of domains in mixtures with a conserved order parameter were also confirmed by visual inspection of interfaces shown in Figure 4.1 to 4.4 using a 3D rendering technique. The ”Label Region” function, a built-in function in Interactive Data Language, which identifies each domain using an index, was also used along with the 3D rendering to verify that there are no independent bodies.

The time evolution of genus per volume, interpreted as a handle or a tunnel density, is shown in Figure 4.18. The log-log plot shows that the genus density is approximately proportional to \( t^1 \) which also agrees with the topological scaling law proposed by Fialkowski et al [23], \( \chi(t) \sim l^d(t) \) where \( \chi(t) \) is the Euler characteristic per volume; \( l(t) \) is the characteristic length; \( d \) is the dimensionality. Since \( l(t) \sim t^{1/3} \), \( d = 3 \), and \( g \sim -\chi/2 \) when \( g \gg 1 \), the genus also obeys the scaling hypothesis, \( g(t) \sim l^3(t) \), in three-dimensions.

We define the scaled genus, \( g_V S_V^{-3} \), where \( g_V \) is the genus density \( (g/V) \) and \( S_V \) is the interfacial area per volume. The characteristic volume is \( S_V^{-3} \) since \( S_V^{-1} \) is the characteristic length. Thus the scaled genus represents the genus per characteristic volume, interpreted
Figure 4.18. A log-log plot of genus density vs time. The fitting equation is \( \log \left( \frac{g}{V} \right) = -0.95 \log t - 0.6695 \) \( (R^2 = 0.9999) \).

as the number of handles or tunnels within a characteristic volume. If the topology scales, then the scaled genus should be time-invariant. The time-evolution of the scaled genus of the mixtures with a nonconserved order parameter is shown in Figure 4.19. The scaled genus is approximately time-invariant. Non-integer numbers of scaled genus are statistically averaged numbers such that the scaled genus of 0.13 corresponds with 13 handles or tunnels within a volume of \( 100S_V^{-3} \). The average and the standard deviation of scaled genii at different times is \( 0.135 \pm 0.001 \). This scaled genus for conserved dynamics is close to that for nonconserved dynamics, \( 0.139 \pm 0.003 \), only 3% difference.
4.2. Asymmetric mixtures

We simulated the coarsening of 3D asymmetric mixtures with volume fractions of 22%, 30%, 36%, and 40%, resulted by quenching homogeneous mixtures with compositions of 0.22, 0.30, 0.36, and 0.40 to a temperature below $T_C$. Although it has been widely assumed that symmetric mixtures have interconnected domains while asymmetric mixtures have droplet domains, it was found in this study that in three-dimensions the bicontinuously interconnected domains are observed in the 36% and 40% mixtures during the late-stage coarsening as shown in Figure 4.25 to 4.28. Furthermore, these mixtures undergo the self-similar coarsening, which will be quantitatively verified in this section. In Figure 4.20, portions of the whole computational domains are presented. All the interfacial shapes look statistically similar. It is hard to see the difference between the scaled interfacial shapes of
the 36% and 40% mixtures. However, by a closer inspection it can be seen that diameters of tube-shaped domains are smaller in the 36% mixtures. When compared to the scaled structures of a symmetric mixture in Figure 4.5, it is clearer that the scaled structures of a 36% mixture have thinner tubes. In fact, their morphologies represented by the scaled ISDs are somewhat different but their topologies represented by the scaled genus are very similar. The bicontinuity was confirmed by the Label Region function, a built-in function in IDL, and visual inspections with the 3D rendering technique as mentioned in Section 3.3. In 22% mixtures, droplet domains are clearly observed (Figure 4.21 and 4.22). In 30% mixtures, domains are interconnected to some degree but not bicontinuous. Instead, there are a number of domains of the minority phase enclosed by an interface. In this sense, the 30% mixtures have clustered domains rather than bicontinuous domains.

In this section, we will present quantitative analyses of the different types of domain structures using the structure function, the interfacial shape distribution, and the genus, all of which are averaged over two simulations at each volume fraction. Only scaled measures will be presented to determine whether each volume fraction yields a self-similar domain structure. Computational box sizes, mesh sizes, and time steps for mixtures with different volume fractions are listed in Table 2.1.

All these mixtures obey the LSW growth law as shown in Figure 4.29. Nevertheless, it is unclear if the 22% and 30% mixtures undergo the self-similar coarsening, which will be shown in the following sections for structure function, interfacial shape distribution, and genus. The kinetic coefficient $k$ in Equation 1.2 decreases with volume fraction unlike the 2D mixtures where the $k$ increases with the area fraction (See Figure 5.4).
(a) a 36% mixture at $t = 25600$ ($1/S_V = 32.0$) (b) a 36% mixture at $t = 640000$ ($1/S_V = 84.9$)

(c) a 40% mixture at $t = 51200$ ($1/S_V = 36.0$) (d) a 40% mixture at $t = 768000$ ($1/S_V = 82.7$)

Figure 4.20. Self-similar evolution of 3D domains in the 36% and 40% mixtures with a conserved order parameter. These are portions taken from the computational domains. An edge length is $6(1/S_V)$. 
Figure 4.21. An asymmetric $\phi$ with volume fraction of 22% at $t = 102400$ ($1/S_V = 72.0$). Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(256\sqrt{2})^3$. 
Figure 4.22. An asymmetric $\phi$ with volume fraction of 22% at $t = 307200$ ($1/S_V = 102.2$). Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(256\sqrt{2})^3$. 
Figure 4.23. An asymmetric $\phi$ with volume fraction of 30% at $t = 102400$ ($1/S_V = 72.0$). Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(256\sqrt{2})^3$. 
Figure 4.24. An asymmetric $\phi$ with volume fraction of 30% at $t = 307200$ ($1/S_V = 82.6$). Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(256\sqrt{2})^3$. 
Figure 4.25. An asymmetric $\phi$ with volume fraction of 36% at $t = 25600$ ($1/S_V = 32.0$). Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(1024\sqrt{2})^3$. 
Figure 4.26. An asymmetric $\phi$ with volume fraction of 36% at $t = 640000$ ($1/S_V = 84.9$). Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(1024\sqrt{2})^3$. 


Figure 4.27. An asymmetric $\phi$ with volume fraction of 40% at $t = 25600$ ($1/S_V = 36.0$). Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(1024\sqrt{2})^3$. 
Figure 4.28. An asymmetric $\phi$ with volume fraction of 40\% at $t = 768000 \quad (1/S_V = 36.0)$. Transparent regions denote the phase with $\phi = 0$, and grey regions denote the phase with $\phi = 1$. This is the entire computational box with the size of $(1024\sqrt{2})^3$. 
Figure 4.29. (Characteristic length, $1/S_V = l)^3$ vs time. The fitting equations are $S_V^{-3}(t) = 3.4474t + 29661 \ (R^2 = 0.9969)$ for 22% mixture, $S_V^{-3}(t) = 1.8652t - 10196 \ (R^2 = 0.9991)$ for 30% mixtures, $S_V^{-3}(t) = 0.9297t + 23295 \ (R^2 = 0.9992)$ for 36% mixtures, $S_V^{-3}(t) = 0.7194t + 14087 \ (R^2 = 0.9998)$ for 40% mixtures, and $S_V^{-3}(t) = 0.6122t + 10179 \ (R^2 = 0.9998)$ for 50% mixtures.

4.2.1. Structure functions

Scaled structure functions of the 36% and 40% asymmetric mixture are presented in Figure 4.30. In the 36% mixture, the scaled SFs at different times are approximately similar. However, the earliest one marked by blue color is slightly different from other ones. A similar tendency appears in the evolution of ISDs and scaled genus (See Section 4.2.2 and 4.2.3). In the 40% mixture, all the scaled SFs are similar without much deviation unlike the 36% mixture. Interestingly, the peak positions ($q_{max}$) of scaled SFs of the 36%, 40%, and 50% mixture are nearly the same (See Figure 4.8(b)). On the other hand,
the maximum intensities are different. The maximum intensity of the 36\% mixture is lower than that of the 40\% mixture, which is lower than that of the 50\% mixture. The scaled SFs of the three mixtures are broader with decreasing volume fraction.

Scaled SFs of the 22\% and 30\% mixtures are presented in Figure 4.31. The statistics are poor because the computational domains for the simulations are too small (See Table 2.1). Thus, it is unclear if the evolution is self-similar because it is possible that the non-self-similar scaled SFs are due to the finite size effects. The peak position in scaled SFs, $q_{\text{max}}$, of the 22\% mixture moves to the right with time while the $q_{\text{max}}$ of the 30\% mixture moves to the left with time.

### 4.2.2. Morphology

Scaled ISDs of the 36\% and 40\% mixtures are shown in Figure 4.32 to 4.39. The overall shape of the scaled ISD of the 40\% mixture is similar to that of 50\% mixtures except that the entire distribution is shifted toward the upper right and is tilted slightly counterclockwise. A closer inspection of the data shows that the ISD of 40\% mixture is not symmetric about $H = H_{\text{avg}}$ (the line $\kappa_2 = -\kappa_1 + 2H_{\text{avg}}$) where $H_{\text{avg}}$ is the area-averaged mean curvature; rather, it is displaced toward the upper-right side of the $H = H_{\text{avg}}$ line. Nevertheless, in the 40\% mixture the scaled ISDs appear to be self-similar. The results of 36\% mixtures are more interesting in that the evolution of probability is not exactly self-similar even in the late-stage where characteristic length is much larger than interfacial thickness ($1/S_V > 5\delta$) where $\delta$ is the interfacial thickness. In comparing the scaled ISDs for the 36\% mixture, we observe that the earlier scaled ISD is more asymmetric about $H = H_{\text{avg}}$ and evolves toward a self-similar morphology. The rightmost portion
(a) Scaled structure functions of 36% mixtures at different times.

(b) Scaled structure functions of 40% mixtures at different times.

Figure 4.30. Evolution of structure functions in 36% and 40% asymmetric mixtures with a conserved order parameter.
(a) Scaled structure functions of a 22% mixture at different times.

(b) Scaled structure functions of a 30% mixture at different times.

Figure 4.31. Evolution of structure functions in 22% and 30% asymmetric mixtures with a conserved order parameter.
of the dark blue region near the dashed line of $\kappa_2 = \kappa_1$ (spherical patches of interface) moves away from this dashed line with time. The scaled ISDs of the 36% mixture are clearly shifted more towards the upper-right position with respect to the $H = 0$ line and are more spread than those of the 40% mixtures. In addition, the peak heights are 8.3% lower in the 36% mixture than in the 40% mixture. The shift toward the right is a result of the asymmetry in volume fraction and the definition of interfacial normals where the direction of normals are from $\phi = 1$-phase (the minority phase) to $\phi = 0$-phase (the majority phase).

The majority of interfaces are hyperbolic (saddle-shaped) ($\kappa_1 \kappa_2 = K < 0$) in these 36% and 40% mixtures. The pair of interfacial curvatures with the highest probability represents the most probable interfacial shape existing in these mixtures. Using the scaled ISDs, the fraction of elliptic interfacial area (FE) present in these mixtures was calculated. The data are shown in Figure 4.40. The FE in the 40% mixture does not change significantly throughout the evolution. The average of FE over different times is $(10.75 \pm 0.29)\%$ where 0.29 is a standard deviation. Average curvatures in the 40% mixtures are $<K/S_V^2> \simeq -1.67 \pm 0.01$ and $<H/S_V> \simeq -0.270 \pm 0.004$. In Figure 4.40 the FE in the 36% mixture rapidly decreases initially and its decreasing rate slows towards approximately 15%. The similar tendency was also seen in the evolution of the scaled ISDs in Figure 4.32 to 4.35. Average curvatures in the 36% mixtures were obtained from the last three data points because this structure is evolving towards the final self-similar structure and thus the last data points are closer to the final structure. The average curvatures are $<K/S_V^2> \simeq -1.64 \pm 0.00$ and $<H/S_V> \simeq 0.391 \pm 0.001$. The average scaled mean curvature, $<H/S_V>$, deviates more from zero ($<H/S_V>= 0$ in symmetric
Figure 4.32. The scaled interfacial shape distribution of the 36% mixture with a conserved order parameter $\phi$ at $t = 25600 \ (1/S_V = 32.0)$. The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{avg}/S_V \ (H = H_{avg})$. 
Figure 4.33. The scaled interfacial shape distribution of the 36% mixture with a conserved order parameter $\phi$ at $t = 179200$ ($1/S_V = 57.8$). The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{avg}/S_V$ ($H = H_{avg}$).
Figure 4.34. The scaled interfacial shape distribution of the 36% mixture with a conserved order parameter $\phi$ at $t = 460800$ ($1/S_V = 76.8$). The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{avg}/S_V$ ($H = H_{avg}$).
Figure 4.35. The scaled interfacial shape distribution of the 36% mixture with a conserved order parameter $\phi$ at $t = 640000$ ($1/S_V = 84.9$). The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{avg}/S_V$ ($H = H_{avg}$).
Figure 4.36. The scaled interfacial shape distribution of the 40% mixture with a conserved order parameter $\phi$ at $t = 51200$ ($1/S_V = 36.0$). The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{avg}/S_V$ ($H = H_{avg}$).
Figure 4.37. The scaled interfacial shape distribution of the 40% mixture with a conserved order parameter $\phi$ at $t = 153600$ ($1/S_V = 50.0$). The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{\text{avg}}/S_V$ ($H = H_{\text{avg}}$).
Figure 4.38. The scaled interfacial shape distribution of the 40% mixture with a conserved order parameter $\phi$ at $t = 332800 \ (1/S_V = 63.5)$. The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{avg}/S_V \ (H = H_{avg})$. 
Figure 4.39. The scaled interfacial shape distribution of the 40% mixture with a conserved order parameter $\phi$ at $t = 768000$ ($1/S_V = 82.7$). The dotted line denote $\kappa_2/S_V = -\kappa_1/S_V + 2H_{\text{avg}}/S_V$ ($H = H_{\text{avg}}$).
mixtures) with decreasing volume fraction. However, mostly importantly, the average scaled Gaussian curvatures of 36% and 40% mixtures are similar those of symmetric mixtures with a nonconserved or a conserved order parameter. All the $< K/S^2_V >$ values of the bicontinuous structures investigated in this study agree within errors of 7.9%, which implies the similar scaled topology of the bicontinuous structures because the $< K >$ is related to the genus.

Scaled ISDs of 22% and 30% mixture are shown in Figures 4.41 to 4.48. Note that the computational domains for simulations of these systems were too small to obtain good statistics. In addition, finite size effects may have occurred. Thus we cannot assert whether these mixtures evolve self-similarly or not, based on our data. However, it may be
sufficient to provide a behavior of these mixtures. Most of all, these 22% and 30% mixtures are not bicontinuous, in contrast with 36%, 40%, and 50% mixtures whose domains are bicontinuous.

Most of the domains in the 22% mixture are droplets. Some domains undergo coalescence as observed in Figure 4.21 to 4.22. The evolution of domains may be better described as the particle coarsening kinetics. However, investigating particle size distribution is out of scope in this study. The scaled ISDs of the 22% mixture are presented in Figure 4.41 to 4.44. The majority of interfacial patches are located near the spherical line represented by a dashed line ($\kappa_2 = \kappa_1$). In all the scaled ISDs of the 22% mixture, there is some probability near the parabolic (cylindrical) interfaces represented by the line $\kappa_1 = 0$ ($K = 0$). This is because some domains undergoing coalescence have necks between the domains. The peak locations of the first two scaled ISDs are nearly the same. The peak moves up along the spherical line at later times. The peak height decreases with contours becoming more spread except between the second and the third times.

In the 30% mixture, the domains are clustered (somewhat interconnected but not bicontinuous). The scaled ISDs of the 30% mixture are presented in Figure 4.45 to 4.48. There are significant amounts of both hyperbolic and elliptic interfaces. The FE is shown in Figure 4.49 where the FE fluctuates around 52.0% with a standard deviation of 0.9%. Thus the fraction of elliptic interfaces is nearly constant. Nevertheless, the shapes of the scaled ISDs change significantly with time. The maximum probability changes significantly with time from 0.64 to 0.73, a 14% increase. The peak location moves to the right. The average scaled Gaussian curvature, $< K/S^2 >$, related to the scaled topology, is $0.474 \pm 0.089$ which was obtained by averaging the values at five different
Figure 4.41. The scaled interfacial shape distribution of the 22% mixture with a conserved order parameter $\phi$ at $t = 102400$ ($1/S_V = 72.0$).
Figure 4.42. The scaled interfacial shape distribution of the 22% mixture with a conserved order parameter $\phi$ at $t = 153600$ ($1/S_V = 82.4$).
Figure 4.43. The scaled interfacial shape distribution of the 22% mixture with a conserved order parameter $\phi$ at $t = 204800$ ($1/S_V = 91.0$).
Figure 4.44. The scaled interfacial shape distribution of the 22% mixture with a conserved order parameter $\phi$ at $t = 307200$ ($1/S_V = 102.0$).
Figure 4.45. The scaled interfacial shape distribution of the 30% mixture with a conserved order parameter $\phi$ at $t = 25600$ ($1/S_v = 35.8$).
Figure 4.46. The scaled interfacial shape distribution of the 30% mixture with a conserved order parameter $\phi$ at $t = 51200$ ($1/S_V = 44.6$).
Figure 4.47. The scaled interfacial shape distribution of the 30% mixture with a conserved order parameter $\phi$ at $t = 179200$ ($1/S_v = 68.1$).
Figure 4.48. The scaled interfacial shape distribution of the 30% mixture with a conserved order parameter $\phi$ at $t = 307200$ ($1/S_V = 82.6$).
times. The scaled topology of the 30% mixture is not expected to be time invariant because the standard deviation of 0.089, about 19% of the average value, is large. In addition, the values of $< K/S_V^2 >$ are positive at all the times unlike those of the bicontinuous structures. The average scaled mean curvature, $< H/S_V >$, is $1.01 \pm 0.02$ which is nearly constant.

### 4.2.3. Topology

While the scaled topologies of the 36% and 40% mixtures having bicontinuous domains are similar to that of the 50% mixture, those of the 22% and 30% are different as shown in Figure 4.50. The scaled genus $g_V S_V^{-3}$ of the 40% mixtures has a nearly time-independent
value of $0.133 \pm 0.001$. As mentioned previously, the scaled genii of 36%, 40%, and 50% mixtures with a conserved order parameter yield the value of $0.133 \pm 0.002$, which was obtained by averaging the scaled genus at different times for each volume fraction and then averaging the scaled genii for different volume fractions.

The scaled genii of 22% and 30% are negative, which means that there are a number of independent bodies of the minority phase, as explained in Section 2.5.3. The two mixtures show a different tendency in the evolution of the scaled genus. In the 22% mixture, the scaled genus decreases in its negative value indicating that the number of independent domains per characteristic volume ($S^{-3}_V$) increases with time. However, this is not true for the systems in the very late-stage where $l$ having an order of computational box dimension
continues to increase and a few of droplets exist within the system. In Figure 4.30, there is a sudden drop at the latest time in the data of the 22% mixture. This is because the increase of the characteristic length is faster than the increase of the negative genus by coalescence. Pinching is hard to occur in the 22% mixture because most domains are droplets. On the other hand, in the 33% mixture, its negative scaled genus is $-0.142 \pm 0.012$ that are averaged over the values at five different times. The standard deviation of 0.012 larger than that in the bicontinuous structures indicates that the number of independent domains per characteristic volume ($S^{-3}_V$) fluctuates significantly with time. Thus it is unclear if the 30% mixtures show the self-similar evolution of their topologies.
CHAPTER 5

Two-Dimensional Mixtures

Phase separation and coarsening in two-dimensional mixtures was simulated. For nonconserved dynamics, only symmetric mixtures were examined while for conserved dynamics symmetric and asymmetric 40%, 44%, and 48% mixtures were examined. All the data were averaged over four simulations per each volume fraction and dynamics (See Table 2.1). The area fraction in two-dimensions corresponds with the volume fraction in three-dimensions. The details of the computational methods including equations and parameters are described in Section 2.1. Periodic boundary conditions were applied.

\[ X(0, y) = X(L, y) \]
\[ X(x, 0) = X(x, L) \]

where \( X \) represents an order parameter (\( \phi \) or \( \eta \)) or a derivative of the energy density with respect to the order parameter (\( df/d\phi \) or \( df/d\eta \)). Many 2D calculations have been using different techniques \[60–62, 66, 67\]. All the calculations show that symmetric mixtures attain interconnected domains and asymmetric mixtures attain droplets in the late-stage coarsening, which is also observed in many experiments of film samples of binary mixtures \[25–29\]. In this chapter, the evolution of two-dimensional phase domains were investigated by means of the distribution of curvature scaled by characteristic length, interfacial length per area.
The interfacial length in a two-dimensional $N \times N$ array of an order parameter was obtained by calculating surface area per volume ($S_V$) of a three-dimensional $N \times N \times 2$ array with $\Delta z = 1$ while $\Delta x = \Delta y = \sqrt{2}$ made by stacking the two-dimensional array twice. All the results presented in this chapter were averaged over four sets of simulations per each area fraction per each dynamics. The systems that were simulated are listed in Table 2.1.

As done for three-dimensional mixtures, all the curvature data were obtained in the mixtures undergoing the late-stage coarsening where the characteristic length is at least five times larger than the interfacial thickness ($\delta = 4\sqrt{2} \approx 5.66$). In two-dimensions, there is only one curvature $\kappa = 1/R$ where $R$ is the radius of curvature. The curvature $\kappa$ is given by the divergence of the interfacial normal [68].

\begin{equation}
\kappa = \nabla \cdot n \quad \text{where} \quad n = -\frac{\nabla X}{|\nabla X|}
\end{equation}

where $n$ is an interfacial normal defined as plus when it points from the $\phi = 1$ phase to the $\phi = 0$ phase; $X$ is an order parameter ($\eta$ or $\phi$).

5.1. Nonconserved dynamics

The evolution of domains in a symmetric mixture with a nonconserved order parameter is presented in Figure 5.1 where black domains represent the phase of $\eta = 0$ and white domains represent the phase of $\eta = 1$. The domain shapes at later times look statistically similar to those at earlier times. The characteristic length $l$ increases as domains coarsen. The time-evolution of $l$ shown in Figure 5.2 obey the Allen-Cahn growth law $l^2(t) = At + B$. 
The correlation coefficient in this case is 0.9997 that is attributed to the lack of simulations sets. Adding more sets of simulations does improve the quality of statistics.

The domain shapes shown in Figure 5.1 are distinctive of nonconserved dynamics and they are complex. The distinctiveness is quantified by the distribution of interfacial curvature. The details of curvature calculation were presented in the Chapter 2. The distributions of scaled curvature at different times that are averaged over four sets of simulations are presented in Figure 5.3. The bin size \( \Delta \tilde{\kappa} = 0.35 \) was selected. This scaled distribution is a little asymmetric about \( \tilde{\kappa} = 0 \), yielding a little larger probability in the positive curvature. It is expected that the curvature distributions are symmetric about \( \tilde{\kappa} = 0 \) if more sets of simulations are included for averaging. The scaled curvature distributions at different times are nearly identical after \( t = 160 \).

### 5.2. Conserved dynamics

The evolution of domains in mixtures with different area fractions is presented in Figure 5.5 to 5.8 where the black domains represent the phase of \( \phi = 0 \) and white domains represent the phase of \( \phi = 1 \). Unlike in the nonconserved dynamics, the white domains do not undergo the self-similar coarsening. In all asymmetric mixtures, there are many initially elongated domains with a high aspect ratio at earlier times. Such elongated domains become circular at later times. A mixture with a lower area fraction has a smaller number of elongated domains or has domains with a less higher aspect ratio at earlier times. Thus the mixture with a lower area fraction attain circular domains earlier. The time-evolution of characteristic length \( l \) averaged over four sets of simulations is shown in Figure 5.4 where the data from the late-stage \( (l > 5\delta) \) are taken. Fitting parameters
Figure 5.1. Evolution of domains in a 50% mixture with a nonconserved order parameter.
Figure 5.2. Characteristic length vs. time during coarsening of mixtures with a nonconserved order parameter. The fitting equation is $l^2(t) = 8.9782t^2 - 122.9$ ($R^2 = 0.9997$).

and correlation coefficients for the LSW growth law $l^3(t) = At + B$ are listed in Table 5.1 where although all the data are in the late-stage the earlier data are located under the fitting line. The correlation coefficients of 48% and 50% mixtures are closer to one than those of 40% and 44% mixtures.

The slope of the lines in Figure 5.4 increases with the amount of the minority phase increased. Unlike 3D mixtures, more asymmetric mixtures yield slower kinetics. No break-up of domains is observed in two-dimensions because the Rayleigh instability occurs only in three-dimensions. Initially elongated domains become circular domains by reducing
Figure 5.3. Distributions of the scaled curvature $\tilde{\kappa} = \kappa \cdot l$ in mixtures with a nonconserved order parameter.

Table 5.1. List of fitting parameters ($A$ and $B$) and correlation coefficient ($R^2$) for the fitting equation $l(t) = At^{1/3} + B$ in conserved dynamics.

<table>
<thead>
<tr>
<th>Phase fraction (%)</th>
<th>$A$</th>
<th>$B$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.4256</td>
<td>24889</td>
<td>0.9974</td>
</tr>
<tr>
<td>44</td>
<td>0.4455</td>
<td>41195</td>
<td>0.9927</td>
</tr>
<tr>
<td>48</td>
<td>0.8756</td>
<td>42443</td>
<td>0.9991</td>
</tr>
<tr>
<td>50</td>
<td>1.419</td>
<td>-20742</td>
<td>0.9993</td>
</tr>
</tbody>
</table>

interfacial curvature. As a result, all asymmetric mixtures have isolated domains in their late-stage. Contrarily, the previously interconnected domains at earlier times in the symmetric mixture become structures with mostly interconnected domains and a few of
Figure 5.4. (Characteristic length)$^3$ vs. time during coarsening of mixtures with a conserved order parameter. The fitting equation of $l^3(t) = At + B$ was used.

droplets during the late-stage coarsening (See Figure 5.8). In addition, the domains in the symmetric mixtures are not bicontinuous because of the presence of islands.

The distributions of scaled curvature of mixtures with a conserved order parameter are presented in Figure 5.9 and 5.10 which contain the distributions at the later four times when the characteristic length is at least five times larger than the interfacial thickness. The bin size $\Delta \kappa = 0.35$ was selected. In Figure 5.9(a) for the 40% mixtures, the scaled
Figure 5.5. Evolution of domains in a 40% mixture with a conserved order parameter.
Figure 5.6. Evolution of domains in a 44% mixture with a conserved order parameter.
Figure 5.7. Evolution of domains in a 48% mixture with a conserved order parameter.
Figure 5.8. Evolution of domains in a 50% mixture with a conserved order parameter.
curvature distributions at different times are nearly identical, indicating that the coarsening of white particles is self-similar and this system is described by particle coarsening kinetics. In Figure 5.9(b) for the 44% mixtures, the distribution at \( t = 24320 \) is different from the others. The domain shapes at \( t = 24320 \) shown in Figure 5.6(c) are more elongated than those at later times. The distributions at the later three times are nearly identical because the majority of particles are circle-shaped.

The 48% mixtures have elongated domains having both positively and negatively interfaces at \( t = 1280 \) and many droplets having mostly positively curved interfaces at \( t = 642560 \) shown in Figure 5.7. The evolution from the elongated domains to the circle-shaped domains is much slower than the 44% mixtures. The curvature distribution at \( t = 21760 \), when elongated or somewhat interconnected domains are observed, has a maximum at zero curvature \((\tilde{\kappa} = 0)\). The peak position moves to the right keeping its height until \( t = 97280 \). Then, the probability at the peak position starts to increase without changing its location. The distributions at the last two times are nearly identical. The 50% mixtures did not yield the self-similar curvature distributions at any time. The distributions are almost symmetric except the distribution at \( t = 768000 \) when the statistics are poor. More importantly, these distributions are not identical in that the peak height is decreasing and the distribution is becoming broader with time.

It is very interesting that all the scaled curvature distributions of asymmetric mixtures having mostly circular-shaped domains have the peak at the \( \tilde{\kappa} = 0.7 \pm 0.175 \) where \( \Delta \tilde{\kappa} = 0.35 \) while those of mixtures having domains with both positively and negatively curved interfaces have a peak at zero curvature.
Figure 5.9. Distributions of the scaled curvature $\tilde{\kappa} = \kappa \cdot l$ in mixtures with a conserved order parameter.
Figure 5.10. Distributions of the scaled curvature $\tilde{\kappa} = \kappa \cdot l$ in mixtures with a conserved order parameter.

(a) 48% mixtures

(b) 50% mixtures
CHAPTER 6

Discussion

6.1. Comparison of symmetric mixtures evolving via nonconserved and conserved dynamics

It has been shown that each of the two dynamics yields a self-similar domain structure having a time-invariant scaled ISD and genus. In this section, the morphologies and the topologies resulting from the two dynamics are compared for the symmetric mixtures. The two dynamics have an essential difference. Coarsening via conserved dynamics takes place by long-range diffusion of mass and thus describes the evolution of a conserved order parameter such as the concentration. On the other hand, nonconserved dynamics does not require long-range diffusion of mass and thus describes the evolution of a nonconserved order parameter like magnetization or compositional order. In both dynamics, the motion of the interface is related to its mean curvature. In coarsening with conserved dynamics, the diffusion field at a point is determined by the mean curvature of the surrounding interfaces. Therefore, the factors influencing the interfacial velocity at that point are nonlocal. In contrast, the velocity of the interface depends only upon its local mean curvature in the nonconserved dynamics case.

The different coupling between interfacial patches results in different scaled morphologies. Figure 6.1 shows the bicontinuous structures resulting from our simulations. Although both interfacial structures are bicontinuous, their morphologies are different in
that more red regions of strongly positive Gaussian curvature (interfaces with large curvatures that are elliptic) appear in systems with a nonconserved order parameter. In Figure 6.1(c) and 6.1(d), more red regions in systems with a nonconserved order parameter represent the larger deviation in scaled mean curvature \( H/S_V \) from zero mean curvature, consistent with weaker coupling between interfacial patches. Interfaces with higher mean values \(|H/S_V|\) evolve faster to decrease \(|H|\). Since \(S_V\) also decreases faster in the system with a nonconserved order parameter, the distribution of \(H/S_V\) is time-invariant. More red and black regions in systems with a nonconserved order parameter implies the faster kinetics of nonconserved dynamics than conserved dynamics.

The time-independent scaled ISD evolving by nonconserved dynamics and conserved dynamics are shown in Figure 6.2. The shapes of the scaled ISDs of two dynamics are clearly different. The stronger coupling in conserved dynamics yields a narrower probability contours than the scaled ISD of mixtures with nonconserved order parameter. Consistent with equal volume fractions of the two phases, both of the scaled ISDs are symmetric about the \(H = 0\) \((\kappa_1 = -\kappa_2)\) line and the average of \(H\) over the structure is zero. The majority of the interfaces are hyperbolic, or saddle-shaped. The peaks of both ISDs are near \(\kappa_iS_V^{-1} \approx 1\), where \(i = 1, 2\), implying that \(S_V\) provides a good order-of-magnitude measure of the interfacial curvature.

The scaled ISD for nonconserved dynamics has a larger deviation from the \(H = 0\) line than that of the conserved dynamics. The standard deviations in scaled mean curvature \((\sqrt{\langle H^2 \rangle}/S_V)\) are 0.94 and 0.34 for nonconserved and conserved dynamics, respectively. All the average curvature values of the two dynamics are compared in Table 6.1. The interfacial velocity for nonconserved dynamics is *local* and is solely a function of the
Figure 6.1. Scaled interfacial morphologies of symmetric mixtures unique to nonconserved ((a) and (c)) and conserved dynamics ((b) and (d)), respectively. These are portions of the interfaces colored with scaled Gaussian curvature $K/S_V^2$ ((a) and (b)) and scaled mean curvature $H/S_V$ ((c) and (d)). All portions are cubic domains with edge lengths of $6(1/S_V)$. In (b), the pair of red regions marked with a red arrow is a remnant of a pinched tube. More red regions are observed in (a) than (b).
mean curvature at a point. By contrast, the interfacial velocity for conserved dynamics is *nonlocal*, governed by the diffusion field established by mean curvatures of surrounding patches. Therefore, the interfacial velocity of an interfacial patch is more strongly coupled with those of surrounding patches in conserved dynamics than in nonconserved dynamics. The coupling results in rapid evolution of an interfacial patch toward reducing the local curvature variation and thus increases the stability of regions with similar curvatures. This nonlocal coupling only exists in conserved dynamics, which leads to the observed smaller deviation in the mean curvature and narrower ISDs. Also evident is the larger fraction of interface with $K > 0$ in the scaled ISD for nonconserved dynamics than for conserved dynamics, as seen in the interfacial structures of Figure 6.1. There are more red regions in structures evolving by nonconserved dynamics. Those red regions have strongly

Figure 6.2. Comparison of the scaled ISDs of symmetric mixtures unique to the nonconserved and the conserved dynamics, respectively.
positive $K$, mostly appear as pairs separated by a relatively small distance, and thus are likely remnants of a thin tube-shaped region of a phase that fissioned into two parts.

By integrating the scaled ISDs over regions 1 and 4, we find that $\sim 20\%$ and $\sim 6\%$ of the interfacial area have $K > 0$ during coarsening by nonconserved and conserved dynamics, respectively. Unlike $H$, the average of $K$ is nonzero in agreement with results presented by Aksimentiev, Moorthi, and Holyst [22]. However, Aksimentiev et al did not find the self-similar evolution in their simulations. The scaled ISDs shown in Figure 6.2 are unique to the corresponding dynamics during the self-similar evolution of bicontinuous structures, and thus are the counterparts to the well known LSW particle-size distribution for a system with spherical particles.

The pair of red regions marked by a red arrow in Figure 6.1(b) is a remnant of a pinched tube. More pairs of regions are observed in Figure 6.1(a) than in Figure 6.1(b). The rate of pinching in both symmetric mixtures is $dg/dl \sim l^2$ because $g(t) \sim t^3(t)$ as described in Section 3.3 and 4.1.3. The scaled genii of the two mixtures are presented in Figure 6.3 where the characteristic length replaces the time in the $x-$axis because the time scales of the two dynamics are too different. The values of the scaled genus for both dynamics are similar, implying nearly identical numbers of tunnels per unit characteristic volume based on the cube of the surface area per unit volume.

<table>
<thead>
<tr>
<th>dynamics</th>
<th>$\sqrt{&lt;H^2/S_V^2&gt;}$</th>
<th>$&lt;K/S_V^2&gt;$</th>
<th>$&lt;\kappa_1/S_V&gt;$</th>
<th>$&lt;\kappa_2/S_V&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$AC$</td>
<td>$0.94 \pm 0.01$</td>
<td>$-1.77 \pm 0.03$</td>
<td>$-1.39 \pm 0.02$</td>
<td>$1.36 \pm 0.01$</td>
</tr>
<tr>
<td>$CH$</td>
<td>$0.34 \pm 0.00$</td>
<td>$-1.70 \pm 0.01$</td>
<td>$-1.18 \pm 0.00$</td>
<td>$1.18 \pm 0.00$</td>
</tr>
</tbody>
</table>

Table 6.1. Area-averaged scaled curvatures in symmetric mixtures. $AC=$nonconserved dynamics (model A), $CH=$conserved dynamics (model B)
Figure 6.3. Genus per characteristic volume ($g V S_V^{-3}$) versus characteristic length ($1/S_V$).

For structures where $g \gg 1$, the Gauss-Bonnet theorem becomes $g \simeq -(4\pi)^{-1} \int_S K dS$. Multiplying both sides by $V^{-1} S_V^{-3}$, we obtain $g V S_V^{-3} \simeq -(4\pi)^{-1} K_{avg} S_V^{-2}$, where $K_{avg} = (V S_V)^{-1} \int_S K dS$. Just like the scaled genus, the scaled average Gaussian curvatures ($K_{avg} S_V^{-2}$) is time-invariant and similar in both dynamics during coarsening. Thus, the scaling of morphologies or ISDs automatically implies the scaling of the topologies. This similar scaled topology with different scaled morphologies is due to the fact that the conserved and nonconserved dynamics result in similar values in $K_{avg} S_V^{-2}$.

The bicontinuous structures from our simulations are compared with Schoen’s G surface, one of the triply-periodic minimal surfaces, having a genus per unit cell of 5, shown in Figure 6.4. This minimal surface has been used as a model for the interfacial structure of the bicontinuous structures in many block copolymer systems [10–12]. We demonstrate
how the bicontinuous structures from phase separation are topologically and morphologically different from the G surface by means of the scaled genus and the ISD. We determine the scaled genus of the G surface with volume fraction of 50:50 and $S_V$ of 0.31, based on the data given by Góźdź et al [59] and obtain the scaled genus of 0.17 for the G surface, which is 21% larger than 0.14 found for the self-similar structures resulting from phase separation. While the difference is modest, it is statistically significant since it is much larger than any fluctuation in the scaled genus obtained in the simulations, indicating that the topology of the self-similar structures differs from that of the G surface. The difference in the ISD is more dramatic. The approximate minimum value of scaled Gaussian curvature ($K/S_V^2 = \kappa_1/S_V \cdot \kappa_2/S_V$) is -1.83 for the G surface (obtained from the histogram given by Góźdź et al) that is much less than -7.84 for structures with conserved dynamics (obtained from the ISDs in Figure 2). The absolute values of standard deviation of the scaled mean curvature of the G surface is zero by definition while the standard
deviations in $H/S_V$ of the self-similar structures given earlier are clearly nonzero. The scaled genus, the Gaussian curvature, and the mean curvature all point to the fact that the self-similar bicontinuous structures originated from phase separation and coarsening are quantitatively different not only in their morphology but also their topology from a minimal surface, regardless of the mechanism of coarsening.

6.2. The effects of volume fraction and dimensionality

The interfacial morphologies in three-dimensional mixtures are strongly dependent of volume fraction. Most importantly, we found that the three-dimensional 36%, 40%, and 50% mixtures evolving with conserved dynamics have bicontinuous domains although it has been assumed for a long time that in even moderately asymmetric mixtures initially percolated structures become clusters or droplets during late-stage coarsening, referred to as percolation-to-clusters transition (PCT) or percolation-to-droplets transition (PDT) [26–29,61,69]. However, most of these conclusions are based on experiments that have been performed in film samples that can be regarded as 2D systems, provided that the characteristic domain size is not significantly smaller than the film thickness. More importantly, we find that the similar scaled genii were found in all the three-dimensional mixtures with bicontinuous domains, also including the symmetric mixtures with a non-conserved order parameter. In two-dimensional calculations in symmetric mixtures for the very late-stage shown in Chapter 5, we also observe both interconnected domains and the droplet-shaped domains. In the numerical investigation of 2D Cahn-Hilliard systems by Gameiro et al [60], they report that the connectivity of phases gradually decreases with increasing asymmetricity in the phase fraction, consistent with our observations.
In this section, we will compare the scaled genii of all three-dimensional mixtures at the different volume fractions employed in this study. Furthermore, we will prove that the PCT or PDT is a result of three-dimensional effects in the earlier stage and two-dimensional effects in the later stage by modeling a three-dimensional system having a rectangular computational box where $L_z \ll L_x$ and $L_z \ll L_y$. We compare different systems as a function of characteristic length that is a function of time, because the time scale of evolution varies due to the different coarsening rates.

Scaled genii of all three-dimensional mixtures examined are presented in Figure 6.5. The 40% and 50% mixtures yield very similar scaled genii, which indicates that both structures are topologically equivalent although their morphologies are different. The topology of the 36% mixture evolves in time, as was the case for its morphology. At
earlier times, it has a value slightly less than the scaled genus of the 40% and 50% structures. However, the scaled genus gradually increases with time and approaches the values of the 40% and 50% mixtures. Thus we find that all the scaled genii attain a value of $0.134 \pm 0.004$ during coarsening following phase separation in isotropic systems with conserved and nonconserved dynamics. This value of the scaled genus is independent of the morphology of the bicontinuous interfaces.

The fact that all of the three bicontinuous structures with different volume fractions have approximately the same scaled genus indicates that they are topologically similar although their detailed local morphologies are different. In addition, the similar scaled genus value implies that the 36%, 40% and 50% mixtures all have a similar area-averaged scaled Gaussian curvature $[54]$.

In three-dimensions, mixtures with volume fraction above a certain limit, we do not observe collapse of bicontinuity reported from experiments using film samples or in simulations. This is because, when the characteristic domain size in the system becomes comparable to the film thickness, it is geometrically impossible to attain completely bicontinuous structure. When one phase is completely continuous, the other phase must be broken up into multiple domains that are disconnected. Therefore, while in an earlier stage the characteristic domain size is much smaller than film thickness and a percolated structure is observed, the bicontinuity cannot be sustained as the system undergoes coarsening. In the later stage where the characteristic length becomes comparable to the film thickness,
Figure 6.6. Portions of interfaces presented in the 36%, 40%, and 50% mixtures with a conserved order parameter at $t = 384,000 \left(1/\mathcal{S}_V = 72.69\right)$, $t = 512,000 \left(1/\mathcal{S}_V = 72.69\right)$, and $t = 588,800 \left(1/\mathcal{S}_V = 71.96\right)$, respectively. An edge length is scaled to be $4\left(1/\mathcal{S}_V\right)$.

the two-dimensional effects ensue and droplets or clusters appear. Morphological transitions observed in experiments [26–29,69] can thus be understood as early-stage three-dimensional coarsening followed by late-stage two-dimensional coarsening. The droplet structures are also observed in two-dimensional numerical simulations [60,61]
Figure 6.7. Evolution of domains in a 40% mixture with a rectangular computational box of $512 \times 512 \times 32$ grids with $\Delta x = \sqrt{2}$ evolving via conserved dynamics. Transparent regions denote the $\phi = 0$ phase and grey regions denote the $\phi = 1$ phase.
To illustrate this, a rectangular system with $512 \times 512 \times 32$ grids with $\Delta x = \sqrt{2}$ was employed with conserved dynamics. All the parameters are the same to the simulations of a $512^3$ box except the z-dimension is much smaller. The evolution of domains are shown in Figure 6.7 where three-dimensionally interconnected domains at $t = 1280$ undergoes the transition to two-dimensional droplets at $t = 46080$. During the transition from interconnected domains to droplets, many pinching events are observed. The plot of cube of characteristic length versus during coarsening of this system is shown in Figure 6.9. The data points are oscillating around the line $l^3(t) = 2.2181t - 7616.6$. The correlation coefficient $R^2 = 0.99$ is the smallest among all the systems examined in this study. It is still unclear if this system obeys the LSW growth law since only one simulation was performed.

The scaled ISDs of this system are presented in Figure 6.8. Note that the grey regions in the $z = 0$ and $z = 32\sqrt{2}$ planes (the bottom and top surfaces, respectively) in Figure 6.7 are not interfaces but artificially created surfaces to denote the $\phi = 1$ phase. The scaled ISD at $t = 1280$ may not have 100% accuracy because the characteristic length is a little less than three times of interfacial thickness ($\delta = 4\sqrt{2} \approx 5.66$). Nevertheless, the scaled ISD at $t = 1280$ resembles that of the 30% mixture shown in Figure 4.45, indicating that the domains are interconnected but not bicontinuous. By integrating the scaled ISDs, it is found that about 38% of interfaces are elliptic ($K > 0$) at $t = 1280$ and about 30% of interfaces are elliptic ($K > 0$) at $t = 15360$. More interfaces are parabolic or cylindrical ($K = 0$) at $t = 26880$ then at earlier times when many droplets exist in the system as shown in Figure 6.7(d). Most importantly, when the characteristic length become similar to the z-dimension ($l \approx L_z = 32\sqrt{2} \approx 45.25$), all interfacial normals are
nearly perpendicular to the z-direction. In Figure 6.7(e) where $t = 409960$ and $1/S_V < L_z$, some interfacial normals are not perpendicular to the z-direction due to the presence of horizontal passages. In Figure 6.7(f) where $t = 64000$ and $1/S_V > L_z$, all interfacial normals are nearly perpendicular to the z-direction.
Figure 6.8. Corresponding scaled ISDs of mixtures present in Figure 6.7.
Figure 6.9. Cube of characteristic length vs. time during coarsening of domains in a rectangular system with $512 \times 512 \times 32$ grids with $\Delta x = \sqrt{2}$. The poorer statistics indicated by the $R^2$ value smaller than other simulations in this study is because only one set of simulation was performed for the PTD.
CHAPTER 7

Conclusions

The evolution of morphology and topology during coarsening of two-phase mixtures originating from phase separation via nonconserved and conserved dynamics were studied in three-dimensions and in two-dimensions. This was done using large-scale phase-field calculations and using variety of methods to analyze the data including the structure function, the interfacial shape distribution, and the genus. For three-dimensional symmetric mixtures evolving via the two dynamics and asymmetric mixtures with volume fractions of 22%, 30%, 36%, and 40% evolving via conserved dynamics were investigated. For two-dimensional mixtures, symmetric mixtures evolving via the two dynamics and asymmetric mixtures with area fractions of 40%, 44%, and 48% evolving via conserved dynamics were investigated. A thin film geometry whose $z-$dimension is much smaller than $x-$ and $y-$dimensions was also investigated to examine the dimensionality effects.

Three-dimensional symmetric mixtures evolving via the two dynamics have bicontinuous domains with complex morphology and topology. It was found that they attain the self-similar scaled morphologies and topologies during late-stage coarsening, characterized by the scaled interfacial shape distributions and the scaled genii, respectively. The time-invariant scaled interfacial shape distributions are unique to the dynamics, with conserved dynamics yielding a narrower distribution of interfacial curvature about zero mean curvature. The difference is attributed to the stronger coupling of interfacial curvatures in the conserved dynamics case. The scaled interfacial shape distributions form the
counterparts for interconnected domains to the particle-size distribution scaled by average particle size. In contrast, both dynamics yield similar scaled topologies characterized by the similar scaled genii of $\sim 0.139$ and $\sim 0.135$ for nonconserved and conserved dynamics, respectively.

It was shown that three-dimensional mixtures with a volume fraction of 36% and 40% evolving via conserved dynamics also have bicontinuous domains during late-stage coarsening and that highly asymmetric mixtures have droplet-shaped domains during the late-stage. Furthermore, the evolution of all the mixtures with bicontinuous domains is self-similar, yielding the scaled interfacial shape distributions different for the volume fraction. However, despite these differences in volume fractions, and whether the order parameter is conserved, the bicontinuous mixtures undergoing the self-similar coarsening have approximately the same genus of $\sim 0.134 \pm 0.004$. This implies that they have nearly the same scaled topology.

Two-dimensional simulations also revealed many interesting points. The results partially agree with the assumption of interconnected domains in symmetric mixtures and droplet domains in asymmetric mixtures during late-stage coarsening. In our results, the 2D symmetric mixtures with a conserved order parameter have both interconnected and droplet domains at the same time during late-stage coarsening. Instead of the interfacial shape distributions and the genus, the evolution of curvature distributions was investigated. Interestingly, all the mixtures with droplet domains yield the maximum probability at the similar scaled curvature of $0.7 \pm 0.175$ while all the mixtures with interconnected domains yield the maximum probability at the similar scaled curvature of zero. The evolution kinetics is faster for high area fractions in two-dimensions while that is faster
for low volume fraction in three-dimensions. Additionally, no pinching was observed in the two-dimensional mixtures unlike in three-dimensional mixtures because the Rayleigh instability can only occur in three-dimensions.

The percolation-to-droplets transition was observed in a simulation of a film sample. Three-dimensional dynamics were observed at earlier times and two-dimensional dynamics were observed at later times. This was shown by a simulation using a rectangular computational box whose one dimension is smaller than the others and conserved dynamics. When the characteristic length is on the order of the box size, droplets began to form.
References


