COMPUTER SIMULATION STUDY OF WATERBORNE TWO-COMPONENT POLYURETHANE FILM FORMATION

Shihai Yang
University of Southern Mississippi

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COMPUTER SIMULATION STUDY OF WATERBORNE
TWO-COMPONENT POLYURETHANE FILM FORMATION

by

Shihai Yang

A Dissertation
Submitted to the Graduate Studies Office
of The University of Southern Mississippi
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy

Approved:

August 2007
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SHIHAI YANG

2007
COMPUTER SIMULATION STUDY OF WATERBORNE
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ABSTRACT

COMPUTER SIMULATION STUDY OF WATERBORNE TWO-COMPONENT POLYURETHANE FILM FORMATION

by Shihai Yang

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In this thesis, a coarse-grained computer simulation model is presented to study the film growth and macroscopic morphological feature (film thickness, surface roughness and longitudinal constituent density profile) in a multi-component polymer system. The mixture consists of reactive hydrophobic (H) and polar groups (P) in a reactive aqueous solvent (A) which is also allowed to evaporate. Characteristics of each component such as hydrophobic and polar interactions, molecular weights, and specific functionality for the covalent bonding are used to describe the waterborne two-component polyurethane (WB 2K-PUR) film growth as an example. Systematic approach is employed to study the film growth step by step starting from the mixture of its basic ingredients. Attempts are made to capture such realistic features as perceived reaction kinetics and polymerization mechanism in the model.

Constituents move stochastically via the Metropolis algorithm to explore thermodynamic equilibration while the kinetic reactions are incorporated through flexible covalent bonding (Bond Fluctuation Model) which may arrest the growth before reaching equilibrium. Film thickness grows and its interface evolves and equilibrates as the simulation continues. Power-law dependence is found for the initial growth of film thickness (\(h\)) and surface roughness (\(W\)) with time (\(t\)), i.e., \(h \propto t^\gamma\), \(W \propto t^\beta\), with all simulations. In addition to the study of film evolution and surface morphology, constituent density profiles along the longitudinal direction are also investigated to develop a deep understanding of film infra-structure as well as to track the post-reaction product distribution. Effects of parameters such as temperature, relative humidity (initial water concentration), stoichiometry
(NCO:OH ratio) and reaction rate are examined specifically in these simulations. Qualitative agreements with laboratory observations are found with our simulation results.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xviii</td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>xix</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>xx</td>
</tr>
<tr>
<td>1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2 WATERBORNE TWO-COMPONENT POLYURETHANES</td>
<td>4</td>
</tr>
<tr>
<td>2.1 Polyurethane Chemistry</td>
<td>4</td>
</tr>
<tr>
<td>2.2 Solventborne and Waterborne Polyurethanes</td>
<td>6</td>
</tr>
<tr>
<td>2.3 Experiments</td>
<td>9</td>
</tr>
<tr>
<td>3 SURFACE AND INTERFACE GROWTH</td>
<td>13</td>
</tr>
<tr>
<td>3.1 Surface and Interface via Particle Deposition</td>
<td>13</td>
</tr>
<tr>
<td>3.2 Deposition of Polymer Chains</td>
<td>18</td>
</tr>
<tr>
<td>3.3 Network Formation in Film Growth</td>
<td>19</td>
</tr>
<tr>
<td>4 COMPUTER MODELLING</td>
<td>23</td>
</tr>
<tr>
<td>4.1 Simulation Methods and Techniques</td>
<td>23</td>
</tr>
<tr>
<td>4.2 Computer Model for Film Formation</td>
<td>29</td>
</tr>
<tr>
<td>5 PRELIMINARY STUDY</td>
<td>38</td>
</tr>
<tr>
<td>5.1 Film Growth</td>
<td>39</td>
</tr>
<tr>
<td>5.2 Equilibrium</td>
<td>54</td>
</tr>
<tr>
<td>5.3 Finite Size Effect</td>
<td>58</td>
</tr>
<tr>
<td>6 FILM IN NON-REACTIVE SOLVENT</td>
<td>65</td>
</tr>
<tr>
<td>6.1 Film Growth</td>
<td>66</td>
</tr>
<tr>
<td>6.2 Equilibrium</td>
<td>80</td>
</tr>
<tr>
<td>6.3 Density Profile</td>
<td>86</td>
</tr>
<tr>
<td>6.4 Finite Size Effect</td>
<td>95</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Section Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 FILM IN REACTIVE SOLVENT</td>
<td>105</td>
</tr>
<tr>
<td>7.1 Film Growth</td>
<td>107</td>
</tr>
<tr>
<td>7.2 Equilibrium</td>
<td>125</td>
</tr>
<tr>
<td>7.3 Density Profile</td>
<td>133</td>
</tr>
<tr>
<td>7.4 Finite Size Effect</td>
<td>143</td>
</tr>
<tr>
<td>8 FILM WITH ISOTROPIC GROWTH</td>
<td>149</td>
</tr>
<tr>
<td>8.1 Film Growth</td>
<td>150</td>
</tr>
<tr>
<td>8.2 Equilibrium</td>
<td>168</td>
</tr>
<tr>
<td>8.3 Density Profile</td>
<td>178</td>
</tr>
<tr>
<td>8.4 Finite Size Effect</td>
<td>192</td>
</tr>
<tr>
<td>9 SUMMARY</td>
<td>198</td>
</tr>
<tr>
<td>APPENDIX</td>
<td></td>
</tr>
<tr>
<td>A COMPUTER ALGORITHM FLOWCHART</td>
<td>204</td>
</tr>
<tr>
<td>B THE METROPOLIS ALGORITHM</td>
<td>205</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>206</td>
</tr>
</tbody>
</table>
# LIST OF ILLUSTRATIONS

## Figure

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Representative structures of polyester and WDPI used in the experiments of this study.</td>
<td>10</td>
</tr>
<tr>
<td>2.2</td>
<td>Topographic AFM image of WB 2K-PUR films crosslinked at 82 %RH and 30 °C recorded from the film-air interface.</td>
<td>11</td>
</tr>
<tr>
<td>2.3</td>
<td>Film-air (F-A) IRIR image of WB 2K-PUR films crosslinked at 82 %RH and 30 °C showing the compositional variations and phase separation. Dark gray area (A) corresponds to PEG-rich (hydrophilic) domain; light gray area (B) corresponds to isocyanurate-rich (hydrophobic) domain.</td>
<td>12</td>
</tr>
<tr>
<td>3.1</td>
<td>The random deposition model. Particles are dropped from random positions above the surface and are deposited on the top of the column under them. The height of the interface in RD does not depend on the height of the neighboring columns.</td>
<td>15</td>
</tr>
<tr>
<td>3.2</td>
<td>Schematic picture of film height $h$ and its surface roughness $W$ on a substrate with length $L$.</td>
<td>16</td>
</tr>
<tr>
<td>3.3</td>
<td>Typical plot of growth of the interface width with time. Two regimes: (i) power law growth, and (ii) saturation.</td>
<td>17</td>
</tr>
<tr>
<td>3.4</td>
<td>A typical picture of cross-linked polymer network.</td>
<td>20</td>
</tr>
<tr>
<td>4.1</td>
<td>Schematic illustration of the bond fluctuation model in three dimensions. An effective monomer blocks a cube containing eight lattice sites for occupation by other monomers.</td>
<td>28</td>
</tr>
<tr>
<td>4.2</td>
<td>Schematic illustration of the chemical reactions involved in waterborne two-component polyurethane systems: A) main reactions between isocyanate groups of crosslinker ($f_H = 3$) and hydroxyl groups of polyol ($f_P = 2$); B) side reactions between isocyanate groups of crosslinker and water ($f_A = 1$) to form an intermediate amine group on the crosslinker ($H^* = 3$) which leads to further consumption of polyisocyanate.</td>
<td>34</td>
</tr>
<tr>
<td>4.3</td>
<td>Snapshots for film formation with components tethered by fluctuating covalent bonds involving reactive hydrophobic (Light gray), polar (Black) and evaporative aqueous groups (Blue). The film consists of all points that are covalently bonded from the substrate. The surface is defined as the locus of all connected points with the maximum height.</td>
<td>37</td>
</tr>
</tbody>
</table>
5.1 Snapshots for film formation with components tethered by fluctuating covalent bonds involving reactive hydrophobic (H), polar (P) and evaporative aqueous groups (A). Red: H before reaction; Yellow: H after reaction; Black: P before reaction; Green: P after reaction; Blue: A. The film consists of all points that are covalently bonded from the substrate. The surface is defined as the locus of all connected points with the maximum height. a) \( t = 0 \), b) \( t = 20 \), c) \( t = 60 \), d) \( t = 100 \), e) \( t = 5000 \), f) \( t = 3 \times 10^4 \). .......... 40

5.2 Growth of the average film thickness \( (h) \) for a range of temperatures with only hardcore interaction among the components (non-reactive aqueous solvent) on a sample \( 40 \times 40 \times 30 \) with 10 independent samples for \( p_H = p_P = 0.01 \) with initial water concentration \( p_A = 0.03 \) and \( f_H = f_P = 4 \) with \( R_{HH} = R_{PP} = R_{HP} = R_{HS} = R_{PS} = 1 \) using EBFM with reaction proceeding from the substrate (case 1). Variation of the saturated and near-saturated thickness \( h_s \) with the temperature is presented in the inset. The statistical errors in data are of the order of symbols sizes. .......... 42

5.3 Growth of the average film thickness \( (h) \) for a range of temperatures with additional interaction among the components (non-reactive aqueous solvent) on a sample \( 40 \times 40 \times 30 \) with 10 independent samples for \( p_H = p_P = 0.01 \) with initial water concentration \( p_A = 0.03 \) and \( f_H = f_P = 4 \) with \( R_{HH} = R_{PP} = R_{HP} = R_{HS} = R_{PS} = 1 \) using EBFM with reaction proceeding from the substrate (case 2). Variation of the saturated and near-saturated thickness \( h_s \) with the temperature is presented in the inset. The statistical errors in data are of the order of symbols sizes. .......... 44

5.4 Variation of water concentration with time steps for a range of temperatures using the same parameter as in Figure 5.3. .......... 45

5.5 Growth of the average film thickness \( (h) \) for a range of temperatures with additional interaction among the components (non-reactive aqueous solvent) on a sample \( 40 \times 40 \times 30 \) with 10 independent samples for \( p_H = p_P = 0.01 \) with initial water concentration \( p_A = 0.03 \) and \( f_H = f_P = 4 \) with \( R_{HH} = R_{PP} = 0, R_{HP} = R_{HS} = R_{PS} = 1 \) using EBFM with reaction proceeding from the substrate (case 3). .......... 46

5.6 Growth of the average film thickness \( (h) \) for a range of temperatures with additional interaction among the components (non-reactive aqueous solvent) on a sample \( 40 \times 40 \times 30 \) with 10 independent samples for \( p_H = 0.015, p_P = 0.023 \) with initial water concentration \( p_A = 0.042 \) and \( f_H = 3, f_P = 2 \) with \( R_{HH} = R_{PP} = 0, R_{HP} = R_{HS} = R_{PS} = 1 \) using EBFM with reaction proceeding from the substrate (case 4). .......... 47

5.7 Evolution of the interface width \( (W) \) of the film surface for a range of temperatures using the same parameters as in Figure 5.2 (case 1). .......... 49

5.8 Evolution of the interface width \( (W) \) of the film surface for a range of temperatures using the same parameters as in Figure 5.3 (case 2). .......... 51

5.9 Evolution of the interface width \( (W) \) of the film surface for a range of temperatures using the same parameters as in Figure 5.5 (case 3). .......... 52
5.10 Evolution of the interface width \( (W) \) of the film surface for a range of temperatures using the same parameters as in Figure 5.6 (case 4). .......................... 53

5.11 Variation of the saturated and near-saturated thickness \( h_s \) with the temperature using the same parameter as in Figure 5.5 (case 3). The statistical errors in data are of the order of symbols sizes. .................................................. 56

5.12 Variation of the saturated and near-saturated thickness \( h_s \) with the temperature using the same parameter as in Figure 5.6 (case 4). The statistical errors in data are of the order of symbols sizes. .......................... 57

5.13 Variation of the saturated and near-saturated roughness \( W_y \) with the temperature using the same parameter as in Figure 5.5 (case 3). The statistical errors in data are of the order of symbols sizes. .................................................. 58

5.14 Variation of the saturated and near-saturated roughness \( W_y \) with the temperature using the same parameter as in Figure 5.6 (case 4). The statistical errors in data are of the order of symbols sizes. .......................... 59

5.15 Evolution of the film thickness \( h \) using EBFM for a temperature \( T = 5 \) with non-reactive aqueous solvent on different sample sizes each with ten independent samples for \( p_H = p_P = 0.01 \) with initial water concentration \( p_A = 0.03 \) (case 2). .................................................. 63

5.16 Evolution of the interface width \( W \) using EBFM for a temperature \( T = 5 \) with non-reactive aqueous solvent on different sample sizes each with ten independent samples for \( p_H = p_P = 0.01 \) with initial water concentration \( p_A = 0.03 \) (case 2). .................................................. 64

6.1 Snapshots for film surface evolution proceeding from the substrate in non-reactive evaporative solvent. The surface is defined as the locus of all connected points with the maximum height. a) \( t = 1 \), b) \( t = 25 \), c) \( t = 50 \), d) \( t = 5 \times 10^4 \) .................................................. 67

6.2 Film-air (F-A) IRIR images of WB 2K-PUR films showing the compositional variations and phase separation .................................................. 68

6.3 Growth of the average film thickness \( (h) \) for a range of temperatures with non-reactive aqueous solvent on a sample \( 40 \times 40 \times 30 \) with 10 independent samples for \( p_H = 0.0115, p_P = 0.023 \) with initial water concentration \( p_A = 0.0422 \) using BFM with reaction proceeding from the substrate. .................................................. 69

6.4 Growth of the average film thickness \( (h) \) for a range of initial water concentrations at temperature \( T = 3 \) with non-reactive aqueous solvent on a sample \( 40 \times 40 \times 30 \) with 10 independent samples for \( p_H = 0.0115, p_P = 0.023 \) using BFM with reaction proceeding from the substrate. .................................................. 72

6.5 Growth of the average film thickness \( (h) \) for a range of NCO:OH ratios at temperature \( T = 3 \) with non-reactive aqueous solvent on a sample \( 40 \times 40 \times 30 \) with 10 independent samples for \( p_H = 0.0115, p_P = 0.023 \) with initial water concentration \( p_A = 0.0422 \) using BFM with reaction proceeding from the substrate. .................................................. 74
6.6 Growth of the average film thickness ($h$) for a range of reaction rates at temperature $T = 3$ with non-reactive aqueous solvent on a sample $40 \times 40 \times 30$ with 10 independent samples for $p_H = 0.0115, p_P = 0.023$ with initial water concentration $p_A = 0.0422$ using BFM with reaction proceeding from the substrate. ........................................................ 75

6.7 Evolution of the interface width ($W$) of the film surface for a range of temperatures using the same parameters as in Figure 6.3. ............................................ 77

6.8 Evolution of the interface width ($W$) of the film surface for a range of initial water concentrations using the same parameters as in Figure 6.4. ......................... 79

6.9 Evolution of the interface width ($W$) of the film surface for a range of NCO:OH ratios using the same parameters as in Figure 6.5. ................................. 80

6.10 Evolution of the interface width ($W$) of the film surface for a range of reaction rates using the same parameters as in Figure 6.6. ................................. 81

6.11 Variation of the saturated and near-saturated thickness $h_s$ with the temperature using the same parameter as in Figure 6.3. The statistical errors in data are of the order of symbols sizes. ...................................................... 83

6.12 Variation of the saturated and near-saturated thickness $h_s$ with the initial water concentration using the same parameter as in Figure 6.4. The statistical errors in data are of the order of symbols sizes. ...................................................... 84

6.13 Variation of the saturated and near-saturated thickness $h_s$ with the NCO:OH ratios using the same parameter as in Figure 6.5. The statistical errors in data are of the order of symbols sizes. ...................................................... 85

6.14 Variation of the saturated and near-saturated thickness $h_s$ with the reaction rates using the same parameter as in Figure 6.6. The statistical errors in data are of the order of symbols sizes. ...................................................... 86

6.15 Variation of the saturated and near-saturated roughness $W_s$ with the temperature using the same parameter as in Figure 6.7. The statistical errors in data are of the order of symbols sizes. ...................................................... 87

6.16 Variation of the saturated and near-saturated roughness $W_s$ with the initial water concentration using the same parameter as in Figure 6.8. The statistical errors in data are of the order of symbols sizes. ...................................................... 88

6.17 Variation of the saturated and near-saturated roughness $W_s$ with the NCO:OH ratios using the same parameter as in Figure 6.9. The statistical errors in data are of the order of symbols sizes. ...................................................... 89

6.18 Variation of the saturated and near-saturated roughness $W_s$ with the reaction rate using the same parameter as in Figure 6.10. The statistical errors in data are of the order of symbols sizes. ...................................................... 90

6.19 Density profile of all components along the longitudinal direction in the long time limit at different temperatures using the same parameter as in Figure 6.3. 91

6.20 Density profile of $P$ component along the longitudinal direction in the long time limit at different temperatures using the same parameter as in Figure 6.3. 92

6.21 Density profile of $H$ component along the longitudinal direction in the long time limit at different temperatures using the same parameter as in Figure 6.3. 93

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
6.22 Density profile of all components along the longitudinal direction in the long
time limit at different initial water concentrations using the same parameter
as in Figure 6.4. ................................................................. 94
6.23 Density profile of P component along the longitudinal direction in the long
time limit at different initial water concentrations using the same parameter
as in Figure 6.4. ................................................................. 95
6.24 Density profile of H component along the longitudinal direction in the long
time limit at different initial water concentrations using the same parameter
as in Figure 6.4. ................................................................. 96
6.25 Density profile of all components along the longitudinal direction in the long
time limit at different NCO:OH ratios using the same parameter as in Figure
6.5. ..................................................................................... 97
6.26 Density profile of P component along the longitudinal direction in the long
time limit at different NCO:OH ratios using the same parameter as in Figure
6.5. ..................................................................................... 98
6.27 Density profile of H component along the longitudinal direction in the long
time limit at different NCO:OH ratios using the same parameter as in Figure
6.5. ..................................................................................... 99
6.28 Density profile of all components along the longitudinal direction in the long
time limit at different reaction rates using the same parameter as in Figure 6.6. 100
6.29 Density profile of P component along the longitudinal direction in the long
time limit at different reaction rates using the same parameter as in Figure 6.6. 101
6.30 Density profile of H component along the longitudinal direction in the long
time limit at different reaction rates using the same parameter as in Figure 6.6. 102
6.31 evolution of the film thickness \(h\) using BFM for a temperature \(T = 5\) with non-
reactive aqueous solvent on different sample sizes each with ten independent
samples for \(p_H = 0.0115\) and \(p_P = 0.023\) with initial water concentration
\(p_A = 0.0422\) (case 5). ........................................................... 103
6.32 evolution of the interface width \(W\) using BFM for a temperature \(T = 5\) with
non-reactive aqueous solvent on different sample sizes each with ten indepen-
dent samples for \(p_H = 0.0115\) and \(p_P = 0.023\) with initial water concentration
\(p_A = 0.0422\) (case 5). ........................................................... 104
7.1 Schematic illustration of the volume of water being (a) included in, or (b)
excluded from the film after its reaction with hydrophobic component. .... 106
7.2 Growth of the average film thickness \((h)\) for a range of temperatures with re-
active aqueous solvent on a sample \(40 \times 40 \times 30\) with 10 independent samples
for \(p_H = 0.0115, p_P = 0.023\) with initial water concentration \(p_A = 0.0422\)
using BFM with reaction proceeding from the substrate (case 6). The upper
plot is for the systems using BFM and the lower plot is for the systems using
EBFM. ................................................................. 109
7.3 (a) Growth of reacted water concentration using EBFM, (b) growth of reacted water concentration using BFM, (c) growth of evaporated water concentration using EBFM, and (d) growth of evaporated water concentration using BFM for a range of temperatures on a 40 x 40 x 30 sample with ten independent samples for $P_H = 0.0115, P_P = 0.023$ with initial water concentration $P_A = 0.0422$.

7.4 Growth of the average film thickness ($h$) for a range of temperatures with reactive aqueous solvent on a sample 40 x 40 x 30 with 10 independent samples for $P_H = 0.0115, P_P = 0.023$ with initial water concentration $P_A = 0.0422$ using BFM with reaction proceeding from the substrate (case 7).

7.5 Growth of the average film thickness ($h$) for a range of initial water concentration at temperature $T = 3$ with reactive aqueous solvent on a sample 40 x 40 x 30 with 10 independent samples for $P_H = 0.0115, P_P = 0.023$ using BFM with reaction proceeding from the substrate (case 7).

7.6 Growth of the average film thickness ($h$) for a range of NCO:OH ratios at temperature $T = 3$ with reactive aqueous solvent on a sample 40 x 40 x 30 with 10 independent samples for $P_H = 0.0115, P_P = 0.023$ with initial water concentration $P_A = 0.0422$ using BFM with reaction proceeding from the substrate (case 7).

7.7 Growth of the average film thickness ($h$) for a range of reaction rates at temperature $T = 3$ with reactive aqueous solvent on a sample 40 x 40 x 30 with 10 independent samples for $P_H = 0.0115, P_P = 0.023$ with initial water concentration using BFM with reaction proceeding from the substrate (case 7).

7.8 Evolution of the interface width ($W$) of the film surface for a range of temperatures using the same parameters as in Figure 7.2.

7.9 Evolution of the interface width ($W$) of the film surface for a range of temperatures using the same parameters as in Figure 7.4.

7.10 Evolution of the interface width ($W$) of the film surface for a range of initial water concentrations using the same parameters as in Figure 7.5.

7.11 Evolution of the interface width ($W$) of the film surface for a range of NCO:OH ratios using the same parameters as in Figure 7.6.

7.12 Evolution of the interface width ($W$) of the film surface for a range of Reaction rates using the same parameters as in Figure 7.7.

7.13 Variation of the saturated and near-saturated thickness $h_s$ with the temperature using the same parameter as in Figure 7.2 (case 6). The statistical errors in data are of the order of symbols sizes.

7.14 Variation of the saturated and near-saturated thickness $h_s$ with the temperature using the same parameter as in Figure 7.4 (case 7). The statistical errors in data are of the order of symbols sizes.

7.15 Variation of the saturated and near-saturated thickness $h_s$ with the initial water concentration using the same parameter as in Figure 7.5 (case 7). The statistical errors in data are of the order of symbols sizes.
7.16 Variation of the saturated and near-saturated thickness \( h_s \) with the NCO:OH ratio using the same parameter as in Figure 7.6 (case 7). The statistical errors in data are of the order of symbols sizes. ............................................................... 129

7.17 Variation of the saturated and near-saturated thickness \( h_s \) with the reaction rate using the same parameter as in Figure 7.7 (case 7). The statistical errors in data are of the order of symbols sizes. ............................................................... 130

7.18 Variation of the saturated and near-saturated roughness \( W_s \) with the temperature using the same parameter as in Figure 7.8 (case 6). The statistical errors in data are of the order of symbols sizes. ............................................................... 131

7.19 Variation of the saturated and near-saturated roughness \( W_s \) with the temperature using the same parameter as in Figure 7.9 (case 7). The statistical errors in data are of the order of symbols sizes. ............................................................... 132

7.20 Variation of the saturated and near-saturated roughness \( W_s \) with the initial water concentration using the same parameter as in Figure 7.10 (case 7). The statistical errors in data are of the order of symbols sizes. ............................................................... 133

7.21 Variation of the saturated and near-saturated roughness \( W_s \) with the NCO:OH ratio using the same parameter as in Figure 7.11 (case 7). The statistical errors in data are of the order of symbols sizes. ............................................................... 134

7.22 Variation of the saturated and near-saturated roughness \( W_s \) with the reaction rate using the same parameter as in Figure 7.12 (case 7). The statistical errors in data are of the order of symbols sizes. ............................................................... 135

7.23 Density profile of all components along the longitudinal direction in the long time limit at different temperatures using the same parameter as in Figure 7.4 (case 7). ............................................................... 136

7.24 Density profile of \( P \) component along the longitudinal direction in the long time limit at different temperatures using the same parameter as in Figure 7.4 (case 7). ............................................................... 137

7.25 Density profile of \( H \) component along the longitudinal direction in the long time limit at different temperatures using the same parameter as in Figure 7.4 (case 7). ............................................................... 138

7.26 Density profile of all components along the longitudinal direction in the long time limit at different initial water concentrations using the same parameter as in Figure 7.5 (case 7). ............................................................... 139

7.27 Density profile of \( P \) component along the longitudinal direction in the long time limit at different initial water concentrations using the same parameter as in Figure 7.5 (case 7). ............................................................... 140

7.28 Density profile of \( H \) component along the longitudinal direction in the long time limit at different initial water concentrations using the same parameter as in Figure 7.5 (case 7). ............................................................... 141

7.29 Density profile of all components along the longitudinal direction in the long time limit at different NCO:OH ratios using the same parameter as in Figure 7.6 (case 7). ............................................................... 142
7.30 Density profile of P component along the longitudinal direction in the long time limit at different NCO:OH ratios using the same parameter as in Figure 7.6 (case 7).

7.31 Density profile of H component along the longitudinal direction in the long time limit at different NCO:OH ratios using the same parameter as in Figure 7.6 (case 7).

7.32 Density profile of all components along the longitudinal direction in the long time limit at different reaction rates using the same parameter as in Figure 7.7 (case 7).

7.33 Density profile of P component along the longitudinal direction in the long time limit at different reaction rates using the same parameter as in Figure 7.7 (case 7).

7.34 Density profile of H component along the longitudinal direction in the long time limit at different reaction rates using the same parameter as in Figure 7.7 (case 7).

7.35 Evolution of the interface width W using BFM for a temperature T = 5 with reactive aqueous solvent on different sample sizes each with ten independent samples for p_H = 0.0115 and p_P = 0.023 with initial water concentration p_A = 0.0422 (case 7).

8.1 Snapshots for film formation proceeding isotropically in space with reactive hydrophobic (H), polar (P) and evaporative aqueous groups (A). Red: H before reaction; Yellow: H after reaction; Black: P before reaction; Green: P after reaction; Blue: A; Pink/Light blue: modified H*.

8.2 Growth of the average film thickness (h) for a range of temperatures with reactive aqueous solvent on a sample 40 x 40 x 30 with 10 independent samples for p_H = 0.0115, p_P = 0.023 with initial water concentration p_A = 0.0422 using BFM with reaction proceeding isotropically in space (case 8).

8.3 Growth of the average film thickness (h) for a range of initial water concentration at temperature T = 3 with reactive aqueous solvent on a sample 40 x 40 x 30 with 10 independent samples for p_H = 0.0115, p_P = 0.023 using BFM with reaction proceeding isotropically in space (case 8).

8.4 Growth of the average film thickness (h) for a range of NCO:OH ratios at temperature T = 3 with reactive aqueous solvent on a sample 40 x 40 x 30 with 10 independent samples for p_H = 0.0115, p_P = 0.023 with initial water concentration p_A = 0.0422 using BFM with reaction proceeding isotropically in space (case 8).
8.5 Growth of the average film thickness ($h$) for a range of reaction rates at temperature $T = 3$ with reactive aqueous solvent on a sample $40 \times 40 \times 30$ with 10 independent samples for $p_H = 0.0115, p_P = 0.023$ with initial water concentration using BFM with reaction proceeding isotropically in space (case 8). .................................................. 159

8.6 Evolution of the interface width ($W$) of the film surface for a range of temperatures using the same parameters as in Figure 8.2. .......................................................... 161

8.7 Evolution of the interface width ($W$) of the film surface for a range of initial water concentrations using the same parameters as in Figure 8.3. ......................... 164

8.8 Evolution of the interface width ($W$) of the film surface for a range of NCO:OH ratios using the same parameters as in Figure 8.4. .................................................. 166

8.9 Evolution of the interface width ($W$) of the film surface for a range of Reaction rates using the same parameters as in Figure 8.5. ................................................... 167

8.10 Variation of the saturated and near-saturated thickness $h_s$ with the temperature using the same parameter as in Figure 8.2 (case 8). The statistical errors in data are of the order of symbols sizes. .............................................. 168

8.11 Variation of the saturated and near-saturated thickness $h_s$ with the initial water concentration using the same parameter as in Figure 8.3 (case 8). The statistical errors in data are of the order of symbols sizes. .............................................. 170

8.12 Variation of the saturated and near-saturated thickness $h_s$ with the NCO:OH ratio using the same parameter as in Figure 8.4 (case 8). The statistical errors in data are of the order of symbols sizes. .............................................. 171

8.13 Variation of the saturated and near-saturated thickness $h_s$ with the temperature using the same parameter as in Figure 8.5 (case 8). The statistical errors in data are of the order of symbols sizes. .............................................. 172

8.14 Variation of the saturated and near-saturated roughness $W_s$ with the temperature using the same parameter as in Figure 8.6 (case 8). .................................................. 174

8.15 Topographic AFM images of WB 2K-PUR films crosslinked at 30%RH and temperature a) $T = 30 ^\circ C$ and b) $T = 50 ^\circ C$ recorded from the film-air interface. .......................................................... 174

8.16 Variation of the saturated and near-saturated roughness $W_s$ with the initial water concentration using the same parameter as in Figure 8.7 (case 8). The statistical errors in data are of the order of symbols sizes. .............................................. 175

8.17 Topographic AFM images of WB 2K-PUR films crosslinked at 30 $^\circ C$ and relative humidity a) $RH = 75\%$ and b) $RH = 82\%$ recorded from the film-air interface. .................................................. 176

8.18 Variation of the saturated and near-saturated roughness $W_s$ with the NCO:OH ratio using the same parameter as in Figure 8.8 (case 8). .................................................. 176

8.19 Topographic AFM images of WB 2K-PUR filmd crosslinked at 82%RH and 30 $^\circ C$ with varying stoichiometries recorded from the film-air interface. ............... 177

8.20 Variation of the saturated and near-saturated roughness $W_s$ with the reaction rate using the same parameter as in Figure 8.9 (case 8). The statistical errors in data are of the order of symbols sizes. .................................................. 178
8.21 Density profile of all components along the longitudinal direction in the long time limit at different temperatures using the same parameter as in Figure 8.2 (case 8). .......................................................... 179
8.22 Density profile of \( H \) component along the longitudinal direction in the long time limit at different temperatures using the same parameter as in Figure 8.2 (case 8). .......................................................... 182
8.23 Density profile of \( P \) component along the longitudinal direction in the long time limit at different temperatures using the same parameter as in Figure 8.2 (case 8). .......................................................... 183
8.24 Schematic illustration of film layers at different temperature region. .... 183
8.25 Density profile of all components along the longitudinal direction in the long time limit at different initial water concentrations using the same parameter as in Figure 8.3 (case 8) .......................................................... 184
8.26 Density profile of \( H \) component along the longitudinal direction in the long time limit at different initial water concentrations using the same parameter as in Figure 8.3 (case 8) .......................................................... 185
8.27 Density profile of \( P \) component along the longitudinal direction in the long time limit at different initial water concentrations using the same parameter as in Figure 8.3 (case 8) .......................................................... 186
8.28 Schematic illustration of film layers under different relative humidities. .... 186
8.29 Variation of the percentage of consumed \( H \) and \( P \) component with initial water concentration. .......................................................... 187
8.30 ATR-FTIR spectra of WB 2K-PUR films crosslinked at 30 C and 11, 32, 49, 75, 82 and 97%RH recorded from the F-A (A) and F-S (B) interfaces, respectively. Arrows indicate intensity changes with increasing RH. 1724 PUR/ester C=O; 1647 PUA C =O; 1560 PUA N-H; 1524 PUR N-H. .... 188
8.31 Density profile of all components along the longitudinal direction in the long time limit at different NCO:OH ratios using the same parameter as in Figure 8.4 (case 8) .......................................................... 189
8.32 Density profile of \( P \) component along the longitudinal direction in the long time limit at different NCO:OH ratios using the same parameter as in Figure 8.4 (case 8) .......................................................... 190
8.33 Density profile of \( H \) component along the longitudinal direction in the long time limit at different NCO:OH ratios using the same parameter as in Figure 8.4 (case 8) .......................................................... 191
8.34 Variation of the percentage of consumed \( H \) and \( P \) component with NCO:OH ratio. .......................................................... 192
8.35 ATR-FTIR spectral absorbance profiles for 1524 and 1560 cm\(^{-1}\) N-H bending modes of WB 2K-PUR films with varied NCO:OH ratios recorded from the F-A interface. .......................................................... 193
8.36 Density profile of all components along the longitudinal direction in the long time limit at different reaction rates using the same parameter as in Figure 8.5 (case 8) .......................................................... 194
8.37 Density profile of $P$ component along the longitudinal direction in the long time limit at different reaction rates using the same parameter as in Figure 8.5 (case 8) ................................................................. 195
8.38 Density profile of $H$ component along the longitudinal direction in the long time limit at different reaction rates using the same parameter as in Figure 8.5 (case 8) ................................................................. 196
8.39 Evolution of the interface width $W$ using BFM for a temperature $T = 5$ with reactive aqueous solvent on different sample sizes each with ten independent samples for $p_H = 0.0115$ and $p_P = 0.023$ with initial water concentration $p_A = 0.0422$ (case 8) ................................................................. 197
LIST OF TABLES

Table

5.1 Parameters used in cases 1-4 ................................................................. 60
5.2 Power-law exponents of initial film growth in cases 1 and 2 .................. 61
5.3 Power-law exponents of initial film growth in cases 3 and 4 ................. 62

6.1 Parameters used in case 5 ................................................................. 66
6.2 Power-law exponents of initial film growth at different temperatures in case 5 70
6.3 Power-law exponents of initial film growth at different initial water concentrations in case 5 ................................................................. 71
6.4 Power-law exponents of initial film growth at different NCO:OH ratios in case 5 ................................................................. 73
6.5 Power-law exponents of initial film growth at different reaction rates in case 5 76

7.1 Parameters used in case 6 and 7 ................................................................. 107
7.2 Power-law exponents of initial film growth at different temperatures in case 7 113
7.3 Power-law exponents of initial film growth at different initial water concentrations in case 7 ................................................................. 115
7.4 Power-law exponents of initial film growth at different NCO:OH ratios in case 7 ................................................................. 115
7.5 Power-law exponents of initial film growth at different reaction rates in case 7 117

8.1 Parameters used in case 8 ................................................................. 150
LIST OF SYMBOLS

A - aqueous component  
B, C - prefactor/constant  
$C_{H/P/A}$ - volume concentration of H/P/A component  
D - density  
E - interaction energy  
$E_g$ - gravitational potential energy  
f - functionality  
g - gravity constant  
H - hydrophobic component  
$H^*$ - modified hydrophobic component  
h - mean surface height (film thickness)  
h$_s$ - steday-state thickness  
i, j - lattice site  
j - interaction  
l - bond length  
$L_{x/y/z}$ - lattice size  
$M_{H/P/A}$ - molecular weight of H/P/A component  
NCO - isocyanate group  
NH$_2$ - amine group  
N$_s$ - number of substrate points  
OH - hydroxyl group  
P - polar component  
$P_{H/P/A}$ - number concentration of H/P/A component  
R - reaction rate  
r - distance between particles  
T - temperature  
t - time step  
t$_x$ - time step for film growth reaching its maximum value  
W - interface width (film roughness)  
$W_s$ - steady-state interface width  
x, y, z - lattice axial orientation  
$\varepsilon$ - interaction strength  
$\gamma$ - leading power-law exponent for thickness growth  
$\beta$ - leading power-law exponent for roughness growth
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated Total Reflectance Fourier Transform Infrared</td>
</tr>
<tr>
<td>BFM</td>
<td>Bond Fluctuation Model</td>
</tr>
<tr>
<td>EBFM</td>
<td>Effective Bond Fluctuation Model</td>
</tr>
<tr>
<td>HAP</td>
<td>Hazardous Air Pollutants</td>
</tr>
<tr>
<td>HDI</td>
<td>Hexamethylene Diisocyanate</td>
</tr>
<tr>
<td>IPDI</td>
<td>Isophorone Diisocyanate</td>
</tr>
<tr>
<td>IRIRI</td>
<td>Internal Reflection Infrared Imaging</td>
</tr>
<tr>
<td>MCS</td>
<td>Monte Carlo Step</td>
</tr>
<tr>
<td>MC</td>
<td>Monte Carlo</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
</tr>
<tr>
<td>PEG</td>
<td>Poly(ethelene glycol)</td>
</tr>
<tr>
<td>PUR</td>
<td>Polyurethane</td>
</tr>
<tr>
<td>PUA</td>
<td>Polyurea</td>
</tr>
<tr>
<td>PUD</td>
<td>Polyurethane Dispersion</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compounds</td>
</tr>
<tr>
<td>WB 2K-PUR</td>
<td>Waterborne Two-component Polyurethane</td>
</tr>
<tr>
<td>WDPI</td>
<td>Water Dispersible Polyisocyanate</td>
</tr>
</tbody>
</table>
Chapter 1
INTRODUCTION

Ever since their discovery by Otto Bayer and co-workers in 1937, polyurethanes (PUR's) have developed as a unique and versatile class of materials with many useful and intriguing properties. They have found use in a wide variety of applications such as foams, elastomers, coatings, sealants, and adhesive based products. Some of the applications of polyurethanes lies in the automotive, furniture, construction, thermal insulation, and footwear industries[1].

Reactive two-component polyurethane coatings historically have been stringently protected from water, but in the early 1990s it was shown that such reactive systems could actually be formulated using water as the carrier and still produce films with outstanding appearance and barrier properties. The introduction of waterborne two-component polyurethanes (WB 2K-PUR) is providing a means to formulate ultra-low volatile organic compounds (VOC) and hazardous air pollutants (HAPs) systems, with performance properties that closely match those of two-component solvent-borne polyurethanes[2, 3]. Despite of the attractive advantage of environment-friendly production processes and comparable high performance of WB 2K-PUR, knowledge concerning film formation of WB 2K-PUR system is very limited. The difficulties rise up mainly because of the greatly increased complexity of the system due to its heterogeneous nature along with simultaneous progression of several parallel physico-chemical processes such as water evaporation, cross-linking reactions, phase separation, and droplet coalescence, to name a few[4] – [11]. The resulted film has heterogeneous, micro-phase separated domains, which may result from thermodynamic incompatibility between soft and hard segments in PUR block copolymers[12] – [16], hydrogen bonding[17, 18], as well as reaction induced
CHAPTER 1. INTRODUCTION

phase separation[19, 20]. A systematic understanding of the global characteristics of the film growth from its basic constituents is highly desirable but not feasible with current experimental tools. Due to complexity, it is also not feasible to incorporate the thermodynamics equilibration involving stochastic mobility of constituents and kinetic reactions with covalent bonding in a self-consistent analytical theory[21]. Therefore, computer simulations[22] – [24] remain the primary tools to complement and understand the laboratory observations.

Our main goal is to develop an appropriate computer simulation model to understand the macroscopic properties evolving from the microscopic details in response to various external and internal stimuli such as temperature, molecular weight, miscibility and reactivity of individual components, evaporation rates, and others in WB 2K-PUR film formation. Desirably, a simulation model shall have following features:

1. It should be effective in capturing the influential factors in WB 2K-PUR film formation and realistic features of the system such as specific reaction kinetics and polymerization mechanism as many as possible.

2. The model should predict the macroscopic properties in response to external and internal stimuli in a qualitative way.

3. Flexibility to apply to other film formation processes of different systems should be offered by the model.

Though a few attempts[25, 26] have been made recently to study the film growth in such a multi-component system via computer simulations, the degrees of freedom for constituent movement is minimal and the film morphology lacks flexibility in these works. Further, efforts have been made to incorporate cross-linking reaction in these models, but no work has been done concerning the reactivity of solvent (water) with the main components which is a significant side reaction in WB 2K-PUR system. Moreover, the polymerization mechanism of polyurethane/urea formation, i.e., step-growth or chain-
growth, is nearly unaddressed in previous studies. Thus, constructing a more realistic model by appropriately addressing these issues is the main focus of this dissertation.

A brief introduction of polyurethane chemistry and waterborne two-component polyurethane systems are provided in Chapter 2. Chapter 3 gives an overview of computer simulation concepts on polymeric systems and theoretical aspects on film formation studies. A detailed description of the model and a systematic approach used in this thesis is covered in Chapter 4. Then in the following four chapters, a systematic progression of studies on film growth and the equilibrium properties of film in response to various external stimuli such as temperature, initial water concentration, the ratio of two major components of polyurethane film and reaction rate, are presented. Chapter 5 starts with our prelude data using simplest parameters on film formation from the substrate in non-reactive aqueous solvent with over relaxed conditions on bond fluctuation. Chapter 6 presents film formation with elimination of the deficiency of over relaxed condition on excluded volume interaction in non-reactive solvent from the substrate. The side reaction between hydrophobic and aqueous component, namely, film formation in reactive solvent, is considered in Chapter 7 where the effect of including or excluding the volume of water after reaction is addressed. Chapter 8 further improves the model by allowing covalent bonding isotropically formed in space in a reactive solvent with excluded volume of water after reaction. Comparison with the experimental observations are also presented in this chapter. Finally, a summary of the work is presented in chapter 9.
Chapter 2

WATERBORNE TWO-COMPONENT POLYURETHANES

2.1 Polyurethane Chemistry

To model the polyurethane/urea film formation, understanding of the chemical reactions is necessary. A brief review of polyurethane chemistry is therefore worth providing[1, 3, 27]. Commercial polyurethane polymers are typically made by the reaction of a diisocyanate with a molecule containing at least two active hydrogens. (An active hydrogen is defined as hydrogen which can be replaced by sodium.)

\[
\text{OCN-R-NCO + HO-R'-OH} \rightarrow -(\text{OOC-HN-R-NH-CO-O-R'})_n
\]

Diisocyanate   Diol   Polyurethane

Where R and R' represent \((\text{CH}_2)_m\) and \((\text{CH}_2)_n\) groups, respectively, m and n are integers. The formation of polyurethane is a polyaddition reaction, but the mechanism of polymerization is step-wise. When an isocyanate reacts with an alcohol, a urethane is formed:

\[
\text{R-NCO + R'-OH} \rightarrow \text{R-NH-CO-O-R'}
\]

Isocyanate   Alcohol   Urethane

If the active hydrogen compound is a primary amine, a substituted urea results:

\[
\text{R-NCO + R'-NH}_2 \rightarrow \text{R-NH-CO-NH-R'}
\]

Isocyanate   Amine   Urea

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CHAPTER 2. WATERBORNE TWO-COMPONENT POLYURETHANES

When the active hydrogen compound is water, the first stage of the reaction is the production of an unstable carbamic acid derivative, \( \text{RHNCOOH} \), which quickly decomposes to the amine, liberating carbon dioxide. The amine can then go on to react further with isocyanate to form a substituted urea:

\[
\text{R-NCO} + \text{H}_2\text{O} \quad \rightarrow \quad \text{R-NH}_2 + \text{CO}_2 \uparrow
\]

*Isocyanate*  *Water*  *Amine*  *Carbon Dioxide (released)*

\[
\text{R-NH}_2 + \text{R-NCO} \quad \rightarrow \quad \text{R-NH-CO-NH-R}
\]

*Amine*  *Isocyanate*  *Urea*

The substituted ureas are themselves active hydrogen compounds, and further reaction can take place with any remaining isocyanate to give the biuret:

\[
\text{R-NH-CO-NH-R} + \text{R'-NCO} \quad \rightarrow \quad \text{R-}(\text{R'}-\text{NH-CO})-\text{N-CO-NH-R}
\]

*Urea*  *Isocyanate*  *Biuret*

Similarly, the urethanes formed from the reaction of isocyanates with alcohols can go on to react with any remaining isocyanate to give allophanates:

\[
\text{R-NCO} + \text{R-NH-CO-O-R'} \quad \rightarrow \quad \text{R-}(\text{R-NH-CO})-\text{N-CO-O-R'}
\]

*Isocyanate*  *Urethane*  *Allophanate*

Biuret and allophanate formation can be encouraged by using a stoichiometric excess of isocyanate. In our system we are mainly concerned about the formation of urethane.
and urea. The crosslinker used in this study has 3 isocyanate groups and the polyol has 2 hydroxyl groups (2 active hydrogens), thus, as the crosslinking polymerization goes on, a three dimensional (3D) network is formed.

2.2 Solventborne and Waterborne Polyurethanes

Some of the most commonly produced PUR coatings systems are the so-called “2K” or two-component systems, in which polyisocyanate is supplied as one component and the polyol is supplied separately. In solvent-based 2K-PUR systems, polyols and polyisocyanates are mixed in an organic solvent and a homogenous solution of both components is obtained. The influence of water in the mixture is minimized by using high-purity solvents with very low water content. Both components are mixed in a solvent prior to application and their reactivity is such that within a few-hour period, such systems become crosslinked. The use of solvents dilutes the concentrations of reactive groups, thereby suppressing the crosslinking reactions until the coating is applied to the substrate. Volatilization of solvents upon application results in a rapid increase in concentration of functional groups, and accelerated reaction rates. The predominant reaction during the pot life is urethane formation. Although in an ideal system, an equal stoichiometry of polyisocyanate and polyol is desired, in reality, 2K systems are usually mixed with a small molar excess of polyisocyanate due to competing reactions of isocyanate with water, which may occur due to the presence of water as an impurity in solvent-based systems. This competing reaction may result in complications for two primary reasons, namely isocyanate groups that are consumed by water are unavailable to crosslink with polyols, which may lead to poor film mechanical properties and the presence of unreacted polyol, and carbon dioxide may form, which could adversely affect film properties. For these reasons, it was long thought that a waterborne reactive system would not be achievable.

In response to a number of environmental concerns, aqueous dispersions of high
molecular weight polyurethanes, or simply polyurethane dispersions (PUD's), became commercially available in 1967. The synthesis of polyurethanes for incorporation into PUD's is very similar to the synthesis of polyurethanes for use in solventborne lacquers. In essence, diisocyanates, diols or macrodiols, chain extenders, catalysts, and other coreactants containing ionizable or non-ionic hydrophilic moieties are combined in an organic solvent and heated in an inert environment to produce the desired polymer. Upon removal of solvent and subsequent neutralization, the polyurethane may be mixed with water under high shear to form the aqueous dispersion. While PUD's offer an environmentally-compliant material, the long-term stability of such colloidal dispersions has been a concern, since PUD's containing ester functionalities may hydrolyze over time due to the presence of water in the formulation, leading to reduction in molecular weight of the PUR and ultimately colloidal instability and poorer film properties.

Although PUD's are capable of providing films with acceptable properties for a number of applications and are relatively easy to apply, there is no doubt that a crosslinked film provides increased durability and chemical resistance when compared to uncrosslinked materials. For this reason, a number of approaches toward reactive 1K PUR waterborne formulations have been taken. Since isocyanate (NCO) functional groups are known to react with water, isocyanate crosslinkers may be reacted with a protective moiety, which may be removed later simply by heating which shifts the reversible equilibrium toward starting materials, thereby regenerating the NCO functional groups on the crosslinker. Protection occurs prior to incorporation into a waterborne formulation. Such protected isocyanates are called blocked isocyanates, and may be used to provide crosslinked coatings and films. In essence, a waterborne formulation containing a blocked isocyanate, a hydroxy-functional coreactant, water, and other ancillary components may be applied to a substrate, and after evaporation of water, a non-crosslinked film results. However, by heating the film to an acceptable "de-blocking temperature" (110-170C), the de-blocking
reaction takes place in which NCO groups are regenerated and may then react with the hydroxy-functional co-reactant to form a urethane crosslink and ultimately a crosslinked film. While waterborne PUR formulations incorporating blocked isocyanates offer an attractive approach toward low VOC crosslinked PUR coatings, such an approach is not without disadvantages. Specifically, such films must be heated to drive the de-blocking reaction, which increases time and energy consumption and somewhat limits the types of substrates that may be used, since some plastics may warp or melt when exposed to heat. Furthermore, the blocking agent ultimately must leave the film, which may pose a threat of toxicity and contributes to VOC or hazardous air pollutants (HAP's).

Due to the inherent limitations of solventborne 2K PUR's, PUD's and 1K PUR's using blocked isocyanates, waterborne two-component polyurethanes (WB 2K-PUR) were developed in the 1990's to address many of the limitations of existing technologies. In essence, WB 2K-PUR systems may be achieved by adapting existing polyurethane reactants to make them more hydrophilic or water-dispersible, followed by mixing both components under high shear into an aqueous dispersion. The basic components of WB 2K-PUR systems typically include a hydroxy-functional water-reducible acrylic or polyester “polyol” resin dispersion, an amine neutralizing agent to facilitate aqueous dispersion of the polyol via neutralization of pendant carboxylic acid groups, an oligomeric polyisocyanate crosslinker derived from hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI) which may or may not be hydrophilically-modified, optional cosolvent(s), and water. Figure 2.1 provides representative structures for components utilized in WB 2K-PUR systems. WB 2K-PUR systems are significantly more complex than their solventborne 2K-PUR counterparts. Separate phases exist in WB 2K-PUR colloidal dispersions since both polyisocyanate and polyol generally have limited hydrophilicity. Furthermore, since isocyanate are known to react with water, such reactions become a critical factor during the pot life as well as upon application. In essence, there are an in-
creased number of variables to monitor and control in WB 2K-PUR systems, for example solution morphology, particle-size distribution, dispersed co-reactant characteristics, and pH, to name a few.

2.3 Experiments

The laboratory experiments and measurements are conducted by our collaborators (Dr. Urban and his group at department of polymer science, University of Southern Mississippi). The WB 2K-PUR system used in the laboratory experiments consists of a polyester polyol aqueous dispersion and a water dispersible polyisocyanate (WDPI). The polyol resin utilized is a complex mixture of products, the precise composition of which is unknown. WDPI crosslinkers used in these studies contain approximately 35 wt% poly(ethylene glycol) (PEG) which were used to facilitate water dispersibility of polyisocyanates. Representative structures for polyester polyol and WDPI are shown in Figure 2.1.

Polyurethane/urea films were prepared [28, 29] by mixing polyol resin aqueous dispersion with WDPI crosslinker using overhead agitation at 1800 rpm for 10 min. The relative amounts of all components were adjusted to yield isocyanate to hydroxyl (NCO:OH) molar equivalent ratios ranging from 1.0 to 2.2, while maintaining 45% w/w solids. Following the mixing process, such mixture was held without agitation for 10–15 min to allow for viscosity reduction, and the mixture was applied to obtain approximately 40 μm (±3 μm) thick dry films on glass slides after crosslinking for 3 days in controlled environment (temperature (30 - 50 °C), relative humidity (11 - 97 %RH)) chamber.

Advanced microscopic and molecular-level spectroscopic characterization approaches have been employed by Urban and coworkers to examine the properties of dried film. The ones used to illustrate or compare with simulation result in this thesis include atomic force
CHAPTER 2. WATERBORNE TWO-COMPONENT POLYURETHANES

Figure 2.1: Representative structures of polyester and WDPI used in the experiments of this study.

microscopy (AFM), attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra and internal reflection infrared imaging (IRIRI). Figure 2.2 illustrates an AFM image of the surface of such a resulted PUR film, which appears to be rough under sufficient magnification. While AFM images describe a qualitative nature of surface morphology, a quantitative measurement is highly desirable but difficult with current laboratory techniques. Questions such as how the process parameters, i.e., temperature, moisture and so on, affect the film evolution and final surface morphology are difficult to probe for experimentalists due to the limited control and monitoring of the process. Interpretation of data with limited knowledge of waterborne two-component polyurethanes could also be challenging. For example, topographical features that appear as "hills" and "valleys" in the AFM image (Figure 2.2) could be attributed to subtle compositional variations in

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polyurethane/polyurea distributions near the film-air interface, as revealed by IRIRI spectroscopy (see Figure 6.2). However, how these global morphological features (physical and chemical) evolve from the microscopic details in response to various external and internal stimuli is unknown. Hence, computer simulations become very important tools to complement our limited understanding of WB 2K-PUR film formation. In the next chapter, we will cover more theoretical background on surfact/interface studies via computer simulations.

Figure 2.2: Topographic AFM image of WB 2K-PUR films crosslinked at 82 %RH and 30 °C recorded from the film-air interface.

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Figure 2.3: Film-air (F-A) IRIR image of WB 2K-PUR films crosslinked at 82 %RH and 30 °C showing the compositional variations and phase separation. Dark gray area (A) corresponds to PEG-rich (hydrophilic) domain; light gray area (B) corresponds to isocyanurate-rich (hydrophobic) domain.

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Surfaces and interfaces are ubiquitous and play a critical role in controlling the properties and function of a broad range of materials. In coating technology, knowledge of the roughness of the polymer layer on the adsorbing surface and surface morphology is key to characterizing the surface properties [30, 31], such as contact and friction, surface diffusion, optical reflection, and electrical conductivity. In this chapter, we will introduce important concepts of surface/interface growth and film density profile within the context of one of the most intensively studied field – deposition of particles or other objects, e.g., polymer chains, onto a substrate.

3.1 Surface and Interface via Particle Deposition

Under sufficient magnification even surfaces that seem smooth to the eye often appear rough. The first question one would like to answer is “How to define a surface? How to characterize quantitatively the morphology of an arbitrary interface such as its roughness?” We are interested not only in the morphology of various interfaces, but also in the dynamics of how the morphology develops in time. Some surfaces are formed as a result of deposition process such as in a molecular beam epitaxy (MBE). Others shrink due to erosion or etching (e.g., in sputter erosion the material is bombarded with an ion beam that hits the surface and kicks out atoms). Some interfaces propagate through inhomogeneous media (e.g., a droplet of coffee impenetrates a paper towel). Thus an interesting set of questions would concern the formation, growth, and dynamics of such interfaces. In the following part, first we introduce concepts such as surface height and its roughness using
a simple growth model, random deposition (RD). Then several other particle deposition models are briefly reviewed to illustrate interface growth with correlations.

In a random deposition, a particle is released from a randomly chosen site over the surface, and falls vertically until it reaches the top of the column under it, whereupon it is deposited (see Figure 3.1). We define the “surface” to be the set of particles in the aggregate that are highest in each column. The mean surface height of the surface, $\bar{h}$, is defined by

$$\bar{h}(t) = \frac{1}{L} \sum_{i=1}^{L} h(i,t),$$

(3.1.1)

where $h(i,t)$ is the height of column $i$ at time $t$, $L$ is the lattice size (here is substrate length). The interface width, $W$, which characterizes the roughness of the interface, is defined by the root mean square fluctuation in the height,

$$W(L,t) = \sqrt{\frac{1}{L} \sum_{i=1}^{L} [h(i,t) - \bar{h}(t)]^2}.$$  

(3.1.2)

A schematic picture of film height and its surface roughness is illustrated in Figure 3.2.

To monitor the roughening process quantitatively, we measure the width of the interface as a function of time. At time zero, the interface is simply a straight line with zero width. As deposition occurs, the interface gradually roughens. As found in many deposition processes, the width grows as a power of time initially,

$$w(L,t) \approx t^\beta \quad [t << t_*].$$

(3.1.3)

The exponent $\beta$ is called the growth exponent, characterizing the time-dependent dynamics of the roughening process. In the RD model, there are no interactions among the columns; the columns grow independently. The interface width in RD grows indefinitely with time, i.e., without saturation, with the growth exponent $\beta = \frac{1}{2}$. However, if
CHAPTER 3. SURFACE AND INTERFACE GROWTH

Figure 3.1: The random deposition model. Particles are dropped from random positions above the surface and are deposited on the top of the column under them. The height of the interface in RD does not depend on the height of the neighboring columns.

interactions are allowed among the columns (e.g., sticking to neighbor columns, lateral migration of particles, etc.) we get correlations in the height of the columns. When the height-to-height correlation length \( \xi_h \) is equal to the substrate length \( L \) the interface width stops growing and saturates to \( W_s \). Figure 3.3 illustrates such a typical plot of the time evolution of the surface width has two regions separated by a "crossover" time \( t_x \). The saturation width \( W_s \) increases as \( L \) increases, and the dependence also follows a power law,

\[
W_s(L) \approx L^\alpha \quad [\xi_h \geq L].
\] (3.1.4)
The exponent $\alpha$ is called the roughness exponent. The crossover time $t_x$ (or saturation time) at which the interface crosses over from the behavior of equation (3.1.3) to that of equation (3.1.4) depends on the system size,

$$t_x \approx L^z, \quad (3.1.5)$$

where $z$ is called the dynamic exponent. The scaling exponents $\alpha, \beta$ and $z$ are not independent. They can be linked by a scaling law,

$$z = \frac{\alpha}{\beta}. \quad (3.1.6)$$

Since there are no correlations in the RD model, the correlation length $\xi_h$ is always zero, the interface does not saturate, and the roughness exponent $\alpha$ is not defined. Many other growth models introduce correlations and lead to correlated surfaces. One simple example is random deposition with surface relaxation [33]. In such a growth model, each particle is allowed to migrate across a number of columns and settle into the lowest position. Thus the newly-arriving particle compares the heights of nearby columns before...
Figure 3.3: Typical plot of growth of the interface width with time. Two regimes: (i) power law growth, and (ii) saturation.

sticking. This process generates correlations among the neighboring heights, which lead to the entire interface being correlated. These correlations eventually lead to the saturation of the interface. Using symmetry principles for a continuous system Edwards and Wilkinson (1982) proposed the equations of motion for the interface [34, 35]

\[
\frac{\delta h(y,z,t)}{\delta \tau} = \nu + \nu \Delta^2 h + \eta(y,z,t),
\]

where \( \nu \) is the average speed of the moving interface, \( \nu \) is a smoothing constant (e.g., surface tension), and \( \eta \) is the noise term uncorrelated in \( y \) and \( z \). Equation (3.1.6) is known as the Edwards-Wilkinson (EW) equation. The term \( \nu \Delta^2 h \) acts to smooth the interface by moving material from the sharpest peaks to areas concave upward.

Another simple growth model introducing correlations is ballistic deposition (BD) [36, 37]. In the BD model, particles are released from randomly chosen positions above the surface and fall vertically until they are adjacent to the substrate or to another particle. The newly-arriving particle sticks to the first nearest-neighbor site it encounters. Thus the height of the new particle will be equal to or larger than that of its neighbors. The height fluctuation will spread laterally, because the next particle deposited near it must
have a height equal or larger as well. The columns are thus correlated. For a continuum equation that describe these systems, Kardar, Parasi and Zhang (KPZ) [38] suggested to add a nonlinear term to the Edwards-Wilkinson equation. The KPZ equation is

\[ \frac{\delta h(y,z,t)}{\delta t} = v + v\Delta^2 h + \frac{\lambda}{2} (\Delta h)^2 + \eta(y,z,t), \quad (3.1.8) \]

Where \( \frac{1}{2} (\Delta h)^2 \) describes the lateral growth and \( \lambda \) is a constant. For a one-dimensional surface the KPZ scaling exponents are \( \beta = 1/3 \) and \( \alpha = 1/2 \), which is in excellent agreement with results from BD simulations [36, 39].

3.2 Deposition of Polymer Chains

While deposition of particles onto a substrate has been intensively investigated, interfacial growth resulting from deposition of polymers is not as well studied. Deposition of polymer onto a substrate is an important process in designing polymeric materials and composites and for coating surfaces ([21, 40]). Complexities arise from the bond constraints along the chain, which leads to entanglement, chain relaxations, etc. As polymer chains are driven by an external field (e.g., electric field, pressure gradient, gravitation, etc.) toward a substrate, the polymer density grows and an interface develops [41, 42, 43]. However, it is not clear how the polymer interface width evolves and scales with chain length \( L_c \) (molecular weight), field \( E \), and temperature \( T \). The degrees of freedom for polymer are constrained by the chemical bonds among the individual monomers, which leads to dynamics quite different from that of particles [44]. In Kardar-Parisi-Zhang (KPZ)-like growth processes of particle deposition [37, 38, 45, 46], particles are not interacted with each other, correlations among the columns are simple (i.e., only height-height correlation involves). Finite-size scaling of the saturated width with the substrate length \( L \) is used to evaluate the roughness exponent \( \alpha \) (i.e., \( W_s \propto L^\alpha \)). Single-parameter scaling of
the asymptotic width with the substrate length $L$ has been verified in detail via extensive simulations in KPZ-like interfacial dynamics where the height-height correlation length $\xi_h$ obeys $\xi_h \geq L$ [44]. In the deposition of polymer chain, however, particles are interacted with each other through covalent bonds. This is significantly more complexed than the simple particle deposition process, as more than one characteristic lengths are involved in interfacial polymer dynamics, e.g., the height-height correlation length $\xi_h$, radius of gyration of chains $R_g$, and density-density correlation $\xi_d$. These correlation lengths are interdependent with each other. Effects of external parameters ($E, T$) on these lengths at the interface are difficult to evaluate. The scaling relations derived from particle deposition growth model fail to apply, and computer simulations are already needed to study such complex interface growth.

In our problem, the scenario becomes even more complex. Multiple components (polyisocyante, polyol, solvent) instead of mono-component are involved. Particles can interact with each other leading to thermodynamic equilibrium. In the meanwhile, cross-linking reactions take place among the reactive units via covalent bonding which can capture the thermodynamic equilibrium. As cross-linking leads to formation of network structure, additional correlation lengths are introduced into the system. It is not clear how the thermal energy and the covalent bonding interplay with each other, and how they affect the interface width growth. Thus computer simulation studies become necessary in probing such a highly complexed system involving thermodynamic equilibration and network formation.

3.3 Network Formation in Film Growth

The film formation processes in WB 2K-PUR involve cross-linking reactions among reactive constituents resulting in a three-dimensional network structure. An illustration of such a network is shown in Figure 3.4. Thus it can be very helpful to look at some chem-
ical/physical phenomena that have already been well studied and share similarities with our system in the process. One such example is gelation.

![Diagram of a cross-linked polymer network](image.png)

**Figure 3.4:** A typical picture of cross-linked polymer network.

A gel is a three-dimensional network of flexible chains cross-linked by chemical or physical bonds, which is generally immersed in a solvent. In the process of gelation, molecules carrying reactive functional groups (with functionality $f \geq 2$) react with each other. Each molecule may form bonds with its neighboring molecules. In such stochastic growth processes, ramified networks of chemical species evolve from a variety of physical and chemical processes leading to entanglement and cross-linking of various order [47]–[51]. As the reaction proceeds, an incipient infinite network can be formed. This infinitely large macromolecule is called a gel. The collection of finite clusters is called a sol. The critical point, $p_c$, at which the infinite cluster appears is referred as the gel point. The formation of gel networks and their conformational properties depend on various factors, such as rate of reactions, growth of bonds and their decay, mobility of monomers, type of solvents, temperature, etc. Two types of reactions, the step and chain polymerization, are

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usually encountered in gelation. In step polymerizations, polymers are formed through a series of steps and large molecules result from a large number of steps. If the functionality $f \geq 3$, then the polymerization leads to polymers with branches and cycles. As the reaction proceeds, an indefinitely large network appears at the gel point. The most common network-forming reaction by a chain polymerization is the free-radical copolymerization, where monomers are activated by external agencies such as radicals. The free radical end can be bonded either to another chain (intermolecular cross link) or to the same chain (cyclization). In this chain polymerization, cross-linking is formed only through a radical center.

Understanding the growth process in polymerization and sol-gel transition via model systems has attracted a considerable interests for a long time [47]—[51]. Flory [47] and Stockmayer [48, 52] proposed a classical percolation approach on Cayley tree, which was the beginning in the theoretical investigation of irreversible kinetic gelation. While simplicity is offered by such models in deriving the closed form expressions for the physical quantities such as volume fraction and weight average degree polymerization, they are lack of excluded volume, steric hindrance, and closed loops. De Gennes and Stauffer [53, 54] take into account the cyclization and branches in their study of percolation [55] on three dimensional lattices. However, their percolation models have drawbacks such as lack of more realistic reaction kinetics and multiplicity of bonds formation. These features have been considered in a more comprehensive computer simulation models for irreversible kinetic gelation [49], [54]—[59].

To incorporate the kinetics more appropriately, the mobility of the solvent, monomers, and the microgel particles have been taken into account in recent computer simulation models [60]—[62]. Several studies on aggregation considers the mobility of the clusters, i.e., cluster of clustering [49]—[51], [63]—[64]. The mobility of the clusters results in an enhanced ramification of the aggregate clusters and a reduced fractal dimension-
ality. However, unlike the kinetic gelation models, functionality of the particles are not restricted and most of these studies emphasize the fractal dimensionality rather than the sol-to-gel transition. Pandey and his coworkers [65] includes the mobility of the particulates for kinetic gelation with step reactions along with factors such as degrees of reversibility, quality of solvent, and temperature. On the other hand, continuum approach [49, 66] provides an alternate way to study kinetic gelation in which the mobility of the particles and clusters are emphasized. In this approach, one studies the Smoluchowski equation and its variants, i.e., the modified differential equations for the growth and decay of the clusters. Though exact mathematical solutions can be achieved for certain kernels, i.e., the rate constant for the aggregation and decay, in more general situations (i.e., for a spatiotemporal dependence of the rate constant), however, solving such equation becomes intractable. Furthermore, it is unclear if the nonlinearity of the medium (i.e., spatial inhomogeneities), and the steric hindrance can be taken into account appropriately in such approaches.
Chapter 4

COMPUTER MODELLING

4.1 Simulation Methods and Techniques

4.1.1 Monte Carlo simulation

Monte Carlo (MC) simulation is a stochastic method. It deals with statistical phase space where energy landscapes are used to explore microstates of various ensembles in order to obtain global (equilibrium) properties. One may sample the phase space directly, or if the potentials are known, use importance sampling via the Boltzmann distribution. The MC method provides a general-purpose numerical approach to problems in statistical physics and chemical physics.

For thermodynamic system, the Monte Carlo method describes the system in terms of a Hamiltonian $H$. A state of the system is denoted by $x = (x_1, x_2, ..., x_n)$, where $n$ is the number of the degree of freedom. The phase space consists of the set of states denoted by $\Omega$ with a distribution function $f$. The ensemble average of an observable $A$ with the partition function $Z$ is given by

$$< A > = Z^{-1} \int_{\Omega} A(x) f(H(x)) \, dx,$$

(4.1.1.1)

where $Z = \int_{\Omega} f(H(x))$. In general, the Monte Carlo method, a stochastic method, gives information about the configurational properties and allows the simulation of models without equations of motion which integrate forward in time.

In principle, one needs to enumerate all configurations of all components in the system in order to calculate physical quantities from the partition function, which is forbiddenly
difficult for most real systems. The Monte Carlo method approaches this problem by constructing a random walk through the configuration space of the considered model space. This gives an approximation to the integral (4.1.1.1)

\[ \langle A \rangle \approx \frac{\sum A(x_t) P^{-1}(x_t) f(H(x_t))}{\sum P^{-1}(x_t) f(H(x_t))}, \]  

(4.1.1.2)

where \( P(x) \) is a probability with which one chooses the states. By constructing a Markov process, one configuration is transitioned to another through a probabilistic evolution. The Markov process probabilistically simulated the continuum dynamics of the physical system. The detailed balance principle [67] is expected to be met for an equilibrium system,

\[ P_{eq}(x) W(x \rightarrow x') = P_{eq}(x') W(x' \rightarrow x), \]  

(4.1.1.3)

Where \( P_{eq}(x) \) is the probability of finding the system in state \( x \), i.e., the canonical distribution of the system. The transition probability \( W(x \rightarrow x') \) satisfies the detailed balance condition (4.1.1.3) to ensure an approach towards an equilibrium. The importance sampling method is used for the study of thermal fluctuations in a system. In an equilibrium system characterized by temperature \( T \), all possible configurations are weighted according to a probability proportional to the Boltzmann factor \( \beta = 1/k_B T \). Thus the detailed balance condition for the transition probability implies

\[ \frac{W(x \rightarrow x')}{W(x' \rightarrow x)} = \exp(-\Delta H/k_B T). \]  

(4.1.1.4)

By this method, one can generate states representing the thermal equilibrium by letting \( P(x_t) \) be \( P(x_t) \approx e^{-H(x_t)/k_B T} \). Equation (4.1.1.2) thus becomes

\[ \langle A \rangle \approx \frac{1}{n} \sum_{t=1}^{n} A(x_t). \]  

(4.1.1.5)
CHAPTER 4. COMPUTER MODELLING

With equation (4.1.1.5) all the averages become a simple arithmetic average over the generated states. This can be accomplished by the Metropolis method (see Appendix B) to choose the successive state independently of each other. If $\Delta H > 0$, $W(x \rightarrow x') = e^{-\beta \Delta H}$, otherwise $W(x \rightarrow x') = 1$ [68].

Two problems that associate with Monte Carlo method are finite observation time and finite system size. In practice, only finite Markov chains can be obtained. Initial configurations of chains may have effect on the correlations in the chains. Thus to guarantee a thermal equilibrium of the system, one has to run the simulation for a sufficiently long time (Monte Carlo steps) in order to relax the system. This time is measured by the number of states generated. Meanwhile, a large number of samples are needed to average the measured properties for a reliable estimate.

In a computer simulation, the system size is always finite. Thus finite-size effects arise inevitably in any computer simulation and must be carefully accounted for before simulation data may be directly compared with experiment or theory. Finite-size effects refer to deviations from bulk properties as sample dimensions are reduced. An intrinsic effect occurs in material systems for which one or more sample dimensions are comparable to the intrinsic length scale of the property being considered. Periodic boundaries are usually used for a good approximation of the infinite system as long as the correlation length $\xi$ does not exceed the linear extension of the system $L$. For critical phenomena such as percolation, finite-size scaling theory is employed to overcome the setback of a finite size system. In addition to the usual random statistical errors associated with averaging over limited numbers of particles, systematic errors may also occur due to the finite size of the model system. Two general types of size effect have been identified. One is the well-known explicit (or ensemble) size effect that results from fixing the number of particles and is commonly encountered in canonical and microcanonical ensemble simulations. The other, and more subtle, is the implicit (or anomalous) size effect, whose origin may
be traced to the (usually periodic) boundary conditions. Both types of size effect can directly influence the microscopic structure of the system, as characterized by the pair- and higher-order correlation functions, and consequently any derived thermodynamic or structural properties.

4.1.2 lattice and off-lattice model

The computer simulation of polymeric systems can be carried out either on a discrete lattice or in a continuum space. The main difference between these two models is how to deal with the motion of the species in the system. In a lattice model, the coordinates of the species are restricted to lattice positions on a regular lattice grid. The fixed bond length is simply the lattice constant. Though spatial resolution is somewhat reduced, this method are easier to implement and analysis, and their regular structure often lends itself naturally to the use of extremely efficient Monte Carlo moves that quickly relax a polymer structure. As integer arithmetic and simplified nearest-neighbor interactions are allowed in the lattice model, computational efficiency is greatly enhanced. In an off-lattice continuum simulation model, species (monomer units) move in continuous space where bonds may make any angle with respect to an adjacent bond. It allows the use of equation of motions with physical dynamics (Newton) or well-controlled approximation to it (variants of Langevin). This method results in good small-scale resolution and is well suited for use with dense melts where possible bond angles are restricted. Continuous models obviously have no lattice or discretisation artifacts. Large degrees of freedom are also achieved in an off-lattice continuum simulation. However, this method is computationally expensive, which limits its application to short times and/or very small systems. Nevertheless, as addressed by Florian Muller-Plathe [69], "there is a priori no speed advantage for either model: Problems of similar complexity need a similar amount of computer time if both models are implemented with a similar degree of sophistication."
4.1.3 Bond Fluctuation Model

The lattice algorithm that is now most widely used for the simulation of many-chain systems is the bond fluctuation model (BFM) [70] – [74]. BFM combines ideas from standard lattice MC methods with the notion that one should allow the bond angle and the bond length to vary to produce a very efficient algorithm. Thus limitations associated with the reduced degrees of freedom on the lattice can be solved by this method. Schematic illustrations of the bond fluctuation model in three dimensions [75] are presented in Figure 4.1. Because the method only involves local moves, it is useful for investigating dynamics as well as static properties. In fact, it has been used to model the dynamics of both two-dimensional [76] and three-dimensional polymer melts [73, 74], the glass transition [77] – [82], polymer blends [83] – [75], polymer networks [85, 86], gel electrophoresis [87], polymer brushes [88] – [93], star polymers [94] and so on, and it was attempted to map it on to real materials. Each monomer consists of $2^d$ lattice sites. In addition to the excluded volume interaction, the bond length $l$ is restricted to a maximum extension to avoid bond crossing. On the square lattice, the bond length $l$ is constrained to be in the range of $1 < l < \sqrt{13}$. On the simple cubic lattice, the length $l$ of the bonds connecting two neighboring cubes along the chain must be taken from the set $l = 2, \sqrt{5}, \sqrt{6}, 3, \sqrt{10}$. Configurations relax by random diffusive hops of the effective monomers by one lattice spacing in a randomly chosen lattice direction. The restriction in the allowed bond lengths assures that the excluded volume interactions simultaneously maintain the constraint that bonds cannot cross each other in the course of random motion of the monomers. This model is in a sense intermediate between the simple lattice models and the off-lattice models, because the vector that connects two monomers can take 36 values (in d=2) or 108 values (in d=3), rather than four or six (square or simple cubic lattice, respectively). While thus the continuum behavior is almost approximated, one still enjoys the advantages of lattice algorithms (integer arithmetics, excluded volume is checked via the occupancy of
lattice sits, etc.) Since each monomer occupies $2^d$ sites, but every jump only requires $2^{d-1}$ empty sites, the method works at relatively high densities. It also suffers less from the nonergodicity problems due to blocked configurations than the standard methods. The method has been widely used to study two- and three-dimensional polymer melts. It also works well for branched and tethered polymers as well as polymer networks and glasses.

*Figure 4.1:* Schematic illustration of the bond fluctuation model in three dimensions. An effective monomer blocks a cube containing eight lattice sites for occupation by other monomers.
CHAPTER 4. COMPUTER MODELLING

4.2 Computer Model for Film Formation

One of our efforts in this work is to construct a computer simulation model which is capable of effectively capturing the characteristics of the film formation process in multi-component polymeric system to study macroscopic properties (interface/surface morphology) of the film. In this section, we present an overview of our proposed simulation models. Variation of the details of the model acquired as a process of systematic improvement will be addressed in latter chapters as appropriate.

4.2.1 Assumptions and Approaches

As previously addressed, chemical details of molecules are to a large extent ignored in the coarse-grained modeling in order to study global properties at large scale. Thus important goals of molecular simulations such as predicting physical properties of particular materials quantitatively from a knowledge of atomistic potentials will not be achieved in our simulations; however, this consequence is inevitable due to the complexity of polymeric systems. In addition to chemical structure coarsening of molecules, additional coarsening for the complex composition, interaction and processes of the film formation is required to further simplify our system. Such approximating/coarsening form the basis of our model which include,

1. The components of WB 2K-PUR system (chapter 2, page 9) can be simplified as 3 types: hydrophobic, hydrophilic, and solvent (water). That is, both hydrophilically-modified and unmodified crosslinkers (WDPI) are taken to be one type, i.e., hydrophobic (H). The polyol resin utilized, a complex mixture of products and the precise composition of which is unknown, is generally taken to be another type, hydrophilic (P). The solvent and other components are treated as water (A) here.

2. Each component is represented by uniform particles. That is, both structural details of components and size differences between different types of components are ignored.
3. Main characteristics of components are captured by phenomenological interactions $E$, molecular weight $M_w$ and reaction functionality $f$.

4. Components are mixed randomly initially ($t = 0$) before starting the crosslinking reaction. That is, the process of colloidal coalescence of reactive droplets prior to applying to the substrate are not considered at this stage.

Two commonly used simulation techniques are Monte Carlo (MC) and Molecular Dynamics (MD). The MC method provides a general-purpose numerical approach to problems in statistical physics and chemical physics. Using this method, one can easily explore the characteristics of specific systems and avoid the approximations introduced in the mean field theory. In this study we use Metropolis algorithm to stochastically move the entities. MC modeling can be performed either on a discrete lattice or in the continuum (off-lattice) space. The main difference between these two methods is how to deal with the motion of the species in the system. The movement of species in a lattice model must be between the lattice sites, whereas the off-lattice model does not have this constraint. We choose lattice algorithm mainly because its advantage of simplicity such as integer arithmetics and easy check of excluded volume condition which is an important constraint in polymer simulation. Limitations associated with the reduced degrees of freedom on the lattice is solved by introduction of the bond fluctuation model (BFM) in this study. BFM is an effective algorithm for simulating the dynamics of polymers in all spatial dimensions. It consists of single bead moves, has Rouse dynamics for all spatial dimensions, allows for dynamics simulations of linear and branched polymers, uses a lattice, and is ergodic[70]. In BFM, an effective monomer blocks a cube containing eight lattice sites for occupation by other monomers. The length $l$ of the bonds connecting two neighboring cubes must be taken from the set $l = 2, \sqrt{5}, \sqrt{6}, 3, \sqrt{10}$ in three dimensions. Configurations relax by random diffusive hops of the effective monomers by one lattice spacing in a randomly chosen lattice direction. The restriction in the allowed bond lengths
assures that the excluded volume interactions simultaneously maintain the constraint that bonds cannot cross each other in the course of random motion of the monomers. BFM combines typical advantages of lattice Monte Carlo methods with those from the continuous Brownian dynamics algorithm[24].

4.2.2 Component Characteristics

We consider three types of particles, hydrophobic (H), hydrophilic (P), and water (A) on a simple three dimensional discrete lattice of size \( L_x \times L_y \times L_z \). A particle is described by a cube occupying its eight lattice sites. The size of each unit (hydrophobic (H), polar (P), and water (A)) are taken to be the same which is the cube, the unit lattice size, to simplify the details in the spirit of coarsening. Excluded volume constraint is implemented by requiring that a site can not be occupied by more than one particle. An isolated particle can move to one of its 26 neighboring sites, a considerable increase of the degrees of freedom for each constituent to execute its stochastic movement is thus achieved in comparison to 6 in previous studies[25, 26]. In addition to excluded volume (hardcore) interaction, we consider an interaction among the particles within a range \( r = \sqrt{10} \). The interaction energy \( E \),

\[
E = \sum_{ij} J(i, j), \tag{4.2.2.1}
\]

where, \( i \) runs over each particle and \( j \) runs over its neighboring sites within a range \( r \).

\[
J(H,H) = J(P,P) = -J(H,A) = J(P,A) = -\epsilon. \tag{4.2.2.2}
\]

In this study we use \( \epsilon = 0, 1 \). There is an attractive interaction between each particle and the adsorbing substrate (S) at the bottom \( z = 1 \),

\[
J(H,S) = J(P,S) = J(A,S) = -2. \tag{4.2.2.3}
\]
Additionally, each component ascribes a molecular weight \( (M_H, M_P, M_A) \) in arbitrary unit to incorporate the effect of gravitational precipitation. The gravitational potential energy at height \( z \) from the bottom in unit of \( g \) the acceleration due to gravity, 

\[
E_g = \frac{M_H}{p_H/a} \cdot z. \tag{4.2.2.4}
\]

In order to implement reaction kinetics, each reacting unit \((H, P)\) is assigned an appropriate functionality \( f \), i.e., it can react up to \( f \) neighboring functional groups including the substrate.

### 4.2.3 Thermodynamics

The stochastic motion of the particles can be controlled by temperature \( T \), a parameter measured in arbitrary unit (i.e., in unit of the Boltzmann constant \( k_B \) and the interaction energy). Initially, particles \( H, P, \) and \( A \) are randomly distributed and mixed thoroughly on fraction \( p_H, p_P, \) and \( p_A \) of the lattice sites. Then each particle attempts to move to one of its randomly selected adjacent site (26) with the Metropolis algorithm. That is, a particle at a site say \( k \) and one of its neighboring adjacent sites \( l \) are selected randomly. If the proposed move does not violate the excluded volume constraint, then the total energies \( E_k \) and \( E_l \) in corresponding configurations with particle at the initial site \( k \) and its proposed move to randomly selected new site \( l \) are evaluated. The particle is moved from site \( k \) to \( l \) with probability \( \exp(E_k - E_l)/T \). Periodic boundary conditions are used along the transverse \((x, z)\) directions for all constituents. Along the longitudinal \((y)\) direction, an open boundary condition at the top (Film-Air interface) and an impenetrable substrate at the bottom (Film-substrate interface, \( y = 1 \)) are implemented. The aqueous constituent \((A)\) can evaporate, i.e., leave the sample from the top if it attempts to do so. However, constituents \( H \) and \( P \) cannot leave the sample, their concentrations are thus conserved. Attempts to move each particle once defines unit Monte Carlo step (MCS) time.
4.2.4 Kinetic Reactions

Each constituent attempts to react with one of its neighboring particles within a range $r$ or the substrate sites with a fixed reaction rate (probability) after each MCS time. The rates (probabilities) of reactions with the substrate and among the functional groups are controllable parameters. Each hopping attempt is followed by covalent bonding among the reacting units. Further, each covalent bond resulting from such reaction kinetics is irreversible. However, its bond length can fluctuate between 2 and $\sqrt{10}$ excluding $\sqrt{8}$ if the bonded unit attempts to move. As mentioned in the experiment section, the main chemical reactions are between isocyanate groups (-NCO) of the crosslinker (hydrophobic, $H$) and hydroxyl groups (-OH) of polyol (hydrophilic, $P$) to form urethane (RNHCOOR'), thus covalent bonds are mainly formed between $H$ and $P$ particles. See figure 4.2 for an illustration of the chemical reactions involved in waterborne two-component polyurethane systems. Covalent bonds may also be formed between $H$ and $A$ particles when $A$ is considered reactive, leading to a modified hydrophobic particle $H^*$ which is capable of further reactions. That is, one of the isocyanate groups (-NCO) of the crosslinker is changed to amine groups (-NH$_2$) after its reaction with water, and the amine group (-NH$_2$) can further react with another isocyanate group (-NCO) to form urea (RNHCONHR'). Since the crosslinker has multiple isocyanate groups, the $H^*$ particle containing both isocyanate groups and amine groups can further react with any other $H$, $P$, $A$ and $H^*$ particles. The number of reactive functional groups $f$ of each $H$, $P$, $A$ and $H^*$ particles are chosen to be 3, 2, 1 and 3, respectively, based on their experimental findings [29].

Cross-linking reactions proceeding from the adsorbing substrate or isotropically at arbitrary sites in the lattice will both be studied. In the former case, covalent bonding occurs between active components, which are either in contact with the substrate, or are already part of the forming film. Thus the film starts from the substrate and grows in
Figure 4.2: Schematic illustration of the chemical reactions involved in waterborne two-component polyurethane systems: A) main reactions between isocyanate groups of crosslinker ($f_H = 3$) and hydroxyl groups of polyol ($f_p = 2$); B) side reactions between isocyanate groups of crosslinker and water ($f_A = 1$) to form an intermediate amine group on the crosslinker ($H^* = 3$) which leads to further consumption of polyisocyanate.

upward direction till most of the reactive units have reacted. In the latter case, covalent bonding occurs isotropically in space and thus the film grows more evenly in every direction. The situation of film starting from substrate is considered mainly for a systematic study purpose and to compare with previous related studies[25, 26]. It somehow captures the features of interface growth of polymer chains by driven deposition[95]. However,
CHAPTER 4. COMPUTER MODELLING

this may not be realistic in our WB 2K-PUR film formation where cross-linking can start anywhere among the reactive components and form clusters of polyurethane/polyurea quickly. Covalent bonding starting isotropically in the lattice is therefore considered a more realistic approximation to the real situation since the step-growth polymerization mechanism in forming polyurethane/polyurea is better captured.

4.2.5 Systematic Implementation

One of the advantages of computer simulations is that complex materials and processes can be studied in a systematic way. This is important in studying complex multi-component systems like ours because the complexity of the problem is greatly decreased when one starts from a simple model and improves it step by step. Thus the development of our model will have following steps: (1) First we would like to consider the system having thermodynamic equilibration as well as cross-linking reactions proceeding from the substrate with much relaxed bond fluctuation while the aqueous component continues to evaporate. This prelude data first starts with system with only hard-core interaction among the components and reaction between $H$ and $P$ components, and then additional interaction, i.e., short range attractive/repulsive interaction among the $H$, $P$ and $A$ components, will be introduced into the system. (2) Next we will study the system involving thermodynamic equilibration as well as cross-linking reaction proceeding from the substrate with more appropriate bond fluctuation constraints while the aqueous component continues to evaporate. Based on that, the side reactions between component $H$ and $A$ will then be included into the model. This can be further divided into two sub-cases where the volume of component $A$ might be included or excluded in the film after its reaction with component $H$. (3) Last we will study the system involving thermodynamic equilibration via stochastic motion of each constituent and segmental moves as well as kinetic cross-linking reaction proceeding isotropically in space while the aqueous com-
ponent continues to evaporate. Additional interaction among the constituents and reactive solvent with volume excluded from the film after reaction will be considered for this case.

### 4.2.6 Quantities Measured

The main quantities that we are interested in the simulation are film thickness \( h \), the interface width/surface roughness \( W \) and density profile of each component along longitudinal direction. The film consists of all points that are covalently bonded from the substrate. The surface is the locus of all connected points with the maximum height. Thus, each substrate point \( i \) has a film height \( h_i \). The film thickness \( h \) is defined as,

\[
h = \frac{1}{N_s} \sum_{i} h_i,
\]

where, the number of substrate points \( N_s = L_x \times L_z \).

The interface width \( W \) of the film surface is defined as the root mean square (RMS) fluctuation of the film height \([32, 45]\), i.e., the thickness,

\[
W^2 = \langle h_i^2 \rangle - h^2,
\]

\[
\langle h_i^2 \rangle = \frac{1}{N_x} \sum_{i} h_i^2.
\]

The density of component \( i \) \((i = H/P/A)\) at layer \( j \) \((y = j)\) is defined as,

\[
D_{ij} = \frac{N_{i,j}}{N_s},
\]

where, \( N_{i,j} \) is the number of component \( i \) particles at layer \( j \).
Figure 4.3: Snapshots for film formation with components tethered by fluctuating covalent bonds involving reactive hydrophobic (Light gray), polar (Black) and evaporative aqueous groups (Blue). The film consists of all points that are covalently bonded from the substrate. The surface is defined as the locus of all connected points with the maximum height.
Chapter 5

PRELIMINARY STUDY

The reacting system is represented by three types of particles: $H$, $P$ and $A$. Each particle occupies a unit cube in a three dimensional lattice observing the excluded volume constraints. In addition, each particle is characterized by its molecular weight, functionality and interaction with other surrounding particles. Particles are randomly distributed in the lattice initially and are moved stochastically afterwards by Metropolis algorithm to approach thermodynamic equilibrium. Covalent bonds can be formed among reactive components within a certain range with specific reaction kinetics. Bonded constituents are capable of fluctuating its bond length within a limited range. This range of bond formation and length fluctuation, i.e., $0 \leq r \leq \sqrt{27}$ is relatively loose in that excluded volume constraints for bonds are ignored measurably though the degrees of freedom for the bond length is enhanced considerably. We refer this prelude model as effective bond fluctuation model (EBFM). A more restricted range for bond length fluctuation, i.e., $0 \leq r \leq \sqrt{10}$ excluding $\sqrt{8}$ is implemented in bond fluctuation model (BFM) which will be covered in latter chapters.

In this chapter we present some data generated by EBFM to illustrate the various prospects of the simulation model and the systematic study of the system. Hence, some assumptions such as reaction kinetics and selection of the parameters may not be realistic in regard to our specific WB 2K-PUR experimental system in some cases. Further, we are restricted to a small set of parameters (e.g., temperature) to illustrate how the effective bond fluctuating model responds to such stimuli as interaction, component reactivity, concentration and functionality in the film growth process. We also focus our discussion
on film formation in non-reactive evaporating aqueous solvent A in the following sections. We document the different cases examined in table 5.1. The results of cases 1 and 2 are published [96].

5.1 Film Growth

5.1.1 Surface Height Growth

In this section, we will examine the evolution of surface height, film thickness $h$, with time. Simulations are run on a simple cubic lattice with sample size $40 \times 30 \times 40$. 10 independent samples are run to get an average estimate of the physical quantities. An illustrative snapshot of the film growth is shown in figure 5.1. Initially, all the component particles, polar, hydrophobic and water (A) are distributed randomly with their number concentrations $p_p = 0.01$, $p_H = 0.01$ and $p_A = 0.03$, respectively. Note that the volume concentrations are eight times larger than the number concentrations as each particle occupies eight lattice sites of a cube. As time progresses, e.g., $t = 5, 10$, cross-linking grows and film begins to propagate in upward direction from the substrate until most of the reactive components are cross-linked ($t = 40$). The film consists of all points that are covalently bonded from the substrate. We define the “surface” to be the set of particles in the aggregate that are highest in each substrate point (with height $h_i$). The film thickness $h$ is defined as:

$$
  h = \frac{1}{N_s} \sum_i h_i,
$$

(5.1.1.1)

where the number of substrate points $N_s = L_x \times L_y$. A remarkable feature of this model is the ability to move cross-linked particles by including the corresponding bond fluctuations even though within a limited range. As a result, the cross-linked film may become more compact if subjected to downward pressure or gravity. In our computer simulation experiments the film thickness reaches a maximum value as water continually evaporates.
and reaches a steady state in asymptotic time limit as discussed in the following.

\[ R_{HH} = R_{HP} = R_{PP} = 1 \]

**Figure 5.1:** Snapshots for film formation with components tethered by fluctuating covalent bonds involving reactive hydrophobic (H), polar (P) and evaporative aqueous groups (A). Red: H before reaction; Yellow: H after reaction; Black: P before reaction; Green: P after reaction; Blue: A. The film consists of all points that are covalently bonded from the substrate. The surface is defined as the locus of all connected points with the maximum height. a) \( t = 0 \), b) \( t = 20 \), c) \( t = 60 \), d) \( t = 100 \), e) \( t = 5000 \), f) \( t = 3 \times 10^4 \).

First let us look at a simple case (case 1) where both the polar (P) and hydrophobic (H) particles can form bonds with each other, i.e., \( R_{HH} = R_{HP} = R_{PP} = 1 \) with functional-
ity \( f_H = f_P = 4 \). In addition, only hardcore interaction between the particles is considered during equilibration resulting from the stochastic motion in film formation, i.e., no interaction among polar, non-polar and water particles was involved in calculating energy for their moves. Figure 5.2 shows the variation of the mean film thickness \( h \) with the time steps for a range of temperatures \( (T = 0.5 - 5) \). Three stages of film growth are observed for all temperatures: an initial fast growth of the mean surface height followed by a relatively slow relaxation (kinetic reaction regime) before approaching a steady state. The first stage of the film growth may be expressed as

\[
h = Bt^\gamma + Ct^\delta + \ldots,
\]

with a leading power law index \( \gamma \) and correction term with exponent \( \delta \) for \( \gamma > \delta \); \( B \) and \( C \) are constants. For example, at temperature \( T = 0.5 \) (indicated by dashed lines) there may be two growth rates described by \( \gamma \approx 2.0 \) followed by \( \gamma \approx 1.6 \) (see figure 5.2). Note that the time span for the power-law growth is relatively small as the kinetic reaction is fast. The unit of time step is arbitrary. If we had to define a unit time step as an attempt to move one particle (rather than all particles, the common practice in Monte Carlo simulation), then the range of time step could be expanded by a large amount.

The initial growth of the film thickness (for \( t \leq 30 \)) is followed by polymerization in the intermediate relaxation regime \( (t \approx 30 - 10^3) \) where most of the functional groups are already reacted. However, the bonded units continue to execute their stochastic movements allowed by corresponding bond fluctuations as the film thickness \( h \) equilibrates to a saturated value \( h_s \). The time need for the film thickness to relax to its steady state value varies for different temperatures. It seems taking longer for higher temperature system to relax to its equilibrium than the lower temperature system. The temperature dependence of saturated film thickness, i.e., \( h_s - T \) will be discussed later.
Figure 5.2: Growth of the average film thickness ($h$) for a range of temperatures with only hardcore interaction among the components (non-reactive aqueous solvent) on a sample $40 \times 40 \times 30$ with 10 independent samples for $p_H = p_P = 0.01$ with initial water concentration $p_A = 0.03$ and $f_H = f_P = 4$ with $R_{HH} = R_{PP} = R_{HP} = R_{HS} = R_{PS} = 1$ using EBFM with reaction proceeding from the substrate (case 1). Variation of the saturated and near-saturated thickness $h_S$ with the temperature is presented in the inset. The statistical errors in data are of the order of symbols sizes.

Now let us examine what happens on including more interaction (attractive interaction between $P$ and $A$, repulsive interaction between $H$ and $A$) among mobile functional groups, i.e., case 2. As show in figure 5.3, the variation of the mean surface height of the film, $h$, with time remains nearly the same as the system with the hardcore interaction alone (see figure 5.2) at higher temperature. The film thickness $h$ at low temperature ($T = 0.5$) exhibits much slower decrease after reaching its maximum. It would be interesting to have a closer look by examining the evaporating water concentration in the
CHAPTER 5. PRELIMINARY STUDY

sample. Figure 5.4 shows the decay of water concentration as it evaporates during the film growth. Evidently, a considerable amount of water still persists in the film at low temperature ($T = 0.5$). This provides an insight into the competition between the interaction energy and thermal energy causing water to evaporate. At low temperature, the mobility of the particles is relatively low. Attractive interaction between water constituents and the polar groups makes it harder for water to escape the lattice which results in a swollen film. In this case (low temperature), the film has not reached a steady state equilibrium. At higher temperature, the overall mobility of particles increases, water evaporation is less hindered by its interaction with polar particles.

With the hard core interaction, the film thickness reaches its saturation (figure 5.2). For constituents with additional hydrophobic and polar interactions, film thickness ($h$) have not reached saturation at all temperatures as pointed out above. The film morphology changes considerably due to added hydrophobic and polar interactions where evaporation of water component becomes difficult (figure 5.4). Thus, it is extremely difficult to have a completely dry film as some humidity do exist in experiments. Our simulations with slow approach to saturated film thickness, may be closer to laboratory experiment.

So far we have taken hydrophobic ($H$) particles and polar ($P$) particles as non-distinctive reactants in the cross-linking reaction. That is, covalent bonds can be formed not only between $H$ and $P$ particles but also between $H$ and $H$, $P$ and $P$ particles. This might not be true in our laboratory experiments as the cross-linkers do not react with themselves nor do the hydroxyl groups of polyol react with other hydroxyl groups. Thus we consider in case 3 covalent bonds only be formed between $H$ and $P$ particles ($R_{HP} = 1$, $R_{HH} = R_{PP} = 0$) and each $H$ or $P$ particle has functionality 4 ($f_H = f_P = 4$). Additional hydrophobic and polar interactions are also taken into account in case 3. As shown in figure 5.5, the variation of the mean surface height of the film, $h$, with time remains almost the same as the
Figure 5.3: Growth of the average film thickness ($h$) for a range of temperatures with additional interaction among the components (non-reactive aqueous solvent) on a sample $40 \times 40 \times 30$ with 10 independent samples for $p_H = p_P = 0.01$ with initial water concentration $p_H = f_f = 0.03$ and $f_H = f_P = 4$ with $R_{HH} = R_{PP} = R_{HP} = R_{HS} = R_{PS} = 1$ using EBFM with reaction proceeding from the substrate (case 2). Variation of the saturated and near-saturated thickness $h_s$ with the temperature is presented in the inset. The statistical errors in data are of the order of symbols sizes.

system in case 2 at higher temperature except a little bit slower film growth in the initial stage... (exponent, reason for slow).... At lower temperature the film thickness not only exhibits a slower growth than the system in case 2 but also a slightly thinner film. This might be due to the slowed down film growth renders more time for water particles to evaporate from the system which leads to a less swollen film by the trapped water particles at low temperature. A less degree of complexity of the formed cross-linking network structure due to the simpler reaction kinetics (i.e., $R_{HH} = R_{PP} = 0$) is also likely to contribute to
Figure 5.4: Variation of water concentration with time steps for a range of temperatures using the same parameter as in Figure 5.3.

the less amount of the trapped water in the film. At very low temperature (e.g., $T = 0.5$), however, the film is likely not saturated as a large amount of water particles are trapped inside due to small mobility of components at low temperature.

A further improvement of the previous cases is to adopt the actual functionality from the laboratory experiments for the reactive components in case 4. That is, we choose functionality 3 for hydrophobic component and 2 for polar component ($f_H = 3, f_P = 2$) as the cross-linker and polyol used in the experiment has three isocyanate groups and two hydroxyl groups, respectively. In addition, the number concentrations of each component are adjusted to be $p_P = 0.0115$, $p_H = 0.023$ and $p_A = 0.0422$ to match the ratio (NCO:OH
CHAPTER 5. PRELIMINARY STUDY

Figure 5.5: Growth of the average film thickness ($h$) for a range of temperatures with additional interaction among the components (non-reactive aqueous solvent) on a sample $40 \times 40 \times 30$ with 10 independent samples for $p_H = p_P = 0.01$ with initial water concentration $p_A = 0.03$ and $f_H = f_P = 4$ with $R_{HH} = R_{PP} = 0, R_{HP} = R_{HS} = R_{PS} = 1$ using EBFM with reaction proceeding from the substrate (case 3).

= 1:2, 55wt% water) used in the laboratory experiment. Again the variation of mean surface height $h$ with time (Figure 5.6) shows little difference in comparison to previous cases except the film initial growth is even more slower, about one magnitude longer than other cases. This is not out of our expectation since the limited functionality reduces the number of possible bonds being formed at a time. The equilibrated film is “thicker” since the concentrations of reactants are higher in case 4 even though many reactive particles (e.g., $H$) left un-reacted at the end of film formation. A list of power-law exponents of initial growth stage for the four cases are documented in tables 5.2 and 5.3.
5.1.2 Interface Width Growth

An important and interesting question to both experimentalists and theorists is how the film morphology, especially surface roughness, responds to various external and internal stimuli such as temperature, relative humidity, component concentration and stoicheometry, interaction, etc.. This information can be critical in understanding the film formation process as well as assisting experimentalists in their experiment design. Thus one of our main interests is to examine the evolution of interface width, a measurement of the film...
roughness, with time and the saturated interface width.

The interface width $W$ of the film surface is defined as the root mean square (RMS) fluctuation of the film height [32, 45], i.e., the thickness,

$$ W^2 = \langle h_i^2 \rangle - h^2, \quad (5.1.2.1) $$

$$ \langle h_i^2 \rangle = \frac{1}{n_s} \sum_{i} h_i^2. \quad (5.1.2.2) $$

To monitor the roughening process quantitatively, we measure the width of the interface as a function of time. By the constraint of film proceeding from the floor, the growth starts from the substrate; the interface at time zero is simply a flat plate, with zero width. As cross-linking occurs, the interface gradually roughens.

Figure 5.7 shows the variation of the interface width $W$ with the time steps at different temperatures corresponding to height variation presented in figure 5.2 (case 1). This case has considered only hardcore interaction among particles. Initially, the interface width, $W$, grows with time $t$ with a power law,

$$ W = B t^\beta, \quad (5.1.2.3) $$

with exponent $\beta$ which changes from $\beta \approx 1.0$ to $\beta \approx 0.80$ in time at the temperature $T = 0.5$ (see figure 5.7). The interface width then decreases with an overshoot (maxima) before stabilizing somewhat with an increasing trend at higher temperatures in the intermediate time regime. It finally relaxes to steady state saturation in the long (asymptotic) time regime. The general non-monotonic approach before reaching saturation persists at all temperatures with obvious change in patterns with the temperature.

Response of the interface width growth can be explained by the three stage development of the film formation similar to evolution of the mean surface height, $h$. At early
stage, films propagate upward unevenly from the substrate resulting in increasing fluctuations in the propagating front. Since the reaction propagates from the substrate, nearby functional groups have high probability to react. As a result, the interface width, i.e., the surface roughness increases with time. Thereafter, it decreases as the film formation propagates to the top where most particles near the film air interface have reacted and become part of the film. The film starts shrinking toward the substrate as the interstitial water evaporates; the consolidation leads to decrease in the surface roughness. The film roughness grows up again due to the stochastic movement of the cross-linked particles and increasing pore space (empty sites) provided by water evaporation. As water content in the film reduces, the film stretches too far with an almost second maximum.

Figure 5.7: Evolution of the interface width ($W$) of the film surface for a range of temperatures using the same parameters as in Figure 5.2 (case 1).
(overshoot) in the interface width (at high temperatures). The bond fluctuations respond and the film roughness eventually reaches a steady state where both the mean surface height and the root mean square interface width remain constant. A somewhat oscillatory response, more pronounced with the fluctuation in the film height, i.e., the interface width, is due to bond fluctuations of covalent bonded functional groups augmented by the interplay between the thermal energy and the free volume due to water evaporation. Such a pronounced non-monotonic and somewhat oscillatory response of the interface width (roughness) during the film formation and equilibration is a unique characteristic that cannot be captured by constant bond length in previous studies.

Corresponding growth of the interface width $W$ for the interacting functional groups (case 2) is presented in figure 5.8 for a range of temperatures. At a first glance, the interface growth pattern for interacting functional groups (figure 5.8) appears similar to that with the hardcore interaction alone (figure 5.7). However, a closer examination reveals important differences. The interface width $W$ grows faster for interacting system with a higher growth exponent. For example, $\beta_1 \approx 1.15 \pm 0.02$ (initially) and $\beta_2 \approx 0.83 \pm 0.02$ (later stage) at $T = 0.5$ (figure 5.8) in comparison to corresponding values $\beta_1 \approx 1.10 \pm 0.02$ and $\beta_2 \approx 0.81 \pm 0.02$ for hardcore constituents (figure 5.7). As mentioned earlier, with additional hydrophobic and polar interaction, the film has not reached equilibrium at low temperature due to significant amount of water trapped in the film. Thus, for temperature lower than 1.25, the oscillatory response of interface width is absent in the intermediate relaxation region.

For system with bonds forming only between hydrophobic and polar particles (case 3), i.e., $R_{HP} = 1, R_{HH} = R_{PP} = 0$, again the interface width variation with time remains almost the same shape at higher temperatures but a slower growth at initial stage in comparison to the previous two cases, see figure 5.9. This trend of slower interface width growth is consistent with the slower surface height growth in case 3. As particles of the
same type cannot form bonds with each other, the number of reactive particles within the bond forming range reduced resulting in a slowed down propagation of film front. This effect is more profound for systems of lower temperatures. At low temperature (e.g., \( T = 0.5 \)), the attractive interaction between the same type of particles (H and H, P and P) competes over the thermal energy, thus the time for H and P particles hopping into the bond forming range is extended especially for the later stage of initial growth (\( \beta_2 = 0.59 \)). The overshoot of the interface width is absent at low temperature (\( T = 0.5 \)) due to this slow approach of interface growth. For higher temperatures, in contrast, the interface width growths exhibit an obvious oscillatory pattern.

*Figure 5.8:* Evolution of the interface width (W) of the film surface for a range of temperatures using the same parameters as in Figure 5.3 (case 2).
Figure 5.9: Evolution of the interface width ($W$) of the film surface for a range of temperatures using the same parameters as in Figure 5.5 (case 3).

It would be interesting to see how the interface width vary with time using experimental values for parameters such as component functionality ($f_H = 3$, $f_P = 2$ instead of $f_H = f_P = 4$) and concentration ratio ($p_P : p_H = 1 : 2$) which is case 4. Bond forming among the same type of particles is forbidden as case 3. As shown in figure 5.10, the overall trend appears somewhat similar to previous cases, but a closer look reveals important differences. First, we notice that the initial fast growth is further slowed down and appears to have three steps of growth which can be fitted by a power law. For example, the growth at temperature $T = 1$ can be scaled by a power law with exponents $\beta_1 = 0.92$ followed by $\beta_2 = 0.78$ and $\beta_3 = 0.44$. Thereafter, the interface width reaches an overshoot and then enters an intermediate steady state before it finally relaxes to the saturated...
value. Unlike the other cases, oscillatory response of the interface width is not obvious or absent for the temperatures we examined. The reduced number of functional groups of reactants not only slows down the film formation process but also considerably changes the structure of network formed by cross-linking reaction. The density of the bonds decreases. The bonded units are less constrained due to the bond fluctuation length limit since the number of their connecting neighbors reduces. More freedom is thus achieved for bonded particles to fluctuate and relax.

![Figure 5.10](image)

*Figure 5.10*: Evolution of the interface width \((W)\) of the film surface for a range of temperatures using the same parameters as in Figure 5.6 (case 4).
CHAPTER 5. PRELIMINARY STUDY

5.2 Equilibrium

As we discussed in previous section, film grows from the substrate with both film thickness and roughness increasing as a power of time initially, i.e., \( h \approx t^a \) and \( W \approx t^b \). The power-law increase does not continue indefinitely, but is followed by a relaxation region before the thickness and the interface width reaches a saturated value, \( h_s \) and \( W_s \), in the asymptotic time limit. The saturation state or equilibrium may correspond to the dry film after cure in the laboratory experiment, thus is of main interest of us to examine how it responds to the various external and internal stimuli. In this section, we examine the temperature dependance of equilibrium film thickness and film roughness for different cases.

5.2.1 Film Thickness

Mobility of the constituents and corresponding bond lengths depends on the temperature, i.e., higher the temperature, larger is the bond length. Accordingly, the equilibrium film thickness \( h_s \) depends on temperature. Variation of \( h_s \) with temperature for case 1 is presented in the inset of figure 5.2 which shows that, on increasing the temperature, a fast linear expansion of the film thickness \( (h_s = 6.21 + 0.30T) \) is followed by relatively slow expansion \( (h_s = 6.54 + 0.20T) \) at high temperatures. Unlike the previous studies [25, 26], where the film thickness (surface height) remains constant after the reaction reaches its equilibrium saturating most of its functional groups, the mean film thickness further relaxes to its equilibrium value due to bond fluctuations in the asymptotic time limit. The mean surface height of the film is larger at higher temperature which may be due to more active vibration of bonded particles at high temperature. It is also clear from these data (figure 5.2) that the relaxation time required to reach equilibrium varies with temperature; films at higher temperatures require longer time to equilibrate.

Figure 5.3 (inset) shows the variation of mean surface height with temperature for
case 2 which shows a sharp decrease of film thickness at low temperatures followed by nearly constant with a slight increase of film thickness at high temperatures. Note the sharp contrast between the non-monotonic variation of the film thickness here with that of the hardcore constituents (case 1) where the film thickness continues to increase with the temperature. As we pointed out earlier, the film at low temperature may have not reached true equilibrium in the time limit of observation due to the added hydrophobic and polar interaction.

Figure 5.11 shows the variation of mean surface height with temperature for case 3 which appears very similar to the trend in case 2. That is, the film thickness decreases sharply at low temperatures and remain almost the same afterwards at high temperatures. This indicates that the constraint of no covalent bonding among components of the same type does slow down the initial film thickness growth a little bit (figure 5.5) but not having much impact on the saturated film thickness.

The variation of mean surface height with temperature for case 4 is shown in figure 5.12. Again the saturated film thickness decreases in low temperature region and increases almost linearly in high temperature region. The film thickness growth slowed down even further than that in case 3 due to the smaller functionalities assigned to the reactive components. However, the saturated film thicknesses are larger than those in previous cases as a result of larger concentrations used in case 4.

5.2.2 Film Roughness

The saturated interface width \( W_s \) of case 1 is found to increase linearly with the temperature as shown in the inset of figure 5.7. Similar to the film thickness (figure 5.2, the saturated interface width, \( W_s \), shows two linear scaling, a fast growth at low temperatures (\( W_s = 1.26 + 0.43T \)) while a relatively slow growth at high temperatures (\( W_s = 1.81 + 0.20T \)). This is in contrast to previous studies [26] where the interface continues
Figure 5.11: Variation of the saturated and near-saturated thickness $h_s$ with the temperature using the same parameter as in Figure 5.5 (case 3). The statistical errors in data are of the order of symbols sizes.

to decay with the temperature.

For case 2, the saturated interface width, i.e., the steady state roughness $W_s$ decreases sharply with the temperature at low temperatures followed by a very slow linear growth on increasing the temperature (figure 5.3). This must be contrasted from the linear increase of $W_s$ with temperature for systems with hardcore interaction alone (figure 5.7) and that of the monotonic decay in previous study [26].

The dependence of the saturated interface width on temperature in case 3 is very similar to that in case 2, as shown in figure 5.13. Again we do not observe much effect of
Figure 5.12: Variation of the saturated and near-saturated thickness $h_s$ with the temperature using the same parameter as in Figure 5.6 (case 4). The statistical errors in data are of the order of symbols sizes.

Constraint covalent bonding between $H$ and $P$ components on the saturated film roughness in comparison to case 2. Figure 5.14 shows the variation of the saturated interface width with temperature in case 4 where more realistic functionalities and concentrations are used. Again the interface width is pretty high at low temperature (e.g., $T = 1$) which may not well equilibrated yet. The film roughness increases with temperature at higher temperatures. While the general shape of film roughness growth with time maintains (figure 5.10), we notice that the initial film roughness is slower and the film saturates more quickly than in previous cases.
CHAPTER 5. PRELIMINARY STUDY

5.3 Finite Size Effect

To make sure that there is no severe finite size effects, simulations are performed with different lattice sizes. Variations of film thickness and the interface width for case 2 for these lattices are presented in figures 5.15 and 5.16 respectively. There is very little effect of the lattice size on the qualitative nature of the dependence of film thickness and its interface width. The data for other cases show similar results.

Figure 5.13: Variation of the saturated and near-saturated roughness \( W_s \) with the temperature using the same parameter as in Figure 5.5 (case 3). The statistical errors in data are of the order of symbols sizes.
Figure 5.14: Variation of the saturated and near-saturated roughness $W_s$ with the temperature using the same parameter as in Figure 5.6 (case 4). The statistical errors in data are of the order of symbols sizes.
Table 5.1: Parameters used in cases 1-4.

<table>
<thead>
<tr>
<th>Case</th>
<th>Condition</th>
<th>Parameters</th>
<th>Results</th>
</tr>
</thead>
</table>
| 1     | $2 \leq r \leq \sqrt{27}$ | $p_F = p_H = 0.01, p_A = 0.03$  
$f_F = f_H = 4, f_A = 0$  
$R_{HH} = R_{PP} = R_{HP} = R_{HS} = R_{PS} = 1$  
$M_P = 0.3, M_H = 1.5, M_A = 0.03$ | film propagates from the substrate |
| 2     | $2 \leq r \leq \sqrt{27}$ | $p_F = p_H = 0.01, p_A = 0.03$  
$f_F = f_H = 4, f_A = 0$  
$R_{HH} = R_{PP} = R_{HP} = R_{HS} = R_{PS} = 1$  
$M_P = 0.3, M_H = 1.5, M_A = 0.03$ | film propagates from the substrate |
| 3     | $2 \leq r \leq \sqrt{27}$ | $p_F = p_H = 0.01, p_A = 0.03$  
$f_F = f_H = 4, f_A = 0$  
$R_{HP} = R_{HS} = R_{PS} = 1, R_{HH} = R_{PP} = 0$  
$M_P = 0.3, M_H = 1.5, M_A = 0.03$ | film propagates from the substrate |
| 4     | $2 \leq r \leq \sqrt{27}$ | $p_F = 0.0115, p_H = 0.0230, p_A = 0.0422$  
$f_F = 2, f_H = 3, f_A = 0$  
$R_{HP} = R_{HS} = R_{PS} = 1, R_{HH} = R_{PP} = 0$  
$M_P = 0.3, M_H = 1.5, M_A = 0.03$ | film propagates from the substrate |
Table 5.2: Power-law exponents of initial film growth in cases 1 and 2.

<table>
<thead>
<tr>
<th>case</th>
<th>T</th>
<th>$\gamma_1(B_1)$</th>
<th>$\gamma_2(B_2)$</th>
<th>$\beta_1(C_1)$</th>
<th>$\beta_2(C_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>case 1</td>
<td>0.5</td>
<td>2.00(0.11)</td>
<td>1.60(0.20)</td>
<td>1.10(0.58)</td>
<td>0.80(0.90)</td>
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<tr>
<td></td>
<td>1.0</td>
<td>1.90(0.11)</td>
<td>1.49(0.22)</td>
<td>1.03(0.65)</td>
<td>0.85(0.87)</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1.88(0.12)</td>
<td>1.62(0.18)</td>
<td>1.11(0.56)</td>
<td>0.81(0.92)</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.88(0.13)</td>
<td>1.52(0.23)</td>
<td>0.99(0.70)</td>
<td>0.85(0.88)</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>1.90(0.12)</td>
<td>1.61(0.20)</td>
<td>1.03(0.66)</td>
<td>0.86(0.87)</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>2.02(0.10)</td>
<td>1.65(0.18)</td>
<td>1.10(0.59)</td>
<td>0.81(0.94)</td>
</tr>
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<td>3.5</td>
<td>2.02(0.10)</td>
<td>1.61(0.20)</td>
<td>1.12(0.58)</td>
<td>0.76(1.08)</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>1.85(0.16)</td>
<td>1.49(0.29)</td>
<td>1.00(0.77)</td>
<td>0.64(1.43)</td>
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<td></td>
<td>4.5</td>
<td>2.02(0.10)</td>
<td>1.67(0.18)</td>
<td>1.14(0.56)</td>
<td>0.81(0.95)</td>
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<tr>
<td></td>
<td>5.0</td>
<td>1.99(0.15)</td>
<td>1.48(0.31)</td>
<td>1.07(0.74)</td>
<td>0.75(1.23)</td>
</tr>
<tr>
<td>case 2</td>
<td>0.5</td>
<td>2.00(0.10)</td>
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<td>1.10(0.50)</td>
<td>0.80(0.88)</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>1.91(0.08)</td>
<td>1.32(0.22)</td>
<td>1.08(0.53)</td>
<td>0.77(0.84)</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.95(0.08)</td>
<td>1.37(0.20)</td>
<td>1.11(0.49)</td>
<td>0.80(0.75)</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>2.02(0.08)</td>
<td>1.45(0.19)</td>
<td>1.15(0.49)</td>
<td>0.86(0.72)</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1.97(0.09)</td>
<td>1.44(0.22)</td>
<td>1.14(0.54)</td>
<td>0.91(0.70)</td>
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<td></td>
<td>2.0</td>
<td>1.87(0.11)</td>
<td>1.54(0.18)</td>
<td>1.04(0.62)</td>
<td>0.78(1.04)</td>
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<tr>
<td></td>
<td>2.5</td>
<td>1.94(0.12)</td>
<td>1.37(0.32)</td>
<td>1.07(0.67)</td>
<td>0.77(0.98)</td>
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<tr>
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<td>3.0</td>
<td>2.00(0.10)</td>
<td>1.46(0.24)</td>
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<td>0.81(0.92)</td>
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<tr>
<td></td>
<td>3.5</td>
<td>1.86(0.13)</td>
<td>1.51(0.23)</td>
<td>1.01(0.62)</td>
<td>0.86(0.87)</td>
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<td></td>
<td>4.0</td>
<td>1.96(0.11)</td>
<td>1.50(0.23)</td>
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<td>0.84(0.93)</td>
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<td>4.5</td>
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<td>1.12(0.56)</td>
<td>0.79(1.03)</td>
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<td>5.0</td>
<td>2.06(0.10)</td>
<td>1.47(0.27)</td>
<td>1.21(0.50)</td>
<td>0.80(1.02)</td>
</tr>
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Table 5.3: Power-law exponents of initial film growth in cases 3 and 4.

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<tr>
<th>case</th>
<th>T</th>
<th>$\gamma_1(B_1)$</th>
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<th>$\gamma_3(B_3)$</th>
<th>$\beta_1(C_1)$</th>
<th>$\beta_2(C_2)$</th>
<th>$\beta_3(C_3)$</th>
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</thead>
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<tr>
<td>3</td>
<td>0.5</td>
<td>1.84(0.05)</td>
<td>1.26(0.12)</td>
<td>0.89(0.28)</td>
<td>1.05(0.36)</td>
<td>0.59(0.70)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.82(0.05)</td>
<td>1.34(0.11)</td>
<td>1.06(0.22)</td>
<td>1.01(0.39)</td>
<td>0.65(0.68)</td>
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<tr>
<td></td>
<td>1.5</td>
<td>1.98(0.05)</td>
<td>1.41(0.12)</td>
<td>1.04(0.28)</td>
<td>1.06(0.40)</td>
<td>0.63(0.79)</td>
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</tr>
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<td></td>
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<td>1.82(0.07)</td>
<td>1.34(0.15)</td>
<td>1.15(0.23)</td>
<td>0.99(0.48)</td>
<td>0.69(0.75)</td>
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</tr>
<tr>
<td></td>
<td>2.5</td>
<td>1.89(0.07)</td>
<td>1.37(0.15)</td>
<td>1.20(0.22)</td>
<td>1.07(0.44)</td>
<td>0.73(0.70)</td>
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<td>1.81(0.08)</td>
<td>1.43(0.14)</td>
<td>1.20(0.22)</td>
<td>1.00(0.48)</td>
<td>0.70(0.77)</td>
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</tr>
<tr>
<td></td>
<td>3.5</td>
<td>1.88(0.07)</td>
<td>1.35(0.17)</td>
<td>1.19(0.27)</td>
<td>1.05(0.46)</td>
<td>0.77(0.72)</td>
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</tr>
<tr>
<td></td>
<td>4.0</td>
<td>1.89(0.08)</td>
<td>1.38(0.16)</td>
<td>1.19(0.24)</td>
<td>1.00(0.51)</td>
<td>0.68(0.84)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>1.91(0.08)</td>
<td>1.32(0.18)</td>
<td>1.24(0.22)</td>
<td>1.08(0.47)</td>
<td>0.72(0.76)</td>
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<tr>
<td></td>
<td>5.0</td>
<td>1.93(0.07)</td>
<td>1.45(0.14)</td>
<td>1.21(0.26)</td>
<td>1.03(0.49)</td>
<td>0.72(0.74)</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1.60(0.030)</td>
<td>1.15(0.08)</td>
<td>0.72(0.29)</td>
<td>0.92(0.25)</td>
<td>0.78(0.33)</td>
<td>0.44(0.74)</td>
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<tr>
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<td>2</td>
<td>1.76(0.027)</td>
<td>1.31(0.07)</td>
<td>0.85(0.22)</td>
<td>1.00(0.24)</td>
<td>0.59(0.53)</td>
<td>0.48(0.69)</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.66(0.044)</td>
<td>1.27(0.08)</td>
<td>0.92(0.19)</td>
<td>0.95(0.34)</td>
<td>0.66(0.52)</td>
<td>0.46(0.82)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.81(0.030)</td>
<td>1.19(0.10)</td>
<td>0.83(0.27)</td>
<td>1.22(0.22)</td>
<td>0.75(0.43)</td>
<td>0.47(0.79)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.61(0.047)</td>
<td>-</td>
<td>0.89(0.24)</td>
<td>0.94(0.34)</td>
<td>0.62(0.59)</td>
<td>0.41(0.97)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1.68(0.049)</td>
<td>1.08(0.15)</td>
<td>0.76(0.36)</td>
<td>0.96(0.36)</td>
<td>0.59(0.65)</td>
<td>0.47(0.82)</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.71(0.046)</td>
<td>1.10(0.14)</td>
<td>0.91(0.23)</td>
<td>0.98(0.35)</td>
<td>0.51(0.76)</td>
<td>0.53(0.74)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.86(0.035)</td>
<td>1.10(0.13)</td>
<td>1.10(0.12)</td>
<td>1.07(0.28)</td>
<td>0.62(0.58)</td>
<td>0.62(0.56)</td>
</tr>
</tbody>
</table>
Figure 5.15: evolution of the film thickness $h$ using EBFM for a temperature $T = 5$ with non-reactive aqueous solvent on different sample sizes each with ten independent samples for $p_H = p_F = 0.01$ with initial water concentration $p_A = 0.03$ (case 2).
Figure 5.16: evolution of the interface width $W$ using EBFM for a temperature $T = 5$ with non-reactive aqueous solvent on different sample sizes each with ten independent samples for $p_H = p_P = 0.01$ with initial water concentration $p_A = 0.03$ (case 2).
In chapter 5, we have had an initial impression of simulating film formation processes, i.e., colloidal aggregation, solvent evaporation, cross-linking reaction and deposition, from its basic constituents. The elastic feature of the film is captured by allowing bonded segments to fluctuate their lengths. This is a big improvement over previous models in which the cross-linked network is rigid as the bonded units are incapable of any additional motions once they are bonded. However, the range for bond formation and fluctuation in EBFM \((0 \leq r \leq \sqrt{27})\) is too big to fully take into account of the excluded volume constraint for bonds. Actually bond crossing each other may occur immediately after the bonds are formed between particles within that range. Thus cross-linking and excluded volume constraints are considered only approximately in the spirit of a mean-field description in EBFM. To solve this problem, a more restricted range for bond length fluctuation is adopted in the simulation model, i.e., a bonded unit can stretch its bond length between 2 and \(\sqrt{10}\) excluding \(\sqrt{8}\), a common practice in the well-known bond fluctuation model on a 3D lattice. Moreover, covalent bonds are constrained to form only between nearest neighbor monomers involved in kinetic reaction. These constraints enforce bond fluctuations and mobility to obey the excluded volume effects in the model, which will be referred as BFM.

In this and later chapters we will focus on film formation using BFM. As part of the systematic study, we investigate film growth proceeding from the substrate in a non-reactive evaporating aqueous solvent in this chapter (case 5, see table 6.1). The results will be compared with those of case 4 of chapter 5 in which EBFM is used. Hence, all
Table 6.1: Parameters used in case 5.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2 \leq r \leq \sqrt{10}$ excluded $\sqrt{8}$</td>
</tr>
<tr>
<td>2</td>
<td>$p_P = 0.0115, p_H = 0.0230, p_A = 0.0422$</td>
</tr>
<tr>
<td>3</td>
<td>$f_P = 2, f_H = 3, f_A = 0$</td>
</tr>
<tr>
<td>4</td>
<td>$R_H P = R_H S = R_P S = 1, R_H H = R_P P = 0$</td>
</tr>
<tr>
<td>6</td>
<td>$M_P = 0.3, M_H = 1.5, M_A = 0.03$</td>
</tr>
<tr>
<td>7</td>
<td>film propagates from the substrate</td>
</tr>
</tbody>
</table>

The parameters and constraints used in case 5 of this chapter remain the same as those in case 4, except for the constraints of bond formation and fluctuation range. In addition, more sets of external parameters such as temperature, NCO:OH ratio, initial water concentration and reaction rate are examined to study their effects on film growth and surface morphology in this chapter.

### 6.1 Film Growth

Initially, all the component particles, polar ($P$), hydrophobic ($H$) and aqueous water ($A$) are distributed randomly with their number concentrations $p_P = 0.0115, p_H = 0.0230$ and $p_A = 0.0422$, respectively on the lattice. Note that the volume concentrations $C_P = 0.092, C_H = 0.184$ and $C_A = 0.3376$ are eight times larger than the number concentrations as each particle occupies eight lattice sites of a unit cube. As time progresses, cross-linking grows and film begins to propagate in upward direction from the substrate until most of the reactive components are cross-linked. With the continual mobility of covalently bonded units, the cross-linked film may further relax as aqueous constituents continue to evaporate; the film reaches a steady state in asymptotic time limit.

Snapshots for film surface evolution proceeding from the substrate are shown in figure...
6.1. The surface is defined as the locus of all connected points with the maximum height from the substrate. As seen, topographical features that appear as "hills" and "valleys" are present in the simulated film surface. These features are attributed to subtle compositional variations in polyurethane/polyurea distributions near the film-air (F-A) interface, as revealed by IRIRI spectroscopy (see figure 6.2).

![Figure 6.1: Snapshots for film surface evolution proceeding from the substrate in non-reactive evaporative solvent. The surface is defined as the locus of all connected points with the maximum height. a) t = 1, b) t = 25, c) t = 50, d) t = 5 × 10⁴](image)

### 6.1.1 Surface Height Growth

First let us look at the effect of temperature on film growth in case 5 with BFM. Figure 6.3 shows the variation of the mean film thickness \( h \) with the time steps for a range of temperatures \( T = 1.5 - 5 \). Similar to case 4 with EBFM, three stages of film growth are observed for most temperatures in case 5 with BFM. That is, an initial fast growth of the mean surface height is followed by a relatively slow relaxation before approaching a steady state. Again, the initial growth of surface height with time can be described by
power-law, i.e., $h = B t^\gamma$ with an index $\gamma$ and a prefactor $B$. There may be more than one power-laws for growth depending on kinetics and time regime. However, a notably much slower growth in the initial stage of film propagation is observed with BFM. For example, at temperature $T = 3$ the three growth rates can be described by $\gamma_1 \simeq 0.85$ followed by $\gamma_2 \simeq 0.56$ and $\gamma_3 \simeq 0.44$ in comparison to $\gamma_1 \simeq 1.66$ followed by $\gamma_2 \simeq 1.27$ and $\gamma_3 \simeq 0.92$ with EBFM (see table 5.3). The time span for the monotonic growth of surface height is about an order larger ($t_x \approx 10^3$) than that in EBFM ($t_x \approx 10^2$, see figure 5.6). In addition, the maximum values that the mean surface height achieves are much smaller in BFM ($h_x = 9.0$ at $T = 3$) than those in EBFM ($h_x = 24.0$ at $T = 3$) and have strong dependence on temperature. These are not out of expectation. As bonds are constrained to form only between nearest neighboring particles and bond lengths are restricted to fluctuate within

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**Figure 6.2**: Film-air (F-A) IRIR images of WB 2K-PUR films showing the compositional variations and phase separation.
a much limited range in BFM, the probability of reaction among appropriate components at each time step is much lower in comparison to EBFM where the range for reaction is quite large ($r \leq \sqrt{27}$). Hence, the cross-linking reactions slow down significantly in BFM. Moreover, the strengthened restriction on bond fluctuation in BFM results in a less stretched film which accounts for the smaller maximum surface heights before the onset of relaxation region. The lower the temperature, the less stretched the film. Another observation is that the time to reach steady state thickness is about the same for both BFM and EBFM, though a slower initial film growth and a retarded onset of relaxation are anticipated in BFM. A list of power-law exponents of initial film growth as a function of temperature are documented in table 6.2.

Figure 6.3: Growth of the average film thickness ($h$) for a range of temperatures with non-reactive aqueous solvent on a sample $40 \times 40 \times 30$ with 10 independent samples for $p_{H} = 0.0115, p_{P} = 0.023$ with initial water concentration $p_{A} = 0.0422$ using BFM with reaction proceeding from the substrate.
Table 6.2: Power-law exponents of initial film growth at different temperatures in case 5.

<table>
<thead>
<tr>
<th>T</th>
<th>$\gamma_1(B_1)$</th>
<th>$\gamma_2(B_2)$</th>
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<th>$\beta_1(C_1)$</th>
<th>$\beta_2(C_2)$</th>
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<td>1.5</td>
<td>0.82(0.058)</td>
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<td>0.38(0.19)</td>
<td>0.36(0.47)</td>
<td>0.18(0.71)</td>
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<td>2.0</td>
<td>0.83(0.067)</td>
<td>0.65(0.09)</td>
<td>0.42(0.18)</td>
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<td>0.22(0.65)</td>
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<tr>
<td>2.5</td>
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<td>0.63(0.10)</td>
<td>0.43(0.18)</td>
<td>0.37(0.48)</td>
<td>0.22(0.68)</td>
</tr>
<tr>
<td>3.0</td>
<td>0.85(0.067)</td>
<td>0.56(0.12)</td>
<td>0.44(0.17)</td>
<td>0.38(0.49)</td>
<td>0.21(0.70)</td>
</tr>
<tr>
<td>4.0</td>
<td>0.86(0.065)</td>
<td>0.57(0.13)</td>
<td>0.46(0.18)</td>
<td>0.37(0.49)</td>
<td>0.21(0.72)</td>
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<tr>
<td>5.0</td>
<td>0.77(0.075)</td>
<td>0.52(0.14)</td>
<td>0.51(0.14)</td>
<td>0.46(0.46)</td>
<td>0.24(0.64)</td>
</tr>
</tbody>
</table>

Experimentally, the reactive dispersion is cured in a controlled chamber under certain relative humidity after its application to the substrate. Differences in environmental humidity result in different rates of evaporation of aqueous solvent. Through attractive/repulsive interaction of solvent (water) with other reactive constituents, the rate of water evaporation might have a great effect on film growth and steady-state film characteristics. For this consideration, we conducted computer simulations to examine the effect of water evaporation rate on the film formation. As higher water evaporation rates (lower relative humidity) correspond to lower water concentration contained in the system at each time step, we use different initial water concentrations to represent different water evaporation rates (so different relative humidity). Figure 6.4 shows the variation of the mean surface height with the time steps for a range of initial water concentrations ($p_A = 0.024 - 0.042$) at temperature $T = 3$. The growth pattern remains the same for all initial water concentrations. That is, an initial growth of mean surface height ($0 - 10^3$) is followed by a relaxation ($10^3 - 10^4$) before approaching a steady state. Again, the initial growth can be described by power-laws, i.e., $h = Br^\gamma$ with an index $\gamma$ and a prefactor $B$. For example, at the initial water concentration $p_A = 0.036$, the two growth rates can be described by $\gamma_1 \simeq 0.83$ followed by $\gamma_2 \simeq 0.48$. Power-law exponents of initial film growth
Table 6.3: Power-law exponents of initial film growth at different initial water concentrations in case 5.

<table>
<thead>
<tr>
<th>PA</th>
<th>$\gamma_1(B_1)$</th>
<th>$\gamma_2(B_2)$</th>
<th>$\beta_1(C_1)$</th>
<th>$\beta_2(C_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.024</td>
<td>0.76(0.12)</td>
<td>0.50(0.22)</td>
<td>0.34(0.63)</td>
<td>0.22(0.80)</td>
</tr>
<tr>
<td>0.027</td>
<td>0.75(0.11)</td>
<td>0.47(0.23)</td>
<td>0.30(0.64)</td>
<td>0.17(0.92)</td>
</tr>
<tr>
<td>0.030</td>
<td>0.81(0.09)</td>
<td>0.48(0.21)</td>
<td>0.35(0.58)</td>
<td>0.21(0.80)</td>
</tr>
<tr>
<td>0.033</td>
<td>0.88(0.07)</td>
<td>0.51(0.17)</td>
<td>0.38(0.53)</td>
<td>0.22(0.74)</td>
</tr>
<tr>
<td>0.036</td>
<td>0.83(0.08)</td>
<td>0.48(0.18)</td>
<td>0.38(0.53)</td>
<td>0.21(0.77)</td>
</tr>
<tr>
<td>0.039</td>
<td>0.85(0.07)</td>
<td>0.48(0.16)</td>
<td>0.36(0.51)</td>
<td>0.21(0.70)</td>
</tr>
<tr>
<td>0.042</td>
<td>0.81(0.07)</td>
<td>0.51(0.14)</td>
<td>0.38(0.49)</td>
<td>0.24(0.67)</td>
</tr>
</tbody>
</table>

for other initial water concentrations are documented in Table 6.3. As can be seen, the two growth rates $\gamma_1 (0.81 \pm 0.07)$ and $\gamma_2 (0.49 \pm 0.02)$ are about the same for all initial water concentrations that are observed though the prefactors $B$ are different. This is evidenced in Figure 6.4 where the initial part of the curves shift to the right parallelly as the initial water concentrations increases. Hence, the initial water concentration does not affect the initial film growth very much in this case, as it does not change the power-law exponents when it varies. The system of higher initial water concentration does have slower growth of mean surface height (the prefactor is smaller) as the presence of larger amount of water dilutes the concentration of reactants in unit volume, but this hindrance is a relatively slight one.

Another important consideration in 2K-PUR film formation is the stoichiometric ratio of isocyanate (NCO) to hydroxyl (OH) functional groups, since this ratio may affect film properties. Compositional changes may strongly affect colloidal dynamics and stability, particle interactions in the colloidal state, reaction rates, phase separation during film formation, and ultimately film physical properties. Investigation of the effect of sto-
Figure 6.4: Growth of the average film thickness \( (h) \) for a range of initial water concentrations at temperature \( T = 3 \) with non-reactive aqueous solvent on a sample \( 40 \times 40 \times 30 \) with 10 independent samples for \( p_H = 0.0115, p_P = 0.023 \) using BFM with reaction proceeding from the substrate.

Figure 6.5 shows the variation of the mean surface height with the time steps for a range of NCO:OH ratios (NCO:OH = 1.0 - 2.2) at temperature \( T = 3 \). The three-step growth, i.e., growth-relaxation-saturation, can still be observed for systems of high NCO:OH ratios, but the intermediate relaxation stage is smoothing out for the low NCO:OH ratio systems (NCO:OH = 1.0, 1.2). The power-law exponents for the initial stage are very close for all the systems of different stoichiometry in WB 2K-PUR systems is thus desired. In our simulation, the concentration of polyol \( (P) \) component is fixed while the concentration of isocyanate \( (H) \) component is adjusted to achieve the desired stoichiometric ratio.
**Table 6.4:** Power-law exponents of initial film growth at different NCO:OH ratios in case 5.

<table>
<thead>
<tr>
<th>NCO:OH</th>
<th>$\gamma_1(B_1)$</th>
<th>$\gamma_2(B_2)$</th>
<th>$\beta_1(C_1)$</th>
<th>$\beta_2(C_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.65(0.07)</td>
<td>0.50(0.11)</td>
<td>0.32(0.50)</td>
<td>0.22(0.66)</td>
</tr>
<tr>
<td>1.2</td>
<td>0.80(0.06)</td>
<td>0.49(0.13)</td>
<td>0.34(0.50)</td>
<td>0.24(0.64)</td>
</tr>
<tr>
<td>1.4</td>
<td>0.77(0.06)</td>
<td>0.49(0.12)</td>
<td>0.38(0.45)</td>
<td>0.24(0.62)</td>
</tr>
<tr>
<td>1.6</td>
<td>0.77(0.06)</td>
<td>0.51(0.12)</td>
<td>0.37(0.47)</td>
<td>0.25(0.63)</td>
</tr>
<tr>
<td>1.8</td>
<td>0.73(0.07)</td>
<td>0.49(0.14)</td>
<td>0.34(0.50)</td>
<td>0.22(0.71)</td>
</tr>
<tr>
<td>2.0</td>
<td>0.75(0.07)</td>
<td>0.50(0.14)</td>
<td>0.35(0.51)</td>
<td>0.23(0.68)</td>
</tr>
<tr>
<td>2.2</td>
<td>0.83(0.06)</td>
<td>0.48(0.15)</td>
<td>0.38(0.49)</td>
<td>0.23(0.68)</td>
</tr>
</tbody>
</table>

NCO:OH ratios in our observation limit, i.e., $\gamma_1 \simeq 0.77$ for early stages and $\gamma_2 \simeq 0.49$ for late stages, as shown in table 6.4. The growth of mean surface height is relatively faster for higher NCO:OH ratios than the lower ones, as more NCO groups are available to react with OH groups. But this difference in growth rates is small as their power-law exponents for initial growth are almost the same. Note that in 2K-PUR systems, an excess amount of NCO is usually used to compensate for any NCO-H$_2$O reactions and to ensure that all available OH groups are consumed by the end of film formation. However, since water is so far considered as non-reactive in case 5, the effect of excess amount of NCO on film growth is not fully revealed as in reactive solvent systems (covered in later chapters).

As cross-linking reactions go on among reactive components ($H$ and $P$), the film develops and the interface front propagates upwardly from the substrate. The thermodynamic equilibrium via stochastic motion of individual constituents can be captured by cross-linking reaction depending on the rate of reaction. Domains of separated hydrophobic and hydrophilic phases may be formed when the reactions are significantly slow increasing difficulties for complete reaction among reactants. Thus it is of importance to
look into the effect of the rate of cross-linking reaction on the film growth and film properties. Figure 6.6 shows the variation of the mean surface height with the time steps for several reaction rates ($R_{HP} = R_{HS} = R_{PS} = 0.01 - 1.0$) at temperature $T = 3$. As can be seen, the intermediate relaxation region for film thickness is smeared out at low reaction rate (e.g., $R = 0.1, 0.01$), while the growth-relaxation-saturation pattern for film growth conserves at high reaction rate. The time for monotonic growth of mean surface height is about one order larger for low reaction rate ($t_x \approx 10^3$) than for high reaction rate ($t_x \approx 10^5$). The early stage of film growth ($t \leq 10$) appears to be independent of reaction
rate as the curves overlap each other for a wide range of reaction rates. The growth rate differs significantly afterwards for different reaction rates, e.g., $\gamma_2 \simeq 0.45$ for $R = 1.0$ in contrast to $\gamma_2 \simeq 0.30$ for $R = 0.01$. The power-law exponents for early and late stages of film thickness growth are documented in table 6.5 for different reaction rates.

![Figure 6.6: Growth of the average film thickness ($h$) for a range of reaction rates at temperature $T = 3$ with non-reactive aqueous solvent on a sample $40 \times 40 \times 30$ with 10 independent samples for $p_H = 0.0115, p_F = 0.023$ with initial water concentration $p_A = 0.0422$ using BFM with reaction proceeding from the substrate.](image)

6.1.2 Interface Width Growth

Now let us examine the effect of constraints on bond formation and length fluctuation on the growth of interface width (film roughness) with BFM. First we look into the variation
Table 6.5: Power-law exponents of initial film growth at different reaction rates in case 5.

<table>
<thead>
<tr>
<th>( R )</th>
<th>( \gamma_1(B_1) )</th>
<th>( \gamma_2(B_2) )</th>
<th>( \beta_1(C_1) )</th>
<th>( \beta_2(C_2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.80(0.068)</td>
<td>0.45(0.18)</td>
<td>0.35(0.51)</td>
<td>0.20(0.76)</td>
</tr>
<tr>
<td>0.5</td>
<td>0.75(0.068)</td>
<td>0.42(0.17)</td>
<td>0.32(0.50)</td>
<td>0.18(0.72)</td>
</tr>
<tr>
<td>0.1</td>
<td>0.75(0.070)</td>
<td>0.38(0.17)</td>
<td>0.35(0.49)</td>
<td>0.14(0.77)</td>
</tr>
<tr>
<td>0.05</td>
<td>0.77(0.069)</td>
<td>0.30(0.22)</td>
<td>0.34(0.47)</td>
<td>0.11(0.84)</td>
</tr>
</tbody>
</table>

of the interface width \( W \) with the time step at different temperatures as shown in figure 6.7 corresponding to height variation presented in figure 6.3. Generally, the interface widths show a non-monotonic growth (with one overshoot) over time for all temperatures. This is in contrast to the oscillatory response (with two overshoots) of the interface width with time in EBFM (see figure 5.10). The interface growth in early stage may however be described by a power law,

\[
W = C t^\beta,
\]

with exponent \( \beta \) which changes from \( \beta_1 \approx 0.38 \) to \( \beta_2 \approx 0.21 \) in time at the temperature \( T = 3 \). These values are much smaller than those in EBFM where \( \beta_1 \approx 0.95 \) is followed by \( \beta_2 \approx 0.66 \) and \( \beta_3 \approx 0.46 \), indicating a slower film growth and roughening. A list of power-law exponents of initial film interface width growth as a function of temperature are documented in table 6.2. The maxima of interface width are smaller in value \( (h_x = 4.8 \) at \( T = 3 \)) and depend more strongly on temperature in BFM than those in EBFM \( (h_x = 9.0 \) at \( T = 3 \)). However, the oscillatory response of interface width in the intermediate stage observed in EBFM at high temperatures is missing due to the restricted bond fluctuation and the slowed down initial growth in BFM. As discussed in chapter 5 (see page 50), the oscillatory response in the interface width is mainly caused by the bond fluctuations of covalent bonded functional groups augmented by the interplay between the thermal energy
and the free volume due to water evaporation. At one hand, the stochastic movement of cross-linked particles is confined in a much narrower range so that the film will not stretch too far before the bond fluctuations respond. On the other hand, the slower approach of film growth due to the strengthened bond formation and fluctuation range renders more time for water particles to evaporate in the duration of cross-linking. This reduces the pore spaces provided by water evaporation in the process of film consolidation. A second maximum in the interface width in the intermediate relaxation region thus disappears in BFM.

Figure 6.7: Evolution of the interface width \(W\) of the film surface for a range of temperatures using the same parameters as in Figure 6.3.

Corresponding growth of the interface width \(W\) for different initial water concentrations at temperature \(T = 3\) is presented in figure 6.8. Similar to the growth pattern of mean surface height, variations of the interface width with time steps have little dependence on
the initial water concentration. This again can be seen from the power-law exponents of early stage of interface width growth, which are shown in table 6.3. The two growth rates, i.e., $\beta_1 \simeq 0.36$ (early stage) and $\beta \simeq 0.21$ (late stage), remain the same with increasing the initial water concentration in the system. The prefactor for high initial water concentration is slightly smaller than the one for low initial water concentration, indicating a relatively slower interface roughening occurs under high initial water concentration. This is consistent with the slower cross-linking reactions under high initial water concentration as water dilutes the concentration of reactants. The maxima of interface width under high initial water concentration, however, are slightly larger than the ones under low initial water concentration. This is likely due to a larger amount of water particles interferes via attractive interactions with hydrophilic ($P$) components. The steady state interface widths, however, seem to overlap each other despite of the differences in initial water concentration.

Figure 6.9 shows the corresponding variation of interface width with time steps for a range of NCO:OH ratios (NCO:OH = 1.0 - 2.2) at temperature $T = 3$. As can be seen, a general monotonic interface width growth persists for all the NCO:OH ratios. The initial growth can be described by power-laws and the exponents are documented in table 6.4. There are two growth rates in the initial stage and each growth rate is about the same for different NCO:OH ratios. Again this indicates the stoicheometry of reacting groups does not have a big impact on the initial growth of interface width with non-reactive aqueous solvent. The system of higher NCO:OH ratio does have higher maxima of interface width in the intermediate stage (and also the steady state value). This is likely due to the higher degree of ramification of the cross-linked network under higher NCO:OH ratio as more NCO groups are available to react with OH groups.

Lastly, we examine the corresponding variation of interface width with time steps for different reaction rates ($R_{HP} = R_{HS} = R_{PS} = 0.01 - 1.0$) at temperature $T = 3$, as shown
Figure 6.8: Evolution of the interface width \((W)\) of the film surface for a range of initial water concentrations using the same parameters as in Figure 6.4.

in figure 6.10. A notable difference in growth pattern is observed between high reaction rate system \((R = 1, 0.5)\) and low reaction rate system \((e.g., R = 0.01)\). In the high reaction rate system, an initial fast growth till reaching some maxima is followed by a relaxation region before achieving the steady state. In the low reaction rate system, however, the interface width growth is very slow and instead of having a “peak” in the intermediate region as in the high reaction rate system, a “valley” is observed before it increases again to reach the steady state. The growth rate of initial stage can be fitted by power-law, which is documented in table 6.5. The early stage of growth seems not be affected by reaction rate, the late stage, however, greatly depends on the reaction rate.
CHAPTER 6. FILM IN NON-REACTIVE SOLVENT

Figure 6.9: Evolution of the interface width (W) of the film surface for a range of NCO:OH ratios using the same parameters as in Figure 6.5.

6.2 Equilibrium

After a non-monotonic growth of film thickness and roughness, a steady state is reached in the asymptotic time limit. This steady state or equilibrium may correspond to the dry film after cure in the laboratory experiment. Various external and internal stimuli can affect the processes of film formation and therefore the final film properties. In this section, we examine the dependence of equilibrium film thickness $h_s$ and film roughness $W_s$ with such parameters as temperature, initial water concentration, NCO:OH ratio and reaction rate in a non-reactive aqueous solvent with BFM.
6.2.1 Film Thickness

Variation of the saturated mean surface height $h_s$, film thickness, with temperature, initial water concentration, NCO:OH ratio and reaction rate are presented in figure 6.11 – figure 6.14, respectively. Mobility of the constituents and corresponding bond lengths depend on the temperature, i.e., higher the temperature, larger is the bond length. Thus, the equilibrium film thickness $h_s$ depends on temperature. Figure 6.11 shows that the film thickness increases on increasing the temperature. At low temperature, mobility of the constituents is small. Attractive interaction among constituents of the same type is dominant in comparison to the thermal energy, increasing the difficulty for complete reactions.
and the time to reach steady state. The film at low temperature may have not reached true equilibrium in the time limit of observation due to the hydrophobic and polar interaction. At high temperature, mobility of the constituents is big and reactions among appropriate constituents are more complete. Moreover, each covalent bond vibrates more resulting in a stretched film with larger film thickness. Figure 6.12 shows that the film thickness decreases linearly on increasing the initial water concentration \( h_s = 7.71 - 6.90 \cdot p_A \).

As water does not participate in the chemical reaction in case 5 and eventually leaves the system via evaporation, this decrease of \( h_s \) with initial water concentration is very slight. Stoicheometry may affect reaction kinetics, particle interactions, phase separation during film formation and ultimately film properties. Figure 6.13 shows that, on increasing the NCO:OH ratio, a fast linear expansion of the film thickness is followed by relatively slow expansion at high NCO:OH ratios. More \( H \) particles (NCO groups) are reacted with \( P \) particles (OH groups) and the substrate at high NCO:OH ratio (concentration of OH groups is fixed) resulting in a thicker film. Competition between thermodynamic equilibrium and cross-linking reaction affect the film formation process as well as the final film properties. Figure 6.14 shows that the film thickness \( h_s \) increases on increasing the reaction rate. At very low reaction rate (e.g., \( R = 0.01 \)), even though the mobility of each constituent is relatively high, many reactants remain un-reacted leading to a thinner film. If the temperature is also very low, cross-linking reaction can be even harder and phase separation may occur. At high reaction rate, on the other hand, thermodynamic equilibrium may be arrested by cross-linking reaction as the mobility of constituents is much limited once they are covalently bonded.

### 6.2.2 Film Roughness

Variation of the saturated interface width \( W_s \), film roughness, with temperature, initial water concentration, NCO:OH ratio and reaction rate are presented in figure 6.15 — fig-
Figure 6.11: Variation of the saturated and near-saturated thickness $h_s$ with the temperature using the same parameter as in Figure 6.3. The statistical errors in data are of the order of symbols sizes.

Figure 6.18, respectively. Temperature not only affects the saturated mean surface height ($h_s$) via mobility of constituents but also affects the saturated interface width ($W_s$). Figure 6.15 shows that on increasing the temperature, film roughness increases with a slow growth at low temperature followed by a fast growth. As temperature increases, the mobility of each constituent increases leading to more active cross-linking reactions as well as bond length fluctuation. As a result, a thicker and rougher film is formed in the asymptotic time limit at high temperatures. Figure 6.16 shows that the steady state film roughness does not depend on the initial water concentration in case 5. As water is considered non-reactive and eventually leaves the system via evaporation, it only affects the growth rates of film thickness and roughness slightly via its dilution effect and its in-
CHAPTER 6. FILM IN NON-REACTIVE SOLVENT

Figure 6.12: Variation of the saturated and near-saturated thickness \( h_s \) with the initial water concentration using the same parameter as in Figure 6.4. The statistical errors in data are of the order of symbols sizes.

Figure 6.17 shows that on increasing the NCO:OH ratio, the steady state film roughness increases linearly with a fast expansion (\( W_s = 1.26 + 0.36 \times (\text{NCO:OH}) \)) followed by a relatively slow expansion (\( W_s = 1.63 + 0.15 \times (\text{NCO:OH}) \)). This trend is consistent with the dependence of steady state film thickness on NCO:OH ratio. As NCO:OH ratio increases, more \( H \) particles involve in the cross-linking reaction leading to a lower density of neighboring bonds for each \( H \) particle (hence a less compact film network). The surface roughens as more dan-
CHAPTER 6. FILM IN NON-REACTIVE SOLVENT

7.0
h = 5.06 + 0.84 * (NCO:OH)
6.5
h = 4.58 + 1.2 * (NCO:OH)
6.0
5.5
1.0
1.5
2.0
2.5
NCO:OH

Figure 6.13: Variation of the saturated and near-saturated thickness $h_s$ with the NCO:OH ratios using the same parameter as in Figure 6.5. The statistical errors in data are of the order of symbols sizes.

gling bonded $H$ particles exist. Figure 6.18 shows that the steady state film roughness $W_s$ increases on increasing the reaction rate. At low reaction rate, many reactive constituents are left behind without bonding to the film network. This results in a thin and relatively smooth film. At high reaction rate, not only the reactions take place much faster but also more reactive particles end up in connecting to each other. Irregularity increases on the film surface.
Figure 6.14: Variation of the saturated and near-saturated thickness $h_s$ with the reaction rates using the same parameter as in Figure 6.6. The statistical errors in data are of the order of symbols sizes.

6.3 Density Profile

In our computer simulation, we are not only able to study the evolution of film growth and the steady state film surface/interface morphology, but also to monitor the bulk properties of the film via density profile. By examining the density profile along the longitudinal direction of the steady state film, we can get important information on film formation such as the distribution of reaction product. This information combined with the film thickness and its interface width can give us insight in the processes involved in the polyurethane film formation. Therefore, it will be interesting to look into the effect of different stimuli.
Figure 6.15: Variation of the saturated and near-saturated roughness $W_s$ with the temperature using the same parameter as in Figure 6.7. The statistical errors in data are of the order of symbols sizes.

on the density profiles of different components.

6.3.1 Effect of Temperature

Figure 6.19 presents the longitudinal density profile of all components in the long time limit at different temperatures ($T = 1.5 - 5.0$). Density ($D$) is defined as the ratio of the number of bonded particles $N_b$ at each layer and the total number of possible particles ($N_{tot}$) occupied at each layer, i.e.,

$$ D = \frac{N_b}{N_{tot}}, \quad (6.3.1.1) $$

Where $N_{tot} = 40 \times 40/4 = 400$. As we can see from Figure 6.19, the layers near the substrate ($y = 0 - 5$, referred as lower layers) are very dense. The density decreases as
Figure 6.16: Variation of the saturated and near-saturated roughness $W_s$ with the initial water concentration using the same parameter as in Figure 6.8. The statistical errors in data are of the order of symbols sizes.

The layers get closer to the film-air interface ($y = 6 - 10$ for low temperature, $y = 6 - 15$ for high temperature, referred as topper layers). At high temperature, the overall film is more expanded than that at low temperature. The density of lower layers increases with increasing the temperature at low temperatures. This is likely due to the incomplete cross-linking reaction among the reactants at very low temperature (e.g., $T = 1.5$), as indicated by the film thickness growth in Figure 6.3. With continual increase of the temperature at high temperatures, the density of lower layers decreases. However, the density of topper layers at high temperature is larger than that at low temperature. This is mainly due to
Figure 6.17: Variation of the saturated and near-saturated roughness $W_s$ with the NCO:OH ratios using the same parameter as in Figure 6.9. The statistical errors in data are of the order of symbols sizes.

the more active bond fluctuation of bonded units at high temperature resulting in a more stretched film.

To track the reaction product distribution, we look at the density profile of individual component along the longitudinal direction. Figure 6.20 shows the density profile of hydrophilic, $P$, component at different temperatures corresponding to Figure 6.19. The density variation of $P$ component with temperature is very similar to the density variation for all components. At low temperature, a peak around $y = 2 - 4$ is observed in the lower layers. At high temperature, a less dense but more uniform film is observed in the lower
CHAPTER 6. FILM IN NON-REACTIVE SOLVENT

Figure 6.18: Variation of the saturated and near-saturated roughness $W_s$ with the reaction rate using the same parameter as in Figure 6.10. The statistical errors in data are of the order of symbols sizes.

layers. The density of $P$ component gradually decreases when the layer gets closer to the film-air interface. At high temperature, the density of $P$ component decreases more slowly than that at low temperature in the topper layers. Thus denser and thicker topper layers are observed at high temperature than at low temperature. Figure 6.21 shows the corresponding density profile of hydrophobic, $H$, component at different temperatures. A peak of $H$ component around $y = 2$ is observed for middle and high temperatures. The density gradually decreases along the upward longitudinal direction with slower decrease at higher temperatures. At low temperature (e.g., $T = 1.5$), however, a valley of $H$ com-

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Figure 6.19: Density profile of all components along the longitudinal direction in the long time limit at different temperatures using the same parameter as in Figure 6.3.

ponent around $y = 3$ is followed by a sharp peak at $y = 6$ in the lower layers. From Figure 6.20 and Figure 6.21, we can see that a dense $P$ layer is formed near the substrate especially at low temperature; a more uniform film with $H$ and $P$ component is achieved at high temperature; a thin $H$ component rich layer is formed in the bulk at low temperature.

6.3.2 Effect of the Initial Water Concentration

Figure 6.22 shows the density profile of all components in the long time limit with different initial water concentrations corresponding to Figure 6.4. As can be seen, a very dense layer ($D = 0.78$) is formed near the substrate. The density then decreases along the longitudinal direction. The initial water concentration seems to have little influence on the density profile as all the curves are almost overlay each other. This is understandable
Figure 6.20: Density profile of $P$ component along the longitudinal direction in the long time limit at different temperatures using the same parameter as in Figure 6.3.

as water particles are not considered reactive so far and eventually leave the system via evaporation.

6.3.3 Effect of NCO:OH Ratio

Figure 6.25 shows the density profile of all components in the long time limit with different NCO:OH ratios corresponding to Figure 6.5. Again, the density decreases along the longitudinal direction after the initial dense layer near the substrate. A slightly less dense film near the substrate and a relatively more dense film in the bulk and near the film-air interface are observed at high NCO:OH ratios. A cross-over appears at $y = 3$ where the density is the same for different NCO:OH ratios. Figure 6.26 and Figure 6.27 show the same trend for density profile of individual $P$ and $H$ components. A smaller density of
Figure 6.21: Density profile of $H$ component along the longitudinal direction in the long time limit at different temperatures using the same parameter as in Figure 6.3.

$P$ component near the substrate exhibits at high NCO:OH ratio than at low ratio. As the content of $P$ component is fixed when the ratio NCO:OH varies, high NCO:OH ratio means more $H$ particles (NCO groups) in the system. More $P$ components react with $H$ in the bulk when $H$ content is high before the $P$ particles fall down to the substrate to react with the substrate. Thus less density of $P$ components exhibits near the substrate at high NCO:OH ratio. However, a slightly larger density of $H$ component near the substrate exhibits at high NCO:OH ratio than at low ratio indicated in Figure 6.27. Again low NCO:OH ratio means less amount of $H$ component present in the system. Hence, the density of $H$ component is smaller throughout the film at low NCO:OH ratio.
Figure 6.22: Density profile of all components along the longitudinal direction in the long time limit at different initial water concentrations using the same parameter as in Figure 6.4.

6.3.4 Effect of Reaction Rate

Figure 6.28 shows the density profile of all components in the long time limit with different reaction rates corresponding to Figure 6.6. A relatively larger film density near the substrate and smaller density near the film-air interface are observed at low reaction rate. Figure 6.29 and Figure 6.30 also show the similar trend for density profile of individual P and H components. This is likely due to the incomplete cross-linking reaction among the reactants and more particles subsiding to the substrate and reacting with the substrate at low reaction rate.
Figure 6.23: Density profile of \( P \) component along the longitudinal direction in the long
time limit at different initial water concentrations using the same parameter as in Figure
6.4.

6.4 Finite Size Effect

To make sure that there is no severe finite size effects, simulations are performed with
different lattice sizes. Variations of film thickness and the interface width for these lattices
are presented in figures 6.31 and 6.32 respectively. There is very little effect of the lattice
size on the qualitative nature of the dependence of film thickness and its interface width.
Figure 6.24: Density profile of H component along the longitudinal direction in the long time limit at different initial water concentrations using the same parameter as in Figure 6.4.
Figure 6.25: Density profile of all components along the longitudinal direction in the long time limit at different NCO:OH ratios using the same parameter as in Figure 6.5.

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Figure 6.26: Density profile of $P$ component along the longitudinal direction in the long time limit at different NCO:OH ratios using the same parameter as in Figure 6.5.
Figure 6.27: Density profile of $H$ component along the longitudinal direction in the long time limit at different NCO:OH ratios using the same parameter as in Figure 6.5.
Figure 6.28: Density profile of all components along the longitudinal direction in the long time limit at different reaction rates using the same parameter as in Figure 6.6.
Figure 6.29: Density profile of $P$ component along the longitudinal direction in the long time limit at different reaction rates using the same parameter as in Figure 6.6.
Figure 6.30: Density profile of H component along the longitudinal direction in the long time limit at different reaction rates using the same parameter as in Figure 6.6.
Figure 6.31: evolution of the film thickness $h$ using BFM for a temperature $T = 5$ with non-reactive aqueous solvent on different sample sizes each with ten independent samples for $p_H = 0.0115$ and $p_P = 0.023$ with initial water concentration $p_A = 0.0422$ (case 5).
Figure 6.32: evolution of the interface width $W$ using BFM for a temperature $T = 5$ with non-reactive aqueous solvent on different sample sizes each with ten independent samples for $p_H = 0.0115$ and $p_P = 0.023$ with initial water concentration $p_A = 0.0422$ (case 5).
Chapter 7

FILM IN REACTIVE SOLVENT

One of our efforts in this work is to construct a computer simulation model which is capable of effectively capturing the characteristics of the film formation process in multi-component polymeric system to study macroscopic properties (interface/surface morphology) of the film.

In previous chapters, we have looked into the film formation with cross-linking reactions taking place between isocyanate \((H)\) and polyol \((P)\) components to form polyurethane. With the presence of a big amount of water in the WB 2K-PUR system, the reaction of isocyanate \((H)\) with water \((A)\) to ultimately form polyurea is unavoidable. Hence, one of our big efforts to make the model more realistic is to incorporate the side reactions between \(H\) and \(A\) components into the model. This is implemented by allowing covalent bonds to be formed between \(H\) and \(A\) particles, leading to a modified hydrophobic particle \(H^*\) which is capable of further reactions. That is, one of the isocyanate groups (-NCO) of the crosslinker is changed to amine groups (-NH\(_2\)) after its reaction with water, and the amine group (-NH\(_2\)) can further react with another isocyanate group (-NCO) to form urea (RNHCONHR\(^{'})\). Two cases are considered concerning the volume of the water particle after its reaction with an \(H\) component. Figure 7.1 illustrates the situation where the volume of water is included (case 6) or excluded (case 7) after reaction. In case 6, water particles remain in and become part of the film network after reaction, thus a much "swollen" film is resulted. The whole combined entity of the \(H\) and \(A\) particle connected with a covalent bond can be viewed as the modified \(H^*\) component, which can form a covalent bond with another \(H\) particle from the side of water particle. The other two unreacted functional
groups of the \( H \) particle can still react with another \( P, A \) or \( H^* \) components. In case 7, water particle vanish or disappear after its reaction with an \( H \) particle. That \( H \) particle, being denoted as \( H^* \) now, "remembers" its reaction with water, hence it can directly form a covalent bond with another \( H, P, A \) or \( H^* \). Though no size distinguish among different components is one of our assumptions to simplify the model, exclusion of water volume from the film after reaction might be more realistic as the hydrolysis reaction of the isocyanate group (-NCO) to form an intermediate amine group (-NH\(_2\)) and release carbon dioxide (CO\(_2\)) shall not change the volume of the cross-linker (\( H \)) much. The number of reactive functional groups \( f \) of each \( H, P, A \) and \( H^* \) particles are chosen to be 3, 2, 1 and 3, respectively, for both cases.

![Figure 7.1: Schematic illustration of the volume of water being (a) included in, or (b) excluded from the film after its reaction with hydrophobic component.](image)

In this chapter, we will investigate various aspects of polyurethane film growth from the substrate in a reactive evaporating aqueous solvent with bond fluctuation model (BFM). The two cases of inclusion or exclusion of the volume of water particle after reaction will be discussed (see table 7.1 for parameters used in these cases). To get more insight of the effect of strengthened bond formation and length fluctuation constraint on film formation in reactive solvent, simulation results of case 6 for a range of temperatures will be compared with the data generated by EBFM. Results will also be compared with film growth in non-reactive solvent. These results are published in [97].
CHAPTER 7. FILM IN REACTIVE SOLVENT

Table 7.1: Parameters used in case 6 and 7.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2 \leq r \leq \sqrt{10}$ excluded $\sqrt{8}$</td>
</tr>
<tr>
<td>2</td>
<td>$p_P = 0.0115$, $p_H = 0.0230$, $p_A = 0.0422$</td>
</tr>
<tr>
<td>3</td>
<td>$f_P = 2$, $f_H = 3$, $f_A = 1$</td>
</tr>
<tr>
<td>4</td>
<td>$R_{HP} = R_{HS} = R_{PS} = R_{HA} = R_{HH} = 1$, $R_{HH} = R_{PP} = 0$</td>
</tr>
<tr>
<td>6</td>
<td>$M_P = 0.3$, $M_H = 1.5$, $M_A = 0.03$</td>
</tr>
<tr>
<td>7</td>
<td>film propagates from the substrate</td>
</tr>
</tbody>
</table>

7.1 Film Growth

7.1.1 Surface Height Growth

First we look at the surface height growth in case 6 where water participates in the chemical reaction and remains in the film after reaction. Figure 7.2 shows the variation of the mean film thickness $h$ with the time steps for a range of temperatures ($T = 1, 1.5, \ldots, 5$) with reactive aqueous solvent on a log-log plot. Two general characteristics are observed at all temperatures, a growth followed by saturation. The film growth may be described by a power-law,

$$h = B t^\gamma,$$

(7.1.1.1)

with an index $\gamma$ and a prefactor $B$. There may be more than one power-laws for growth depending on kinetics and time regime. For example, at temperature $T = 5$ (indicated by dashed lines) we see two growth rates, a relatively rapid growth described by $\gamma \approx 0.97$ followed by $\gamma \approx 0.77$ (see figure 7.2). For comparison, we also present the evolution of film thickness with the effective bond fluctuation model (EBFM) [96] in figure 7.2. At a first glance, the wider range for a bond formation and its length fluctuation with EBFM does not change the pattern of film growth, i.e., an initial power-law growth is followed...
by a steady state saturation. However, a closer look reveals important differences. First, a much faster initial growth is observed in EBFM with $\gamma \approx 1.84$ followed by $\gamma \approx 1.34$ at temperature $T = 5$, i.e., with almost twice the value of corresponding exponents in BFM. The crossover time from film growth to saturation in BFM is about an order larger ($t_x \approx 10^2$) at high temperature and two orders ($t_x \approx 10^3$) at low temperature than that in EBFM. This shows a notably slower film growth with BFM as expected. Further, the saturated film thicknesses are smaller in BFM than those in EBFM especially at low temperatures.

Aqueous solvent (i.e., the humidity) plays an important role in controlling the film morphology including its surface roughening [4, 25, 28]. Therefore, it is worth examining the evaporation fraction of the aqueous component involved in reaction. In figure 7.3, we present the variation of reacted aqueous component with the time step. We see that the fraction of reacted aqueous component increases before reaching a steady state saturation $C_S$. The steady-state concentration of aqueous component ($C_S$) in EBFM is found to be insensitive to temperature. In contrast, the steady-state concentration ($C_S$) of reacted aqueous component in BFM, depends on temperature particularly in low temperature regime. For example, $T = 5$, $C_S \approx 65\%$ of its initial concentration $C_A$. $C_S$ decreases on reducing the temperature, i.e., $C_S \approx 20\%$ of $C_A$ at $T = 1$. As bonds are constrained to form between nearest neighboring particles and bond lengths are restricted to fluctuate within a much limited range in BFM in comparison to EBFM, the cross-linking reactions slow down significantly in BFM. This is due to lower probability of reaction among appropriate components within their nearest neighbor range ($r = 2$) in BFM than that in EBFM where the range of reaction is relatively large ($r \leq \sqrt{27}$). The differences become more pronounced at low temperature where the overall mobility of each component is small and many aqueous constituents evaporate before they move next to hydrophobic components for reaction to occur. The film is thus much less “swollen” in BFM by the
Figure 7.2: Growth of the average film thickness \( (h) \) for a range of temperatures with reactive aqueous solvent on a sample \( 40 \times 40 \times 30 \) with 10 independent samples for \( p_H = 0.0115, p_D = 0.023 \) with initial water concentration \( p_A = 0.0422 \) using BFM with reaction proceeding from the substrate (case 6). The upper plot is for the systems using BFM and the lower plot is for the systems using EBFM.

The volume of reacted water at low temperatures as much of the aqueous constituents eventually leave the system via evaporation. The high mobility of each constituent at high temperature leads to a high reaction probability as the probability of a particle to come next to reacting particles is higher. A substantial portion of water particles are thus able to react with \( H \) components at high temperature. Therefore, the restriction on bond length has less effect on film thickness at high temperature where film thickness in BFM is comparable to that in EBFM.
Figure 7.3: (a) Growth of reacted water concentration using EBFM, (b) growth of reacted water concentration using BFM, (c) growth of evaporated water concentration using EBFM, and (d) growth of evaporated water concentration using BFM for a range of temperatures on a 40 x 40 x 30 sample with ten independent samples for $p_H = 0.0115, p_P = 0.023$ with initial water concentration $p_A = 0.0422$.

We would also like to point out that the growth pattern of mean surface height with reactive aqueous solvent $A$ (in BFM or EBFM) differs from their corresponding systems with non-reactive solvent $A$ in which three stages of film growth are clearly observed at all temperatures (case 4, 5). That is, an initial fast growth of the mean surface height followed by a relatively slow relaxation before approaching a steady state. With the reactive aqueous solvent, however, the intermediate stage of film relaxation is lost; at least it is much less obvious due to the side reaction between hydrophobic ($H$) component and water ($A$) (see figure 4.2). Since the initial water concentration is high, a significant amount of water
particles participate in hydrolysis reaction of isocyanate groups (H) leading to modified H* particles before they have a chance to evaporate from the top surface. The side reaction between H and A components consumes only one isocyanate group of H particle at a time but the modified hydrophobic group H* can further react with another H leading to more consumption of H components in the system. Moreover, since the aqueous constituents are retained in the film after reaction, it further contributes to a “swollen” film. As pointed out above, 65% of initial aqueous component is retained via reaction while 35% evaporates at T = 5 (see figure 7.3), in contrast to 100% water evaporates from the system at the temperature T = 5 in non-reactive aqueous solvent [96]. The decay of film thickness due to film consolidation via water evaporation is considerably reduced with the reactive aqueous solvent in comparison to non-reactive aqueous solvent [96]. The film thickness, hence, remains nearly constant (more stable) after its initial growth with reactive aqueous solvent.

Figure 7.4 shows the variation of the mean film thickness h with the time steps for a range of temperatures (T = 1 – 5) in case 7 where the volume of aqueous component is excluded after its reaction with hydrophobic component. In comparison to case 6 (see figure 7.2, several obvious differences exhibit in the film thickness growth in case 7. First, a slower initial growth is observed in case 7 with γ₁ ≈ 0.88 followed by γ₂ ≈ 0.67 and γ₃ ≈ 0.41 at temperature T = 5 in comparison to γ ≈ 0.97 followed by γ ≈ 0.77 in case 6. The crossover time from film growth to saturation in case 7 is about an order larger (tₓ ≈ 10⁴ for low temperature and tₓ ≈ 10³ for high temperature) than that in case 6 (tₓ ≈ 10³ for low temperature and tₓ ≈ 10² for high temperature). Second, the intermediate maximum thickness and saturated thickness are much smaller in value in case 7 than those in case 6. For example, the saturated film thickness in case 6 at T = 5 (hₛ = 27.0) is about two times of the value in case 7 at the same temperature (hₛ = 12.5). Moreover, an overshoot of film thickness exhibits at high temperatures in case 7 while such an overshoot is absent in case...
6. Since the concentration of water used in these simulations is high comparing to other reactive components, the side reaction between hydrophobic component and water is very significant. As the volume of water is excluded out of the film after reaction in case 7, the "swollen" effect by reactive aqueous component no long exists. Thus a significantly slower film growth and thinner film is produced as a result. A list of power-law exponents of initial film growth as a function of temperature are documented in table 7.2.

Figure 7.4: Growth of the average film thickness ($h$) for a range of temperatures with reactive aqueous solvent on a sample $40 \times 40 \times 30$ with 10 independent samples for $p_H = 0.0115$, $p_p = 0.023$ with initial water concentration $p_A = 0.0422$ using BFM with reaction proceeding from the substrate (case 7).

Figure 7.5 shows the variation of the mean surface height with the time steps for a range of initial water concentrations ($p_A = 0.024 - 0.042$) at temperature $T = 3$ in case 7. As can be seen, a slightly slower growth in the initial stage and a slightly larger steady...
Table 7.2: Power-law exponents of initial film growth at different temperatures in case 7.

<table>
<thead>
<tr>
<th>T</th>
<th>$\gamma_1(B_1)$</th>
<th>$\gamma_2(B_2)$</th>
<th>$\beta_1(C_1)$</th>
<th>$\beta_2(C_2)$</th>
<th>$\beta_3(C_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.76(0.059)</td>
<td>0.52(0.13)</td>
<td>0.36(0.46)</td>
<td>0.26(0.57)</td>
<td>0.15(0.90)</td>
</tr>
<tr>
<td>1.5</td>
<td>0.83(0.053)</td>
<td>0.55(0.13)</td>
<td>0.42(0.43)</td>
<td>0.32(0.52)</td>
<td>0.22(0.73)</td>
</tr>
<tr>
<td>2.0</td>
<td>0.80(0.062)</td>
<td>0.53(0.16)</td>
<td>0.38(0.48)</td>
<td>0.30(0.56)</td>
<td>0.20(0.79)</td>
</tr>
<tr>
<td>3.0</td>
<td>0.83(0.066)</td>
<td>0.67(0.10)</td>
<td>0.40(0.48)</td>
<td>0.32(0.55)</td>
<td>0.26(0.66)</td>
</tr>
<tr>
<td>4.0</td>
<td>0.88(0.061)</td>
<td>0.67(0.11)</td>
<td>0.44(0.46)</td>
<td>0.32(0.58)</td>
<td>0.27(0.67)</td>
</tr>
<tr>
<td>5.0</td>
<td>0.88(0.063)</td>
<td>0.67(0.12)</td>
<td>0.41(0.48)</td>
<td>0.32(0.58)</td>
<td>0.21(0.86)</td>
</tr>
</tbody>
</table>

state film thickness exhibit at higher initial water concentration. Even though the higher initial water concentration creates more opportunity for $H$ component to react with water particles initially, the film growth is hindered by the dilution effect of high water concentration which decreases the possibility that a modified $H^*$ particle is next to another $H$ particle for further reaction to occur. Thus a slightly slower initial film growth is observed with higher initial water concentration. In the intermediate time region, however, the dilution effect decreases as a significant amount of water has left the system via evaporation. The film growth rate with high initial water concentration catches up. In the long time limit, more water particles are reacted and hence more $H$ components are consumed with the higher initial water concentration than the lower ones resulting in a slightly thicker film with higher initial water concentrations. A list of power-law exponents of initial film growth as a function of initial water concentration are documented in table 7.3.

Figure 7.6 shows the variation of the mean surface height with the time steps for a range of NCO:OH ratios (NCO:OH = 1.0 - 2.2) at temperature $T = 3$ in case 7. As increasing the NCO:OH ratio, the film thickness grows faster in all time regions and a thicker saturated film achieves in the long time limit. This is well understandable. As NCO:OH
Figure 7.5: Growth of the average film thickness ($h$) for a range of initial water concentration at temperature $T = 3$ with reactive aqueous solvent on a sample $40 \times 40 \times 30$ with 10 independent samples for $p_H = 0.0115, p_P = 0.023$ using BFM with reaction proceeding from the substrate (case 7).

Ratio increases, more hydrophobic particles $H$ are present in the system, increasing the probability of reacting with both the $P$ component and the aqueous component $A$. The modified $H^*$ component can further react with other $H$ components, so more $H$ particles are consumed at higher NCO:OH ratios. A list of power-law exponents of initial film growth as a function of NCO:OH ratio are documented in table 7.4.

Figure 7.7 shows the variation of the mean surface height with the time steps for several reaction rates ($R_{HP} = R_{HS} = R_{PS} = 0.01 - 1$) at temperature $T = 3$ in case 7. As can be seen, a two-stage monotonic growth followed by a saturation stage without the
CHAPTER 7. FILM IN REACTIVE SOLVENT

Table 7.3: Power-law exponents of initial film growth at different initial water concentrations in case 7.

<table>
<thead>
<tr>
<th>$p_A$</th>
<th>$\gamma_1(B_1)$</th>
<th>$\gamma_2(B_2)$</th>
<th>$\beta_1(C_1)$</th>
<th>$\beta_2(C_2)$</th>
<th>$\beta_3(C_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.024</td>
<td>0.92(0.09)</td>
<td>0.64(0.16)</td>
<td>0.43(0.56)</td>
<td>0.27(0.72)</td>
<td>0.13(1.21)</td>
</tr>
<tr>
<td>0.027</td>
<td>0.87(0.10)</td>
<td>0.60(0.17)</td>
<td>0.39(0.59)</td>
<td>0.25(0.76)</td>
<td>0.17(1.01)</td>
</tr>
<tr>
<td>0.030</td>
<td>0.87(0.08)</td>
<td>0.68(0.13)</td>
<td>0.41(0.55)</td>
<td>0.28(0.69)</td>
<td>0.15(1.10)</td>
</tr>
<tr>
<td>0.033</td>
<td>0.79(0.09)</td>
<td>0.69(0.11)</td>
<td>0.37(0.57)</td>
<td>0.28(0.66)</td>
<td>0.18(0.97)</td>
</tr>
<tr>
<td>0.036</td>
<td>0.79(0.08)</td>
<td>0.71(0.10)</td>
<td>0.37(0.54)</td>
<td>0.32(0.58)</td>
<td>0.18(0.97)</td>
</tr>
<tr>
<td>0.039</td>
<td>0.86(0.07)</td>
<td>0.72(0.09)</td>
<td>0.37(0.51)</td>
<td>0.31(0.56)</td>
<td>0.23(0.77)</td>
</tr>
<tr>
<td>0.042</td>
<td>0.83(0.06)</td>
<td>0.72(0.08)</td>
<td>0.39(0.48)</td>
<td>0.31(0.55)</td>
<td>0.23(0.74)</td>
</tr>
</tbody>
</table>

Table 7.4: Power-law exponents of initial film growth at different NCO:OH ratios in case 7.

<table>
<thead>
<tr>
<th>NCO : OH</th>
<th>$\gamma_1(B_1)$</th>
<th>$\gamma_2(B_2)$</th>
<th>$\gamma_3(B_3)$</th>
<th>$\beta_1(C_1)$</th>
<th>$\beta_2(C_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.87(0.06)</td>
<td>0.73(0.07)</td>
<td>0.54(0.12)</td>
<td>0.41(0.45)</td>
<td>0.30(0.56)</td>
</tr>
<tr>
<td>1.2</td>
<td>0.90(0.06)</td>
<td>0.70(0.08)</td>
<td>0.59(0.11)</td>
<td>0.42(0.46)</td>
<td>0.29(0.58)</td>
</tr>
<tr>
<td>1.4</td>
<td>0.87(0.06)</td>
<td>0.75(0.08)</td>
<td>0.58(0.13)</td>
<td>0.40(0.48)</td>
<td>0.30(0.58)</td>
</tr>
<tr>
<td>1.6</td>
<td>0.95(0.05)</td>
<td>0.71(0.08)</td>
<td>0.66(0.09)</td>
<td>0.44(0.44)</td>
<td>0.31(0.53)</td>
</tr>
<tr>
<td>1.8</td>
<td>0.90(0.06)</td>
<td>0.80(0.07)</td>
<td>0.64(0.11)</td>
<td>0.42(0.47)</td>
<td>0.30(0.59)</td>
</tr>
<tr>
<td>2.0</td>
<td>0.95(0.06)</td>
<td>0.75(0.09)</td>
<td>0.64(0.12)</td>
<td>0.43(0.46)</td>
<td>0.29(0.61)</td>
</tr>
<tr>
<td>2.2</td>
<td>0.90(0.06)</td>
<td>0.75(0.08)</td>
<td>0.67(0.10)</td>
<td>0.41(0.48)</td>
<td>0.28(0.62)</td>
</tr>
</tbody>
</table>

intermediate relaxation region is observed for all reaction rates at $T = 3$. The early stage of film growth ($t \leq 10$) appears to be independent of reaction rate as the curves overlap each other for a wide range of reaction rates. The growth rate then differs significantly afterwards for different reaction rates, e.g., $\gamma_2 \simeq 0.68$ for $R = 1.0$ in contrast to $\gamma_2 \simeq 0.28$ for $R = 0.01$. The time for monotonic growth of mean surface height is about one
Figure 7.6: Growth of the average film thickness \((h)\) for a range of NCO:OH ratios at temperature \(T = 3\) with reactive aqueous solvent on a sample \(40 \times 40 \times 30\) with 10 independent samples for \(p_H = 0.0115, p_P = 0.023\) with initial water concentration \(p_A = 0.0422\) using BFM with reaction proceeding from the substrate (case 7).

order larger for low reaction rate \((t_x \approx 10^4)\) than for high reaction rate \((t_x \approx 10^3)\). These characteristics are somewhat similar to the film thickness variation with time in case 5 where the aqueous component is non-reactive. The power-law exponents for early and late stages of film thickness growth are documented in table 7.5 for different reaction rates.
CHAPTER 7. FILM IN REACTIVE SOLVENT

Figure 7.7: Growth of the average film thickness \( h \) for a range of reaction rates at temperature \( T = 3 \) with reactive aqueous solvent on a sample \( 40 \times 40 \times 30 \) with 10 independent samples for \( p_H = 0.0115 \), \( p_p = 0.023 \) with initial water concentration using BFM with reaction proceeding from the substrate (case 7).

Table 7.5: Power-law exponents of initial film growth at different reaction rates in case 7.

<table>
<thead>
<tr>
<th>( R )</th>
<th>( \gamma_1(B_1) )</th>
<th>( \gamma_2(B_2) )</th>
<th>( \beta_1(C_1) )</th>
<th>( \beta_2(C_2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.84(0.065)</td>
<td>0.68(0.10)</td>
<td>0.37(0.50)</td>
<td>0.28(0.62)</td>
</tr>
<tr>
<td>0.5</td>
<td>0.74(0.071)</td>
<td>0.56(0.12)</td>
<td>0.32(0.52)</td>
<td>0.25(0.61)</td>
</tr>
<tr>
<td>0.1</td>
<td>0.71(0.071)</td>
<td>0.37(0.18)</td>
<td>0.29(0.52)</td>
<td>0.14(0.78)</td>
</tr>
<tr>
<td>0.05</td>
<td>0.74(0.070)</td>
<td>0.28(0.25)</td>
<td>0.32(0.51)</td>
<td>0.10(0.87)</td>
</tr>
</tbody>
</table>

7.1.2 Interface Width Growth

Now let us examine the growth of the interface width \( W \) for case 6. Figure 7.8 shows the variation of the interface width \( W \) with the time step at different temperatures (see figure...
7.2 for growth in film thickness). Generally, the interface widths show a non-monotonic growth over time for all temperatures with visible changes in pattern with temperature, for both BFM and EBFM systems. The interface growth in early stage may however be described by a power-law, i.e., \( W = C t^\beta \), where \( C \) is a constant and \( \beta \) is an index. The growth exponent depends on time regime and details of the model. Since important improvements are made in BFM over EBFM, a more realistic film growth results with the former which can be illustrated better by pointing out differences in results. First, we observe that the overall fluctuation in interface width data at each temperature is much smaller in BFM than that in EBFM. Since the shortcoming of over bond-fluctuation and over-relaxed constraints on exclude volume with EBFM has been corrected in BFM, a better relaxed and equilibrated film surface is achieved with BFM as a result. Second, the initial growth of the interface width \( (W = C t^\beta) \) is much slower in BFM with power law exponent \( \beta_1 \approx 0.40 \) (initially) and \( \beta_2 \approx 0.25 \) (later stage) in comparison to \( \beta_1 \approx 1.05 \) (initially) and \( \beta_2 \approx 0.60 \) (later stage) in EBFM at the temperature \( T = 5 \). This is attributed to a sharply reduced probability of available reactive particles due to narrow range of bond formation \( (r = 2) \) and its fluctuation range with BFM. The overall slowing down of the film growth in BFM leads to a more gradual interface development rendering more time for surface relaxation.

Third, the restriction in bond formation and fluctuation affects the rate of water reaction and water evaporation during film formation resulting in different patterns of interface growth in the intermediate time region, which is more pronounced at higher temperatures. For example, at the temperature \( T = 5 \), Figure 7.3 shows that about the same amount of water participates in the steady-state kinetic reaction (65%, \( p_A = 0.0273 \)) in both EBFM and BFM despite of different bond length constraints. However, different rate of water reaction and water evaporation results at different time region in these systems (see figure 7.3). With EBFM, a slow concentration increase occurs in the region \( t = 10^2 - 10^3 \) for
both water reaction and evaporation (figure 7.3a and 7.3c), resulting in an intermediate stable stage for the interface width (see figure 7.8). The slowing down of water reaction and evaporation in this region is likely due to the substantially reduced free water concentration as water reaction is very fast at the initial stage in EBFM. In the following time region ($t = 10^3 - 10^4$), however, no water further reacts but a significant amount (17%) of water continues to evaporate (figure 7.3c) from the system. This is almost half of the total amount of water evaporated, leading to a second time increase of the interface width as water evaporation provides more free space for the stochastic movement of particles.

In BFM system, in contrast, water evaporates at a relatively and constant high rate before
the time step \( t = 10^3 \), no water further evaporates afterwards (figure 7.3d). Yet a gradual decrease of interface width is detected in the following time region \( t = 10^3 - 10^4 \) (see figure 7.8) which is likely due to the additional amount of water (12%) participated in the reaction. Differences in the bond formation and bond fluctuation constraints using EBFM and BFM lead to different patterns in interface relaxation due to interplay and competition between water reaction and water evaporation. Lastly, we would like to point out that the non-monotonic growth of the interface width in this study distinguishes from the oscillatory response of the interface width in a non-reactive aqueous solvent system [96] where the interface width has two overshoots before it finally relaxes to a saturated value. The oscillatory response of the interface width in non-reactive solvent system is mainly caused by the free volume due to water evaporation [96]. The large amount of water retention via the side reaction in this study appears to smooth (smear) out the interface width just after its first overshoot and leads to a more stable relaxation afterwards.

Figure 7.9 shows the variation of the interface width \( W \) with the time steps for a range of temperatures \( (T = 1 - 5) \) in case 7 corresponding to figure 7.4. In comparison to case 6 in which water particle retains in the film after its reaction, notable differences are observed in case 7. First, the initial interface width growth is comparable for case 6 and 7. For example, at temperature \( T = 5 \) an initial growth with \( \beta_1 \simeq 0.41 \) followed by \( \beta_2 \simeq 0.32 \) and \( \beta_3 \simeq 0.21 \) in case 7 is in comparison to \( \beta \simeq 0.40 \) followed by \( \beta \simeq 0.25 \) in case 6. However, the crossover time from film growth to relaxation in case 7 is about an order larger (\( t_x \approx 10^4 \) for low temperature and \( t_x \approx 10^3 \) for high temperature) than that in case 6 (\( t_x \approx 10^3 \) for low temperature and \( t_x \approx 10^2 \) for high temperature). Second, the intermediate maximum thickness have a strong temperature dependence and are smaller in value in case 7 than those in case 6. Since the volume of water is excluded out of the film after reaction in case 7, the "swollen" effect by reactive aqueous component no long exists. As the temperature decreases, the overshoot which is previously magnified
by the "swollen" effect becomes smaller in case 7. Moreover, the relaxation time for the interface width to reach steady-state value is much longer in case 7 than that in case 6.

Figure 7.9: Evolution of the interface width (W) of the film surface for a range of temperatures using the same parameters as in Figure 7.4.

Corresponding growth of the interface width W for different initial water concentrations at temperature $T = 3$ in case 7 (see figure 7.5 for film thickness growth) is presented in figure 7.10. Again, increasing the initial water concentration, a slightly slower interface width growth in the early growth stage is followed by a slightly faster interface width growth in the late growth stage. The crossover of this different growth stage for different initial water concentrations is around $t = 10^2$. As a result, a larger value overshoot is found for the system with higher initial water concentration. The saturated interface widths, however, are about the same for different initial water concentrations. As the film growth can be hindered by the presence of huge amount of water which delays the ad-
adjacent contact of the main reactants ($H, P$ and $H^*$), a slightly slower initial film growth is observed with higher initial water concentration. As water continues to evaporate, this "dilution" effect by the aqueous component attenuates. Now more $H$ particles are consumed in high initial water concentration system as more $H^*$ particles exist as a result of active $H - A$ reaction in the earlier stage. The interface width growth rate with high initial water concentration thus catches up. Though a slightly thicker film results with high initial water concentration, the saturated film roughness for different initial water concentrations does not have much difference.

![Figure 7.10](image)

*Figure 7.10:* Evolution of the interface width ($W$) of the film surface for a range of initial water concentrations using the same parameters as in Figure 7.5.

Figure 7.11 shows the corresponding variation of interface width with time steps for a

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range of NCO:OH ratios (NCO:OH = 1.0 - 2.2) at temperature $T = 3$ in case 7 (see figure 7.6 for film thickness growth). As can be seen, the general growth-relaxation-saturation pattern persists for all the NCO:OH ratios. The initial growth can be described by power-laws and the exponents are documented in table 7.4. There are two growth rates in the initial stage and the growth rate of later stage is slightly larger for higher NCO:OH ratios. Moreover, the system of higher NCO:OH ratio has higher steady-state interface width in the long time limit. This is likely due to the higher degree of ramification on the surface of the cross-linked network under higher NCO:OH ratio as more dangling $H^*$ particles are present near the film-air interface due to higher initial $H$ concentration in the system.

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{figure7.11.png}
\caption{Evolution of the interface width ($W$) of the film surface for a range of NCO:OH ratios using the same parameters as in Figure 7.6.}
\end{figure}

The corresponding variation of interface width with time steps for different reaction rates ($R_{HP} = R_{HS} = R_{PS} = 0.01 - 1$) at temperature $T = 3$ in case 7 is shown in figure

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7.12. A notable difference in growth pattern is noticed between high reaction rate system \((R = 1, 0.5)\) and low reaction rate system (e.g., \(R = 0.01\)). In the high reaction rate system, an initial fast interface width growth with an overshoot is followed by a relaxation region before reaching the steady-state film roughness. In the low reaction rate system, in contrast, a very slow interface width growth is followed by a "valley" instead of a "peak" in the intermediate region before the interface width increases again to reach the steady state. This uncommon pattern of interface width growth is also observed at low reaction rate in case 5 where the aqueous component is treated as non-reactive. The growth rate of initial stage can be fitted by power-law, which is documented in table 6.5. The early stage of growth seems not be affected by reaction rate, the late stage, however, greatly depends on the reaction rate.

![Figure 7.12: Evolution of the interface width (W) of the film surface for a range of Reaction rates using the same parameters as in Figure 7.7.](image-url)
7.2 Equilibrium

7.2.1 Film Thickness

Variation of the steady-state film thickness \( h_s \) with the temperature for case 6 is presented in figure 7.13. Clearly, there are two growth regimes, the fast growth of the film thickness in low temperature slows down considerably in the high temperature regime. This implies that temperature plays more important role in low temperature regime in orchestrating the film thickness. For comparison we have also presented corresponding variation with EBFM, where the growth rate of steady-state film thickness with temperature is lower than that in BFM. The steady-state film thickness \( h_s \) increases on increasing the temperature which is qualitatively consistent with laboratory observation.

Variation of the saturated film thickness \( h_s \) with temperature, initial water concentration, NCO:OH ratio and reaction rate in case 7 are presented in figure 7.14 — figure 7.17, respectively. Figure 7.14 shows that the film thickness increases on increasing the temperature. There are two stages of growth, i.e., a fast linear expansion at low temperatures is followed by a relatively slow linear expansion at high temperatures. At low temperature, reactions may not be complete as mobility of the constituents is small. A thin film is resulted at low temperature with many reactive constituents left unreacted. At high temperature, mobility of the constituents is big and reactions among appropriate constituents are more complete. Moreover, each covalent bond vibrates more resulting in a stretched film with larger film thickness. Figure 7.15 shows that the film thickness increases linearly on increasing the initial water concentration \( h_s = 7.59 + 50.95 p_A \). As water participates in the chemical reaction, more hydrophobic \( H \) particles are consumed as a result of the side reaction. The higher the initial water concentration, the thicker the film. Figure 7.16 shows that the film thickness increase linearly on increasing the NCO:OH ratio \( h_s = 4.71 + 2.46 \times (\text{NCO}:\text{OH}) \). As \( H \) component can react with either \( P \)
CHAPTER 7. FILM IN REACTIVE SOLVENT

Figure 7.13: Variation of the saturated and near-saturated thickness $h_s$ with the temperature using the same parameter as in Figure 7.2 (case 6). The statistical errors in data are of the order of symbols sizes.

component or A component and the latter reaction can lead to further consumption of H component, more H particles are able to be a part of the film at high NCO:OH ratio resulting in a thicker film. Figure 7.17 shows that the film thickness $h_s$ increases on increasing the reaction rate. At very low reaction rate (e.g., $R = 0.01$), even though the mobility of each constituent is relatively high, many reactants remain un-reacted leading to a thin film. If the temperature is also very low, cross-linking reaction can be even harder and phase separation may occur. At high reaction rate, on the other hand, thermodynamic equilibrium may be arrested by cross-linking reaction as the mobility of constituents is

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much limited once they are covalently bonded.

\[ h = 5.48 + 1.39 \times T \]
\[ h = -0.31 + 4.3 \times T \]

Figure 7.14: Variation of the saturated and near-saturated thickness \( h_s \) with the temperature using the same parameter as in Figure 7.4 (case 7). The statistical errors in data are of the order of symbols sizes.

7.2.2 Film Roughness

Variation of saturated interface width, i.e., the steady state roughness \( W_s \), with temperature in case 6 is presented in figure 7.18. For comparison we have also presented corresponding variation with EBFM. Generally, the saturated or near-saturated interface width \( W_s \) is found to increase slightly with the temperature at lower temperatures. However, it decreases on further increasing the temperature. At low temperature, the systems do not
CHAPTER 7. FILM IN REACTIVE SOLVENT

Figure 7.15: Variation of the saturated and near-saturated thickness $h_s$ with the initial water concentration using the same parameter as in Figure 7.5 (case 7). The statistical errors in data are of the order of symbols sizes.

seem to have reached full equilibrium within our observation time limit due to the low mobility of the constituents. Therefore, corresponding data are not as reliable (see a large fluctuation in data at low $T$ with BFM). At high temperatures on the other, logarithmic scalings are found to fit the data $W_s = A + Bln(T)$ with coefficient $B = -1.39$ for BFM system and $B = -0.94$ for EBFM system. This is in contrast to previous study with non-reactive aqueous solvent where the interface continues to increase with the temperature.

At higher temperatures, the density of the film becomes higher as the cross-linking increases, which reduces the fluctuation (i.e., heterogeneity) and hence the interface width,
even though the film expands on raising the temperature (figure 7.13). It is, however, consistent with earlier work [26] where a fixed bond length model is employed. It is important to point out that the saturated or near-saturated interface width is smaller in BFM than that in EBFM at each temperature, indicating a smoother film surface is achieved by BFM over EBFM.

Variation of the saturated interface width $W_s$, film roughness, with temperature, initial water concentration, NCO:OH ratio and reaction rate in case 7 are presented in figure 7.19 – figure 7.22, respectively. Figure 7.19 shows that on increasing the temperature, film

$$h_s = 4.71 + 2.46 \times \text{(NCO:OH)}$$

*Figure 7.16*: Variation of the saturated and near-saturated thickness $h_s$ with the NCO:OH ratio using the same parameter as in Figure 7.6 (case 7). The statistical errors in data are of the order of symbols sizes.
roughness first increases at low temperature and then decreases sharply at higher temperature followed by slight increase as continue to increase temperature. At low temperature, the reactions are hardly complete and the film hardly relaxes to its full extent due to the small mobility of segments under low temperature. As temperature increases, the mobility of each constituent increases leading to more complete cross-linking reactions which reduce the film roughness. As temperature continues to increase, the roughness goes up slightly due to the more active bond length fluctuation at high temperatures. Figure 7.20 shows that the steady state film roughness first decreases and then increases on increasing
Figure 7.18: Variation of the saturated and near-saturated roughness $W_s$ with the temperature using the same parameter as in Figure 7.8 (case 6). The statistical errors in data are of the order of symbols sizes.

The initial water concentration though the overall changes are not very big in case 7. As the hydrophobic component can react with water, film roughness decreases as the extra consumed $H$ particles due to hydrolysis reaction tend to decrease the heterogeneity of the film structure. On the other hand, more dangling $H$ and $H^*$ particles are produced near the surface as a result of the side reaction. Thus film roughness goes up at high initial water concentrations. Figure 7.21 shows that on increasing the NCO:OH ratio, the steady state film roughness first decreases at low NCO:OH ratio and then increases at higher NCO:OH ratios. At low NCO:OH ratio, increasing NCO:OH ratio enables more
CHAPTER 7. FILM IN REACTIVE SOLVENT

$H$ particles to involve in the cross-linking reaction reducing the pore of the film structure. The film roughness decreases a little bit with increasing the NCO:OH ratio. At higher NCO:OH ratio, however, the surface roughens if increasing the NCO:OH ratio as more dangling bonded $H$ and $H^*$ particles hanging at the surface area. Figure 7.22 shows that the steady state film roughness $W_s$ slightly increases on increasing the reaction rate. At low reaction rate, many reactive constituents are left behind without bonding to the film network. This results in a thin and relatively smooth film. At high reaction rate, not only the reactions take place much faster but also more reactive particles end up in connecting to each other. Irregularity increases on the film surface.

\[ W_s \]

\[ \begin{array}{c}
\text{Figure 7.19: Variation of the saturated and near-saturated roughness } W_s \text{ with the temperature using the same parameter as in Figure 7.9 (case 7). The statistical errors in data are of the order of symbols sizes.}
\end{array} \]
CHAPTER 7. FILM IN REACTIVE SOLVENT

7.3 Density Profile

7.3.1 Effect of Temperature

Figure 7.23 presents the combined density profile of all components in the long time limit at different temperatures \( T = 1.0 - 5.0 \) in case 7. The film starts with some relatively dense layers near the substrate and the density increases for the middle bulk layers \( (y = 2 - 7) \) and then decreases gradually till getting to the film-air interface. At low temperatures \( T = 1.0, 1.5 \), the overall film density is small and a density "peak" occurs near the substrate \( (y = 1) \). As temperature increases, the density for each layer increases also.
The "peak" moves towards middle layers, e.g., \( y = 4 - 5 \) for \( T = 2.0 \). The bulk layers are getting denser and wider at higher temperatures \( (T = 3.0, 4.0) \). As further increases the temperature, the bulk density decreases a little bit while the upper layers are getting denser. In a word, the film is thicker and more stretched in longitudinal direction with more even bulk layers at high temperature. The density profile of individual \( P \) component (figure 7.24) shows that there is a peak of \( P \) component in the middle layers of film at low to middle temperatures \( (T = 1.0 - 2.0) \). This peak moves towards higher layers and is getting sharper and narrower as temperature increases \( (T = 2.0) \). At higher tem-
temperature \((T = 4.0 - 5.0)\), the density pattern changes to several dense layers \((y = 0 - 6)\) evenly starting out from the substrate followed by gradual decrease along the longitudinal direction. No sharp density peaks of \(P\) component exist in the middle layers at high temperature. The density profile of individual \(H\) component for different temperatures (figure 7.25) on the other hand shows a very similar trend to the density profile of all components we just discussed. One feature we notice is that at relatively low temperature \((T = 2.0)\) a \(P\) component rich layer with relatively deficient \(H\) component density exists around \(y = 4\), indicating a polyurethane-rich layer exhibits in the middle part of the film.
CHAPTER 7. FILM IN REACTIVE SOLVENT

7.3.2 Effect of Initial Water Concentration

Figure 7.26 shows the combined density profile of all components in the long time limit at different initial water concentrations ($p_A = 0.024 - 0.042$) in case 7 corresponding to the Figure 7.5. As shown in Figure 7.26, the initial water concentration does not change the density variation pattern which is simply $1 - 2$ relatively dense layers followed by $3 - 4$ layers dense bulk and then gradual decrease of the density in the upper layers. With increasing the initial water concentration, the density of lower layers decreases but the density of upper layers increases. The crossover occurs at $y = 3$. Density profiles of individual $P$ and $H$ components (see Figure 7.28 and Figure 7.27) might give more insights about the product distribution. Again the density pattern for both components is likewise. By increasing the initial water concentration, density of $P$ component at lower
and middle bulk layers decreases while the density of $H$ component at lower layer is about the same and increases at middle layers. This indicates polyurethane is relatively rich in those lower layers at low initial water concentration. At upper layers, however, situation is different. By increasing the initial water concentration, we see no or very slightly increase of $P$ component density at each upper layer, but the density of $H$ component increases for each middle and upper layer. This suggests more $H$ or $H^*$ particles (thus more polyurea) are present in the upper part of the film at high initial water concentrations while the content of $P$ particles remains constant. This also supports more dangling $H$ and $H^*$ particles distribute near the surface increasing the film roughness at high initial water concentrations.

Figure 7.24: Density profile of $P$ component along the longitudinal direction in the long time limit at different temperatures using the same parameter as in Figure 7.4 (case 7).
7.3.3 Effect of NOC:OH Ratio

Figure 7.29 shows the combined density profile of all components in the long time limit with different NOC:OH ratios corresponding to Figure 7.6. The film starts with a medium dense layer at the substrate and then getting denser for a couple of layers before reaching maximum density for another 3 – 4 layers and then density declines for the upper layers. As increasing the NOC:OH ratio, the density for each layer increases also. For lower layers \((y = 0 - 3)\), the density increases with increase of the NOC:OH ratio at low NOC:OH ratios (NOC:OH = 1.0 – 1.4); the density remains almost constant at higher NOC:OH ratios (NOC:OH = 1.6 – 2.0). For middle and upper layers \((y \geq 4)\), the density increases on increasing the NOC:OH ratios and the film stretches farther at high NOC:OH ratios. When look at the density profiles of individual \(P\) and \(H\) component (see Figure
7.30 and Figure 7.31), more information is revealed. At low NCO:OH ratios (NCO:OH = 1.0 – 1.4), the density of $P$ component increases on increasing the NCO:OH ratio at each layer. At higher NCO:OH ratios (NCO:OH = 1.6 – 2.2), however, the density of $P$ component decreases on increasing the NCO:OH ratio at lower layers ($y = 0 – 3$), but increases on increasing the NCO:OH ratio at upper layers ($y > 4$). Now look at the density profile of $H$ component in Figure 7.31 which shows a transition from a sharp and narrow density “peak” in the middle layers at low NCO:OH ratios to a round and wide density “arc” in the middle bulk layers at high NCO:OH ratios. At lower layers ($y = 0 – 3$), the density of $H$ component increase on increasing the NCO:OH ratio even at high NCO:OH ratios where the $P$ density starts to decrease. This seems to imply the lower layers at high

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NCO:OH ratio are polyurea-rich. While at low NCO:OH ratios these polyurea-rich layers have shifted to middle layers ($y = 4 - 5$). At upper layers polyurethane and polyurea are more mixed for all the NCO:OH ratios. As the cross-linking reactions are constrained to start from the substrate, for polyurea-rich layers to occur at lower layers requires relatively high concentration of both $H$ and $A$ components near the substrate when reaction starts. Since water particles can evaporate from the top, the water concentration near the substrate is relatively high especially at high NCO:OH ratios as water particles are more trapped by the surrounding constituents. Moreover, since the molecular weight of $H$ component is relatively small, high NCO:OH ratio provides more $H$ particles near the substrate in the beginning before they hop to middle and upper layers. Thus polyurea-rich
layers occur close to the substrate at high NCO:OH ratios as the reactions are constrained to start from the substrate. At low NCO:OH ratios, however, as the concentration of $H$ component is small throughout the layers initially, thin polyurea-rich layers are formed in the middle layers after more $H$ and $A$ components concentrate there as a result of low molecular weights. By the time cross-linking reactions propagate to the upper layers, more mixed $H$, $P$ and $A$ components lead to more even upper layers for different NCO:OH ratios.
Figure 7.29: Density profile of all components along the longitudinal direction in the long time limit at different NCO:OH ratios using the same parameter as in Figure 7.6 (case 7).

7.3.4 Effect of Reaction Rate

Figure 7.32 shows the combined density profile of all components in the long time limit with different reaction rates corresponding to Figure 7.7. The films start from one relatively high density at the substrate, get denser for a couple of layers till reach the maximum density and then decline as the layers move towards the film-air interface. With increasing the reaction rate, density for each layer also increases. The film at high reaction rate is thicker than the lower ones. The density of individual $H$ component (Figure 7.34) shows almost the same trend. A more prominent “arc” of $H$ density appears at the high reaction rate. The density of individual $P$ component (Figure 7.33), however, decreases on increasing the reaction rate at lower and middle layers. At upper layers the $P$ density increases on increasing the reaction rate. At low reaction rate, reactions are not
CHAPTER 7. FILM IN REACTIVE SOLVENT

143

Figure 7.30: Density profile of P component along the longitudinal direction in the long time limit at different NCO:OH ratios using the same parameter as in Figure 7.6 (case 7).

complete resulting low density and thin films. In addition, more P particles which have relatively large molecular weight subside to and react with the substrate at low reaction rate, leading to a larger density of P at lower layers at low reaction rate.

7.4 Finite Size Effect

The finite size effect is checked by performing simulations on different lattice sizes. Variations of interface width in case 6 for these lattices are already presented in the inset figure 7.8. Variations of interface width in case 7 for different lattice sizes are presented in figure 7.35. As can be seen, there is no severe effect of the lattice size on the qualitative nature of the growth of the interface width. Similar checks on the film thickness show the same result.
Figure 7.31: Density profile of H component along the longitudinal direction in the long time limit at different NCO:OH ratios using the same parameter as in Figure 7.6 (case 7).
Figure 7.32: Density profile of all components along the longitudinal direction in the long time limit at different reaction rates using the same parameter as in Figure 7.7 (case 7).
Figure 7.33: Density profile of $P$ component along the longitudinal direction in the long time limit at different reaction rates using the same parameter as in Figure 7.7 (case 7).
Figure 7.34: Density profile of $H$ component along the longitudinal direction in the long time limit at different reaction rates using the same parameter as in Figure 7.7 (case 7).
Figure 7.35: evolution of the interface width $W$ using BFM for a temperature $T = 5$ with reactive aqueous solvent on different sample sizes each with ten independent samples for $p_H = 0.0115$ and $p_P = 0.023$ with initial water concentration $p_A = 0.0422$ (case 7).
Chapter 8

FILM WITH ISOTROPIC GROWTH

In previous chapters, we have shown a systematic improvement of our model by introducing fluctuating covalent bonds, including additional interaction among components, and adopting more realistic reaction kinetics (i.e., reaction with aqueous solvent with and without including its excluded volume). A common procedure in earlier examinations (chapter 5-7) is propagation of the cross-linking reaction from the substrate. Historically, the initiation of film formation for particle or polymer chain deposition involved substrate, an area extensively studied both experimentally as well as theoretically for decades. A motivation for initiating the reaction from the substrate is to compare results with earlier studies [26] of the same system with a fixed bond length model. Unlike the film formation by chain deposition or particle deposition, reactions occur isotropically. Clusters of bonded units grow isotropically via cross-linking reaction everywhere in the sample, until a spanning network appears. This isotropic approach is more realistic in capturing the step-growth polymerization mechanism in polyurethane formation, a systematic improvement of the simulation model.

In this chapter, we will investigate polyurethane film with the isotropic growth in a simultaneously reacting and evaporating aqueous solvent with the bond fluctuation model (BFM). Since the size of H$_2$O molecule is very small in comparison to $H$ and $P$ components, the volume of water particle is excluded after its reaction with $H$ component (see figure 7.1). We refer it to case 8 (see table 8.1). The evolution of film thickness and its interface width with time along with its equilibrium state in the asymptotic time limit are examined for a set of parameters, i.e., temperature, the initial water concentration,
CHAPTER 8. FILM WITH ISOTROPIC GROWTH

Table 8.1: Parameters used in case 8.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2 \leq r \leq \sqrt{10}$ excluded $\sqrt{8}$</td>
</tr>
<tr>
<td>2</td>
<td>$p_P = 0.0115$, $p_H = 0.0230$, $p_A = 0.0422$</td>
</tr>
<tr>
<td>3</td>
<td>$f_P = 2$, $f_H = 3$, $f_A = 1$</td>
</tr>
<tr>
<td>4</td>
<td>$R_{HP} = R_{HS} = R_{PS} = R_{HA} = R_{HH} = 1$, $R_{HH} = R_{PP} = 0$</td>
</tr>
<tr>
<td>6</td>
<td>$M_P = 0.3$, $M_H = 1.5$, $M_A = 0.03$</td>
</tr>
<tr>
<td>7</td>
<td>film propagates from isotropically in space</td>
</tr>
</tbody>
</table>

NCO:OH ratio and the reaction rate. Results will be compared with the experimental observations as well as previous cases (chapter 5-7). Density profile and finite size effect will also be discussed.

8.1 Film Growth

An illustration of film formation of case 8 is provided in Figure 8.1. As before (chapter 5-7), initially, all the component particles, polar ($P$), hydrophobic ($H$) and aqueous solvent ($A$) are distributed randomly with their number concentrations $p_P = 0.0115$, $p_H = 0.0230$ and $p_A = 0.0422$, respectively on the lattice. As simulation proceeds, clusters of bonded units start to form isotropically via cross-linking. As the time progresses, new clusters evolve and earlier clusters aggregate/grow. A huge spanning cluster eventually forms at a certain point. This cluster continues to grow till most of the reactants have cross-linked and finally relaxes to its steady state via the continual mobility of covalently bonded units and evaporation of aqueous solvent. Though the cross-linking reaction is not constrained to proceed from the substrate as before (chapter 5-7), the definition of the film and its surface is still the same. That is, the film consists of all points that are covalently bonded from the substrate. The surface is the locus of all connected points in the film with the
maximum height from the substrate. Note that all clusters of bonded particles are not a part of the growing film at least in the beginning of the simulation. However, most of these bonded particles become part of the film in the later stage of film formation as the reaction continues to propagate isotropically in all directions.

8.1.1 Surface Height Growth

Let us first look into the general characteristics of film growth. Figure 8.2 shows the variation of the mean film thickness $h$ with the time steps for a range of temperature ($T = 2 – 8$). Though the general growth-relaxation-saturation pattern still persists, important differences exist in comparison to case 7 as a result of different film propagation mode: (i), the initial growth proceeds in steps (i.e., two relatively fast growths ($t = 1 – 10, t = 40 – 100$) are connected by an intermediate slow growth (Figure 8.2)) in contrast to one gradual growth in Figure 7.4. (ii), the film thickness at early time steps with isotropic propagation mode is much larger than the one with substrate-biased propagation. For example, at time step $t = 1$, the film thickness is one order larger here ($h \approx 0.9$) than that in case 7 ($h \approx 0.05$, Figure 7.4). (iii), the film growth is much faster in the initial stage with isotropic propagation mode than the one with substrate-biased propagation mode. The time ($t \approx 10^2$) used to reach the maximum thickness ($h_T = 24.0$) is about one order smaller here than the time ($t \approx 10^3$) required to reach even a smaller thickness ($h_T = 16.0$) at temperature $T = 5$ in case 7 (Figure 7.4). These differences are however expected. With the substrate-biased propagation mode, un-reacted particles can form a bond only when they are next to the substrate or to a particle that are already part of the film network. Thus the initial cross-linking reactions can only take place among the particles that are near the substrate in substrate-biased mode. This results in a smaller initial film thickness initially. Afterwards, the film propagates upward from the substrate in a gradual fashion. The overall film growth is slow and smooth. With this relatively
Figure 8.1: Snapshots for film formation proceeding isotropically in space with reactive hydrophobic (H), polar (P) and evaporative aqueous groups (A). Red: H before reaction; Yellow: H after reaction; Black: P before reaction; Green: P after reaction; Blue: A; Pink/Light blue: modified $H^*$. a) $t = 0$, b) $t = 3$, c) $t = 5$, d) $t = 20$, e) $t = 1 \times 10^4$, f) $t = 5 \times 10^6$. To make the clusters in the initial film growth more visible, the unbonded particles are not shown in figures b) and c).

In the slow reaction mode, a lot of water particles have already left the system via evaporation before they get a chance to react with H components. With the isotropic propagation...
mode, in contrast, reactive particles can be cross-linked immediately once they are next to each other, no matter whether they are near the substrate or far away from it. This leads to a fast initial growth in the beginning. Growth slows down a little bit after its first boost due to the smaller mobility of bonded segments (clusters) than the single particles. The fast growth reappears later when these isolated dispersed clusters are connected with the cluster(s) directly bonded to the substrate. The relaxation time for isotropic cross-linking system, however, is notably longer than the system with reaction proceeding from the substrate. Again this may due to the smaller mobility of bonded segments as well as an over-expanded network in a short time. Nevertheless, the time to reach steady state is about the same order. It is important to point out that with isotropic propagation mode, much more water particles are able to participate in the reaction with $H$ component; resulting modified $H^*$ particles are capable of further reactions with other $H$ particles. Thus more $H$ particles are consumed in the reaction with isotropic propagation mode resulting in a thicker film.

As shown in Figure 8.2, temperature does not change the general growth pattern of film thickness in the range of observation. Increasing the temperature has little effect on initial film growth as the curves at different temperatures are very close to each other (except $T = 2.0$). This is understandable with isotropic propagation mode as the covalent bonding can happen as soon as the reactants are next to each other without the need to move near to the substrate or film propagation front as in substrate-biased growth. Thus the temperature is not a dominant factor at initial growth as cross-linking reactions take place so fast. It, however, does have some impact on the relaxation process and steady state film thickness. At high temperature the film network tends to expand more due to the more active bond fluctuation. In contrast, the film thickness growth has a strong temperature dependence with the substrate-biased propagation mode as shown in Figure 7.4. At relatively low temperature (e.g., $T = 2.0$), film thickness gradually grows till reach
CHAPTER 8. FILM WITH ISOTROPIC GROWTH

Figure 8.2: Growth of the average film thickness \((h)\) for a range of temperatures with reactive aqueous solvent on a sample \(40 \times 40 \times 30\) with 10 independent samples for \(p_H = 0.0115, p_P = 0.023\) with initial water concentration \(p_A = 0.0422\) using BFM with reaction proceeding isotropically in space (case 8).

A steady state without the intermediate relaxation. At very low temperature (e.g., \(T = 1.0\)), film grows even more slowly and hardly reaches the steady state. As cross-linking is required to proceed from the substrate, mobility of constituents becomes significant. At low temperature, it takes more time for constituents to travel near to the substrate and the propagation front. The film grows very slowly and hence has more time to relax its structure in the mean while of growth. A monotonic approach to the saturation of film thickness is thus observed at low temperatures in case 7, i.e., with the substrate-biased propagation mode.

Figure 8.3 shows the variation of the mean surface height with the time steps for a range of initial water concentrations \((p_A = 0.024 - 0.042)\) at temperature \(T = 3\). As can
be seen, the initial water concentration has little effect on the film thickness growth. The curves are almost overlay each other in every time region, from initial film growth to steady state, for all the initial water concentrations. This is different than the dependence of film thickness growth on initial water concentration in case 7 (substrate-biased growth) where a slightly slower growth in the initial stage and a slightly larger steady state film thickness exhibit at higher initial water concentration (see Figure 7.5). In the initial stage of film growth, there are two effects caused by the high initial water concentration that can intercede the film growth rate. On one hand, the higher initial water concentration creates more opportunity for \( H \) component to react with water particles. On the other hand, the higher initial water concentration effectively "dilutes" \( H \) and \( P \) concentration which are

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*Figure 8.3:* Growth of the average film thickness \( (h) \) for a range of initial water concentration at temperature \( T = 3 \) with reactive aqueous solvent on a sample \( 40 \times 40 \times 30 \) with 10 independent samples for \( p_H = 0.0115, p_P = 0.023 \) using BFM with reaction proceeding isotropically in space (case 8).
reactive components. (Of course, the number concentrations of \( H \) and \( P \) components are fixed throughout the simulation. Here “dilution” means more solvent particles are packed on the way of the main reactants \( H \) and \( P \).) As the volume of water particle is excluded after its reaction with \( H \), the first factor is not efficient in increasing the cross-linking rate as further reaction of the modified \( H^* \) component with another \( H \) is hindered by the second factor, dilution effect of high water concentration. Thus a slightly slower initial film growth is observed with higher initial water concentration in case 7. This effect is more evident with the substrate-biased propagation mode where cross-linking reactions are constrained to take place at the propagation front which is near the substrate initially. In the intermediate time region, however, the first factor (i.e., the higher initial water concentration creates more opportunity for \( H \) component to react with water particles) plays more weight as a significant amount of water has left the system via evaporation with substrate-biased mode. The film growth rate with high initial water concentration catches up \((t \approx 10^3, \text{Figure 7.5})\). In the long time limit, more water particles are reacted and hence more \( H \) components are consumed with the higher initial water concentration than the lower ones. Thus a slightly thicker film is observed in the steady state in case 7 with higher initial water concentrations. With the isotropic propagation mode, in contrast, the effect of initial water concentration on the steady state film thickness is minimal. This is because the much faster and more evenly film propagation in space ensures that most of the possible \( H - A \) reactions occur before water evaporation becomes a significant factor. The steady state film thickness in case 8 here (Figure 8.3) is larger than that in case 7 (Figure 7.5) for each initial water concentration as more water particles are able to participate in the reaction here before they evaporate.

Figure 8.4 shows the variation of the mean surface height with the time steps for a range of NCO:OH ratios (NCO:OH = 1.2 - 2.0) at temperature \( T = 3 \) and initial water concentration \( p_A = 0.0422 \). As can be seen, the NCO:OH ratio does change the general
CHAPTER 8. FILM WITH ISOTROPIC GROWTH

157

Figure 8.4: Growth of the average film thickness \( (h) \) for a range of NCO:OH ratios at temperature \( T = 3 \) with reactive aqueous solvent on a sample \( 40 \times 40 \times 30 \) with 10 independent samples for \( p_H = 0.0115, p_P = 0.023 \) with initial water concentration \( p_A = 0.0422 \) using BFM with reaction proceeding isotropically in space (case 8).

growth pattern of film thickness. At early growth stage, the film thickness growth rates are about the same for all NCO:OH ratios. At later growth stage \((t = 10 - 100)\), the film grows faster (Figure 8.4) and reaches a larger intermediate value with larger NCO:OH ratio. The film thickness reaches a larger steady state value in the long time limit with larger NCO:OH ratios. As the concentration of \( P \) particles is fixed, a larger NCO:OH ratio means a larger concentration of \( H \) component in the system. Though more \( H \) particles are able to participate in the side reaction with water initially at larger NCO:OH ratio, the volume of water particle has been excluded. Thus the film mean surface heights do not distinguish much from each other at the early initial stage \((t \leq 10)\). As more \( H \) particles are consumed by further reaction with \( H^* \) at later stage \((t = 10 - 10^2)\), the film thickness
grows faster for larger NCO:OH ratios. A thicker film is also thus resulted with larger NCO:OH ratios. This dependence of film growth with NCO:OH ratio is similar to that in case 7 (substrate-biased growth, chapter 7).
Figure 8.5 shows the variation of the mean surface height with the time steps for a range of reaction rates ($R = 0.01 - 1.0$) at temperature $T = 3$ and initial water concentration $p_a = 0.0422$. Again, the early growth stage ($t \leq 10$) is not affected by the reaction rate much. At later growth stage ($t \approx 10 - 10^4$), however, the film growth is significantly slower at low reaction rate. For example, the time to reach maximum film thickness is about 2 order larger at low reaction rate ($t \approx 10^4$ for $R = 0.01$) than that at high reaction rate ($t \approx 10^2$ for $R = 1.0$). The steady state film thickness is much smaller at very low reaction rate ($R = 0.01$) than those at higher reaction rates. However, for the wide range of reaction rates from $R = 0.05$ to $R = 1.0$, the steady state values are very close to each other despite of different rates in growth and relaxation. This is in contrast to the more
dependent film growth with reaction rate in case 7 (substrate-biased growth, chapter 7). With the isotropic propagation mode, the overall film growth is faster as covalent bonding is not constrained to be near the substrate or propagation front. This especially promotes more water particles and hydrophobic particles to participate in reaction before a large fraction of water evaporates. This is even true for relatively low reaction rate such as $R = 0.05$ in our study. With the substrate-biased propagation mode, the slower film propagation mode in addition to the low reaction rate gives more time for more water particles to leave the system via evaporation. Thus less $H$ particles are consumed through the side reaction with water, and a greater dependence of film thickness on reaction rate is resulted in case 7 (substrate-biased growth, chapter 7).

8.1.2 Interface Width Growth

Let us examine now the general growth pattern of the interface width $W$, a measure of the film roughness, in a reactive aqueous solvent with isotropic propagation mode. Figure 8.6 shows the variation of the interface width $W$ with the time step at different temperatures (see Figure 8.2 for corresponding growth in film thickness). Remarkable differences in the growth of the interface width between the isotropic mode here (case 8) and the substrate-biased mode (case 7). First, the interface width growth shows a general non-monotonic and oscillatory pattern (Figure 8.6) at all temperatures that are studied here. These patterns appear in the following sequence.

- An uncommon "valley" (i.e., minimum) of interface width appears in the very early stage ($t \leq 10$, Figure 8.6).

- A consistent fast growth of the interface width is then followed until it reaches the maximum ($t = 10 - 100$).

- A sharp decrease of the interface width is then followed immediately after the
"peak" \( (t = 100 - 300) \).

- The interface reaches a steady state plateau \( (t \approx 10^3) \) with a slight increase in the intermediate region before it finally relaxes to its lower value in the steady state in the asymptotic time limit.

The multiple growth and relaxation pathways (Figure 8.6) are in sharp contrast to the growth pattern of interface width \( W \) in case 7 with substrate-biased mode where a gradual growth is followed by a relaxation to the steady state at high temperature and a simple monotonic growth of \( W \) at low temperature (chapter 7, Figure 7.9).

\[ \text{Figure 8.6: } \text{Evolution of the interface width (W) of the film surface for a range of temperatures using the same parameters as in Figure 8.2.} \]

Second, the overall initial growth of interface width here is much faster than that in case 7. The time for reaching the maximum of \( W \) is one order smaller with the
isotropic propagation mode ($t_x \approx 10^2$) than that with the substrate-biased propagation mode ($t_x \approx 10^3$) at high temperatures (Figure 7.9). A closer look of interface width growth at the initial 15 steps reveals more specific differences. For example, the starting roughness ($W \approx 1.55$) here right in the beginning is already significantly larger than that ($W \approx 0.45$) in case 7. However, the interface width starts decreasing slightly before embarking on its fast growth here ($t = 10 - 100$, Figure 8.6). The "valley" in the initial interface width growth is likely due to the temporary smoothing of the growing film near the substrate: reactive components are relatively evenly cross-linked throughout the layers adjacent to the substrate because of the fast isotropic propagation mode. The growing film is compressed somewhat as the cross-linked network drops on the substrate due to its high weight. With the substrate-biased propagation mode, in contrast, a consistent increase of interface width ($W \propto t^{\beta_1}, \beta_1 \approx 0.41$) in the initial stage is observed as the film propagates less evenly due to the constraint that the reactive components can form bonds only with those that are already part of the film.

Third, the intermediate relaxation pattern after the maximum and the followed steady state exhibits somehow oscillatory response very similar to the system with effective bond fluctuation model having reactions proceeding from the substrate (see Figure 5.8, case 2). Here the isotropic propagation mode brings a similar effect in the sense of fast film growth in a short amount of time resulting in a quite stretched film. An overshoot in growth of interface width and its decay is thus observed. Though the network structure here should be more compact in comparison to the one with EBFM because of the more restricted bond length limit, the oscillatory pattern apparently persists for its structure relaxation in the consolidation process.

As shown in Figure 8.6, growth of the interface width with time depends on temperature; the effect of temperature is more pronounced in the long time regime. At initial film growth, the effect of temperature on film thickness (Figure 8.2) and its interface
Chapter 8. Film with Isotropic Growth

Width (Figure 8.6) is relatively small. Again this is due to the faster cross-linking reaction among the appropriate reactants in an isotropic propagation mode. The mobility of individual constituent depends on temperature. The higher mobility enhances their chance to encounter other constituents, this increases the probability of reaction at higher temperature/mobility. Initially the reactive particles do not require much movement in order to form bonds with other particles, therefore the temperature plays a less significant role in initial film growth. The power-law exponents \( W \propto t^\beta \) for fitting the fast growth \( (t = 10^1 - 10^2) \) are about the same for \( T = 2 (\beta \simeq 0.58) \) and for \( T = 8 (\beta \simeq 0.62) \) (Figure 8.6). The maximum interface widths are also about the same in value \( (W_x \approx 8.0) \) and in the time \( (t \approx 100) \) they appear for low \( (T = 2.0) \) and high temperatures \( (T = 8.0) \). In relaxation to steady state region, however, temperature has a more significant impact on the film morphology and its roughness. At low temperature (e.g., \( T = 2.0, 2.5 \)), the interface width has not reached complete equilibrium in our observation time limit \( (t = 10^6, \text{Figure 8.6}) \). One reason for this slow relaxation is the presence of cross-linked clusters; global motion of larger clusters is slower, especially at low temperatures. At high temperature \( (T = 6.0, 8.0) \), more active bond fluctuations due to higher particle mobility and segmental mobility lead to a more stretched film structure (i.e., Figure 8.2 for film growth). As a result, the irregularity in the interface (and therefore fluctuation in \( W \) ) increases; note that the fluctuation of data in the steady state is higher at high temperatures, indicating a more active fluctuation of the film surface. The interface width growth with the substrate-biased propagation mode (case 7) also depends on temperature (see Figure 7.4) and the results (chapter 7) are discussed briefly for comparison. The influence of temperature becomes obvious (Figure 7.9) since the latter stage of film initial growth \( (t = 10^2 - 10^3) \) resulting in a wide difference in the maximum value of the interface width \( (W_x = 2.9 - 6.7) \) achieved for different temperatures \( (T = 1.5 - 5.0) \). The higher the temperature, the larger the maximum value and the earlier it appears. At very low temperature (e.g., \( T = 1.0 \)), a

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monotonic growth of the interface width is observed. Due to the slow approach (Figure 7.9) of the substrate-biased propagation mode, interaction among constituents over competes with the thermal energy at low temperature. Aggregations among components of the same type are formed retarding the further reactions to occur. Thus many reactants still remain un-reacted at low temperatures in case 7. This is evidenced in the density profile (see Figure 7.23) which indicates that a very thin film has been formed at very low temperature.

![Graph showing interface width evolution](image)

**Figure 8.7**: Evolution of the interface width (W) of the film surface for a range of initial water concentrations using the same parameters as in Figure 8.3.

Figure 8.7 shows the variation of the interface width with time steps for a range of initial water concentrations ($P_A = 0.024 - 0.042$) at temperature $T = 3$ (corresponding mean surface height presented in Figure 8.3). As can be seen, the initial water concentration does not change the general pattern of the growth of the film interface width, i.e.,

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CHAPTER 8. FILM WITH ISOTROPIC GROWTH

non-monotonic and oscillatory growth with the time steps (Figure 8.7). However, the initial water concentration affects the growth of the interface width at different time regimes and its steady state value $W_s$. At initial growth stage ($t \leq 30$), the higher initial water concentration leads to a slightly slower interface width growth due to the solvent “dilution” effect (explained earlier) on the reactant ($H$ and $P$) concentration. Though solvent $A$ is also reactive, its functionality is only one and its volume is excluded from the system. The further reaction of modified $H^*$ with another $H$ is also hindered somehow because more solvent particles are on the way for another $H$ component to move within a reacting distance. As solvent (water) continues to evaporate, this “blocking” effect becomes less and less while the side reaction of $H$ component and water comes to play more role.

Growth of the interface width speeds up in the later growth region ($t = 30 - 100$) for higher initial water concentration system ($p_A = 0.0422$, Figure 8.7)). In the relaxation region ($t \approx 10^2 - 10^5$), the interface width at higher initial water concentration relaxes a little bit slower and to a larger steady state $W_s$. While the steady state film thicknesses $h_s$ are about the same for all the initial water concentrations, this slightly larger saturated interface width $W_s$ at high initial water concentration may indicate more dangling ends of $H$ or $H^*$ near the film surface. The effect of initial water concentration on growth of the interface width at different time regions ($t = 1 - 10^2, t = 10^2 - 10^3, t = 10^3 - 10^4$) in case 7 (see Figure 7.10) is very similar to here except the maximum interface width is larger at higher initial water concentration ($W_x = 4.7$) than that at lower ones ($W_x = 3.5$).

Figure 8.8 shows the variation of the interface width with time steps for a range of NCO:OH ratios (NCO:OH = 1.0 - 2.2) at temperature $T = 3$ (corresponding mean surface height presented in Figure 8.4). As can be seen, NCO:OH ratio has little effect on the initial growth of the interface width. However, a significant change in pattern is observed during the intermediate growth region. At low NCO:OH ratio (e.g. NCO:OH = 1.0), the interface width stays at a stable stage ($W \approx 2.35$) for a long time ($t = 10^2 - 10^3$).
CHAPTER 8. FILM WITH ISOTROPIC GROWTH

166

Figure 8.8: Evolution of the interface width ($W$) of the film surface for a range of NCO:OH ratios using the same parameters as in Figure 8.4.

after its initial growth to the maximum value ($W_x = 2.8$) and then gradually reaches its steady state value ($W_i = 2.45$). At high NCO:OH ratio (NCO:OH = 2.2), an overshoot of interface width with a sharp and narrow "peak" ($t \approx 10^2$) after the initial growth is followed by a relatively stable stage ($t \approx 10^2 - 10^4$) before it finally decays to steady state value. This transition from no overshoot (i.e., NCO:OH = 1.0) to sharp overshoot (i.e., NCO:OH = 2.2) becomes more obvious on increasing the NCO:OH ratio.

Figure 8.9 shows the variation of the interface width with time steps for a range of reaction rates ($R = 0.01 - 1.0$) at temperature $T = 3$ (corresponding mean surface height presented in Figure 8.5). A changing of growth pattern is noticed between high reaction rate system ($R = 1.0, 0.5$) and low reaction rate system (e.g., $R = 0.01$). The interface widths for the initial time steps are very close at different reaction rates. Afterwards

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Figure 8.9: Evolution of the interface width ($W$) of the film surface for a range of Reaction rates using the same parameters as in Figure 8.5.

($t \geq 5$), a fast interface width growth with an overshoot ($t = 10^2$) is followed by a flat stage ($t \approx 200 - 5000$) and relaxation region ($t \approx 5000 - 10^5$) before reaching the steady-state film roughness for the high reaction rate ($R = 1.0$). In the low reaction rate ($R = 0.01$), in contrast to high $R$, the interface width decreases after first few steps and remains in a flat “valley” for a long time ($t \approx 30 - 10^3$) before it climbs up again for a slight overshoot ($t \approx 10^4$) and then relaxes to a saturated value. The time for reaching the overshoot at low reaction rate ($R = 0.01$, $t \approx 10^4$) is about 2 orders larger than that at high reaction rate ($R = 1.0$, $t \approx 10^2$). The magnitude of maximum value of the interface width is also smaller at low reaction rate. The steady state film roughness at different reaction rates, however, are relatively close to each other.
8.2 Equilibrium

8.2.1 Film Thickness

Figure 8.10: Variation of the saturated and near-saturated thickness $h_s$ with the temperature using the same parameter as in Figure 8.2 (case 8). The statistical errors in data are of the order of symbols sizes.

Variation of the steady-state film thickness ($h_s$) with the temperature is presented in Figure 8.10. The steady state film thickness $h_s$ decreases with temperature at low temperatures and increases with temperature at high temperatures. This is in contrast to the monotonic growth of $h_s$ with temperature in case 7. With the isotropic propagation mode, cross-linking reactions take place among the reactive constituents very quickly; a big tethered film network is formed in a relatively short amount of time (see Figure 8.2). It takes longer for the tethered network to relax its structure and morphology as the mobility of
bonded segments is confined by the fluctuation length limit. This effect is more evident at low temperatures where both the cross-linking reaction and the followed structure relaxation are slowed down due to smaller mobility of free particles and bonded units. The film may have not achieved complete equilibrium at low temperatures, which is more evidenced by looking at the film roughness variation with time (see Figure 8.6). A film with less condense layers in the lower and middle part of the film and more fluctuating bumps in the topper part is formed at low temperature (e.g., $T = 2.0$), which is indicated by the density profile along longitudinal direction (see discussion in the next section). Thus the film thickness $h_s$ exhibits a higher value at low temperature. As temperature increases, the mobility of constituents increases, thus the film network is more relaxed and the particles are more evenly distributed throughout the layers. The steady state thickness $h_s$ decreases when temperature increases from $T = 2.0$ to $T = 3.0$. As temperature further increases, the bond fluctuation becomes even more active and the film network stretches its structure in space. The steady state film thickness $h_s$ thus increases on increasing the temperature in high temperature regime.

Variation of the steady state film thickness ($h_s$) with the initial water concentration is presented in Figure 8.11. As can be seen, the steady state film thickness $h_s$ remains almost the same or decreases very slightly on increasing the initial water concentration. This is in contrast to the monotonic increase of steady state film thickness $h_s$ with the initial water concentration in case 7. Further, the steady state thickness is larger in case 8 with the isotropic propagation mode than that in case 7 with the substrate-biased propagation mode for each initial water concentration. With the isotropic propagation mode, the cross-linking reactions occur very quickly in space. Thus more water particles are able to participate in the reaction before they leave the system via evaporation. More $H$ particles, as a result, become part of the film network due to their side reactions with water and further reactions with other $H$ particles. A thicker film is resulted in case 8 in comparison
CHAPTER 8. FILM WITH ISOTROPIC GROWTH

Figure 8.11: Variation of the saturated and near-saturated thickness $h_s$ with the initial water concentration using the same parameter as in Figure 8.3 (case 8). The statistical errors in data are of the order of symbols sizes.

to that in case 7. However, the initial water concentration does not have much effect on varying the steady state film thickness in case 8. This is likely due to the saturated reaction among $H$ component and water even with a small initial water concentration (e.g. $p_A = 0.024$) when the cross-linking reactions take place so fast.

Variation of the steady-state film thickness ($h_s$) with the NCO:OH ratio is presented in Figure 8.12. It shows that the film thickness increase linearly on increasing the NCO:OH ratio ($h_s = 0.69 + 5.23\ast (\text{NCO:OH})$). As more $H$ particles are consumed through the side reaction at high NCO:OH ratio, a thicker film is resulted at high NCO:OH ratios.
CHAPTER 8. FILM WITH ISOTROPIC GROWTH

Figure 8.12: Variation of the saturated and near-saturated thickness $h_s$ with the NCO:OH ratio using the same parameter as in Figure 8.4 (case 8). The statistical errors in data are of the order of symbols sizes.

Moreover, the growth rate of steady-state film thickness with NCO:OH ratio (the slope) is bigger in case 8 than that in case 7. This is due to the faster growth in isotropic propagation mode leading to more water and eventually more $H$ particles reacted and become part of the film. Variation of the steady-state film thickness ($h_s$) with the reaction rate is presented in Figure 8.13. As seen, the steady-state film thickness remains about the same for a wide range of reaction rates ($R = 0.05 - 1.0$) in case 8. Only at very low reaction rate (e.g., $R = 0.01$), a significant decrease of steady-state film thickness occurs. This implies with isotropic propagation mode, the big chance of reactants next to each other available for cross-linking reaction assures sufficient amount of side reaction despite of the low probability of successful attempts for covalent bonding. With substrate-biased
propagation mode (case 7), however, the steady-state film thickness has much greater dependence on reaction rate (see figure 7.7). Many water particles have been evaporated at low reaction rate in case 7, resulting in less \( H \) particles consumed. Moreover, the steady-state thickness is greater in case 8 than that in case 7 for each reaction rate. The reason is obvious.
8.2.2 Film Roughness

Variation of saturated interface width, i.e., the steady state roughness $W_s$, with temperature is presented in Figure 8.14. Similar to the film thickness, the steady state interface width $W_s$ decreases with temperature at low temperatures ($T = 2 - 3$) and increases with temperature at high temperatures ($T = 3 - 8$). The reasons to this trend have been discussed in previous section (see page 169). AFM images for film surface at temperature $T = 30 \, ^{\circ}C$ and $T = 50 \, ^{\circ}C$ are shown in figure 8.15, which indicates a lower roughness at higher temperature. This may correspond to the low temperature region ($T = 2 - 3$) in our simulation. However, due to the non-monotonic nature of roughness dependence with temperature predicted in our simulation, more experimental data are needed at different temperatures in order to verify our prediction.

Variation of saturated interface width, i.e., the steady state roughness $W_s$, with the initial water concentration is presented in Figure 8.16. The steady state film roughness $W_s$ increases linearly with the initial water concentration ($W_s = 0.8 + 25.1 \times p_A$). This is consistent with the previous study [26]. The steady state film thicknesses are about the same for all the initial water concentrations (see Figure 8.16), indicating the total amount of components ($H$ and $P$) reacted are about the same. Density profile (which will be discussed in next section) shows that more $H$ components are consumed and more dangling ends of bonded $H$ or $H^*$ components are near the top layers ($y = 10 - 13$) under higher initial water concentration ($p_A = 0.042$, see Figure 8.26). This extra consumed $H$ or $H^*$ particles near the surface are likely contribute to the consistent increase of steady state film roughness with increasing initial water concentration. Experimental observations (AFM images of film surface) also indicate the same trend, see figure 8.17. Note the longitudinal scale of AFM surface image at 75 %RH is 70 nm (left) while the longitudinal scale of AFM surface image at 82 %RH (right) is remarkably larger, 300 nm. While the
Figure 8.14: Variation of the saturated and near-saturated roughness $W_s$ with the temperature using the same parameter as in Figure 8.6 (case 8).

Figure 8.15: Topographic AFM images of WB 2K-PUR films crosslinked at 30%RH and temperature a) $T = 30^\circ$C and b) $T = 50^\circ$C recorded from the film-air interface.
AFM images provide a qualitative impression of the surface morphology, our computer simulations are able to provide quantitative formula for the roughness dependence with process parameters such as relative humidity (initial water concentration). With such a formula, one can easily predict the roughness at any certain relative humidity, which is usually cumbersome for experimentalists to do.

Variation of saturated interface width, \( W_s \), with the NCO:OH ratio is presented in Figure 8.18. On increasing the NCO:OH ratio, the steady state film roughness increases. This is consistent with the experimental observations as shown in the AFM images for...
Figure 8.17: Topographic AFM images of WB 2K-PUR films crosslinked at 30 °C and relative humidity a) $RH = 75\%$ and b) $RH = 82\%$ recorded from the film-air interface.

Figure 8.18: Variation of the saturated and near-saturated roughness $W_s$ with the NCO:OH ratio using the same parameter as in Figure 8.8 (case 8).
different NCO:OH ratios, see Figure 8.19. At low NCO:OH ratio (e.g., NCO:OH = 1.1), the surface appears to be smooth with many tiny “hills” and “valleys” evenly distributed along the surface. As the NCO:OH ratio increases, the “hills” and “valleys” becomes more obvious and bigger in size. At high NCO:OH ratio (e.g., NCO:OH = 2.2), the surface appears even rougher with more irregular and larger “hills” and “valleys”. Our simulation prediction agrees with the experimental results very well qualitatively. At higher NCO:OH ratio, more dangling bonded $H$ and $H^*$ particles are formed near the surface area resulting in a rougher film surface.

Variation of steady state roughness $W_s$ with the reaction rate is presented in Figure 8.20. As seen, it is difficult to find a trend (increase or decrease) of the steady state film roughness $W_s$ with the reaction rate due to fluctuation in data points. More samples are
CHAPTER 8. FILM WITH ISOTROPIC GROWTH

Figure 8.20: Variation of the saturated and near-saturated roughness $W_s$ with the reaction rate using the same parameter as in Figure 8.9 (case 8). The statistical errors in data are of the order of symbols sizes.

needed for the simulation to have a meaningful interpretation.

8.3 Density Profile

Film thickness, interface width, and the surface roughness are studies in depth in preceding sections. To characterize the physical and chemical properties of the entire film, however, it is crucial to understand how the constituents of the film-network are distributed throughout, e.g. from substrate to the surface, in addition to surface roughness. Investigation of the density profiles of these constituents could be useful in this regard.
As described in the beginning in this chapter, the aqueous solvent is considered reactive and its volume is excluded from the film soon after its reaction with the $H$ component to implement the reaction kinetics and to account into relative volume appropriately [28]. The cross-linked film network is thus composed of bonded $H$ and $P$ particles connected by either $H - H^*$ bonds or $H - P$ bonds. By tracking the density profile of $P$ components along the longitudinal direction, one can get an idea of how the polyurethane (PUR) is distributed in the film, as suggested in Figure 4.2. Similarly, one can get insight into the distribution of the polyurea (PUA) by studying the density profile of $H$ components.

### 8.3.1 Effect of Temperature

![Density profile graph](image_url)

*Figure 8.21*: Density profile of all components along the longitudinal direction in the long time limit at different temperatures using the same parameter as in Figure 8.2 (case 8).
The density of component $i$ ($i = H/P/A$) at layer $j$ ($y = j$) is defined as,

$$D_{i,j} = \frac{N_{i,j}}{N_i},$$

where, $N_{i,j}$ is the number of component $i$ particles at layer $j$. Figure 8.21 shows the combined density profile of all components, i.e. the sum of the planar densities of $H$ and $P$ components in the long time limit for a range of temperatures ($T = 2.0 - 8.0$) (corresponded thickness variation with time is shown in Figure 8.2). A general trend for the density profile seems to emerge as follows: (i) one to two relatively dense layers near the substrate are followed by (ii) a dense bulk layers before series of layers with much lower densities in a decreasing order appear near the film surface or film-air interface. With increasing the temperature, the film expands more while the bulk density decreases. At low temperature (e.g., $T = 2.0$), the density variation seems to be exceptional to the general trend.

The density profile of individual $H$ and $P$ components (see Figure 8.22 and Figure 8.23) reveals the trend of density variation with temperature more clearly. For example, a narrow and sharp peak (around $y = 5 - 7$ with $D = 0.67$) of density appears in the bulk layers of $H$ component density profile at low temperature. The peak is close to be symmetric. As the temperature increases, this peak becomes wider and shorter in height. At temperature $T = 8$, a wide flat stage of density ($y = 3 - 13$ with $D = 0.35$) instead of a peak presents in the bulk layers. On the other hand, the density profile of $P$ component shows a totally different shape. Highly dense layers near the substrate are followed by bulk layers of decreasing density (see Figure 8.23). At relatively low to middle temperature ($T = 2.5 - 4.0$), oscillations of $P$ densities are observed, i.e., a valley (around $y = 5 - 7$) followed by a peak (around $y = 9 - 10$) exists in the middle layers. This is interesting. When this information is combined with Figure 8.22, we find that the valley for the $P$ component density is corresponding to the peak for the $H$
component. As we know from the reaction kinetics involved in water borne polyurethane film formation (Figure 4.2), the bonded $P$ components are the traces for the product of polyurethane, while the bonded $H$ components give us an idea where the by-product of polyurea is. Thus the density profiles of $H$ and $P$ components seem to indicate that a polyurea-rich layer is exhibited in the lower parts of bulk film at middle temperatures. In the following upper layers ($y = 11 - 14$), however, a more mixed polyurethane and polyurea film is indicated by the density profile at middle temperatures (e.g., $T = 3.0$). When the temperature continues to increase (e.g., $T = 8.0$), the starting density of $P$ component (Figure 8.23) near the substrate is much smaller ($D = 0.2$) and the overall density of $P$ component throughout the film ($y = 1 - 25$) is more gradually decreased in a monotonic fashion without valleys and peaks. The density is also more spread out along the longitudinal direction at high temperature. Both the density profiles for $H$ component and $P$ component at low temperature ($T = 2.0$) seem to be exceptional to the general variation trend with temperature, which shows overall smaller densities in the film. This is likely due to the incomplete cross-linking reaction or non-equilibrium of the system at low temperature as mobility of the constituents are small. A schematic graph of the different film layers is presented in figure 8.24.

### 8.3.2 Effect of Initial Water Concentration

Figure 8.25 shows the combined density profile of all components in the long time limit for a range of initial water concentrations ($p_A = 0.024 - 0.042$) (corresponded thickness variation with time is shown in Figure 8.3). As indicated by Figure 8.25, the initial water concentration seems have little impact on the combined density profile in the film as all the curves almost overlap onto one curve for all the layers in the observation range of initial water concentration. The density starts from $D = 0.6$ at the substrate, goes up to $D = 0.7 - 0.8$ for about 7 layers and then decreases to $D = 0.0$ in another 7 or 8 layers.
Figure 8.22: Density profile of $H$ component along the longitudinal direction in the long time limit at different temperatures using the same parameter as in Figure 8.2 (case 8).

However, when the density profiles of individual $H$ and $P$ component are examined (see Figure 8.26 and Figure 8.27), noticeable changes on density profile are observed for different initial water concentrations. For example, in Figure 8.26, at $p_A = 0.024$, the density of $H$ component starts from $D = 0.25$ at the substrate, achieve the maximum $D = 0.6$ at $y = 4 - 5$ and then decreases almost linearly ($y = 7 - 11$) to $D = 0.0$ ($y = 15$). At $p_A = 0.042$, the density of $H$ component starts smaller, around $D = 0.1$ at the substrate, goes up to a higher maximum $D = 0.65$ at $y = 4 - 7$ and then decreases linearly ($y = 7 - 11$) to $D = 0.0$ ($y = 15$). A shape of "hill" is presented with all the initial water concentrations, showing some symmetric characteristics. The "hill" is higher and narrower and has been shifted to the upper layers at high initial water concentration. On the other hand, the density profile of $P$ component (see Figure 8.27) carries a different
look. Generally, the density starts at a big value from the substrate, then decreases to some relatively stable value in the bulk layers ($y = 4 - 9$) before it finally declines to zero above the surface. With higher initial water concentration ($p_A = 0.042$), the starting density at the substrate is bigger ($D = 0.47$) and the intermediate density in the bulk is smaller (about $D = 0.1$). Furthermore, a non-monotonic variation of the density appears in the bulk layers, i.e., a small “valley” followed by a slight “hill”, at high initial water concentration.
More importantly, the “valley” in the $P$ component density ($y = 4 - 7$) is corresponding to the high “peak” in the $H$ component density. This indicates a polyurea-rich layer exists at around $y = 4 - 7$ at high initial water concentration. This is understandable. As more water are present in the system initially, the side reaction between $H$ component and water which ultimately leads to polyurea formation is more prevalent than the system with less initial water content. Thus a few layers relatively rich in polyurea are formed in the middle part of the film where water concentrations are more condensed. The density of $P$ component (see Figure 8.27) goes up a little bit after that “valley” as the water concentration is smaller due to more evaporation in the upper layers ($y = 8 - 9$). At low initial water concentration ($p_A = 0.024$), a relatively more uniformly distributed
CHAPTER 8. FILM WITH ISOTROPIC GROWTH

polyurea/polyurethane film is formed in the bulk. A schematic graph of the different film layers is presented in figure 8.28. ATR-FTIR spectra data (see figure 8.30) suggests that on increasing the relative humidity, more polyurea and less polyurethane are formed in the film. This is supported by our simulation result when we plot out the variation of the percentage of consumed $H$ and $P$ component with initial water concentration (see figure 8.29).

![Figure 8.26](image)

*Figure 8.26: Density profile of $H$ component along the longitudinal direction in the long time limit at different initial water concentrations using the same parameter as in Figure 8.3 (case 8).*

8.3.3 Effect of NCO:OH Ratio

Figure 8.31 shows the combined density profile of all components in the long time limit for a range of NCO:OH ratios (NCO:OH = 1.0 - 2.2) (corresponded thickness variation
Figure 8.27: Density profile of $P$ component along the longitudinal direction in the long time limit at different initial water concentrations using the same parameter as in Figure 8.3 (case 8).

Figure 8.28: Schematic illustration of film layers under different relative humidities.

with time is shown in Figure 8.4). The film starts with a relatively small density near the substrate and then gets denser till reaching a maximum density around $y = 5$. The film density then starts declining in upper layers. On increasing the NCO:OH ratio, the density for each layer also increases.

When look at the density profiles of individual $P$ and $H$ component (see Figure 8.32...
and Figure 8.33), more information is revealed. The density of $P$ component increases at the lower layers ($y = 0 - 2$) and then decreases to and remains a certain value ($D = 0.04$ at NCO:OH = 1.2 and $D = 0.14$ at NCO:OH = 2.2) in the middle layers ($y = 5 - 10$) before finally declines to zero at the film-air interface. On increasing the NCO:OH ratio, the density of $P$ component decreases at lower layers, but increases at middle and upper layers. The density profile of $H$ component appears very similar to the overall density in figure 8.31. On increasing the NCO:OH ratio, the density of $H$ component increases both at lower layers and at upper layers. This implies relatively polyurea-rich layers may exist at lower part of the film at high NCO:OH ratios. At middle layers ($y = 5 - 10$), how-
Figure 8.30: ATR-FTIR spectra of WB 2K-PUR films crosslinked at 30 C and 11, 32, 49, 75, 82 and 97% RH recorded from the F-A (A) and F-S (B) interfaces, respectively. Arrows indicate intensity changes with increasing RH. 1724 PUR/ester C=O; 1647 PUA C=O; 1560 PUA N-H; 1524 PUR N-H.
Figure 8.31: Density profile of all components along the longitudinal direction in the long time limit at different NCO:OH ratios using the same parameter as in Figure 8.4 (case 8).

ever, concentration of polyurethane is increasing as indicated by the stable layers of relatively dense $P$ component (Figure 8.32) and decreased $H$ component density (Figure 8.33). ATR-FTIR spectra profile (see figure 8.35) suggests that on increasing the NCO:OH ratio, more polyurea and polyurethane are formed in the film. This is also supported by our simulation result when we plot out the variation of the percentage of consumed $H$ and $P$ component with NCO:OH ratios (see figure 8.34).
CHAPTER 8. FILM WITH ISOTROPIC GROWTH

Figure 8.32: Density profile of $P$ component along the longitudinal direction in the long time limit at different NCO:OH ratios using the same parameter as in Figure 8.4 (case 8).

8.3.4 Effect of Reaction Rate

Figure 8.36 shows the combined density profile of all components in the long time limit with different reaction rates ($R = 0.01 - 1.00$) (corresponded thickness variation with time is shown in Figure 8.5). Again the film starts with a relatively small density near the substrate and then gets denser till reaching a maximum value ($D = 0.75$) around $y = 5$. The density declines at following upper layers. With decreasing the reaction rate, the density fluctuates around $D = 0.75$. Specifically, on decreasing the reaction rate, the density first decreases and then increases at lower and middle layers ($y = 0 - 8$), but opposite trend applies at upper layers ($y = 9 - 16$). At very low reaction rate ($R = 0.01$), the density is slightly bigger at lower layers but much smaller at middle and upper layers.

Figure 8.37 and Figure 8.38 show the density profiles of individual $P$ and $H$ compo-
Figure 8.33: Density profile of $H$ component along the longitudinal direction in the long time limit at different NCO:OH ratios using the same parameter as in Figure 8.4 (case 8).

The density of $P$ component is relatively high near the substrate and then decreases along the longitudinal direction. The density remains stable for a few layers in the middle part of the film ($y = 5 - 9$) for high reaction rates. With decreasing the reaction rate, the density of $P$ component first decreases and then increases at lower layers. A very sharp "peak" of $P$ density ($D = 0.43$) exists at lower layers ($y = 2$) at very low reaction rate ($R = 0.01$). At upper layers, however, the density of $P$ component keeps decreasing on decreasing the reaction rate. The density of $H$ component has the typical "hill" shape and almost symmetric. On decreasing the reaction rate, the $H$ density decreases at lower layers ($y = 0 - 5$). The "peak" however shifted a little bit toward higher layers with higher density on decreasing the reaction rate. At upper layers, the $H$ density fluctuates on decreasing the reaction rate.
8.4 Finite Size Effect

The finite size effect is checked by performing simulations on different lattice sizes. Variations of interface width for these lattices are presented in the figure 8.39. As can be seen, there is no severe effect of the lattice size on the qualitative nature of the growth of the interface width in case 8. Similar checks on the film thickness show the same result.
Figure 8.35: ATR-FTIR spectral absorbance profiles for 1524 and 1560 cm\(^{-1}\) N-H bending modes of WB 2K-PUR films with varied NCO:OH ratios recorded from the F-A interface.
Figure 8.36: Density profile of all components along the longitudinal direction in the long time limit at different reaction rates using the same parameter as in Figure 8.5 (case 8).
CHAPTER 8. FILM WITH ISOTROPIC GROWTH

Figure 8.37: Density profile of \( P \) component along the longitudinal direction in the long time limit at different reaction rates using the same parameter as in Figure 8.5 (case 8).
Figure 8.38: Density profile of $H$ component along the longitudinal direction in the long time limit at different reaction rates using the same parameter as in Figure 8.5 (case 8).
Figure 8.39: evolution of the interface width $W$ using BFM for a temperature $T = 5$ with reactive aqueous solvent on different sample sizes each with ten independent samples for $p_H = 0.0115$ and $p_P = 0.023$ with initial water concentration $p_A = 0.0422$ (case 8).
In this thesis, a coarse-grained computer simulation model is presented to study the film growth and macroscopic morphological feature (film thickness, surface roughness and longitudinal constituent density profile) in a multi-component polymer system. Main features of this model are: acceptable qualitative approximation to the real film formation processes, simple and easy to implement, easy to vary a relatively large number of parameters, suitable for visual study of the physical phenomenon, complementary to experimental observations, and extensive and flexible to apply to other systems.

The mixture consists of reactive hydrophobic (H) and polar groups (P) in a reactive aqueous solvent (A) which is also allowed to evaporate. Characteristics of each component such as hydrophobic and polar interactions, molecular weights, and specific functionality for the covalent bonding are used to describe the waterborne two-component polyurethane (WB 2K-PUR) film growth as an example. Constituents move stochastically via the Metropolis algorithm to explore thermodynamic equilibration while the kinetic reactions are incorporated through flexible covalent bonding (Bond Fluctuation Model) which may arrest the growth before reaching equilibrium. The excluded volume constraints and cross-linking for bonds are implemented via limiting the range for bond formation to $r = 2$, the nearest neighbor distance between the reacting units and the bond length fluctuation to $2 \leq r \leq \sqrt{10}$ excluding $\sqrt{8}$. These constraints are relaxed considerably with effective bond fluctuation model (EBFM) where cross-linking and excluded volume constraints are considered only approximately in the spirit of a mean-field description.
A systematic approach has been employed to develop the model. Considerable improvements over the recent studies on modeling the film formation in a waterborne polyurethane film have been achieved by our proposed model while maintaining the efficiency of a discrete lattice. The degrees of freedom for each constituent to move and better relax is much larger, 26 in this study in comparison to 6 in previous studies [25, 26]. In contrast to fixed bond length and immobile bonded units in previous studies, the flexibility of fluctuating covalent bonds between the reacted functional groups with ability to perform their stochastic movement not only make it a more realistic film growth but also adds elastic nature to the film. This larger degree of freedom and flexibility is introduced via using bond fluctuation model. Another big effort of this work is to include realistic reaction kinetics pertaining to the waterborne two-component polyurethane system. Thus in addition to the main reaction between hydrophobic and polar groups, the hydrolysis reaction between hydrophobic groups and aqueous components is included to make it a more realistic film growth [11] — [17]. It also helps to elucidate the role of water in WB 2K-PUR film formation more clearly. The situations of including or excluding the volume of water after its reaction with hydrophobic component are both considered. A further improvement of the model is to allow film propagate evenly in spatial dimensions. This implementation of cross-linking starting isotropically in space not only take into account the specific mechanism involved in WB 2K-PUR but also increase the flexibility of the model to apply to other film formation processes.

Independent parameters in these simulations are concentration of hydrophobic component, hydrophilic component, and water, their relative interaction strengths (ε), molecular weight ($M_w$), temperature ($T$), and reactivity ($R$). Film thickness/roughness evolution with time and effects of temperature, relative humidity (initial water concentration), stoichiometry (NCO:OH ratio), and reaction rate on film morphology are examined specifically. Film thickness grows and its interface evolves and equilibrates as the simulation...
continues. Generally, the growth pattern for film thickness and its interface width can be described by three stages: initial growth, relaxation, and saturation. Power-law dependence is found for the initial growth of film thickness and surface roughness, i.e., $h \propto t^\gamma$, $W \propto t^\beta$, with all simulations. Such power-law dependences are more than one for the initial growth of film thickness and surface with most simulations. Information on product distribution is also analyzed by examining the density profile of each component in the film network.

The effect of hydrophobic and polar interaction within the framework of EBFM is explored for a range of temperature in chapter 5. With additional interaction among the constituents, a much slower relaxation of film thickness is found at low temperature due to the competition between the interaction energy and thermal energy causing water to evaporate. Another interesting observation is an oscillatory response of interface width due to bond fluctuations of covalent bonded functional groups augmented by the interplay between the thermal energy and the free volume due to water evaporation. With the hardcore interaction alone, the saturated film thickness $h_s$ and its interface width $W_s$ increase linearly with two stages on increasing the temperature. With additional hydrophobic and polar interaction, in contrast, a sharp decrease of $h_s$ and $W_s$ at low temperature is followed by slight increase at high temperature.

Cross-linking reaction from an adsorbing substrate with appropriate bond fluctuation and excluded volume constraint in a non-reactive aqueous solvent is discussed in chapter 6. With the more strict range for bond formation and bond length fluctuation, the film growth slows down significantly and the oscillatory response of interface width growth disappears. The initial water concentration and NCO:OH ratio have little influence on the growth pattern of mean surface height and its interface width. At low reaction rate, however, the relaxation region of film thickness is smeared out and a "valley" of interface width appears in the intermediate stage. The saturated film thickness $h_s$ and its interface
width $W_s$ are found to increase on increasing the temperature, the NCO:OH ratio and reaction rate due to the more complete reaction and more active bond vibration at high temperature, more dangling bonded $H$ particles at the surface at high NCO:OH ratio, and more complete reaction at high reaction rate. The initial water concentration does not affect much the saturated film thickness and roughness since the hydrolysis reaction has not been taken into consideration. Density profiles along longitudinal direction show that a more uniform film with $H$ and $P$ component is achieved at high temperature; a dense $P$ layer near the substrate and a thin $H$ component rich layer in the bulk are formed at low temperature. More $H$ components are present near the substrate at high NCO:OH ratio.

Cross-linking reaction from an adsorbing substrate in a reactive aqueous solvent is examined in chapter 7 where two cases, including and excluding the volume of water, are discussed. A significant feature of the former system is the "swollen" effect due to the inclusion of volume of reacted water which cuts out the intermediate stage of film thickness relaxation. Saturated film thickness increases with temperature with two stage linear expansion, while saturated film roughness first increase on increasing the temperature and then decrease on further increasing the temperature. With volume of reacted water excluded from the film, the "swollen" effect is also excluded leading to a slower initial film growth and a thinner film. Saturated film thickness $h_s$ increases on increasing temperature, initial water concentration, NCO:OH ratio and reaction rate. The dependence of saturated film roughness $W_s$ with these parameters becomes more complexed due to the interplay and coercion of different factors such as reaction completeness, degree of bond vibration, presence of extra consumed $H$ particles and bonded dangling $H$ or $H^*$ particles near the surface. Density profiles indicate that polyurethane-rich layers are present in the middle part of the film at low temperature and in the lower part of the film at low initial water concentration; polyurea-rich layers are present in the topper part of the film at high initial water concentration and in the middle part of the film at low NCO:OH ratio and in
the lower part of the film at high NCO:OH ratio.

Cross-linking reaction starting isotropically in space in a reactive aqueous solvent with exclusion of the volume of reacted water is the main focus of chapter 8. The isotropic propagation mode creates a step in the initial film growth and a bigger starting thickness and roughness. The film growth is much faster than the one starting from the substrate. Thus a thicker film is resulted as much more aqueous solvent are able to react and hence more hydrophobic components are consumed. The much faster and more even growth result in a “valley” in the very early stage of roughness growth due to the temporary smoothing of film near the substrate. An oscillatory relaxation pattern of film roughness is also observed likely due to the fast growth in a short amount of time resulting in a quite stretched film in the intermediate stage. As cross-linking takes place so fast, temperature, initial water concentration and NCO:OH ratio have little effect on the initial thickness and interface width growth, but have more impact on the relaxation and saturation stage. A film with less condense layers in the lower and middle part of the film and more fluctuating bumps in the topper part is formed at low temperature; and polyurea-rich layers are formed in the lower part of the film at middle temperature. Both the steady state film thickness and roughness decrease with temperature in low temperature region and increase with temperature in high temperature region. The roughness increases on increasing the initial water concentration and NCO:OH ratio, but fluctuates on increasing the reaction rate. Density profiles indicate that some polyurea-rich layers are formed in the middle part of the film at high initial water concentration and in the lower part of the film at high NCO:OH ratio. Polyurethane relatively rich layers are formed in the middle part of the film at high NCO:OH ratios. Simulation data suggest that with increasing the initial water concentration, more polyurea and less polyurethane are formed in the film; with increasing the NCO:OH ratio, however, both contents of polyurea and polyurethane increases. These results are qualitatively consistent with the spectroscopic data (FTIR).
and microscopic morphology images (AFM).

The proposed research is highly interdisciplinary involving polymer material science, computer science, physics and chemistry. The computer simulation model provides information on film evolution and equilibration in time on a microscopic scale. It gives valuable hints for the interpretation of experimental results on a macroscopic level. Connection between experiment and the computer simulation model lies in the implementation of the perceived reaction kinetics, i.e., with unchecked hypothesis. This is primarily guided by the ongoing experiments. Despite enormous amount of theoretical (analytical and scaling) work [32, 45] on the growth of the interface width and scaling of the roughness on relatively simpler systems (e.g., one component (mono-dispersed) particle deposition models), we are not aware of any theoretical work that involves such a complex system with multi-component constituents participating in specific reaction kinetics without conserving the solvent concentration. Because of complexity and lack of theoretical work, early attempts were made with very simplified models (a minimalist approach with minimum degrees of freedom). In this work, attempts are made to include a much larger degree of freedom with appropriate excluded volume interaction while incorporating the realistic reaction kinetics as well as polymerization mechanism. As a result a more realistic simulation of film formation is achieved with such a simple model. We hope that this study will stimulate experimental studies on appropriate systems and a more realistic and efficient computer simulation modeling. In addition, we expect more application and extension of the model to other film formation processes in the future.
Appendix A

COMPUTER ALGORITHM FLOWCHART

Start

Generate initial state

Attempt to move each particle

Attempt to form a bond between particles

Calculate quantities

\[ t_{\text{max}} = t_{\text{max}} - 1 \]

\[ t_{\text{max}} = 0 \] ?

\[ Y \]

\[ s_{\text{max}} = s_{\text{max}} - 1 \]

\[ s_{\text{max}} = 0 \] ?

\[ Y \]

Calculate the average of the quantities over \( s_{\text{max}} \)

Output the results

End
Appendix B

THE METROPOLIS ALGORITHM

1) Choose a starting configuration state $X$ and compute the Hamiltonian $H(X)$.

2) Choose a new trial state $X'$ and find the difference $\Delta H = H(X') - H(X)$ in the Hamiltonian from the old state.

3) If $\Delta H$ is negative, then set $X = X'$. Otherwise pick a random number $r$ between zero and one. If $r < e^{-\frac{\Delta H}{kT}}$ then set $X = X'$, but otherwise do nothing.

4) If at equilibrium, add the desired quantities $a_1(X), a_2(X), \ldots$ to their respective sums $A_1(X), A_2(X), \ldots$ and increment the counter $N$.

5) Repeat from step 2 until the average of the quantities in step 4 converge.

6) Divide the sums by the number of iterations to get the physical quantity, $A_1(X)/N, A_2(X)/N, \ldots$. 

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