Dynamics of spinodal decomposition in polymer blends/

Mahesh A. Kotnis
University of Massachusetts Amherst

Follow this and additional works at: https://scholarworks.umass.edu/dissertations_1

Recommended Citation
https://scholarworks.umass.edu/dissertations_1/807

This Open Access Dissertation is brought to you for free and open access by ScholarWorks@UMass Amherst. It has been accepted for inclusion in Doctoral Dissertations 1896 - February 2014 by an authorized administrator of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.
DYNAMICS OF SPINODAL DECOMPOSITION IN POLYMER BLENDS

A Dissertation Presented
by
MAHESH A. KOTNIS

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

February 1993
Polymer Science and Engineering Department
DYNAMICS OF SPINODAL DECOMPOSITION IN POLYMER BLENDS

A Dissertation Presented

by

MAHESH A. KOTNIS

Approved as to style and content by:

M. Muthukumar, Chair

David A. Hoagland, Member

James A. Donovan, Member

William J. MacKnight, Department Head
Polymer Science and Engineering
DEDICATION

This dissertation is dedicated to my parents who have always believed and practised that education, apart from being a means of achieving money and power, is a vital means of nourishing a healthier and a broader perspective in life. I sincerely desire and hope that my future pursuits in life are motivated by and are consistent with these thoughts.
I would like to thank my dissertation committee members, Dr. David Hoagland, Dr. James Donovan, and Dr. M. Muthukumar for their contributions and sincere interest. I would also like to thank Dr. Henning Winter for his suggestions and contributions. I would like to acknowledge Dr. Amitabh Chakrabarti for his help in numerical methods and Mr. Kleanthes Koniaris for his help in computer graphics.

I would like to sincerely thank my thesis advisor, Dr. M. Muthukumar, for his patience and insightful guidance throughout this research work. I came to Umass to specifically work for him, with a desire to learn fundamental polymer science. I must say that it was a very rich experience and the training I received in his group has surely broadened my scientific skills and thinking.

I would like to thank my friends in the department and in particular, Michael Graff, Malika Menasveta, Cristina Urdaneta, Wilson Cheung, Bob Jennings and Ajay Parkhe, for their support and friendship.

I have no good words to express my gratitude to my parents and my wife, Deepa, who always encouraged and cherished my academic dream, even in times when I myself felt like I was chasing a mirage.
ABSTRACT

DYNAMICS OF SPINODAL DECOMPOSITION IN POLYMER BLENDS

FEBRUARY 1993

MAHESH A. KOTNIS, B.CHEM., UNIVERSITY OF BOMBAY

M.S., UNIVERSITY OF TENNESSEE

Ph.D., UNIVERSITY OF MASSACHUSETTS

Directed by: Professor M. Muthukumar

A numerical study investigating the dynamics of spinodal decomposition in polymer blends in three dimensions has been performed. The objective of this research was to investigate the effects of the chain-like nature of polymer molecules on the formation and growth of the phase separating domains and to interpret the results of this numerical study to get a better understanding of the experimental observations that are unique to polymeric systems.

The relative contributions of the enthalpic and entropic parts of the interfacial free energy of the inhomogeneous mixture have been computed for the non-hydrodynamic regime of spinodal decomposition in the quiescent polymer blend. It has been shown that the dominance of the entropic contribution leads to the freezing of the dispersed domain morphology and a coarsening mechanism based on the transport of long chain molecules parallel to the interface can explain this novel feature characteristic of polymer blends.

Calculations have been also made to study spinodal decomposition under simple shear flow by making a mean field
approximation for the velocity field. The domain growth has been found to be highly anisotropic with enhanced growth along the flow direction than in the directions perpendicular to the flow.

The potential of the computational scheme used in the present calculations, for applications in other systems, is also discussed.
# TABLE OF CONTENTS

| Page |
|-----------------|-----------------|
| ACKNOWLEDGEMENTS | Page |
| ABSTRACT | vi |
| LIST OF FIGURES | x |

Chapter

1. INTRODUCTION
   - Phase Behavior of Polymer Blends
     - Phase Separation Mechanisms
   - Spinodal Decomposition in Polymer Blends
     - Technological Applications
     - Experimental Studies
     - Theoretical Studies
     - Spinodal Decomposition Under External Flow
   - Research Objectives
   - Dissertation Outline with a Brief Summary of Results

2. MODELING OF SPINODAL DECOMPOSITION
   - Spinodal Decomposition in Small Molecule Mixtures
     - Free Energy of Inhomogeneous Small Molecular Mixtures
   - Models for Spinodal Decomposition in Polymer Blends
     - Free Energy of Inhomogeneous Polymer Mixtures
     - Spinodal Decomposition in Quiescent Mixtures
     - Spinodal Decomposition Under External Flow
     - Mean Field Approximation
   - System of Investigation
   - Computational Scheme
     - Input
     - Numerical Calculations
     - Euler Method
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vector Programming</td>
<td>51</td>
</tr>
<tr>
<td>Fast Fourier Transform</td>
<td>52</td>
</tr>
<tr>
<td>Output</td>
<td>52</td>
</tr>
<tr>
<td>Computer Graphics</td>
<td>52</td>
</tr>
<tr>
<td>Structure Factor</td>
<td>53</td>
</tr>
<tr>
<td>Pair Correlation Function</td>
<td>54</td>
</tr>
<tr>
<td>3. RESULTS AND DISCUSSION</td>
<td>60</td>
</tr>
<tr>
<td>Spinodal Decomposition in the Quiescent State</td>
<td>60</td>
</tr>
<tr>
<td>Spinodal Decomposition under Simple shear Flow</td>
<td>69</td>
</tr>
<tr>
<td>4. CONCLUSIONS AND FUTURE WORK</td>
<td>102</td>
</tr>
<tr>
<td>Conclusions</td>
<td>102</td>
</tr>
<tr>
<td>Future Work</td>
<td>104</td>
</tr>
<tr>
<td>APPENDIX: REPRESENTATIVE PROGRAMS</td>
<td>110</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>123</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Typical phase diagram of a binary polymer blend with upper critical solution temperature.</td>
<td>18</td>
</tr>
<tr>
<td>1.2</td>
<td>Schematics of the structure development in the phase separation by the nucleation and growth mechanism.</td>
<td>19</td>
</tr>
<tr>
<td>1.3</td>
<td>Schematics of the structure development in the phase separation by the spinodal decomposition mechanism.</td>
<td>20</td>
</tr>
<tr>
<td>1.4</td>
<td>Experimental data by Hashimoto et al. showing time dependence of $q_m$ for critical mixtures of polystyrene and poly(vinyl methyl ether) blend, reproduced from the Ref. 8.</td>
<td>21</td>
</tr>
<tr>
<td>1.5</td>
<td>Experimental data by Bates et al. showing time dependence of $q_m$ for critical mixtures of deuterated and protonated 1,4 polybutadienes, reproduced from the Ref. 10.</td>
<td>22</td>
</tr>
<tr>
<td>1.6</td>
<td>Experimental data by Hashimoto et al. showing time dependence of $q_m$ for off-critical mixtures of polystyrene and a random copolymer of styrene and butadiene, reproduced from the Ref. 11.</td>
<td>23</td>
</tr>
<tr>
<td>2.1</td>
<td>Schematics of the simple shear flow geometry.</td>
<td>56</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic representation of the computational methodology used in the present study.</td>
<td>57</td>
</tr>
<tr>
<td>3.1</td>
<td>The spherically averaged structure factor $S(k, \tau)$ vs. $k$ for different values of $\tau$ calculated for the critical mixture ($\phi_o=0.5$) quenched to 49°C.</td>
<td>73</td>
</tr>
<tr>
<td>3.2</td>
<td>The spherically averaged pair correlation function $g(x, \tau)$ vs. $x$ for different values of $\tau$ calculated for the critical mixture ($\phi_o=0.5$) quenched to 49°C.</td>
<td>74</td>
</tr>
</tbody>
</table>
3.3 Time dependence of domain size $R$ for critical ($\phi_0=0.5$) and off-critical ($\phi_0=0.4$) mixtures. The critical mixture is quenched to 54.5(○), 49(●) and 25(Δ)°C. The off-critical mixture is quenched to 35(■) and 15(▲) °C.

3.4 Time dependence of $k_m$ for critical ($\phi_0=0.5$) and off-critical ($\phi_0=0.4$) mixtures. The critical mixture is quenched to 54.5(○), 49(●) and 25(Δ)°C. The off-critical mixture is quenched to 35(■) and 15(▲) °C.

3.5 Computer images of the evolving phases as a function of reduced time $\tau_1$ for (a) critical mixture, $\phi_0=0.5$ and (b) off-critical mixture, $\phi_0=0.4$ quenched at 35°C.

3.6 An off-critical mixture of composition $\phi_0=0.4$ is quenched to three different quench temperatures; 15(■), 30(●) and 35(▲). Sizes of the frozen domains are smaller for shallower quench depths.

3.7 The domain growth is arrested for the off-critical mixture of composition $\phi_0=0.45$ when quenched to 50°C(△). The same composition shows unarrested coarsening of domains when quenched to 46°C(●).

3.8 Images of the evolved domains at $\tau_1=250$ are shown for the off-critical composition $\phi_0=0.45$ quenched to 50°C (a), 46°C (b) and 25°C (c). Dispersed domains are formed in (a) while interconnected domains are formed in (b) and (c).

3.9 Calculated binodal (— — —) and spinodal curves (———) for the particular polymer blend in this study. The dotted line (— — —) represents the transition from the percolated to dispersed morphology based on the percolation threshold of 0.37.
3.10 Time dependence of domain size $R$ for the off-critical ($\phi_0=0.4$) mixture quenched to 35(●) and 40(o) °C. Here the free energy functional has only the enthalpic contribution to the gradient term. ..............83

3.11 Computer images of the evolving phases as a function of reduced time $\tau$ for the off-critical mixture ($\phi_0=0.4$) quenched to 35°C. .......84

3.12 $R(\tau)$ data for the critical mixture quenched to 54.5°C is plotted as a function of $\tau^{1/3}$. .......85

3.13 $R(\tau)$ data for the critical mixture quenched to 54.5°C is plotted as a function of $\tau^{1/4}$. .......86

3.14 $I(k,\tau)$ $k_m(\tau)^3$ is plotted as a function of $(k/k_m)$ on log-log scale for $\phi_0=0.5$ and $T=35°C$. .............................................87

3.15 $I(k,\tau)$ $k_m(\tau)^3$ is plotted as a function of $(k/k_m)$ on log-log scale for $\phi_0=0.45$ and $T=50°C$. .............................................88

3.16 $I(k,\tau)$ $k_m(\tau)^3$ is plotted as a function of $(k/k_m)$ on log-log scale for $\phi_0=0.45$ and $T=25°C$. .............................................89

3.17 $I(k,\tau)$ $k_m(\tau)^3$ is plotted as a function of $(k/k_m)$ on log-log scale for $\phi_0=0.4$ and $T=35°C$. .............................................90

3.18 Calculated scattered intensity in the x direction for SD in a critical mixture at $T=35°C$ and under the dimensionless shear of 0.1, is plotted as a function of $k$ for various $\tau$. .............................................91

3.19 Calculated scattered intensity in the z direction for SD in a critical mixture at $T=35°C$ and under the dimensionless shear of 0.1, is plotted as a function of $k$ for various $\tau$. .............................................92
3.20 Calculated scattered intensity in the y direction for SD in a critical mixture at T=35°C and under the dimensionless shear of 0.1, is plotted as a function of k for various τ. .................................93

3.21 Time dependence of $k_m$ in x(□), y(■), and z(◆) directions is shown for the SD in a critical mixture at T=35°C and under the dimensionless shear of 0.1. ...............................94

3.22 Computer images of the evolving phases in XY plane as a function of reduced time $\tau$ are shown for the SD in a critical mixture at T=35°C and under the dimensionless shear of 0.1. .................................95

3.23 Computer images of the domains in the XY, XZ, and YZ planes evolved during the SD in a critical mixture at T=35°C and under the dimensionless shear of 0.1 are shown for the reduced time $\tau = 400$. .................................96

3.24 Characteristic $k_m$ in the x direction is plotted as a function of $\tau$ for the SD in a critical mixture at T=35°C under different dimensionless shears of 0.1 (a), 0.05 (◆), 0.5 (□), and 1.0 (■). ...............................97

3.25 Characteristic $k_m$ in x, y, and z directions are plotted as a function of $\tau$ in parts (a), (b), and (c) respectively, to determine the growth exponents in the three directions for the SD in a critical mixture at T=35°C under two different dimensionless shears of 0.1 (□) and 0.05 (◆). ...............................98

4.1 A schematic showing various effects of the chain-like nature of polymer molecules on the phase behavior of polymer mixtures. ......108
CHAPTER 1
INTRODUCTION

Phase Behavior of Polymer Blends

Polymer blends are mixtures of two or more polymers dispersed in each other either by mechanical means using compounding devices such as roll mills or twin screw extruders or by chemical methods such as precipitation polymerization, emulsion polymerization, or compositional quenching\(^1\). The incentives to make polymer blends usually stem from the need to reduce the cost of the final product or from the need to develop new materials for specific end applications by modifying the properties of the component polymers.

The chain-like nature of polymer molecules results in the small entropy of mixing and consequently most of polymer blends are thermodynamically immiscible. It is well known that the morphological and interfacial properties of these multiphase systems play an important role in most of their practical applications. A large number of polymer blends have been commercialized and their ubiquitous presence in the consumer and specialty products is testimony to their current and potential technological importance. From a theoretical standpoint, the problem of understanding phase behavior of polymer blends has been long lasting. The well known Flory-Huggins theory\(^2\) and several modifications\(^3\) of the same by
going beyond the mean field approximation, are able to capture the essentials of the thermodynamics of polymer mixtures. However, theoretical advances in the thermodynamics of inhomogeneous polymer mixtures and in the dynamics of the phase separation process, have been relatively difficult due to the mathematical complexity in treating the non-linear effects and also due, to the lack of complete understanding of polymeric interfaces. Thus the study of phase separation in polymer blends has been of considerable importance from a theoretical as well as from a technological perspective.

**Phase Separation Mechanisms**

A typical phase diagram of a binary polymer blend with upper critical solution temperature (UCST) is shown in Figure 1.1. The binodal curve marks the boundary between the one phase and the two phase regions while the spinodal curve delineates the boundary between the unstable and the metastable regions within the two phase region. If the polymer blend is quenched from the one phase region into the metastable region (say to point B in Figure 1.1) then the blend would undergo phase separation by the nucleation and growth (NG) mechanism. In this mechanism there exists a barrier for the nucleation step and once the stable nuclei are formed in the mother phase, they subsequently grow to form a typical dispersed domain morphology. These phase separated domains undergo coarsening wherein, the larger domains grow at the expense of the smaller domains. This
coarsening process is known as Ostwald rippening\textsuperscript{1}. The structure development in the NG mechanism is schematically shown in Figure 1.2. If the quench is made into the unstable region of the phase diagram (say to point C in Figure 1.1) then the phase separation would occur spontaneously by the spinodal decomposition (SD) mechanism. In this mechanism, the concentration fluctuations grow without any barrier and this spontaneity of the SD process results from the thermodynamic instability of the mixture, which is clear from the free energy verses composition diagram in Figure 1.1. The region between the inflexion points on the free energy verses composition curve corresponds to the thermodynamically unstable region and any mixture belonging to this region can lower its free energy by forming two phases until the compositions of the co-existing phases reach the equilibrium values as shown in the same Figure 1.1. The structure formed in the early stage of the spinodal process is characteristically percolating irrespective of the initial composition of the mixture. As the phase separation proceeds and the two phases try to reach their equilibrium compositions, the percolated morphology can undergo a transition to the dispersed domain morphology depending upon the relative volume fractions of the two co-existing phases. The structure development in the SD process is schematically shown in Figure 1.3.
Spinodal Decomposition in Polymer Blends

Technological Applications

The percolating structures resulting from the SD process have been exploited in a number of technological applications. A large variety of membranes used in microfiltration, gas separation, dialysis are prepared by the phase inversion technology which involves the SD of polymer solutions to obtain a polymer rich phase and a solvent rich phase. Solvent is then removed from the system by freeze drying to obtain a highly porous polymer membrane. Another important example is that of the compositional quenching technology where a solution of two or more polymers in a common solvent is adiabatically flashed in a twin screw extruder to obtain a microscale dispersion of the component polymers in each other. This process is used commercially to manufacture some of the impact modified plastics used in every day life such as high impact polystyrene, impact modified ABS, Noryl™ (polybutadiene microdispersed in an alloy of polyphenylene ether and polystyrene). In all these manufacturing processes, it is very important to have control over the morphology in terms of the size of the phase separating domains. When the SD has occurred to a sufficient extent, giving the domain size as required by a particular application, morphology is 'frozen in' or 'locked in' by quenching the mixture, by removing the solvent, or by initiating the chemical cross linking agent. Thus in these technological applications, kinetics of spinodal
decomposition in polymer mixtures plays a key role in determining the structure-property relationship. Even though these technologies have been widely used and are well developed, they involve lot of trial and error type approach and understanding of the SD process in polymer mixtures from a molecular point of view would greatly help in the design and modeling aspects of these processes.

**Experimental Studies**

The earliest attempts to study the kinetics of SD in polymer blends were due to Nishi et al.\(^5\) and Mcmaster\(^6\). They studied the phase diagram and the phase separation dynamics by light transmission, optical microscopy, and pulsed NMR methods but their analyses were more on the qualitative side. Recently, time resolved light scattering coupled with temperature jump method has been employed to obtain quantitative data on the kinetics of SD in polymer mixtures\(^7\). Owing to molecular entanglement the characteristic relaxation time for undiluted polymers is typically many orders of magnitude larger than that of simple liquids (small molecular liquids) and this allows the investigation of the SD kinetics over a much greater range of phase space than is feasible when studying simple liquid mixtures. In the time resolved light scattering technique, the kinetics is traced by measuring the scattered intensity \(I(k)\), as a function of the wave vector, \(k\) at various times during the phase separation process. The spherically averaged scattered intensity \(I(k)\) shows a maximum for a characteristic magnitude of \(k\), denoted
here by $k_m$, the reciprocal of which corresponds to the
dominant length scale of the phase separating domains. As
the phase separation proceeds, the size of the phase
separated domains increases and the maximum in $I(k)$ shifts to
lower values of $k_m$. $k_m$ can be plotted as a function of time $t$
to yield power laws for the domain growth, $k_m \sim t^{-n}$, where the
exponent $n$ depends upon the extent of phase separation. The
important experimental systems that have been widely studied
so far are: polystyrene and poly(vinyl methyl ether)$^{7-9}$,
deuterated and protonated polybutadienes$^{10}$, polybutadiene and
a styrene/butadiene random copolymer$^{11}$.

Experiments on the above mentioned systems have
demonstrated that the value of the exponent $n$ varies over a
wide range from 0 to 0.8. The value of the exponent $n$ is
associated with a particular mechanism of domain coarsening
and hence, depending upon its value, the kinetics of SD has
been traditionally characterized by three time regimes:
early, intermediate and late stages. In the early stage, the
value of $k_m$, denoted here by $k_{0m}$, is independent of time (i.e.
the growth law is $k_m \sim t^0$) and the scattered intensity $I(k)$
increases exponentially with time. Thus the wavelength of
the concentration fluctuations, which is proportional to
reciprocal $k_{0m}$, is constant while the amplitude of the
concentration fluctuations, the square of which is
proportional to the intensity of scattered light, increases
with time. These experimental findings have varified the
predictions of the linear theories of SD in polymer mixtures
by de Gennes\textsuperscript{12} and by Binder\textsuperscript{13}. The end of the early stage and the onset of the intermediate stage, is marked by the shift in the value of $k_m$ to values lower than $k_m^0$ and by the departure of the intensity increase with time from the exponential behavior. In the intermediate stage, both the wavelength and the amplitude of the concentration fluctuations increase as a function of time. Experimental results have shown that the characteristic value of the exponent $n$ for the intermediate stage is 0.33 in the asymptotic limit. The end of the intermediate stage and the onset of the late stage is marked by the dominant presence of the hydrodynamic interactions in the phase separating mixture. The asymptotic exponent characteristic of the late stage has been observed to have a value closer to 1. Because of the lack of the theoretical studies in the intermediate and late stages of SD in polymer systems, the experimental data is usually compared with the predictions of the theories and models developed for domain growth during the SD in small molecule mixtures.

In order to compare the unmixing behavior in different systems, experimental data is usually plotted in terms of the dimensionless quantities which are motivated by the linear theories of SD. Data\textsuperscript{8} by Hashimoto et al. on the critical mixtures of polystyrene and poly(vinyl methyl ether) is shown in Figure 1.4. It clearly indicates that the growth law for the critical mixtures is independent of the quench depth. Such phase separation behavior showing quench depth
independent growth law is also found in small molecule systems and hence, Hashimoto et al. claimed to observe the "universality" in the phase separation behavior. Figure 1.5 shows data\textsuperscript{10} by Bates et al. on the critical mixtures of deuterated and protonated polybutadienes. These data, contrary to Hashimoto's data, show quench depth dependent growth laws indicating the violation of the universality in the phase separation behavior. In both the studies, validity of dynamical scaling was observed at sufficiently late times during the phase separation, indicating the self-similarity in the structures formed at different times in the later stages.

In the case of off-critical mixtures, the growth of the phase separating domains has been observed to stop after a certain characteristic time, called the freezing time, which depends upon the quench depth and the initial composition of the off-critical mixture. This freezing of the morphology has been referred as 'pinning' in the literature and is not observed in the off-critical mixtures of small molecules, but is unique to polymer mixtures. A representative data\textsuperscript{11} on the pinning phenomenon is shown in Figure 1.6. The characteristic wave number $k_m$ decreases initially but soon flattens out indicating no further domain growth. Also, the shallower the quench, the earlier is the pinning and the smaller is the size of the pinned domains.
Theoretical Studies

The concept of SD is universally accepted today but it was only three decades ago that it was introduced for the first time by Cahn and Hilliard in the context of phase behavior of metal alloys. Even today, the theoretical understanding of the SD process is based on the Cahn-Hilliard (CH) formulation. de Gennes extended the original CH formulation to polymer blends. Analytical studies of these models have been reasonably successful in describing the early time behavior of the phase separation process but due to their linearized nature, they are not useful in the later stages. Because of the mathematical complexity of incorporating non-linear effects, it is very difficult to do analytical work describing the intermediate and late stages of the SD process.

There have been two approaches to derive domain growth laws for the intermediate and late stages. In the first approach, domain growth law is derived based on a proposed molecular mechanism underlying the coarsening of the phase separated domains. In the second approach, the non-linear version of the CH formulation is solved by making suitable simplifying assumptions. Lifshitz and Slyozov examined the case of widely spaced domains of one phase growing and shrinking in the matrix of the second phase. They found that the domain growth is limited by the diffusion through the matrix and based on their evaporation-condensation type coarsening mechanism, they obtained an asymptotic domain.
growth law, $k_m \sim t^{-1/3}$. Voorheese and Glicksman\textsuperscript{17} modified the Lifshitz-Slyozov theory by considering the interactions between the dispersed domains and found that the growth law $k_m \sim t^{-1/3}$ is unchanged. Both of these analyses are applicable when the volume fraction of the minority phase is much smaller than that of the majority phase. These models have to be modified when the volume fractions of the two phases are comparable, as in the critical or a nearly critical quench, where the geometry of the resulting domains is highly interconnected rather than being dispersed. Huse\textsuperscript{18} generalized the Lifshitz-Slyozov theory for the coarsening of percolated domains and obtained $k_m \sim A + Bt^{-1/3}$ where $A$ and $B$ are numerical constants. Binder and Stauffer\textsuperscript{19} proposed that the coarsening of the dispersed domains occurs by the diffusion and coalescence of the clusters and also obtained a growth law $k_m \sim t^{-1/3}$. Siggia\textsuperscript{20} accounted for the hydrodynamic interactions in the later stages and proposed a capillary flow model to take into account the motion of the interface driven by the interfacial tension. He obtained $k_m \sim t^{-1}$.

Langer, Baron and Miller\textsuperscript{21} (LBM) solved the non-linear continuity equation in the CH formulation by using the 'decoupling approximation'. Their theory gives the growth law, $k_m \sim t^{-0.212}$. Kawasaki and coworkers\textsuperscript{22} have generalized the LBM theory by introducing hydrodynamic interactions. Their theory gives no simple growth law but predicts a time dependent exponent varying between 0 to 0.6.
All these models and theories are developed for small molecular systems and naturally do not account for the chain-connectivity in polymer molecules, none the less, they have been useful in analyzing the data in polymer systems. In this regard, Kawasaki and Sekimoto\textsuperscript{23} have recently developed a theory for the coarsening of polymeric domains and have obtained a growth law, $k_m \sim t^{-1/4}$.

In the light of the mathematical difficulty in the analytical treatments, numerical studies and Monte Carlo simulations have been found extremely useful to understand and predict the late time behavior of the SD process in small molecule systems\textsuperscript{24-29}. Similar techniques have been recently employed to gain insight into the late stage dynamics of SD in polymer mixtures. Monte Carlo simulations of SD in a ternary system consisting of two polymers and a solvent have been reported by Sariban and Binder\textsuperscript{30}. Chakrabarti et al.\textsuperscript{31} have reported the numerical study of SD in a symmetric polymer blend in three dimensions. In their study, the Onsager coefficient was taken as constant and only the dynamics of critical mixtures was explored. They found that the growth law for the characteristic domain size was independent of the final quench temperature for critical mixtures of a symmetric polymer blend.

**Spinodal Decomposition Under External Flow**

Polymers are subjected to external flow in most processing operations e.g. shear flow in extrusion, elongational flow in fiber spinning and in film blowing, etc.
The phase behavior of polymer mixtures can be significantly altered by the imposed flow. This strong coupling between the phase behavior and the external flow is characteristic of polymeric systems and is a manifestation of the chain-like nature of polymer molecules. The effect of flow on the phase behavior is two fold: first, it changes the phase diagram i.e. the boundaries between the one phase and the two phase regions, and secondly, it affects the kinetics of phase separation and the resulting morphology.

The effect of flow on the phase separation behavior of small molecules was first analytically tackled by Onuki and Kawasaki\textsuperscript{32}. They predicted a lowering of critical temperature $T_c$ under shear, and the anisotropic growth of the phase separating domains showing elongation in the flow direction. Their predictions were experimentally confirmed by Beysen's et al\textsuperscript{33}. There have been many experimental reports about the effect of flow on the phase separation behavior of polymer solutions\textsuperscript{34-37} and polymer blends\textsuperscript{38-40}. Like the small molecular case, in most two component polymer solutions and polymer blends, shear flow suppresses the concentration fluctuations and lowering of the spinodal temperature is observed. These mixtures show what is termed as flow induced homogenization. However in the case of entangled polymer + solvent systems\textsuperscript{34-36} (high molecular weight of polymer) and some polymer blends\textsuperscript{39}, it appears that shear flow shows significant increase in concentration fluctuations. It has been reported\textsuperscript{34-36} that flowing polystyrene solutions with
high molecular weights of $2 \times 10^6$ became turbid at temperatures much higher than the spinodal temperature of quiescent solutions. Whether or not this enhanced scattering is indicative of the true shift in the transition temperature is controversial. There have been two separate theories by Onuki\textsuperscript{41} and by Helfand and Fredrickson\textsuperscript{42} to find the cause of this enhanced scattering above the quiescent spinodal temperature. They predicted conflicting results. In both the theories, however, there is a common theme of including the elastic effects in the phase separation of polymer solutions. These elastic effects arise only in the case of polymer mixtures because of the change in the conformation of polymer chains due to the stresses in the imposed flow field. Recent experiments on SD under shear flow by Fuller and coworkers\textsuperscript{35} have shown that domains grow along the flow direction (x direction) at low shear rates but at higher shear rates, when elastic effects become predominant, domains flip from the x direction to the neutral direction (z direction). Fuller et al. have attributed these observations to the strong 'elastic effects' in the SD in polymer mixtures with rheologically different components. Theories by Helfand and Fredrickson and by Onuki study SD only in the xy plane (x is the flow direction, and y is the gradient direction) and do not predict domain growth along z, the neutral direction.

Research Objectives

The chain-like nature of polymer molecules not only affects the thermodynamic properties (which are static in
nature) of polymer mixtures, but also affects the dynamic properties such as the kinetics of phase separation and the molecular mechanisms of domain coarsening. As discussed in the previous section, recent experimental studies have revealed some of the unique features of the SD process in polymeric systems which have not been completely understood on the theoretical grounds. Our aim in undertaking this study was to explore the effect of the chain-like nature of polymer molecules on the kinetics of SD in polymer blends and how the SD in polymer mixtures differs from the SD in the small molecule mixtures.

In order to achieve this goal, it is necessary to investigate the non-linear regime of the SD process. Apart from the analytical methods, which involve difficult mathematical endeavors to include the non-linear effects, other possible means are either Monte Carlo simulations or numerical studies. Monte Carlo simulations in the dense polymer systems, like homopolymer melts and concentrated solutions, are computationally exhaustive compared to the small molecular systems mainly due to the many degrees of freedom in polymer molecules. The numerical studies which involve the integration of the non-linear continuity equation can be made computationally very efficient by the use of recent vector or massively parallel machines.

The derivation of the continuity equation requires an explicit expression for the free energy functional for the mixture undergoing SD. Embodied in this free energy
functional are the microscopic characteristics of the homogeneous phases and 'interphases' (the interfacial region) of the phase separating mixture. The chain-like nature of polymer molecules affects the free energy of mixing in the homogeneous region and also affects the interfacial region by having a significant entropic contribution to the interfacial free energy unlike their small molecular counterparts. The essential physics of the formation and coarsening of the domains resulting from the complex interfacial dynamics can be captured using this numerical technique.

The objective of this thesis has been to model the non-linear dynamics of the SD process in polymer blends and interpret the results of this numerical study to get a better understanding of the experimental results that are uniquely observed in the SD in polymer blends.

Dissertation Outline with a Brief Summary of Results

Within the framework of the existing theories for inhomogeneous polymer mixtures, we have formulated a model for SD in polymer blends and have developed a computational scheme to investigate the dynamics of the SD process in a binary blend of two flexible chain polymers. The computational scheme mimics the 'Quench Experiment', where the polymer blend is quenched from a homogeneous state into a thermodynamically unstable state and the evolution of the structure is monitored. This computational scheme is specifically used to predict the unmixing behavior of a symmetric blend of deuterated and protonated 1,4
polybutadienes, a system that has been primarily investigated by Bates and coworkers\textsuperscript{43} using scattering experiments. This scheme has been also extended to study the SD under simple shear flow and these calculations adopt a mean field approximation for the velocity field.

Chapter 2 outlines the present theoretical framework for understanding SD in binary mixtures. It describes how the models for SD in small molecule mixtures can be modified and extended to SD in polymer systems. The computational scheme used in the present calculations is schematically shown and the methods used for numerical integration and domain size determination are also discussed.

In Chapter 3 results are presented and are discussed so as to bring out the effects of the chain-like nature of polymer molecules on the domain growth laws and on the molecular mechanisms underlying domain coarsening. The relative contributions of the enthalpic and entropic parts of the inhomogeneous polymer mixture are discussed and it is shown that the dominance of the entropic contribution leads to the emergence of a new region in the phase diagram, where the growth of the phase separated domains is frozen even though the mixture belongs to the thermodynamically unstable state. This new region called the “Transnodal Region”, lies between the spinodal line and the region around the critical composition. A coarsening mechanism based on the molecular transport parallel to the interface is proposed to explain this novel feature characteristic of off-critical polymer
blends. Calculations on the SD under simple shear flow show pronounced anisotropy of the phase separated domains with the domains elongated along the direction parallel to the flow than in the perpendicular directions. The domain growth laws seem to be in reasonable agreement with a more rigorous theory of Kawasaki and Onuki\textsuperscript{32}.

The conclusions and suggestions for future work are presented in Chapter 4. The future work portion of this section primarily deals with the extension of the present computational scheme to other binary mixtures such as a blend of rigid rod polymer with flexible chain polymer and a binary blend having at least one crystallizable polymer as its component.

Appendix comprises the last portion of this dissertation and includes the representative programs used in the present calculations.
Figure 1.1

Typical phase diagram of a binary polymer blend with upper critical solution temperature.
Figure 1.2
Schematics of the structure development in the phase separation by the nucleation and growth mechanism.
Figure 1.3

Schematics of the structure development in the phase separation by the spinodal decomposition mechanism.
Figure 1.4

Experimental data by Hashimoto et al. showing time dependence of $q_m$ for critical mixtures of polystyrene and poly(vinyl methyl ether) blend, reproduced from the Ref.8.
Figure 1.5

Experimental data by Bates et al. showing time dependence of $q_m$ for critical mixtures of deuterated and protonated 1,4 polybutadienes, reproduced from the Ref.10.
Figure 1.6

Experimental data by Hashimoto et al. showing time dependence of $q_m$ for off-critical mixtures of polystyrene and a random copolymer of styrene and butadiene, reproduced from the Ref. 11.
References


(3) Muthukumar, M. J. Chem. Phys. 1986, 85, 4722 and the references there in,


(34) Rangel-Nafaile, C.; Metzner, A. B.; Wissburn, K. F. Macromolecules 1984, 17, 1187 and references there in.


Spinodal Decomposition in Small Molecule Mixtures

In a binary mixture each of the components can either be a small molecule or a polymer. Thus, the binary mixture can represent any one of the following cases: small molecule mixture, a polymer in a small molecule solvent, or a polymer-polymer mixture. Further, the polymer itself can either be a flexible coil or a rigid rod. The mathematical description of the SD process in a binary mixture depends upon the type of the mixture, and when at least one of the components is a polymer, then the chain connectivity of the polymer chain has to be appropriately accounted for. The case of a small molecule binary mixture, which has been studied extensively in the literature, is discussed first and modifications of the same for the polymer case are discussed in the subsequent sections.

Consider a volume element of the phase separating binary mixture of small molecule components A and B. For this volume element, in principal one can write the equations for the conservation of mass, momentum, and energy. Since we are dealing here with an isothermal phase separation process, it suffices to consider only the mass and momentum balance equations.
Mass balance:

If $\phi(r,t)$ is the volume fraction of the component A at the position $r$ and time $t$, then the rate of accumulation of $A$, $\frac{d\phi(r,t)}{dt}$, is given by

$$\frac{d\phi(r,t)}{dt} = - \nabla \cdot J_A + \eta(r,t)$$

(2.1)

where $J_A$ is the local current of the component A, and $\eta$ is the local thermal noise. The local current $J_A$ has a contribution from a diffusive flux, $J_D$ and a convective flux, $J_C$. The diffusive flux, $J_D$ is driven by the gradient of the chemical potential and is described by

$$J_D = - \frac{\Lambda(\phi)}{k_BT} \nabla \left( \frac{\delta F(\phi(r))}{\delta \phi} \right)$$

(2.2)

where $\Lambda(\phi)$ is the Onsager transport coefficient and $\frac{\delta F(\phi(r))}{\delta \phi}$ is a pseudopotential given by the functional derivative of a coarse grained free energy functional $F(\phi(r))$ w.r.t $\phi(r)$. $F(\phi(r))$ describes the free energy of the inhomogeneous mixture by accounting for the excess interfacial free energy due to the presence of the composition gradients resulting from the phase separation. The convective flux, $J_C$ is caused by the transport of the component A due to the local velocity $v(r)$, imparted at the point $r$ from the bulk flow, and is given by
\[ \mathbf{J}_C = \phi(r) \mathbf{v}(r) \]  

Substituting the expressions for \( \mathbf{J}_D \) and \( \mathbf{J}_C \), the mass balance equation (of the component A) can be written as

\[ \frac{d\phi(r,t)}{dt} = \nabla \cdot \left( \Lambda(\phi) \nabla \frac{\delta F(\phi(r))}{\delta \phi} \right) - \nabla \cdot (\phi \mathbf{v}(r)) + \eta(r,t) \]  

If it is assumed that the Onsager coefficient \( \Lambda \) is independent of composition \( \phi \) (and is equal to a constant \( M \), in units of \( K_B T \)), the above equation becomes

\[ \frac{d\phi(r,t)}{dt} = M \nabla^2 \frac{\delta F(\phi(r))}{\delta \phi} - \nabla \cdot (\phi \mathbf{v}(r)) + \eta(r,t) \]  

Making use of the incompressibility condition \( \nabla \cdot \mathbf{v} = 0 \)

Equation 2.5 simplifies to

\[ \frac{d\phi(r,t)}{dt} = M \nabla^2 \frac{\delta F(\phi(r))}{\delta \phi} - \mathbf{v}(r) \cdot \nabla (\phi(r)) + \eta(r,t) \]  

Momentum Balance:

For the momentum balance over the volume element under consideration one has to account for the momentum transport due to the bulk flow and also due to simultaneous phase separation. The Momentum balance equation for such a fluctuating hydrodynamic field\(^1,2\) is given by
\[
\rho \frac{d\mathbf{v}(r,t)}{dt} = T \cdot \left\{ -\mathbf{v} \cdot \nabla \mathbf{v} + \nabla \sigma + (\nabla \phi) \frac{\delta F(\phi(r))}{\delta \phi} \right\} + \eta_v
\]

(2.7)

where \( \rho \) is the density, \( \sigma \) is the stress tensor, and \( \eta_v \) is the local noise term. \( T \) is the transverse projection operator and eliminates the pressure term by using the incompressibility condition \( \nabla \cdot \mathbf{v}(r) = 0 \).

As is seen from Equations 2.6 and 2.7, the mass and momentum balance equations are intercoupled, and in order to study the evolution of the order parameter \( \phi(r,t) \), it is required to solve these two equations simultaneously. This description of the SD process, using both the mass and the momentum balance equations, is known as model H in the language of the critical phenomenon\(^1,2\). For the SD in a binary mixture not subjected to external flow (i.e. in the quiescent state), it can be argued that the local velocity \( \mathbf{v}(r) \) is vanishingly small and the convective mode of transport can be totally neglected so that the SD process in the quiescent mixtures can be described only by the mass balance equation with \( \mathbf{v}(r) = 0 \). This description is termed as model B or the time dependent Ginsburg-Landau (TDGL) model\(^1\). When the SD occurs under external flow, the convective flux is significant and model H description is required in this case. However, certain simplifying assumptions are usually made to reduce the mathematical complexity in solving the two non-linear coupled differential
equations. Thus the two widely studied models in the SD of small molecule mixtures are:

model B (SD in the quiescent state)

\[
\frac{d\phi(r,t)}{dt} = M \nabla^2 \left( \frac{\delta F(\phi(r))}{\delta \phi} \right) + \eta(r,t)
\]

(2.8)

model H (SD under external flow)

\[
\frac{d\phi(r,t)}{dt} = M \nabla^2 \left( \frac{\delta F(\phi(r))}{\delta \phi} \right) - \mathbf{v}(r) \cdot \nabla \phi(r) + \eta(r,t)
\]

(2.9)

and

\[
\rho \frac{d\mathbf{v}(r,t)}{dt} = T \cdot \left\{ -\rho \mathbf{v} \cdot \nabla \mathbf{v} + \nabla \cdot \sigma + (\nabla \phi) \left( \frac{\delta F(\phi(r))}{\delta \phi} \right) \right\} + \eta_v(r,t)
\]

(2.10)

**Free Energy of Inhomogeneous Small Molecular Mixtures**

The explicit form for \( F(\phi(r)) \) is derived here based on the original Cahn-Hilliard formulation\(^3\). The local free energy density, \( f \), in a region of non-uniform composition is assumed to depend upon the local composition \( \phi \), and on the composition of the immediate environment. The free energy density \( f \) therefore can be expressed as the sum of two contributions, which are functions of local composition \( \phi \) and the local composition derivatives respectively. It is assumed that the composition gradient is small compared with the reciprocal of the intermolecular distance. Further it is
assumed that $\phi$ and its derivatives are independent variables and that $f$ is a continuous function of these variables. $f$ can be expanded in a Taylor series about $f_0$, the free energy density of a mixture of uniform composition $\phi$, to obtain

$$f(\phi, \nabla \phi, \nabla^2 \phi, \ldots) = f_0(\phi) + \kappa_1 \nabla^2 \phi + \kappa_2 (\nabla \phi)^2 + \ldots$$

where the coefficients $\kappa_1$, $\kappa_2$, ... can in general be functions of $\phi$. Integrating over a volume $V$ of the inhomogeneous mixture the total free energy of the volume element, $F$, can be written as

$$F(\phi(r)) = \int_V \left[ f_0(\phi) + \kappa_1 \nabla^2 \phi + \kappa_2 (\nabla \phi)^2 + \ldots \right] dv$$

By applying the divergence theorem,

$$\int_V dv \left[ \kappa_1 \nabla^2 \phi \right] =$$

$$- \int_V dv \left[ \frac{d\kappa_1}{d\phi} (\nabla \phi)^2 \right] + \int_S \left[ (\kappa_1 \nabla \phi) \cdot ds \right]$$

Since we are not concerned with the effects at the external surface, we can choose a boundary of integration in Equation 2.13 in such a manner that $\nabla \phi \cdot ds = 0$ and hence the surface integral vanishes. $F$ can now be written as
\[ F(\phi(r)) = \int_V dv \ [ f_0(\phi) + \kappa (\nabla \phi)^2 + \ldots ] \]

where,

\[ \kappa = -\frac{d\kappa}{\phi} + \kappa_2 \]

Thus the free energy of a volume element of an inhomogeneous mixture can be expressed as the sum of two contributions, one being the free energy that the volume element would have in a homogeneous state and the other a 'gradient energy' which is a function of local composition gradient. Equation 2.14 was first derived by Van der Waals but its current popularity is attributed to Cahn and Hilliard who used this functional to analyze the SD in metallic alloys. The square gradient term, \( \kappa (\nabla \phi)^2 \), accounts for the excess interfacial free energy and has an enthalpic, \( \kappa_{\text{Entha}} (\nabla \phi)^2 \) and an entropic contribution, \( \kappa_{\text{Entro}} (\nabla \phi)^2 \). Cahn and Hilliard calculated the value of \( \kappa \) using the lattice model and the regular solution theory for binary mixtures. According to the regular solution theory, \( f_0 \), the free energy of a homogeneous mixture is given by

\[ f_0 = \{ \phi \ln \phi + (1-\phi) \ln (1-\phi) \} + \chi \phi (1-\phi) \]
where $\chi$ is the interaction parameter between the two species A and B. They obtained $K_{\text{Entha}} = \chi \lambda^2$ where $\lambda$ is the effective interaction length between the molecules. The enthalpic contribution stems from the molecular interactions in the inhomogeneous region having composition gradient. They also showed that there is no contribution to the entropy from a composition gradient and consequently $K_{\text{Entro}}$ is zero. Thus the parameter $\kappa$ is independent of the composition $\phi$ for binary mixture of small molecules. Using Equation 2.16 and $\kappa = \chi \lambda^2$, the Cahn-Hilliard functional describing the free energy of an inhomogeneous mixture of small molecules takes the form

$$F(\phi(r)) = \int_V \text{dv} \left[ \phi \ln \phi + (1-\phi) \ln (1-\phi) + \chi \phi (1-\phi) + \chi \lambda^2 (\nabla \phi)^2 \right]$$

Cahn and Hilliard have used the functional in Equation 2.17 to determine the interfacial properties of the small molecule mixtures and have shown that the interfacial width, $\omega \sim (T_c - T)^{1/2}$ and the interfacial tension, $\theta \sim (T_c - T)^{3/2}$. These results have been found to be in agreement with the experimental data$^3$. 

34
Models for Spinodal Decomposition in Polymer Blends

The framework described in earlier sections can be extended to SD in polymer blends by appropriate modifications of model B and model H.

Free Energy of Inhomogeneous Polymer Mixtures

An extension of the Cahn-Hilliard functional to describe the free energy of inhomogeneous polymer blends was developed by de Gennes. The chain-like nature of polymer molecules results in the non zero entropic contribution to the interfacial free energy unlike the small molecular case and hence $\kappa_{\text{Entro}}$ is also non zero. de Gennes evaluated the $\kappa_{\text{Entro}}$ for the polymer mixtures within the framework of Random Phase Approximation (RPA). The RPA result for homogeneous polymer blend gives

$$\frac{1}{S(k)} = \frac{1}{S_A(k) \phi} + \frac{1}{S_B(k)(1-\phi)} - 2\chi$$

(2.18)

where $S(k)$ is the structure factor of the homogeneous blend, $S_A(k)$ and $S_B(k)$ are the structure factors of the component polymers A and B respectively. For the case of binary polymer blend of two flexible chain-like polymers, $S_A(k)$ (and analogously $S_B(k)$) is given by the Debye structure factor as

$$S_A(k) = \frac{2N_A}{k^4R_g^4} \left( \exp(-k^2R_g^2) - 1 + k^2R_g^2 \right)$$

(2.19)
where \( N_A \) is the degree of polymerization and \( R_g \), equal to \( \frac{N_A l_A^2}{6} \), is the radius of gyration of the polymer A chain.

In the limit \( k \to 0 \),

\[
S_A(k) = N_A \left( 1 - \frac{k^2 N_A l_A^2}{18} + \ldots \right) \tag{2.20}
\]

For a symmetric polymer blend, \( N_A = N_B = N \) and \( l_A = l_B = a \).

Substituting \( S_A(k) \) (and analogously \( S_B(k) \)) from Equation 2.20 into Equation 2.8, we get

\[
\frac{1}{S(k)} = \frac{1}{N} \phi + \frac{1}{N (1-\phi)} - 2\chi + \frac{k^2 a^2}{18} \left( \frac{1}{\phi} + \frac{1}{(1-\phi)} \right) + O(k^4) \tag{2.21}
\]

For \( k = 0 \),

\[
\frac{1}{S(k)} = \frac{d^2 f_0}{d\phi^2} \tag{2.22}
\]

where \( f_0 \) is the Flory-Huggins free energy for a symmetric polymer blend and is given by

\[
f_0 = 1/N \left\{ \phi \ln \phi + (1-\phi) \ln (1-\phi) \right\} + \chi \phi (1-\phi) \tag{2.23}
\]

de Gennes generalized this result for \( k \neq 0 \) and obtained the following functional, describing the free energy of an inhomogeneous symmetric polymer blend, as
Thus analogous to the Cahn-Hilliard functional for small molecule mixtures, the free energy of inhomogeneous polymer blends can be written as a sum of two contributions: \( f_o \), the free energy of homogeneous blend and a square gradient part originating from the excess interfacial free energy. The prefactor of the square gradient term, \( \frac{a^2}{36\phi(1-\phi)} \), is composition dependent and is a manifestation of the chain-like nature of polymer molecules. It is to be noted here that the RPA approach does not yield the enthalpic contribution to the interfacial free energy. Tang and Freed\(^7\) have rederived the free energy functional in Equation 2.24 using density functional theory of inhomogeneous polymer blends.

A similar set of RPA calculations can be performed to evaluate the free energy functional for inhomogeneous polymer solutions. In this case (A=polymer and B=solvent) \( S_A(k) \) is the Debye structure factor while \( S_B(k) = 1 \). This yields a composition dependent prefactor of the square gradient term as, \( \frac{a^2}{18\phi} \). Szleifer and Widom\(^8\) performed self consistent calculations on the lattice model of polymer solutions by taking into account the anisotropic biases in the chain conformations due to composition gradients in the interface
and were able to derive the enthalpic and entropic contributions to the prefactor $K$. They obtained, $K_{\text{Entro}} \sim \frac{a^2}{\phi}$ and $K_{\text{Entha}} \sim \chi a^2$. Their $K_{\text{Entro}}$ is of the same form as that obtained from the RPA approach. They have shown that the origin of the composition dependent prefactor obtained from the RPA approach is entropic in nature and stems from the loss of conformational entropy of the polymer chain within the interfacial region.

Another approach to treat the problem of inhomogeneous polymer mixtures and study the nature of polymer-polymer interfaces was pioneered by Helfand. Helfand and co-workers constructed a self consistent field theory of polymer-polymer interfaces by solving the segmental diffusion equation across the interface. They showed that the interfacial tension $\theta$ and the interfacial thickness $\omega$ for a symmetric polymer blend are given by

$$\theta = (K_B T/a^2)(\chi/6)^{1/2}$$

and

$$\omega = 2a/(6\chi)^{1/2}$$

Thus, the interfacial thickness $\omega$ can be of the order of a few Kuhn lengths, much smaller than the actual size of the polymer chain. Helfand’s approach using the self consistent field theory increased the understanding of the polymer interfaces, but it was not useful in treating the SD in polymer mixtures since it did not yield an explicit expression for the free energy functional for inhomogeneous
mixtures. However the equivalence between de Gennes’s square gradient formulation and Helfand’s self consistent field theory was brought out by Sanchez\textsuperscript{10} who wrote “de Gennes’s square gradient theory is in harmony with the microscopic theory of Helfand and co-workers although the latter treats the polymer interfaces from a completely different point of view.”

**Spinodal Decomposition in Quiescent Mixtures**

For a volume element of the phase separating polymer blend, not subjected to external flow, evolution of the order parameter $\phi(r,t)$ can be described by

$$
\frac{d\phi(r,t)}{dt} = \nabla \cdot \left( \frac{\Lambda(\phi)}{K_B T} \nabla \left( \frac{\delta F(\phi(r))}{\delta \phi} \right) \right) + \eta(r,t)
$$

where $F(\phi(r))$ is the generalized functional motivated by Cahn-Hilliard and de Gennes approaches and for the symmetric polymer blend it can be written (in units of $K_B T$) as

$$
F(\phi(r)) = \int d^3 r \left[ f_0(\phi(r)) + \frac{a^2}{36\phi(1-\phi)} + \chi \lambda^2 \right] |\nabla \phi(r)|^2
$$

The effective interaction length $\lambda$ is taken equal to the Kuhn length, $a$. The Onsager coefficient $\Lambda(\phi)$ consistent with the Flory-Huggins free energy can be shown equal to $D_{AB} \phi (1-\phi)$ where $D_{AB}$ is the interdiffusion coefficient of the binary blend\textsuperscript{5}. There are two conflicting theories, popularly known
as 'Slow theory'\textsuperscript{11} and 'Fast theory'\textsuperscript{12}, which relate the interdiffusion coefficient $D_{AB}$ to the self-diffusion coefficients $D_A$ and $D_B$ of the two component polymers A and B respectively. According to the slow theory,

$$\frac{1}{D_{AB}} = \frac{1-\phi}{D_AN_A} + \frac{\phi}{D_BN_B}$$

According to the fast theory,

$$D_{AB} = (1-\phi) D_A N_A + \phi D_B N_B$$

Note that while the slow theory predicts that $D_{AB}$ is controlled by the diffusion of the slower moving component, the fast theory says that it is controlled by the faster moving one. There are experimental results that support both the theories, though most of the recent experimental evidence is in favor of the fast theory. However, for the case of a symmetric polymer blend of deuterated and protonated polymers of otherwise identical chemical structure, $N_A = N_B$, $D_A = D_B$ and both the theories yield the same result that $D_{AB} = N_A D_A = N_B D_B = N_D$. Substituting the values of $\frac{\delta F(\phi(r))}{\delta \phi}$ and $\Lambda(\phi)$ in Equation 2.26, the final equation for the evolution of the order parameter $\phi(r,t)$ is
\[
\frac{d\phi(r,t)}{dt} = ND \nabla \phi \left(1 - \phi\right) \nabla \left[ \ln \frac{\phi}{1 - \phi} + \chi \left(1 - 2\phi\right) - 2\chi a^2 \nabla^2 \phi \right]
- \frac{a^2}{18\phi(1 - \phi)} \nabla^2 \phi + \frac{(1 - 2\phi) a^2}{36\phi^2(1 - \phi)^2} \left(\nabla \phi\right)^2 \right] \} \tag{2.30}
\]

The noise term is not included in the Equation 2.30. It has been shown in small molecule systems that the noise term only increases the number of time steps needed to obtain the asymptotic growth law\textsuperscript{13,14}. The exclusion of the noise term drastically reduces the required computer time since the repeated use of the random number generator is eliminated. Analytical studies by de Gennes\textsuperscript{5} and later on by Binder\textsuperscript{15}, involve linearization of the above equation and hence are valid only in the early time scales of the phase separation. We compliment these studies by numerically solving Equation 2.30, which helps us to explore the kinetics of phase separation even at later time scales.

In order to facilitate comparison of demixing behavior in various systems, following rescaled variables are usually defined so that the experimental data can be plotted in terms of the dimensionless quantities\textsuperscript{16,17}.

\[
x = k^o_m r \quad \text{and} \quad \tau = D_{app} (k^o_m)^2 t \tag{2.31}
\]

where \(k^o_m\) is the wave number corresponding to the maximum in the structure factor at time=0 and \(D_{app}\) is the apparent diffusivity. \(k^o_m\) and \(D_{app}\) can be calculated from the linear
theory. In our study, we have used the following rescaled variables,

\[ x_1 = \frac{(\chi - \chi_s)^{1/2}}{a} \quad \text{and} \quad \tau_1 = \frac{D (\chi - \chi_s)^2}{a^2 \chi_s} t \]  

(2.32)

The values of \( \chi \) at critical and spinodal points are given by \( \chi_c = 2/N \) and \( \chi_s = 1/(2N\phi_0(1-\phi_0)) \) respectively, where \( \phi_0 \) is the volume fraction of component A in the mixture. With these substitutions Equation 2.30 becomes

\[
\frac{d\phi(x_1, \tau_1)}{d\tau_1} = \frac{1}{2\phi_0(1-\phi_0)} \nabla \cdot \left[ \phi (1-\phi) \nabla \left( \frac{\chi_c}{2(\chi - \chi_s)} \ln \frac{\chi}{1-\phi} - \frac{2\chi \phi}{\chi - \chi_s} \right) \right. \\
- 2\chi \nabla^2 \phi - \frac{1}{18\phi(1-\phi)} \nabla^2 \phi + \frac{(1-2\phi)}{36\phi^2(1-\phi)^2} \left( \nabla \phi \right)^2 )
\]  

(2.33)

**Spinodal Decomposition Under External Flow**

The time averaged conformation of the polymer chain subjected to an external flow is different from the conformation in the equilibrium quiescent state. The changes in the chain conformation result in the unique rheological properties of polymer melts and solutions such as rate dependent viscosity, normal stresses, etc. The same elastic effects are also manifested in the phase behavior of flowing polymer mixtures. To develop a model for the SD in flowing polymer mixtures, let’s consider a volume element fixed in space through which the polymer blend is flowing and also
undergoing simultaneous phase separation. For such a volume element following mass and momentum balance equations can be written.

Mass balance:

\[
\frac{d\phi(r,t)}{dt} = - \nabla \cdot J_A + \eta(r,t)
\]

(2.34)

where \(J_A\), the local current of the component A, is given by

\[
J_A = J_D + J_C + J_E
\]

(2.35)

The diffusive flux, \(J_D\) and the convective flux, \(J_C\) are present in small molecule mixtures, but the additional contribution to the local current, which is called here as the 'elastic flux', \(J_E\) is unique to polymeric systems and arises due to the elasticity of the polymer chain. There are two different theories for describing the elastic flux, \(J_E\), one by Helfand and Fredrickson\(^{18}\) and the other by Onuki\(^{19}\).

Helfand and Fredrickson derived their expression for \(J_E\) from the hydrodynamic equations of the microscopic Rouse model and they obtained,

\[
J_E = \frac{v_m D_{AB}}{k_B T} (\nabla \cdot \sigma_p)
\]

(2.36)
where $\sigma_p$ is the deviatoric part of the stress tensor and $v_m$ is the volume of the monomeric unit.

Onuki proposed that the free energy change due to the changes in the conformations of the chain is additive to the free energy change due to mixing. According to Onuki,

$$J_E = -\frac{\Lambda(\phi)}{k_B T} \nabla \left( \frac{\delta F_{EL}}{\delta \phi} \right)$$

He defined a tensorial variable $W_{ij}$ to characterize the distortions of the polymer chain under external flow. He expressed the excess free energy due to the imposed flow, $F_{EL}$, as,

$$F_{EL} = \frac{k_B T}{4} \int d^3r \left[ E(\phi) \, \text{Tr}(W)^2 \right]$$

where $E(\phi)$ is the elastic modulus of the mixture, $W_{ij} = \xi \left( \frac{dv_i}{dx_j} + \frac{dv_j}{dx_i} \right)$ and $\xi$ is the relaxation time of $W_{ij}$. This idea of defining the stored elastic free energy of the chain due to imposed flow is originally due to Marrucci$^{20}$ who defined a similar functional in terms of the deviatoric stress tensor, $\sigma_p$ as

$$F_{EL} = \frac{1}{2} \int d^3r \left[ \text{Tr}(\sigma_p) \right]$$
Thus in both the Helfand-Fredrickson and Onuki models the coupling between the concentration fluctuations and the flow field occurs through the composition dependent rheological properties: the stress tensor, $\sigma_p(\phi)$ in the Helfand-Fredrickson model and the elastic modulus, $E(\phi)$ in the Onuki model.

Momentum balance\textsuperscript{18,19}:

\begin{equation}
\rho \frac{d\mathbf{v}(r,t)}{dt} = T \left\{-\rho \mathbf{v} \cdot \nabla \mathbf{v} + \nabla \cdot \sigma + (\nabla \phi) \frac{\delta F(\phi(r))}{\delta \phi} \right\} + \eta_v
\end{equation}

where $T$ is the transverse projection operator and $\sigma$ is the stress tensor. Embodied in $\sigma$ are the rheological characteristics of the polymer mixture. The mass and momentum balance equations have to be solved simultaneously to study the evolution of the order parameter $\phi$.

A major simplification occurs if we consider a polymer blend with the two components having similar rheological properties. This means that the viscosity, stress tensor and the elastic modulus are independent of the composition $\phi$.

For such a blend in a homogeneous flow field (eg. simple shear flow) the contribution of the elastic effects to the mass and momentum transport is zero by both the Helfand-Fredrickson and Onuki models. Thus the polymer case reduces to the former H model used for SD under flow in small molecule mixtures, except for the use of the modified Cahn-
Hilliard functional to account for the entropic contribution to the interfacial free energy.

**Mean Field Approximation.** For such a blend with rheologically similar components, another simplification can be made by invoking mean field approximation for the velocity field. It is possible to make this approximation only because, even by assuming an unperturbed velocity field in the presence of a fluctuating concentration field, the continuity of the stress field is not violated due to composition independence of the rheological properties.

The local velocity \( \mathbf{v}(r,t) \) can be written as a sum of the average velocity \( \mathbf{u}(r) \) and a fluctuating component \( \mathbf{v}'(r,t) \). If the fluctuating component \( \mathbf{v}' \) is neglected assuming that the imposed velocity field \( \mathbf{u}(r) \) is unperturbed by the fluctuating concentration patterns, then in the mean field limit, mass and momentum balance equations can be decoupled. For a symmetric polymer blend undergoing SD in a simple shear geometry, which is shown in Figure 2.1, the evolution of the order parameter \( \phi(r,t) \) can be described by

\[
\frac{d\phi}{dt} = N D_c \mathbf{\nabla} \cdot \phi (1-\phi) \mathbf{\nabla} \left[ \frac{1}{N} \ln \frac{\phi}{1-\phi} + \chi (1-2\phi) - 2\alpha a^2 \mathbf{\nabla}^2 \phi \right] - \frac{a^2}{18\phi(1-\phi)} \mathbf{\nabla}^2 \phi + \frac{(1-2\phi) a^2}{36\phi^2(1-\phi)^2} (\mathbf{\nabla} \phi)^2 \left( \mathbf{\nabla}^2 \right) - \gamma \frac{d\phi}{dx}
\]  

where \( \gamma \) is the shear rate.
Using the same reduced variables as in the quiescent state, Equation 2.41 can be recast in the dimensionless form as,

\[
\frac{d\phi(x_1, t_1)}{dt_1} = \frac{1}{2\phi_0(1-\phi_0)} \nabla \cdot \left[ \phi(1-\phi) \nabla \left( \frac{\chi_c}{2(\chi-\chi_s)} \ln \frac{\phi}{1-\phi} - \frac{2\chi\phi}{\chi-\chi_s} - 2\chi \nabla^2 \phi - \frac{1}{18\phi(1-\phi)} \nabla^2 \phi + \frac{(1-2\phi)}{36\phi^2(1-\phi)^2} (\nabla \phi)^2 \right) \right] - \frac{a^2 \chi_s \gamma}{D(\chi-\chi_s)^2} \gamma \frac{d\phi}{dx_1}
\]

where \( \frac{a^2 \chi_s \gamma}{D(\chi-\chi_s)^2} \) is the dimensionless shear rate.

We have investigated the structure development in SD under shear flow by numerically solving Equation 2.42.

**System of Investigation**

Binary mixtures of deuterated and protonated polymers of otherwise identical structure have been recently shown to form nonideal solutions exhibiting an upper critical solution temperature in contradiction to the long held assumption of ideal solution behavior of isotopic mixtures. Bates and coworkers\(^{21}\) have systematically investigated the phase behavior of protonated and deuterated 1,4 polybutadienes using small angle neutron scattering. They showed that the scattering from these isotopic mixtures in the homogeneous phase can be well described by de Gennes theory for homogeneous polymer blends based on RPA. They have also investigated the kinetics of SD in the same system using time resolved light scattering; but in this case, they observed
the non-universal phase separation behavior unexplained by any of the existing theories. The same symmetric blend of deuterated and protonated 1,4 polybutadienes has been taken as the model polymer system for the present numerical study. For this system the UCST is 62°C and the dependence of $\chi$ on temperature, T is given by

$$\chi = \frac{0.326}{T} - 0.00023$$

The data on the interdiffusion coefficient $D_{AB}$ for this symmetric system has also been reported in the literature.

**Computational Scheme**

Figure 2.2. illustrates the computational scheme used in the present calculations for performing the 'quench experiment' on the computer. In a real quench experiment, a homogeneous blend of initial composition $\phi_0$ is quenched to a final temperature $T$ in the unstable region of the phase diagram and the evolution of this initially homogeneous system to an inhomogeneous system having phase separated domains is monitored as a function of time. In our computations, perturbations are introduced in the homogeneous system to generate a randomly perturbed initial state, which is allowed to phase separate at the chosen quench temperature in the unstable region. For every initial composition $\phi_0$ and final quench temperature $T$, 12 runs were made using different randomly perturbed initial states and the data was collected.
by averaging out over these runs. Thus the randomness enters the system through the initial condition and the noise term is not considered in the course of phase separation. The algorithm can be divided into three parts: (1) Input, (2) Numerical calculations, and (3) Output, each of these is described below.

**Input**

The system parameters viz. $\chi$ and $T_c$ appropriate to the system under consideration, experimental parameters viz. final quench temperature, initial composition and dimensionless shear rate, and ISEED for the random number generator, are fed as the input to the program.

**Numerical Calculations**

The differential equation governing the dynamics of the phase separation process is solved by numerical integration over a simple cubic lattice of $32^3$ having periodic boundary conditions. The numerical integration is done using the Euler method$^{22}$ which is well suited for vector programming and offers tremendous advantage in the speed in spite of its simplicity and requirement of the relatively small time step in the numerical integration. Time steps of 0.01 and 0.001 have been used in the calculations for SD in the quiescent state and for SD under simple shear flow respectively. Periodic boundary conditions take care of the conservation of the order parameter.
**Euler Method.** At any point \( r \) on the discretized grid, the differential equations encountered in the present study can be put in the general form as,

\[
\frac{d\phi(t)}{dt} = g(\phi, t)
\]

(2.44)

where \( g \) is a complicated non-linear function of \( \phi \) involving local gradient terms like \( \nabla \phi \), \( \nabla^2 \phi \) and with the initial condition \( \phi(t_0) = \phi_0 \). In principal, a step by step solution of the above differential equation may be developed to any degree of accuracy by a Taylor expansion as,

\[
\phi(t_0 + \Delta t) = \phi(t_0) + \Delta t \, \phi'(t_0) + \frac{\Delta t^2}{2!} \, \phi''(t_0) + \ldots + \frac{\Delta t^n}{n!} \, \phi^n(t_0) + \ldots
\]

(2.45)

where \( \Delta t \) is some small interval and \( \phi^n \) is the \( n \)th order derivative of \( \phi \) w.r.t. \( t \). The initial value \( \phi(t_0) \) is known and \( \phi'(t_0) \) is given as \( g(\phi_0, t_0) \). In principal the higher order derivatives may be obtained by differentiating \( \phi'(t) = g(\phi, t) \). In practice this differentiation can be very tedious and is required when the interval \( \Delta t \) is not sufficiently small for achieving numerical stability. However, with the advent of fast computers it is possible to choose small values of \( \Delta t \) and do the integration by truncating the Equation 2.45 after first two terms as
\[ \phi(t_0 + \Delta t) = \phi(t_0) + \Delta t \, g(\phi_0, t_0) \]

The numerical integration performed in this simplistic manner becomes computationally very efficient using the vector programming techniques.

**Vector Programming.** Vector computers are a type of supercomputers which are able to accomplish many simultaneous operations by 'vector' processing, that is, by using powerful instructions to feed arrays of operands through a 'pipeline' or assembly line of operations. This pipeline concept is a streamlining of the conventional scalar processor, a recognition that during the most intense use, a computer is almost in a loop, doing the same operations to many different operands. These computers can be programmed to perform in a conventional manner, that is, in the scalar mode. However, if the programming and compilation is done in the specific manner as required by the vector architecture of the computer, then the performance of the machine can be increased tremendously as compared to the scalar mode of operation. This programming technique for achieving high performance on the vector computer is generically called 'vector programming' and its details can be found in a variety of books on this subject\(^2\).

All the calculations in the present study were performed on Alliant Fx/8 computer. This computer has 4 vector processors and is usually classified as a
'minisupercomputer', since it has slower clock cycle than the conventional supercomputer like a CRAY-3 but has all the architectural attributes of a supercomputer.

**Fast Fourier Transform.** The Fast Fourier Transform (FFT) subroutine used in this study for the calculation of the structure factor and the pair correlation function, has been adopted from the book 'Numerical Recipes'\(^\text{24}\). This routine requires a special format for input and output arrays and the details of its usage and its applicability are discussed in the Ref.24.

**Output**

After each time step \(\Delta t\) in the numerical integration, the volume fraction at all the \(32^3\) points on the discretized grid are updated and the system evolves to a new pattern. This development of the structure formation can be followed graphically and also more quantitatively by determining the domain size through the calculation of the structure factor and the pair correlation function as a function of time. These quantities can be measured experimentally by the scattering techniques, and data on the system in the present study has been reported in the literature\(^\text{17}\).

**Computer Graphics.** A color code is assigned for the volume fractions ranging from 0 to 1. With this color code the numerical data file of the volume fractions at all the \(32^3\) points on the grid can be converted to computer images of the pattern formation. With the graphics software used in the present study, it was difficult to present the three
dimensional images, and hence, the two dimensional images are presented. These are able to effectively bring out the essentials of the morphological evolution.

**Structure Factor.** Dynamical scaling and domain growth laws have been traditionally analyzed\(^{25}\) in terms of the structure function \(S(k, \tau)\) defined as

\[
S(k, \tau) = \frac{1}{N} \sum \sum \exp(ik \cdot x) \left[ \phi(x+x', \tau) \phi(x', \tau) - \langle \phi \rangle^2 \right]
\]

where the sum runs over the lattice and the \(k\) vectors belong to the first Brillouin zone in the reciprocal space, i.e.,

\[
k = \left( \frac{2\pi}{L} \mu \right), \mu = (\mu_x, \mu_y, \mu_z), \text{ and } 0 < \mu_x, \mu_y, \mu_z < L-1, \ L=32
\]

The scattered intensity \(I(k, \tau)\) is proportional to the structure factor \(S(k, \tau)\). For the SD in the quiescent state, the structure formed as a result of the SD process is isotropic and hence \(S(k, \tau)\) can be spherically averaged to obtain a spherically averaged structure factor, \(S(k, \tau)\), as

\[
S(k, \tau) = \sum_{(k-\Delta k)} \frac{S(k, \tau)}{n(k, \Delta k)}
\]

where \(n(k, \Delta k)\) denotes the number of lattice points in a spherical shell of width \(\Delta k\) centered around \(k\). For a given \(\tau\), the spherically averaged \(S(k, \tau)\) shows a maximum for a characteristic magnitude of \(k\) denoted by \(k_m\) and the value of \(k_m\) quantifies the most dominant length scale of the isotropic
domains for that $\tau$. We have fitted the three points near the maximum of $S(k,\tau)$ to a parabolic form and calculated the value of $k_m$ by maximizing the fitted function.

For the SD under simple shear flow, the structure formed can be highly anisotropic and hence the scattered intensity can not be spherically averaged but instead the characteristic domain sizes in the $x$, $y$, and $z$ directions are determined by calculating the magnitude of $k$ for which the maximum in the scattered intensity occurs in the $x$, $y$, and $z$ directions.

**Pair Correlation Function.** Scaling and growth laws have also been analyzed in terms of the real space pair correlation function $G(x,\tau)$, defined as

$$G(x,\tau) = \sum_k \exp(i k \cdot x) S(k,\tau)$$

For the SD in the quiescent state, the spherical averaging procedure is used to obtain the spherically averaged pair correlation function $G(x,\tau)$. A normalized correlation function can be defined as

$$g(x,\tau) = G(x,\tau)/G(x,0)$$

such that $g(0,\tau) = 1$. For the case of the conserved order parameter, a damped oscillatory behavior in $g(x,\tau)$ is typically seen. This allows one to give a quantitative measure of the domain size $R$ as the location of the first
zero of the correlation function. This value of R is calculated by fitting the four points in g(x,t) closest to its first zero to a cubic polynomial of x and by defining R as the value of x where this fitted curve vanishes.
$X = \text{Flow Direction}$

$Y = \text{Gradient Direction}$

$Z = \text{Neutral Direction}$

Figure 2.1

Schematics of the simple shear flow geometry.
Uniform Composition
One Phase Region

Temperature Quench
In The Unstable Region

Introduction Of
Concentration
Perturbations

Growth Of
Concentration
Perturbations

Solve The Non-Linear
Continuity Equation
Governing The Phase
Separation Dynamics

Trace The Kinetics Of Phase Separation

Calculate The
Characteristic Domain
Size As A Function Of
Time

Computer
Generated
Images

Figure 2.2

Schematic representation of the computational methodology used in the present study.
References


Spinodal Decomposition in the Quiescent State

Our results, obtained by numerical integration of Equation 2.33, for critical ($\phi_o=0.5$) and off-critical mixtures at several quench temperatures are presented here. For critical mixture, we have taken the quench temperatures of 25, 35, 49 and 54.5° C. Typical results of the structure factor calculation are shown in Figure 3.1 where $S(k,\tau)$ has been calculated in a particular run for the critical mixture quenched to 49°C. For a given $\tau$ the scattered intensity shows a maximum for a characteristic magnitude of the wavevector, $k_m$ and the value of $k_m$ quantifies the most dominant length scale of the domains for that $\tau$. Typical results for the normalized correlation function $g(x,\tau) = \frac{G(x,\tau)}{G(x,0)}$ for different $\tau$ are shown in the Figure 3.2. Such damped oscillatory behavior of $g(x,\tau)$ has been found characteristic for the conserved order parameter systems$^{1,2}$. Our calculated results of $R(\tau)$ determined through $g(x,\tau)$ are given in Figure 3.3. Similarly, results for the domain size determined through $k_m$ are plotted in Figure 3.4. From both of these figures it is clear that for critical mixtures the growth law does not depend on the quench temperature. The average growth law exponent calculated (for $\tau>100$) from these log-log plots is given by 0.24 ($\pm 0.02$). This result is similar to the earlier study$^3$, although the Onsager coefficient is now
concentration dependent and the noise is left out. Our results for an off-critical mixture ($\phi_0=0.4$) quenched to 35 and 15°C are also shown in Figures 3.3 and 3.4. The phase separated domains stop to coarsen after a certain characteristic time, $\tau_f$ which is clearly seen to depend upon the quench depth; and thus the universality of the growth law is violated for the off-critical mixtures.

Knowing the values of the volume fractions at every point on our 32 x 32 x 32 grid, we can generate computer images of the resulting structures at a given time during the phase separation. Typical evolution of morphology in an arbitrary plane is presented in Figure 3.5. X and Y sides of such a plane represent 32 units of the dimensionless distance which is defined in Equation 2.32. We have used different shades of grey color to represent the composition of evolving phases where complete white corresponds to volume fraction of the component A=1 and complete black corresponds to volume fraction of A=0. It is seen from Figure 3.5(a), that the A-rich and B-rich domains are bicontinuous at all times. In Figure 3.5(b) we see a percolated structure at $\tau_f=2$ for $\phi_0=0.4$ at 35°C and the pattern is similar to that of the critical quench. The contrast between the phases is weak because the phases are away from their final equilibrium compositions. However at $\tau_f=10$ the phases are not percolated for $\phi_0=0.4$ and the size of the domains is unchanged for $\tau_f=10$ and 200. In contrast, we see in Figure 3.5(a) that coarsening continues with $\tau_f$ for the critical quench. Therefore we conclude that a
The morphological pattern is frozen for $\phi_o=0.4$ at 35°C even though this condition belongs to the SD regime.

The effect of quench depth on the growth of domains in the case of off-critical mixtures is illustrated from the $R(T)$ data for $\phi_o=0.4$ and $\phi_o=0.45$ plotted in Figures 3.6 and 3.7 respectively. As seen from Figure 3.6 we find that for $\phi_o=0.4$ freezing occurs at all the three quench temperatures (15, 30 and 35°C) studied here. It is also clear that the freezing occurs earlier at shallower quench depths and the corresponding domain sizes are smaller. From Figure 3.7 we see that the domain growth is not arrested for $\phi_o=0.45$ quenched to $T=46°C$ but the domain growth is arrested when quenched to 50°C. For these cases, the typical morphology in an arbitrary plane at time $T_i=250$ is shown in Figure 3.8. In Figure 3.8 (a) the domains of the minority phase are dispersed in the majority phase and the coarsening is stopped as is seen from Figure 3.7. While in Figure 3.8 (b) it is seen that the two phases are highly interconnected and the coarsening of domains is not arrested in this case. Thus when the mixture of initial composition $\phi_o=0.45$ is quenched to 46°C the volume fraction of the minority phase is sufficiently high so as to form interconnected domains and these domains coarsen unlike the dispersed domains which are formed when the same mixture is quenched to 50°C. From Figures 3.8(a) through 3.8(c) it is seen that the volume fraction of the minority phase is higher for deeper quench depths and so is the interconnectivity of the domains. The
relative volume fractions of the equilibrium phases for a given $\phi_0$ and $T$ are obtained from the lever rule. If the volume fraction of the minority phase is less than the percolation threshold the structure has dispersed domains of the minority phase in the matrix of the majority phase. Thus, for a given phase diagram there is a region inside the unstable region where the two equilibrium phases can be percolated and is associated with the unarraestined coarsening of the domains. There is also a region where the domains of the minority phase will have dispersed clusters and is associated with the arrested coarsening of the phase separated domains. The boundary of this region of frozen morphology inside the unstable region is obtained by repeating the above calculations for different values of $\phi_0$ and $T$. For the system studied here this region is given in Figure 3.9 along with the binodal and spinodal curves. We call this new region of frozen morphology as the 'transnodal region'.

While the transition from percolated to dispersed clusters occurs for all off-critical systems, whether small or large molecules, the freezing of the patterns is triggered only for the polymer case. (Note that the significance of 'off-criticality' in the present context is closely related to the symmetry of the phase diagram). This can be directly verified by suppressing the entropic contribution to the interfacial free energy in Equation 2.27 and repeating the
calculations. In this spirit we also performed calculations starting with the following free energy functional,

\[
F(\phi(r)) = \int d^3r \left[ f(\phi(r)) + K_{\text{Entha}} |\nabla \phi(r)|^2 \right]
\]

(3.1)

where \( f(\phi) \) is the Flory-Huggins free energy and \( K_{\text{Entha}} |\nabla \phi|^2 \) is the enthalpic contribution to the free energy density from the local composition gradients. Now the reduced variables are defined as

\[
x = \frac{(\chi - \chi_s)^{1/2}}{\chi^{1/2} \lambda} r \quad \text{and} \quad \tau = \frac{D (\chi - \chi_s)^2}{\chi \lambda^2 \chi_s} t
\]

(3.2)

After rescaling the corresponding differential equation with the above variables and solving the resulting differential equation in the same previously mentioned manner we have plotted our results of the domain size, \( R(T) \) for \( \phi_o=0.4 \) and \( T=35 \) and \( 40^\circC \) in Figure 3.10. Clearly the free energy functional of Equation 3.1 does not show freezing of the morphology for the off-critical mixtures at the same quench temperatures as before. Typical evolution of morphology in an arbitrary plane is shown in Figure 3.11. In sharp contrast to Figure 3.5(b), Figure 3.11 reveals that the droplets of the dispersed phase grow without any freezing as in small molecular systems where larger droplets cannibalize smaller droplets. The only difference between Figures 3.5(b)
and 3.11 is the entropic contribution to the interfacial free energy.

The free energy functional of Equation 3.1 is similar to the small molecular case in terms of a composition independent prefactor of the gradient term and only differs in the homogeneous free energy which in the case of polymers is given by the Flory-Huggins free energy. The results obtained with the free energy functional of Equation 3.1 are not surprising in view of the known experimental and numerical results in the phase separation of off-critical mixtures of small molecular systems\textsuperscript{5-7}. In Equation 3.1, \( \lambda \) is the effective interaction length between polymer molecules. In the Cahn-Hilliard-de Gennes (CHD) free energy functional in Equation 2.27, \( \lambda \) is taken equal to the Kuhn length, \( a \) and hence for small values of \( \chi \), as for the polymer blend in this study, CHD free energy functional has dominance of the entropic contribution to the interfacial free energy. However, if \( \lambda \) is of the order of radius of gyration of the chain then it is possible to realize a significant enthalpic contribution to the interfacial free energy. In fact Debye\textsuperscript{8} has obtained the value of \( \lambda \) equal to \( R_g/6 \) for inhomogeneous polymer solutions where \( R_g \) is the radius of gyration of the polymer chain.

Lifshitz and Slyozov\textsuperscript{9} and later on Voorhees and Glicksman\textsuperscript{10} analyzed the growth of dispersed domains and found that the asymptotic growth law is of the form \( R(t) \sim t^{1/3} \). In both of these analyses the volume fraction of the minority
phase is considered small enough so as to form isolated domains in the matrix of the majority phase and the coarsening occurs by the transport of molecules perpendicular to the interface. Huse\textsuperscript{11} argued that when the volume fractions of the two phases are comparable then the resulting domain structure is highly percolated and there exists another mode of transport which is parallel to the interface in addition to the transport occurring perpendicular to the interface. He generalized the Lifshitz-Slyozov law by adding corrections of the order $1/R(t)$ to account for the transport parallel to the interface as follows,

\[
\frac{dR(t)}{dt} = \frac{C_2}{R^2(t)} + \frac{C_3}{R^3(t)} + O(R^{-4})
\]

where $C_3$ and $C_2$ are numerical coefficients. For dispersed domains $C_3=0$, $C_2>0$ and we obtain Lifshitz-Slyozov growth law $R(t) \sim t^{1/3}$. For percolated domains, $C_3 > 0$ and we obtain at large $R$ and $t$,

\[
R(t) = (C_3/2C_2) + (3C_2 t)^{1/3}
\]

If the chain transport perpendicular to the interface is totally absent then $C_2=0$, $C_3>0$ and one obtains the growth law $R(t) \sim t^{1/4}$. Kawasaki and Sekimoto\textsuperscript{12} have also obtained similar growth law by considering the transport parallel to the interface as the mechanism of coarsening. Our results of
the calculations for the critical mixtures using the FHD functional can be fitted to the growth law of the form \( R(t) \sim t^n \) as in Figure 3.3 with the exponent \( n=0.24(\pm 0.02) \), which is close to the 'quarter' power law described before. \( R(T) \) data for the critical mixture quenched to 54.5°C is plotted as a function of \( T^{1/3} \) in Figure 3.12. These data can be fitted to the generalized growth law in Equation 3.3 with \( C_2=0.018 \) and \( C_3=0.094 \) suggesting that the coarsening is dominated by the transport parallel to the interface. We can also fit the data to the generalized power law of the type, \( R(t) = A_2 + B_2 \ t^{1/4} \) as shown in Figure 3.13. Although the quarter power law fit is slightly better than the one-third power law fit we can not conclusively say that the growth is described by any particular form of the growth law. On the other hand our results of the calculations for the off-critical mixture \( (\phi_o=0.4) \) using the free energy functional of Equation 3.1 can be fitted to the growth law of the type \( R(t) \sim t^n \) with the exponent \( n=0.32 \ (\pm 0.02) \) which is very close to the Lifshitz-Slyozov predictions. This free energy functional has no entropic contribution to the interfacial free energy and shows the unarrested coarsening of the isolated domains by the classical Lifshitz-Slyozov type evaporation-condensation mechanism.

We have also analyzed our data to test the validity of the dynamical scaling at late time scales during the SD process. The scaling hypothesis states that there exists only one length scale dominating the dynamics in the scaling
regime and the topology scales with time. This dominant length scale is the characteristic size of the domains, $R(\tau)$. According to the dynamical scaling ansatz\textsuperscript{1,2,13} there exists a time independent function $F(k R(\tau))$ such that $I(k, \tau) = R(\tau)^d F(k R(\tau))$ where $I(k, \tau)$ is the scattered light intensity and $d$ is the space dimensionality. We have tested the dynamical scaling law by plotting $I(k, \tau) k_m(\tau)^3$ as a function of $(k/k_m)$ as shown in Figures 3.14 through 3.17 for various compositions and quench temperatures and by checking if the function $F(k/k_m)$ is independent of time. In each of the cases we get a time independent scaling function $F(k/k_m)$ and thus we observe the validity of the dynamical scaling law at late time scales in the SD process. Figure 3.14 shows the functional form of $F(k/k_m)$ for a critical mixture $\phi_0=0.5$ quenched to 35°C. The scaling function shows a weak shoulder and it follows a $k^{-3.6}$ power law for large $k$. The presence of a weak shoulder has been observed in the recent experimental and simulation studies\textsuperscript{13-15}. Similar behavior is observed for the critical mixture quenched to 49 and 25°C. We have constructed similar plots for the off-critical mixture $\phi_0=0.45$ quenched to 50 and 25°C in the Figures 3.15 and 16 respectively. We know that the off-critical mixture $\phi_0=0.45$ quenched to 50°C shows freezing of the morphology and in this case we observe that the scaling function does not show a shoulder and follows $k^{-4}$ law for large $k$ as seen from Figure 3.15. This is to be contrasted with the form of the scaling function shown in the Figure 3.16. In this case ($\phi_0=0.45$ and
we have found above that the system has highly interconnected domains of the two coexisting phases and shows unarrested coarsening of the phase separated domains. Here we see the emergence of the shoulder and the scaling function follows $k^{-3.6}$ law for large $k$. In the Figure 3.17 we have plotted the data for the off-critical mixture $\phi_o=0.4$ quenched to 35°C which shows freezing of the morphology and we see behavior similar to that of Figure 3.15. The observation of the scaling behavior, $F(x) \propto x^{-4}$ (where $x=k/k_m$) for large $k$ in these numerical calculations is in agreement with the expected Porod’s law for large $k$ values\textsuperscript{13}. This law should appear whether the system’s morphology is frozen or not, as observed in the present calculations. However if the composition and temperature are such that the system is not in the transnodal regime then the $F(x) \propto x^{-6}$ behavior characteristic of percolated structures\textsuperscript{13} is expected for $1 < x < 2$. The crossover from the approximately $x^{-6}$ behavior for $1 < x < 2$ to $x^{-4}$ behavior for $x>2$ is seen in Figures 3.14 and 3.17. On the other hand $x^{-6}$ behavior should be absent in the transnodal regime as observed in Figures 3.15 and 3.17. These observations offer further support to the phase diagram presented in Figure 3.9.

### Spinodal Decomposition under Simple Shear Flow

We have investigated the structure development during SD in a critical mixture ($\phi_o=0.5$), quenched to 35°C and under the imposed dimensional shears of 0.05, 0.1, 0.5 and 1.0, by numerically integrating Equation 2.42. The flow geometry is
as shown in Figure 2.1 with x as the flow direction, y as the direction of the velocity gradient and z as the neutral direction.

Figures 3.18 through 3.20 show calculated scattered intensities in the x, y, and z directions for various $\tau$ during the SD of the critical mixture under the dimensionless shear of 0.1. For early times during the phase separation the scattered intensity is isotropic but soon, for $\tau>50$, it becomes markedly anisotropic with enhanced scattering along the flow direction than in the perpendicular directions. Also, the characteristic wavenumber in the x direction shifts to lower values much faster than in the y and z directions. Figure 3.21 shows the variation of the characteristic wavenumbers in the x, y, and z directions as a function of $\tau$. In Figure 3.21, three distinct time regimes can be identified as: early regime, where all the three directions have similar growth behavior showing isotropic scattered intensity (2) intermediate regime, where the growth in the three directions follows different power laws and the intensity is highly anisotropic, and (3) late regime, where the phase separated domains reach their steady state sizes.

Figure 3.22 shows the development of structure in an arbitrary XY plane for various $\tau$. Each side of such a plane corresponds to 32 units of the dimensionless distance defined in Equation 2.31 and the vertical and horizontal directions correspond to x and y directions respectively. The color code used for this series of pictures is also shown in Figure
3.22. From these pictures, the anisotropy of growing domains is clear for $\tau > 50$. Because of the convection and rotation due to the imposed shear, domains undergo complex interfacial dynamics until the steady state is reached, where the domains are seen to be elongated along the flow direction. Figure 3.23 shows computer images of arbitrary XY, XZ, and YZ planes of the evolving structure for $\tau = 400$. These images suggest that the domains are elongated in the flow direction as seen in XY and XZ planes but are randomly arranged in the YZ plane which is perpendicular to the flow direction.

Figures 3.24 shows variation of the characteristic $k_m$ in the x direction as a function of $\tau$ for different shear rates. There are numerical difficulties in these calculations at higher shear rates and are evident from the data in Figure 3.24 for the shear rates of 0.5 and 1.0. From the log-log plots in Figures 3.25(a) through 3.25(c) the growth laws in x, y, and z directions have been determined as, $k_x \sim \tau^{-1}$, $k_y \sim \tau^{-0.18}$, and $k_z \sim \tau^{-0.25}$ respectively.

In these calculations, mean field approximation for the velocity field has been used and this neglects the perturbations in the velocity field due to composition fluctuations coming from the phase separation process. This approximation can be made, only because, the 'continuity of stress' is not violated due to the composition independence of the stress tensor in this particular case. The domain growth laws obtained here can be compared with a more rigorous theory of Onuki and Kawasaki\textsuperscript{16} which calculates the
growth laws by solving the intercoupled mass and momentum balance equations. They have obtained an exponent of 1 for the flow direction and 0.22 for the perpendicular direction (they have averaged the growth in the two directions perpendicular to the flow). Their theory is for small molecules and employs the corresponding free energy functional for inhomogeneous small molecule mixtures. Our calculations made for the polymer case, with the CHD functional and with the mean field limit of the velocity field, yield similar growth laws as those of Onuki and Kawasaki.
Figure 3.1
The spherically averaged structure factor $S(k, \tau)$ vs. $k$ for different values of $\tau$ calculated for the critical mixture ($\phi_0=0.5$) quenched to 49°C. The symbols are as follows: ■ ($\tau=22$), □ ($\tau=112$), ▲ ($\tau=225$), △ ($\tau=337$), ● ($\tau=675$).
Figure 3.2
The spherically averaged pair correlation function $g(x, T)$ vs. $x$ for different values of $T$ calculated for the critical mixture ($\phi_c=0.5$) quenched to 49°C. The symbols are as follows. ■($T=22$) □($T=112$) ▲($T=337$) ●($T=675$).
Time dependence of domain size $R$ for critical ($\phi_o=0.5$) and off-critical ($\phi_o=0.4$) mixtures. The critical mixture is quenched to 54.5(o), 49(●) and 25(△) °C. The off-critical mixture is quenched to 35(■) and 15(▲) °C.
Time dependence of \( k_m \) for critical (\( \phi_o = 0.5 \)) and off-critical (\( \phi_o = 0.4 \)) mixtures. The critical mixture is quenched to 54.5(o), 49(●) and 25(Δ)°C. The off-critical mixture is quenched to 35(□) and 15(▲) °C.
Figure 3.5

Computer images of the evolving phases as a function of reduced time $\tau_1$ for (a) critical mixture, $\phi_0=0.5$ and (b) off-critical mixture, $\phi_0=0.4$ quenched at 35°C. Here the free energy functional has the entropic contribution to the gradient term. Morphology does not change for off-critical mixture at $\tau_1 > 10$. This is to be contrasted to the growth of the percolated domains which are seen to coarsen at the same time scales as seen from Figure 3.5(b) on the next page.

Continued on the next page
Figure 3.5 Continued
An off-critical mixture of composition $\phi_0=0.4$ is quenched to three different quench temperatures; 15(■), 30(●) and 35(○). Sizes of the frozen domains are smaller for shallower quench depths.
The domain growth is arrested for the off-critical mixture of composition $\phi_o=0.45$ when quenched to $50^\circ C$ (□). The same composition shows unarrested coarsening of domains when quenched to $46^\circ C$ (■).
Images of the evolved domains at $T_1=250$ are shown for the off-critical composition $\phi_0=0.45$ quenched to 50°C (a), 46°C (b) and 25°C (c). Dispersed domains are formed in (a) while interconnected domains are formed in (b) and (c).
Calculated binodal (----) and spinodal curves (-----) for the particular polymer blend in this study. The dotted line (-----) represents the transition from the percolated to dispersed morphology based on the percolation threshold of 0.37. This percolation threshold is calculated based on the data points (shown in dark circles on this line) where the growth of the domains was no longer arrested. The shaded region between the spinodal curve and the dispersed to percolated clusters transition line depicts the transnodal region.
Figure 3.10

Time dependence of domain size $R$ for the off-critical ($\phi_0=0.4$) mixture quenched to 35(●) and 40(○) °C. Here the free energy functional has only the enthalpic contribution to the gradient term.
Figure 3.11

Computer images of the evolving phases as a function of reduced time $\tau$ for the off-critical mixture ($\phi_0=0.4$) quenched to 35°C. Here the free energy functional has only the enthalpic contribution to the gradient term similar to the small molecular case. The growth of the dispersed domains is seen to occur by the classical mechanism where larger domains grow at the expense of smaller domains. $\tau$ is defined in Equation 3.2.
Figure 3.12

$R(\tau)$ data for the critical mixture quenched to 54.5°C is plotted as a function of $\tau^{1/3}$. 
Figure 3.13

$R(\tau)$ data for the critical mixture quenched to $54.5^\circ C$ is plotted as a function of $\tau^{1/4}$. 
$I(k, \tau) k_m(\tau)^3$ is plotted as a function of $(k/k_m)$ on log-log scale for $\phi_0 = 0.5$ and $T = 35^\circ C$. The symbols are as follows: $\triangle (T = 225)$ $\bullet (T = 337)$ $\diamondsuit (T = 450)$ $\circ (T = 675)$ $\blacksquare (T = 787)$ $\square (T = 900)$. The solid line shows the $k^{-4}$ behavior.
$I(k, \tau) k_m(\tau)^3$ is plotted as a function of $(k/k_m)$ on log-log scale for $\phi_o=0.45$ and $T=50^\circ$C. The symbols are as follows: $\Delta$ ($T=225$) $\bullet$ ($T=337$) $\bullet$ ($T=450$) $\circ$ ($T=675$) $\Box$ ($T=787$) $\Box$ ($T=900$). The solid line shows the $k^{-4}$ behavior.
Figure 3.16

$I(k, \tau) k_m(\tau)^3$ is plotted as a function of $(k/k_m)$ on log-log scale for $\phi_0=0.45$ and $T=25^\circ C$. The symbols are as follows: ▲ ($\tau=225$), ◦ ($\tau=337$), ◆ ($\tau=450$), ○ ($\tau=675$), □ ($\tau=787$), □ ($\tau=900$). The solid line shows the $k^{-4}$ behavior.
\( I(k, \tau) k_m(\tau)^3 \) is plotted as a function of \( (k/k_m) \) on log-log scale for \( \phi_0 = 0.4 \) and \( T=35^\circ C \). The symbols are as follows: \( \triangle \) (\( \tau=225 \)) \( \bullet \) (\( \tau=337 \)) \( \blacklozenge \) (\( \tau=450 \)) \( \circ \) (\( \tau=675 \)) \( \blacksquare \) (\( \tau=787 \)) \( \square \) (\( \tau=900 \)). The solid line shows the \( k^{-4} \) behavior.
Calculated scattered intensity in the x direction, for SD in a critical mixture at $T=35^\circ C$ and under the dimensionless shear of 0.1, is plotted as a function of $k$ for various $\tau$. The symbols are as follows: $\triangle (T=20)$ $\square (T=55)$ $\blacksquare (T=90)$ $\triangle (T=125)$ $\circ (T=160)$ $\bullet (T=200)$ $\lozenge (T=250)$. $\tau$ is defined in Equation 2.31 and is same as the one in the quiescent state.
Figure 3.19

Calculated scattered intensity in the z direction, for SD in a critical mixture at $T=35^\circ C$ and under the dimensionless shear of 0.1, is plotted as a function of $k$ for various $\tau$. The symbols are as in Figure 3.18.
Calculated scattered intensity in the y direction, for a critical mixture at $T=35^\circ C$ and under the dimensionless shear of 0.1, is plotted as a function of $k$ for various $\tau$. The symbols are as in Figure 3.18.
Figure 3.21

Time dependence of $k_m$ in $x(\square)$, $y(\blacksquare)$, and $z(\Diamond)$ directions is shown for the SD in a critical mixture at $T=35^\circ C$ and under the dimensionless shear of 0.1.
Figure 3.22

Computer images of the evolving phases in XY plane as a function of reduced time $\tau$ are shown for the SD in a critical mixture at $T=35^\circ C$ and under the dimensionless shear of 0.1.
Computer images of the domains in the XY, XZ, and YZ planes evolved during the SD in a critical mixture at $T=35^\circ C$ and under the dimensionless shear of 0.1 are shown for the reduced time $\tau = 400$. 

Figure 3.23
Figure 3.24

Characteristic $k_m$ in the x direction is plotted as a function of $\tau$ for the SD in a critical mixture at $T=35^\circ C$ under different dimensionless shears of 0.1 (□), 0.05 (●), 0.5 (▲), and 1.0 (■).
Characteristic $k_m$ in $x$, $y$, and $z$ directions are plotted as a function of $\tau$ in parts (a), (b), and (c) respectively, to determine the growth exponents in the three directions for the SD in a critical mixture at $T=35^\circ C$ under two different dimensionless shears of 0.1 ( ) and 0.05 ( ).

Continued on the next page
Figure 3.25 Continued
Figure 3.25 Continued
References


(4) Di Marzio, E. A. suggested the name transnodal.


CHAPTER 4
CONCLUSIONS AND FUTURE WORK

Conclusions

Within the framework of the Cahn-Hilliard theory and its modification by de Gennes for inhomogeneous polymer mixtures, we have formulated a model for SD in polymer blends and have developed a computational scheme to investigate the evolution of morphology during SD in a binary blend of two flexible chain polymers. Specifically, we have studied the non-hydrodynamic regime of SD in the quiescent blend (i.e. not subjected to external flow) and an additional case of SD under simple shear flow by making the mean field approximation for the velocity field.

For SD in the quiescent mixtures, domain growth is solely controlled by diffusion in the absence of hydrodynamic interactions and for this case, we have computed the relative contributions of the entropic and enthalpic parts of the free energy of inhomogeneous polymer mixture to the kinetics of phase separation. We have demonstrated the effect of these contributions on the molecular mechanisms underlying the interfacial dynamics and on the resulting morphological evolution. The dominance of the entropic contribution favors the diffusion of molecules parallel to the interface while the dominance of the enthalpic contribution favors the diffusion of molecules perpendicular to the interface. For polymer blends having very small values of $\chi$ say, $10^{-3}$ to
10^{-5}, as in most isotopic blends, entropic contribution dominates and results in the arrested growth of the dispersed domains but shows unarrested growth of the percolated domains. The dominance of the enthalpic contribution results in the classical Lifshitz-Slyozov type evaporation-condensation mechanism for the coarsening of dispersed domains, showing no freezing of the morphology whatsoever. In many polymer systems, the magnitude of $\chi$ can be in the range of $10^0$ to $10^{-2}$ and the phase separation behavior in these systems would be intermediate to the two extreme cases of enthalpic and entropic dominance studied here.

For the SD under simple shear flow (in the absence of elastic effects), convection dominates the domain growth along the flow direction giving a growth exponent close to 1, while diffusion controls the domain growth along the other two directions giving growth exponents close to 0.25. This convection dominated exponent in the flow case should be reconciled with the experimentally observed exponent for the late stage SD in quiescent mixtures (when hydrodynamic interactions are supposed to be dominant), which is also close to unity. Infact Siggia\textsuperscript{1} has derived an exponent of unity for the domain growth in the late stage SD in the quiescent mixtures by proposing a capillary flow model for the interfacial dynamics.

The present calculations for SD under shear flow can be made mathematically more rigorous by going beyond the mean field approximation for the velocity field and this would
increase the potential of the present scheme for studying SD under flow in systems where the component polymers have different rheological properties. This would necessitate a more sophisticated numerical technique to solve two non-linear simultaneous differential equations of mass and momentum balances. Also, a justified model for accounting the elastic flux would be required in the mass balance equation.

This research work has made it possible to relate the microscopic properties of polymer mixtures such as molecular weights and \( \chi \) parameter, which characterize the chemistry of the materials and diffusion coefficients, which characterize the transport properties of the materials, to the macroscopic phase separation behavior of the system in real time and in real space (by appropriately converting dimensionless quantities). This work also has further potential for extension to other systems and is discussed in the next section.

**Future Work**

In the present calculations, we have used a mean field Flory-Huggins free energy for the homogeneous polymer mixture and also, we have not included the thermal noise term in the diffusion equation, mainly for numerical difficulties. This study can be further extended to probe the effects of the thermal noise and of the monomer density fluctuations on the dynamics of spinodal decomposition in polymer mixtures.
The present scheme of calculations can in principle be adopted for investigating the dynamics of SD in a variety of binary mixtures such as a blend of rigid rod polymer and a flexible coil polymer, a blend of ionomers, a blend having at least one crystallizable component etc., provided the free energy of the inhomogeneous mixture under consideration can be expressed in the form,

\[ F(\phi(r)) = \int d^3r \left[ f_0 + (\kappa_{\text{Entro}} + \kappa_{\text{Entha}}) |\nabla\phi(r)|^2 \right] \]  

(4.1)

In practice, it may be very cumbersome to derive such a functional which is able to capture the correct microscopic description of both the homogeneous and the interfacial regions of the inhomogeneous mixture. The system of flexible coil and rigid rod polymers appears interesting from theoretical as well as technological perspectives. In this case, the free energy \( f_0 \), of the homogeneous phase is described by the Flory-Huggins-Onsager formulation\(^2,3\). The presence of rod like molecules in the mixture affects the entropy of mixing by giving an extra contribution from the orientational entropy in addition to the contribution from more commonly encountered conformational entropy. The presence of rod like molecules in the interfacial region would also affect the prefactor of the square gradient term. The \( \kappa_{\text{Entro}} \) will now have to account for the chain-like nature
of flexible coil molecules and also, for the rod like nature of rigid molecules. It would be interesting to study the structure development in this system, since the morphological characteristics of the phase separated system bears a significant impact on the potential of this system to be used as a molecular composite.

Another extension is to a system of two flexible coil polymers with one component crystallizing at the temperatures in the unstable region of the phase diagram. In this case there would be three phases present in the system: two resulting from the SD process and the third being the pure crystallized component polymer. Such a system is of great practical significance because many of the industrial blends such as polycarbonate and polyester, polystyrene and polypropylene oxide, polyether ether ketone and polyimide etc. have a crystallizable polymer as one of the components of the blend. SD has been used in these systems, though not yet successfully, to generate structures having the crystalline and amorphous phases percolating in each other. Modifications to be done in the present scheme of calculations will have to include the extra term in the mass balance equation due to crystallization.

There has been considerable interest in developing models for the phase inversion process and the compositional quenching process used for manufacturing membranes and impact modified plastics respectively. The main aim is to relate the final product properties in terms of the size of the
phase separated domains (usually called as the "pore size") to the processing parameters and to the properties of the processed material. The understanding of the free energy of inhomogeneous polymer mixtures can be extended to the modelling of these processes.
Effect of Chain Like Nature of Polymer Molecules on the Phase Behavior of Polymer Mixtures

Thermodynamics

Small Entropy of Mixing

Composition and M.W. Dependence of chin Parameter

Dynamics

Slow Rates of Phase Separation

Domain Growth Laws Affected by Relative Contributions of Enthalpic and Entropic Parts of Interfacial Free Energy

Freezing of Dispersed Domain Morphology in the Case of Dominant Entropic Contribution to Interfacial Free Energy

Strong Effect of External Flow on the Phase Separation Kinetics and the Resulting Morphologies

Figure 4.1

A schematic showing various effects of the chain-like nature of polymer molecules on the phase behavior of polymer mixtures.
References


APPENDIX

REPRESENTATIVE PROGRAMS

PROGRAM POL3D

PARAMETER (L=32)
PARAMETER (L3=28)

C L3=L/2/BINSI*SQRT(3)+0.5
C **************************************************************
C WE WILL DEFINE THE VARIABLES AND THEIR TYPES
C **************************************************************
COMMON /BINS/ BINSI
REAL P(L*L*L), Q(L,L,L)
REAL W1(L*L*L), QR1(0:L-1,0:L-1,0:L-1)
REAL W2(L*L*L)
REAL W3(L*L*L)
REAL W4(L*L*L)
REAL XGRADP(L*L*L)
REAL SHEAR(L*L*L)
REAL ETA(L*L*L)
REAL V1(L,L,L), V2(L,L,L)

COMPLEX VDATA(L,L,L)
COMPLEX DATA(L*L*L)

INTEGER NN(3)
INTEGER N1(L*L*L)
INTEGER N2(L*L*L)
INTEGER N3(L*L*L)
INTEGER N4(L*L*L)
INTEGER N5(L*L*L)
INTEGER N6(L*L*L)
INTEGER NY(L*L*L)

REAL GR(0:L3)
REAL SK(0:L3)
REAL RA(0:L3)

REAL SKX(L)
REAL SKZ(L)
REAL SKY(L)

EQUIVALENCE (W1(1),QR1(0,0,0))
EQUIVALENCE (P(1),Q(1,1,1))
EQUIVALENCE (W1(1),V1(1,1,1))
EQUIVALENCE (W2(1),V2(1,1,1))
EQUIVALENCE (DATA(1),VDATA(1,1,1))

EXTERNAL DRAN
DOUBLE PRECISION DRAN
C *************************************************
C FOLLOWING SECTION READS AND WRITES THE INPUT AND
C OUTPUT FILES.
C **************************************************

OPEN (UNIT=7, FILE='INPUTFHD')
READ (7, *) DT, IRUN, NUPDA, NMEAS, TEMP, TC, PZERO, GAMMA, INOISE

IF (GAMMA.EQ.0.0) THEN

OPEN (UNIT=9, FILE='RGFHD')
OPEN (UNIT=10, FILE='GRFHD')
OPEN (UNIT=11, FILE='SKFHD')

DO 26 I=9,11
WRITE (I, *) ' 3-D. POLYMER SYSTEM SIDE = ', L
WRITE (I, *) ' CONSERVED ORDER PARAMETER & FHD FREE
ENERGY'
WRITE (I, *) ' DT IRUN NUPDA NMEAS TEMP TC PZERO'
WRITE (I, 6010) DT, IRUN, NUPDA, NMEAS, TEMP, TC, PZERO
WRITE (I, *)
26 CONTINUE

WRITE (9, *) ' TIME
WRITE (9, *) ' RG'

WRITE (10, *) ' TIME
WRITE (10, *) ' G(R,T) R=0,1,.....,L/2*SQRT(3)'
WRITE (10, *)

WRITE (11, *) ' TIME'
WRITE (11, *) ' S(K,T) KX=0,1,.....,L/2*SQRT(3)'
WRITE (11, *)

ELSE

OPEN (UNIT=12, FILE='SKX')
OPEN (UNIT=13, FILE='SKZ')
OPEN (UNIT=14, FILE='SKY')

DO 27 I=12,14
WRITE (I, *) ' 3-D. POLYMER SYSTEM SIDE = ', L
WRITE (I, *) ' CONSERVED ORDER PARAMETER, FHD FREE ENERGY UNDER
FLOW'
WRITE (I, *) ' DT IRUN NUPDA NMEAS TEMP TC PZERO GAMMA'
WRITE (I, 6011) DT, IRUN, NUPDA, NMEAS, TEMP, TC, PZERO, GAMMA
WRITE (I, *)
27 CONTINUE

WRITE (12, *) ' TIME'
WRITE (12, *) ' SKX(K,T) KX=0,1,.....'
WRITE (12, *)
WRITE(13,*), ' TIME ' 
WRITE(13,*), ' SKZ(K,T)  KZ=0,1,.....' 
WRITE(14,*), ' TIME ' 
WRITE(14,*), ' SKYZ(K,T)  KY=0,1,.....' 

ENDIF

6010 FORMAT (1X,F8.4,3(I8),2(F8.2),2X,F5.3) 
6011 FORMAT (1X,F8.4,3(I8),2(F8.2),2X,F5.3) 

C  ***********************************************
C FOLLOWING SECTION DEFINES VARIOUS CONSTANTS IN THE
C CALCULATIONS AND SOME OF THEM CHARACTERIZE A
C PARTICULAR SYSTEM LIKE ALPHA, TC, CHI AND CHIC ETC.
C  ***********************************************

N=L*L*L 
IL=L/2 
LWORK=3*L 
RN=N 
SQN=SQRT(RN) 
BINSI=1.00 

ALPHA=0.326 
CHI=ALPHA/(273.15+TEMP)-0.00023 
CHIC=ALPHA/(273.15+TC)-0.00023 

CHIS=CHIC/(4.0*PZERO*(1.0-PZERO)) 

CPO=0.5/(PZERO*(1.0-PZERO)) 

D1=(CHIC*CPO)/(2.0*(CHI-CHIS)) 

D2=2.0*CPO*CHI/(CHI-CHIS) 

EPS=SQRT(CHI-CHIS) 

C  ***********************************************
C FOLLOWING SECTION SETS UP THE ARRAYS FOR THE NEAREST
C NEIGHBORS FOR ANY POINT IN THE GRID DEFINED WITH
C PERIODIC BOUNDARY CONDITIONS.
C  ***********************************************

CALL COMPRA(RA,L3,L) 

DO 1 I=1,L 
DO 1 J=1,L 
DO 1 K=1,L 
IJK=NCORD(L,I,J,K,0,0,0) 
N1(IJK)=NCORD(L,I,J,K,1,0,0) 
N2(IJK)=NCORD(L,I,J,K,-1,0,0) 
N3(IJK)=NCORD(L,I,J,K,0,1,0) 
N4(IJK)=NCORD(L,I,J,K,0,-1,0) 
112
N5(IJK) = NCORD(L, I, J, K, 0, 0, 1)
N6(IJK) = NCORD(L, I, J, K, 0, 0, -1)
NY(IJK) = J - 1

1 CONTINUE

C *******************************************************
C INITIALIZE
C *******************************************************

DO 501 I=1,N
501 P(I) = PZERO
TIME = 0.0
ISEED = 234567 + IRUN*10

C ********************************************************
C FOLLOWING SECTION SOLVES THE DIFFERENTIAL EQUATION
C USING
C FINITE DIFFERENCE SCHEME.
C ********************************************************

IF (GAMMA.EQ.0.0) THEN
DO 2 IJ=1,NMEAS
DO 3 ISTEP=1,NUPDA

IF (IJ.LE.1) THEN
IF (ISTEP.LE.INOISE) THEN

DO 701 I=1,N
W1(I) = SQRT(3.0)*(2.0*DRAN(ISEED) - 1.0)
W2(I) = SQRT(3.0)*(2.0*DRAN(ISEED) - 1.0)
W3(I) = SQRT(3.0)*(2.0*DRAN(ISEED) - 1.0)
701 CONTINUE

DO 702 I=1,N
ETA(I) = W1(N1(I)) - W1(I) + W2(N3(I)) - W2(I) + W3(N5(I)) - W3(I)
702 CONTINUE
ELSE
DO 709 I=1,N
ETA(I) = 0.0
709 CONTINUE
ENDIF
ELSE
DO 710 I=1,N
ETA(I) = 0.0
710 CONTINUE
ENDIF

DO 703 I=1,N
W1(I) = P(N1(I)) + P(N2(I)) + P(N3(I)) + P(N4(I)) +
& \ P(N5(I)) + P(N6(I))
& \ - 6.0 * P(I)
703 \ CONTINUE

DO 704 I = 1, N
W2(I) = 0.25 * ((P(N1(I)) - P(N2(I))) ** 2 + (P(N3(I)) - P(N4(I))) ** 2 + (P(N5(I)) - P(N6(I))) ** 2)
& \ CONTINUE
704 \ CONTINUE

DO 705 I = 1, N
W3(I) = D1 * ALOG(P(I) / (1.0 - P(I))) - D2 * P(I)
& \ + ((1.0 - 2.0 * P(I)) * W2(I) / (36.0 * (P(I) ** 2) * (1.0 - P(I))) ** 2) * CPO
& \ -(W1(I) / (18.0 * P(I) * (1.0 - P(I)))) * CPO
705 \ CONTINUE

DO 706 I = 1, N
W1(I) = (W3(N1(I)) - W3(I)) * P(I) * (1.0 - P(I))
W2(I) = (W3(N3(I)) - W3(I)) * P(I) * (1.0 - P(I))
W4(I) = (W3(N5(I)) - W3(I)) * P(I) * (1.0 - P(I))
706 \ CONTINUE

DO 707 I = 1, N
P(I) = P(I) + DT * (W1(N1(I)) - W1(N2(I)) + W2(N3(I))
& \ - W2(N4(I))
& \ + W4(N5(I)) - W4(N6(I))) * 0.5
& \ + SQRT(EPS * DT) * ETA(I)
707 \ CONTINUE
3 \ CONTINUE

TIME = TIME + NUPDA * DT
C
C \**********************************************
C \COMPUTE STRUCTURE FACTOR
C \**********************************************
DO 36 I = 1, N
W1(I) = P(I) - PZERO
36 \ W2(I) = 0.0

DO 111 K = 1, L
DO 111 J = 1, L
DO 111 I = 1, L
VDATA(I, J, K) = CMPLX(V1(I, J, K), V2(I, J, K))
111 \ CONTINUE

NN(1) = L
NN(2) = L
NN(3) = L

CALL FFTMD(VDATA, NN, 3, 1)
DO 37 I=1,N
W1(I) = (CABS(DATA(I)))**2

CALL MEANV(W1,W1AV,N)
CALL SPHER(QR1,SK,RA,L,L3,IL)
P0=0.0
DO 78 I=0,L3
78 P0=P0+RA(I)*SK(I)
P0=P0/N
CALL MEANV(P,P1AV,N)
CALL MEASQV(P,P2,N)
PTEST=P2-P1AV**2
WRITE(11,* ) TIME
WRITE(11,156) (SK(I),I=0,L3)
CALL FLUSH(11)

156 FORMAT(5(F15.3))

C *************************************************
C COMPUTE CORRELATION FUNCTION
C *************************************************

DO 38 I=1,N
W1(I)=W1(I)/SQN
38 W2(I)=0.0

DO 112 K=1,L
DO 112 J=1,L
DO 112 I=1,L
VDATA(I,J,K)=CMPLX(V1(I,J,K),V2(I,J,K))
112 CONTINUE

CALL FFTMD(VDATA,NN,3,1)

DO 113 I=1,N
W1(I) = REAL(DATA(I))
113 CONTINUE

CALL MEANV(W1,W1AV,N)
CALL SPHER(QR1,GR,RA,L,L3,IL)
P0=0.0
DO 79 I=0,L3
79 P0=P0+RA(I)*GR(I)
P0=P0/N

CALL RCAL(L3,GR,RG)
 CALL MEASQV(P,P2,N)

WRITE(9,67) TIME, RG*BINSI
67 FORMAT(F7.3,1(1X,F14.6))
CALL FLUSH(9)
WRITE(10, *) TIME
WRITE(10, 156) (GR(I), I=0, L3)
CALL FLUSH(10)

2 CONTINUE

ELSE

PRINT*, 'USE SHEAR PROGRAM'

ENDIF

STOP
END

******************************************************************************
* FOLLOWING SECTION HAS THE SUBROUTINES USED IN THE MAIN PROGRAM *
******************************************************************************

SUBROUTINE DISPLA(X, TT1, KK, ORPAR, L)
REAL X(L, L, L)
CHARACTER*1 FIGURE(100)

N=L*L*L
WRITE(8, 6300) TT1

DO 111 J=1, MIN(10, L)
  111 WRITE(8, 6000) (X(J, I, KK), I=1, MIN(10, L))

6000 FORMAT(1H ,10(F7.2))
WRITE(8, *)
DO 105 IJK=1, 5

105 WRITE(8, *)
WRITE (8, *) ' ORDER PARAMETER=', ORPAR
DO 222 I=1, L
  DO 210 J=1, L
    FIGURE(J)='
  210 IF (X(I, J, KK) .GT. 0.5) FIGURE(J)='*
  222 WRITE(8, 6100) (FIGURE(J), J=1, L)

DO 205 IJK=1, 5

205 WRITE(8, *)
RETURN

6100 FORMAT(1H ,100(A1))
6300 FORMAT(1H ,'TIME = ', F8.4)

END
SUBROUTINE RCAL(L3, GCORR, RG)
REAL GCORR(0:L3)
REAL C(4)
DO 10 IR1=0, L3
IF (GCORR(IR1) .LT. 0.0) GO TO 11
10 CONTINUE
11 CONTINUE
IF (IR1 .LT. L3 .AND. IR1 .GT. 1) THEN
R1=IR1
G1=GCORR(IR1)
G2=GCORR(IR1-1)
G3=GCORR(IR1-2)
G4=GCORR(IR1+1)
C(1)=(3.0*G2-3.0*G1-G3+G4)/6.0
C(2)=(G1-2.0*G2+G3-6.0*C(1)*(R1-1.0))/2.0
C(3)=G1-G2-C(2)*(2*R1-1)-C(1)*(3*R1*R1-3*R1+1)
C(4)=G1-C(1)*R1**3-C(2)*R1*R1-C(3)*R1
RG=R1-0.5
CALL ROOT(C, RG)
ELSE
RG=0.0
ENDIF
RETURN
END

SUBROUTINE ROOT(C, X0)
REAL C(4)
FMIN=1.0E-3
1 F=C(1)*X0**3+C(2)*X0**2+C(3)*X0+C(4)
FD=3.*C(1)*X0**2+2.*C(2)*X0+C(3)
D=F/FD
X0=X0-D
IF (ABS(D) .LT. FMIN) RETURN
GO TO 1
END

SUBROUTINE SPHER(X, XR, RA, L, L3, IL)
COMMON /BINS/ BINSI
REAL XR(0:L3)
REAL RA(0:L3)
REAL X(0:L-1,0:L-1,0:L-1)
DO 969 I=0,L3
XR(I)=0.0

DO 1 IX=0,L-1
I1=IX
IF (I1.GT.IL) I1=I1-L
DO 1 IY=0,L-1
I2=IY
IF (I2.GT.IL) I2=I2-L
DO 1 IZ=0,L-1
I3=IZ
IF (I3.GT.IL) I3=I3-L

R=I1*I1+I2*I2+I3*I3
R=SQRT(R)/BINSI+0.5
I=R
XR(I)=XR(I)+X(IX,IY,IZ)
1 CONTINUE

DO 2 I=0,L3
IF(RA(I).LT.1.0E-6) GOTO 2
XR(I)=XR(I)/RA(I)
2 CONTINUE

RETURN
END

SUBROUTINE COMPRA(RA,L3,L)
COMMON /BINS/ BINSI
REAL RA(0:L3)
DO 973 I=0,L3
RA(I)=0.0
IL=L/2
DO 1 I=0,L-1
I1=I
IF (I1.GT.IL) I1=I1-L
DO 1 J=0,L-1
I2=J
IF (I2.GT.IL) I2=I2-L
DO 1 K=0,L-1
I3=K
IF (I3.GT.IL) I3=I3-L
R=I1*I1+I2*I2+I3*I3
R=SQRT(R)/BINSI+0.5
IJK=R
RA(IJK)=RA(IJK)+1
1 CONTINUE
RETURN
END
SUBROUTINE MEANV(X, XX, N)
REAL X(N)
XX=0.0
DO 1 I=1, N
XX=XX+X(I)
XX=XX/N
RETURN
END

SUBROUTINE MEASQV(X, XX, N)
REAL X(N)
XX=0.0
DO 1 I=1, N
XX=XX+X(I)*X(I)
XX=XX/N
RETURN
END

FUNCTION NCORD(L, I, J, K, IX, IY, IZ)
I1=I+IX
IF(I1.GT.L) I1=I1-L
IF(I1.LT.1) I1=I1+L
I2=J+IY
IF(I2.GT.L) I2=I2-L
IF(I2.LT.1) I2=I2+L
I3=K+IZ
IF(I3.GT.L) I3=I3-L
IF(I3.LT.1) I3=I3+L
NCORD=I1+(I2-1)*L+(I3-1)*L*L
RETURN
END

SUBROUTINE FFTMD(DATA, NN, NDIM, ISIGN)
REAL*8 WR, WI, WPR, WPI, WTEMP, THETA
DIMENSION NN(NDIM), DATA(*)

NTOT=1
DO 11 IDIM=1, NDIM
NTOT=NTOT*NN(IDIM)
11 CONTINUE

NPREV=1

DO 18 IDIM=1, NDIM
N=NN(IDIM)
NREM=NTOT/(N*NPREV)
IP1=2*NPREV
\[ IP2 = IP1 \times N \]
\[ IP3 = IP2 \times NREM \]
\[ I2REV = 1 \]

\[ \text{DO 14 } I2 = 1, IP2, IP1 \]
\[ \quad \text{IF} (I2 < I2REV) \text{ THEN} \]
\[ \quad \quad \text{DO 13 } I1 = I2, I2+IP1-2, 2 \]
\[ \quad \quad \quad \text{DO 12 } I3 = I1, IP3, IP2 \]
\[ \quad \quad \quad \quad I3REV = I2REV + I3 - I2 \]
\[ \quad \quad \quad \quad TEMPL = DATA(I3) \]
\[ \quad \quad \quad \quad TEMPI = DATA(I3+1) \]
\[ \quad \quad \quad \quad DATA(I3) = DATA(I3REV) \]
\[ \quad \quad \quad \quad DATA(I3+1) = DATA(I3REV+1) \]
\[ \quad \quad \quad \quad DATA(I3REV) = TEMPL \]
\[ \quad \quad \quad \quad DATA(I3REV+1) = TEMPI \]

\[ \quad \quad \text{CONTINUE} \]
\[ \quad \quad \text{CONTINUE} \]

\[ \quad \text{ENDIF} \]

\[ IBIT = IP2 / 2 \]

\[ \text{IF} (IBIT \geq IP1) \text{ AND } (I2REV \geq IBIT) \text{ THEN} \]
\[ \quad I2REV = I2REV - IBIT \]
\[ \quad IBIT = IBIT / 2 \]

\[ \text{GO TO 1} \]

\[ \text{ENDIF} \]

\[ I2REV = I2REV + IBIT \]

\[ \text{CONTINUE} \]

\[ \text{IFP1} = IP1 \]

\[ \text{IF} (IFP1 < IP2) \text{ THEN} \]
\[ \quad \text{IFP2} = 2 \times IFP1 \]
\[ \text{THETA} = \text{ISIGN} \times 6.28318530717959D0 / (IFP2 / IP1) \]
\[ \text{WPR} = -2.0 \times \text{DSIN}(0.5D0 \times \text{THETA}) \times 2 \]
\[ \text{WPI} = \text{DSIN}(\text{THETA}) \]
\[ \text{WR} = 1.0 \]

\[ \text{WI} = 0.0 \]

\[ \text{DO 17 } I3 = 1, \text{IFP1}, IP1 \]
\[ \quad \text{DO 16 } I1 = I3, I3+IP1-2, 2 \]
\[ \quad \quad \text{DO 15 } I2 = I1, IP3, \text{IFP2} \]
\[ \quad \quad \quad K1 = I2 \]
\[ \quad \quad \quad K2 = K1 + \text{IFP1} \]
\[ \quad \quad \quad TEMPL = \text{SNGL}(WR) \times \text{DATA}(K2) - \text{SNGL}(WI) \times \text{DATA}(K2+1) \]
\[ \quad \quad \quad TEMPI = \text{SNGL}(WR) \times \text{DATA}(K2+1) + \text{SNGL}(WI) \times \text{DATA}(K2) \]
\[ \quad \quad \quad \text{DATA}(K2) = \text{DATA}(K1) - TEMPL \]
\[ \quad \quad \quad \text{DATA}(K2+1) = \text{DATA}(K1+1) - TEMPI \]
\[ \quad \quad \quad \text{DATA}(K1) = \text{DATA}(K1) + TEMPL \]
\[ \quad \quad \quad \text{DATA}(K1+1) = \text{DATA}(K1+1) + TEMPI \]

\[ \quad \text{CONTINUE} \]
\[ \quad \text{CONTINUE} \]

\[ \text{WTEMP} = WR \]
\[ \text{WR} = \text{WR} \times \text{WPR} - \text{WI} \times \text{WPI} + \text{WR} \]
\[ \text{WI} = \text{WI} \times \text{WPR} + \text{WTEMP} \times \text{WPI} + \text{WI} \]

\[ \text{CONTINUE} \]

\[ \text{IFP1} = \text{IFP2} \]
GO TO 2
ENDIF
NPREV=N*NPREV
CONTINUE
RETURN
END

DOUBLE PRECISION FUNCTION DRAN(IY)
IMPLICIT NONE
INTEGER IY

C DRAN IS A UNIFORM RANDOM NUMBER GENERATOR BASED ON THEORY AND
C SUGGESTIONS GIVEN IN D. E. KNUTH (1969), VOL. 2. THE INTEGER IY
C SHOULD BE INITIALIZED TO AN ARBITRARY INTEGER PRIOR TO THE FIRST
C CALL TO DRAN. THE CALLING PROGRAM SHOULD NOT ALTER THE VALUE OF IY
C BETWEEN SUBSEQUENT CALLS TO DRAN. VALUES OF DRAN WILL BE RETURNED
C IN THE INTERVAL (0,1).
C
INTEGER IA, IC, ITWO, M2, M, MIC
DOUBLE PRECISION HALFM, S
DOUBLE PRECISION DATAN, DSQRT

C ** ALLIANT: SUGGESTED SAVE STMT
C
SAVE IA, IC, M2, MIC, S, ITWO
C
DATA M2/0/, ITWO/2/
IF (M2 .NE. 0) GO TO 20
C
IF FIRST ENTRY, COMPUTE MACHINE INTEGER WORD LENGTH.
C
M = 1
10 M2 = M
M = ITWO * M2
IF (M .GT. M2) GO TO 10
HALFM = M2
C
COMPUE MULTIPLIER AND INCREMENT FOR LINEAR CONGRUENTIAL METHOD.
C
IA = 8*IDINT(HALFM * DATAN(1.0D0) / 8.0D0) + 5
IC = 2*IDINT(HALFM * (0.5D0 - DSQRT(3.0D0)/6.0D0)) + 1
MIC = (M2 - IC) + M2
C
S IS THE SCALE FACTOR FOR CONVERTING TO FLOATING POINT.
C
S = 0.5 / HALFM
C
COMPUE NEXT RANDOM NUMBER.
THE FOLLOWING STATEMENT IS FOR COMPUTERS WHERE INTEGER
OVERFLOW AFFECTS THE SIGN BIT.

IY = IAND(IY, '7FFFFFFF'X)

DRAN = DBLE(IY) * S
RETURN
END


34. Rangel-Nafaile, C.; Metzner, A. B.; Wissburn, K. F. Macromolecules 1984, 17, 1187 and references there in.


