INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.
Phase separation kinetics of binary liquid crystal-polymer mixtures

Kim, Jae Yon, Ph.D.
Kent State University, 1992
PHASE SEPARATION KINETICS OF BINARY LIQUID CRYSTAL-POLYMER MIXTURES

A dissertation submitted to the Kent State University Graduate College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

by

Jae Yon Kim

May, 1992
Dissertation written by

Jae Yon Kim

B.A., Jeonbuk National University, 1985
Ph.D., Kent State University, 1992

Approved by

[Signatures]
Chair, Doctoral Dissertation Committee
Members, Doctoral Dissertation Committee

Accepted by

[Signatures]
Chair, Department of Physics
Dean, Graduate College
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Figures</td>
<td>v</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>viii</td>
</tr>
<tr>
<td><strong>Chapter I — Introduction</strong></td>
<td>1</td>
</tr>
<tr>
<td>1.1 Liquid crystals</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Polymer dispersed liquid crystal (PDLC) materials</td>
<td>11</td>
</tr>
<tr>
<td>1.3 Binary mixtures</td>
<td>14</td>
</tr>
<tr>
<td>1.4 Studies of phase separation</td>
<td>15</td>
</tr>
<tr>
<td><strong>Chapter II — Phase Separation</strong></td>
<td>18</td>
</tr>
<tr>
<td>2.1 Overview</td>
<td>18</td>
</tr>
<tr>
<td>2.2 Phase separation in thermally quenched binary mixtures</td>
<td>29</td>
</tr>
<tr>
<td>2.2.1 Nucleation theories</td>
<td>29</td>
</tr>
<tr>
<td>2.2.2 Early stage theories of spinodal decomposition</td>
<td>30</td>
</tr>
<tr>
<td>2.2.3 Late stage growth theories</td>
<td>36</td>
</tr>
<tr>
<td>2.2.4 Scaling theories for structure factors</td>
<td>44</td>
</tr>
<tr>
<td>2.3 Polymerization induced phase separation (PIPS)</td>
<td>46</td>
</tr>
<tr>
<td>2.3.1 Flory-Huggins model – binary systems</td>
<td>46</td>
</tr>
<tr>
<td>2.3.2 Complex multicomponent systems</td>
<td>47</td>
</tr>
<tr>
<td><strong>Chapter III — Light Scattering</strong></td>
<td>55</td>
</tr>
<tr>
<td>3.1 Light scattering theory</td>
<td>55</td>
</tr>
<tr>
<td>3.2 Dynamic light scattering</td>
<td>58</td>
</tr>
<tr>
<td>3.2.1 Photon correlation</td>
<td>58</td>
</tr>
<tr>
<td>3.2.2 Director fluctuation in PDLC materials</td>
<td>59</td>
</tr>
<tr>
<td><strong>Chapter IV — Experimental Details and Results</strong></td>
<td>63</td>
</tr>
<tr>
<td>4.1 Experimental details</td>
<td>63</td>
</tr>
<tr>
<td>4.1.1 Sample preparation</td>
<td>63</td>
</tr>
<tr>
<td>4.1.2 Experimental setup</td>
<td>67</td>
</tr>
<tr>
<td>4.2 Experimental results</td>
<td>80</td>
</tr>
<tr>
<td>4.2.1 Resistance and capacitance measurements</td>
<td>80</td>
</tr>
</tbody>
</table>
List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Schematics of liquid crystalline phases.</td>
<td>2</td>
</tr>
<tr>
<td>2. Canonical deformations of a nematic liquid crystal.</td>
<td>6</td>
</tr>
<tr>
<td>3. Schematic illustration concerning the refractive index of a nematic liquid crystal for an obliquely incident light.</td>
<td>10</td>
</tr>
<tr>
<td>4. Schematic illustration of optoelectronic response of a PDLC film.</td>
<td>13</td>
</tr>
<tr>
<td>5. Free energy and corresponding phase diagram of a two component mixture.</td>
<td>22</td>
</tr>
<tr>
<td>6. The free energy changes during phase separation of a metastable phase of concentration $\phi_0$.</td>
<td>24</td>
</tr>
<tr>
<td>7. Spontaneous disappearance of concentration fluctuations and diffusion towards a nucleus in a system undergoing nucleation and growth.</td>
<td>25</td>
</tr>
<tr>
<td>8. The free energy changes during phase separation of an unstable phase of concentration $\phi_0$.</td>
<td>26</td>
</tr>
<tr>
<td>9. Temporal change in concentration profile in a system undergoing spinodal decomposition.</td>
<td>28</td>
</tr>
<tr>
<td>10. The growth rate in the early stage predicted by the Cahn-Hilliard theory.</td>
<td>33</td>
</tr>
<tr>
<td>11. Four different stages of spinodal decomposition.</td>
<td>38</td>
</tr>
<tr>
<td>12. n-mer distribution as function of time and size.</td>
<td>50</td>
</tr>
<tr>
<td>13. Schematic of the scattering geometry.</td>
<td>56</td>
</tr>
<tr>
<td>14. Illustration of the droplet director of an elongated cavity in the presence of an electric field.</td>
<td>60</td>
</tr>
<tr>
<td>15. The chemical structures of the components of the nematic liquid crystal E7.</td>
<td>64</td>
</tr>
<tr>
<td>16. Molecular structures of Epon 828 and Capcure 3-800.</td>
<td>65</td>
</tr>
<tr>
<td>17. Refractive indices of the pure liquid crystal E7 and the pure polymer as function of temperature.</td>
<td>68</td>
</tr>
<tr>
<td>18. Experimental setup for resistance measurement during curing process.</td>
<td>69</td>
</tr>
<tr>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
<td></td>
</tr>
<tr>
<td>19. Capacitance and resistance measurement by a GenRad capacitance bridge.</td>
<td>71</td>
</tr>
<tr>
<td>20. Light scattering setup I.</td>
<td>73</td>
</tr>
<tr>
<td>21. Light scattering setup II.</td>
<td>74</td>
</tr>
<tr>
<td>22. Schematic of a microscope and a VCR arrangement to study phase separation while curing.</td>
<td>76</td>
</tr>
<tr>
<td>23. Schematic of the experimental arrangement to see the effect of shear during phase separation.</td>
<td>77</td>
</tr>
<tr>
<td>24. Experimental arrangement for detecting the fluctuating scattered light from the PDLC film.</td>
<td>79</td>
</tr>
<tr>
<td>25. Resistance of a sample as a function of time during phase separation I.</td>
<td>81</td>
</tr>
<tr>
<td>26. Resistance of a sample as a function of time during phase separation II.</td>
<td>82</td>
</tr>
<tr>
<td>27. Capacitance and resistance during phase separation.</td>
<td>83</td>
</tr>
<tr>
<td>28. Onset time of phase separation as a function of composition.</td>
<td>85</td>
</tr>
<tr>
<td>29. Temporal evolution of the diffraction pattern.</td>
<td>86</td>
</tr>
<tr>
<td>30. Scattered intensity as functions of angle and time.</td>
<td>87</td>
</tr>
<tr>
<td>31. Variation of $-M\frac{\delta^2 f}{\delta \delta^2}$ and $\delta M$ with time.</td>
<td>88</td>
</tr>
<tr>
<td>32. Typical scattered intensity from a diffraction grating.</td>
<td>89</td>
</tr>
<tr>
<td>33. Graph of intensity vs. time.</td>
<td>91</td>
</tr>
<tr>
<td>34. Scattered intensity vs. $q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$ at different times I.</td>
<td>92</td>
</tr>
<tr>
<td>35. Scattered intensity vs. $q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$ at different times II.</td>
<td>93</td>
</tr>
<tr>
<td>36. Plot of the scaled structure factor $I_{nor} = q_{max}^3$ vs. the scaled wavevector $q/q_{max}$</td>
<td>94</td>
</tr>
<tr>
<td>37. Log-log plot of the scaled structure factor $F(q/q_{max})$ vs. the scaled wavevector $q/q_{max}$ I.</td>
<td>95</td>
</tr>
<tr>
<td>38. Log-log plot of the scaled structure factor $F(q/q_{max})$ vs. the scaled wavevector $q/q_{max}$ II.</td>
<td>97</td>
</tr>
<tr>
<td>39. $\ln q_{max}$ vs. $\ln (t-t_0)$.</td>
<td>98</td>
</tr>
<tr>
<td>40. $\ln I_{max}$ vs. $\ln (t-t_0)$.</td>
<td>99</td>
</tr>
<tr>
<td>41. Scanning electron micrograph (SEM) of the cured PDLC material. It consists of 33% liquid crystal E7 by weight.</td>
<td>101</td>
</tr>
<tr>
<td>42. Scanning electron micrograph (SEM) of the cured PDLC material. It consists of 45% liquid crystal E7 by weight.</td>
<td>102</td>
</tr>
<tr>
<td>43. Micrographs of cascade phenomena while curing at 45°C.</td>
<td>104</td>
</tr>
</tbody>
</table>
44. Illustration of Gibbs-Thomson effect. .......................................................... 110
45. SEM micrographs of the sample in the presence of shear during phase separation. .......................................................... 112
46. Autocorrelation function of the scattered light with time. The polarization is $V_Y$ and no electric field is applied. ........................................... 114
47. Autocorrelation function of the scattered light with time. The polarization is $V_H$ and no electric field is applied. ........................................... 115
48. Autocorrelation function of the scattered light with time. The polarization is $V_Y$ and the applied electric field is 10 volt at 1 KHz. .... 116
49. Autocorrelation function of the scattered light with time. The polarization is $V_H$ and the applied electric field is 10 volt at 1 KHz. .... 117
50. Autocorrelation function of the scattered light with time. The polarization is $V_H$ and the applied electric field is 10 volt at 1 KHz. Sample time and experimental duration are longer than those of Fig. 50. .......................................................... 118
51. Schematic diagram of the experimental setup and the feedback circuit. .................................................................................................................. 121
52. Sample transmittances as a function of applied voltage. ....................... 123
53. Measured response of the system with negative feedback. ....................... 125
54. Calculated response of the system with negative feedback. ....................... 126
55. Measured response of the system with positive feedback. ....................... 127
56. Calculated response of the system with positive feedback. ....................... 128
57. Sketch showing the intersection of the sample transmittance and feedback response curves to determine the operating point. ....................... 130
A.1. Schematic of Freedericksz transition due to an electric field applied perpendicular to the cell. .......................................................... 142
Acknowledgements

It has been a great pleasure and tremendous opportunity for me to study at Kent for the last six years. I have met many distinguished scholars and friends who have opened new horizons in my life and gave me a new way of thinking. I need hardly mention that one of them is my supervisor, Peter Palffy-Muhoray, who has always helped me through tough problems which I have confronted during my study. His eagerness for science gave me a taste of the true scientific world. Without his patient guidance, this dissertation can not exist today.

Part of works have been done in Professor Thein Kyu's laboratory at the Institute of Polymer Engineering located at The University of Akron. I am pleased to express my appreciation to him for helpful discussions and his permission for use of his light scattering equipment.

I can never forget my parents' self-sacrificing support throughout my life. With their continuous encouragement, I have enjoyed my school life and finished my doctoral study. I am in debt to my sisters who made sacrifices to educate me.

I should not forget Drs. Kee Bang Lee, Hyung Jae Lee, Jung Hong Kim, and Young Hee Lee's guidance and teachings through my undergraduate school life in Jeonbuk National University back Korea. Friends, staff, and faculty's kind help from the Liquid Crystal Institute and Department of Physics are gratefully acknowledged.
Chapter I

Introduction

1.1 Liquid crystals

Liquid crystals exhibit intermediate phases (also known as ‘mesophases’) between the crystalline solid and the isotropic liquid [de Gennes, 1974]. Ordinary liquids are characterized by fluidity and isotropy while crystals possess long range positional order. The key characteristic of liquid crystals is the orientational order of the constituent molecules. Liquid crystals are typically composed of organic molecules with anisotropic properties which are manifest in the diamagnetic and dielectric susceptibilities and the optical birefringence.

Generally, two types of liquid crystalline material are distinguished; \textit{thermotropic} and \textit{lyotropic}. Thermotropic liquid crystalline materials show mesomorphic phases as the temperature is changed. Lyotropic liquid crystalline materials exhibit mesophases depending on the relative concentrations of the constituent components. Liquid crystals in thermotropic and lyotropic materials can be made up of molecules with a rod-like or a disk-like structure.

There are several types of liquid crystalline phase and they are classified mainly into three categories: \textit{nematic}, \textit{cholesteric}, and \textit{smectic}. Schematics of a few common phases are shown in Fig. 1. The nematic phase is the least ordered liquid crystalline phase. This type of mesophase is usually formed by elongated molecules which have a long range orientational order. The direction of the long
Fig. 1. Schematics of liquid crystalline phases.
range orientational order is denoted by the unit vector $n$ and called the director. The parallel and perpendicular components of the macroscopic properties of the nematic with respect to the director exhibit different values. If the values of two components perpendicular to each other as well as to the director are the same, then the nematic is called a uniaxial phase. Otherwise, it is called a biaxial phase. The exhibition of either a uniaxial or a biaxial phase depends on the shape of the constituent molecules. Either rod-like (uniaxial) or book-like (biaxial) shapes can be considered. Theoretical considerations of book-like molecules lead to predictions of biaxial phases [Straley, 1974]. Biaxial nematic phases in lyotropic liquid crystals were found experimentally by Yu and Saupe [1980], in thermotropic polymer by Hessel and Finkelmann [1986] and in thermotropic monomeric systems by Malthête et al. [1986]. The cholesteric is very similar to the nematic in which the mesophase exhibit helical structure along the preferred direction. Smectic phases are characterized by a one-dimensional positional order as well as a long range orientational order.

The orientational order of nematic liquid crystals can be defined considering a cylindrically symmetric molecule in an external magnetic field $H$. The induced molecular magnetic moment $\mu$ can be expressed as

$$\mu = \kappa_\parallel (H \cdot \mathbf{l}) + \kappa_\perp \left\{ H - (H \cdot \mathbf{l}) \mathbf{l} \right\}$$

where $\mathbf{l}$ is a unit vector along the symmetry axis of the molecule and $\kappa_\parallel$ and $\kappa_\perp$ are components of the molecular magnetic susceptibility parallel and perpendicular to the long axis of the molecule, respectively. Extracting the isotropic part of the molecular magnetic susceptibility,
\[
\mu = \pi H + \frac{2}{3} \Delta \kappa \frac{1}{2} \{3(H \cdot l)l - H\} \tag{1.2}
\]

where the molecular susceptibility anisotropy and the average molecular susceptibility are defined as

\[
\Delta \kappa = \kappa_\parallel - \kappa_\perp \quad \text{and} \quad \bar{\kappa} = \frac{\kappa_\parallel + 2 \kappa_\perp}{3}. \tag{1.3}
\]

The bulk diamagnetic susceptibility can be written as

\[
\chi_{\alpha \beta} = \rho_n \bar{\kappa} \delta_{\alpha \beta} + \rho_n^2 \Delta \kappa <\frac{1}{2}(3l_\alpha l_\beta - \delta_{\alpha \beta})> \tag{1.4}
\]

where \(\rho_n\) is the number density and the brackets \(< >\) denote the ensemble average. The orientational order parameter is defined as

\[
Q_{\alpha \beta} = <\frac{1}{2}(3l_\alpha l_\beta - \delta_{\alpha \beta})>. \tag{1.5}
\]

In the principal axis frame, the order parameter is diagonalized, and can be written as

\[
Q_{\alpha \beta} = \begin{bmatrix}
-\frac{1}{2}(S - P) & 0 & 0 \\ 0 & -\frac{1}{2}(S + P) & 0 \\ 0 & 0 & S
\end{bmatrix}. \tag{1.6}
\]

where \(S\) and \(P\) are called the uniaxial and the biaxial order parameter,
respectively. Both order parameters depend on the temperature. In this frame, the unit vector of the axis associated with the eigenvalue $S$ is called the director $\mathbf{n}$. It represents the direction of average alignment of molecules.

For a uniaxial nematic liquid crystal, the biaxial order parameter, $P$, vanishes and molecules tend to align parallel to each other with partial ordering of their long molecular axes. In this case,

$$Q_{\alpha\beta} = S \cdot \frac{1}{2} (3n_\alpha n_\beta - \delta_{\alpha\beta})$$  \hfill (1.7)

where $S$ is the local orientational order of the rod-like molecules and $n_\alpha$ is the components of the director $\mathbf{n}$. The directions $\mathbf{n}$ and $-\mathbf{n}$ are physically equivalent. From Eq. (1.5), the molecular order parameter is represented by

$$S=Q_{zz} = \frac{1}{2} <3 \cos^2 \theta - 1>$$  \hfill (1.8)

In some systems, the director varies with positions. The notation of $<P_2>$ is sometimes used for the order parameter instead of $S$ since the second order Legendre polynomial, $P_2(\cos \theta)$, is equal to $(3\cos^2 \theta - 1)/2$. Note that by tradition, the order parameter in an order-disorder transition is usually defined such that $S=1$ in the perfectly ordered system and $S=0$ for the completely disordered system.

Three canonical elastic deformations commonly found in nematic liquid crystals are illustrated in Fig. 2; (a) undeformed state, (b) splay mode, (c) twist mode and (d) bend mode. Each mode is associated with an elastic constant; the splay constant, $K_1$, the twist constant, $K_2$, and the bend constant, $K_3$. The elastic
Fig. 2. Canonical deformations of a nematic liquid crystal.
free energy [Frank, 1958] associated with the deformations is expressed by

\[ F = \frac{1}{2} \int [K_1 ( \nabla \cdot n)^2 + K_2 (n \cdot \nabla \times n)^2 + K_3 (n \times \nabla \times n)^2] \, dx. \] (1.9)

A model describing the nematic-isotropic phase transition was established by Maier and Saupe [Maier and Saupe, 1958; 1959; 1960]. In the theory, the molecules are assumed to be nonpolar and to have intermolecular interactions. However, this mean field approach ignores fluctuations in the short range order so that the results of the theory are approximate. The single particle pseudopotential is given by

\[ \varepsilon(\cos \theta) = -USP_2(\cos \theta) + \frac{1}{2}US^2 \] (1.10)

where \( \theta \) is the angle between the symmetry axis of the molecule and the nematic director and \( U \) is a measure of the strength of the average anisotropic pair interaction [Palffy-Muhoray and Dunmur, 1982]. The second term arises from the requirement that the average potential energy per molecule equals one half of the average potential energy per a pair of molecules. The orientational partition function for one molecule is

\[ z = \frac{1}{2} \int_0^\pi e^{-\beta \varepsilon(\cos \theta)} \sin \theta \, d\theta \] (1.11)

where \( \beta = (k_B T)^{-1} \). The orientational free energy per molecule \( F = -(k_B T / U) \ln z \) becomes
\[ F = \frac{1}{2} S^2 - \frac{1}{2} \ln \frac{1}{\alpha} \int_0^\pi e^{\alpha S P_2(\cos \theta)} \sin \theta \, d\theta \]  

(1.12)

where \( \alpha = U/k_B T \). Extremal values of \( F \) are obtained when \( \partial F / \partial S = 0 \), that is, when

\[ S = \frac{\int_0^\pi P_2(\cos \theta) e^{\alpha S P_2(\cos \theta)} \sin \theta \, d\theta}{\int_0^\pi e^{\alpha S P_2(\cos \theta)} \sin \theta \, d\theta} \]  

(1.13)

The solution of the self-consistent Eq. (1.13) gives the values of the temperature dependent order parameter.

The dielectric tensor has the same form as the magnetic susceptibility tensor (Eq. (1.4)):

\[ \varepsilon_{\alpha \beta} = \varepsilon_0 \delta_{\alpha \beta} + \frac{2}{3} \varepsilon_0 \Delta \varepsilon S^2 \left( 3n_\alpha n_\beta - \delta_{\alpha \beta} \right) \]  

(1.14)

where

\[ \Delta \varepsilon = \varepsilon_\parallel - \varepsilon_\perp \text{ and } \varepsilon = \frac{\varepsilon_\parallel + 2\varepsilon_\perp}{3} \]  

(1.15)

and \( \varepsilon_\parallel \) and \( \varepsilon_\perp \) are components of the dielectric constants parallel and perpendicular to the director, respectively. Choosing z-axis along the director, \( \varepsilon_{\alpha \beta} \) can be diagonalized and the parallel and perpendicular components of the refractive indices, \( n_\parallel \) and \( n_\perp \), with respect to the nematic director have the following relationship.

\[ n = \sqrt{\varepsilon}, \]  

(1.16)

\[ n_\parallel = \sqrt{\varepsilon_{xx}} \]  

(1.17)
and

\[ n_\perp = \sqrt{\varepsilon_{xx}} = \sqrt{\varepsilon_{yy}}. \]  

(1.18)

\( n_{\parallel} \) is the extraordinary refractive index (also represented by \( n_e \)) and \( n_\perp \) the ordinary refractive index (also represented by \( n_o \)) of the uniaxial nematic liquid crystal. The mean refractive index \( \bar{n} \) of the liquid crystal is given by

\[ \bar{n} = \sqrt{(2n_o^2 + n_e^2)/3}. \]  

(1.19)

When the principal direction of molecular orientation (or director) \( \mathbf{n} \) makes an angle \( \theta \) with the propagation vector \( \mathbf{k} \), the refractive index \( n_{\text{eff}} = n_{\parallel} \) for light linearly polarized parallel to the \((\mathbf{n}, \mathbf{k})\) plane varies with \( \theta \) and is given by Fig. 3.

\[ n_{\text{eff}} = n_{\parallel} (\theta) = \frac{n_e n_o}{(n_e^2 \cos^2 \theta + n_o^2 \sin^2 \theta)^{1/2}} \]  

(1.20)

The refractive index \( n_\perp \) for light linearly polarized perpendicular to the \((\mathbf{n}, \mathbf{k})\) plane shows no dependence on the angle \( \theta \) and is given by

\[ n_\perp = n_o \]  

(1.21)

It can be understood that in the above situation, for an incident light beam perpendicular to the director, the linearly polarized light perpendicular to both the director of the liquid crystal and the propagation vector \( \mathbf{k} \) will not be scattered since there is no refractive index variation along its path. The other
Fig. 3 Schematic illustration of the refractive index of a nematic liquid crystal for an obliquely incident light.
component of the light will be scattered strongly due to large variation of refractive index along its path. For $\theta=0^\circ$, $n_\parallel=n_o$ and $\theta=90^\circ$, $n_\parallel=n_e$.

1.2 Polymer dispersed liquid crystal (PDLC) materials

Polymer dispersed liquid crystal (PDLC) materials have received considerable attention recently for fundamental scientific reasons as well as for their potential in display applications [Doane et al., 1986 and 1989; Drzaic, 1986; Vaz et al., 1987; Montgomery and Vaz, 1987]. They are composite materials consisting of micron-sized liquid crystal droplets in a polymer matrix, formed by phase separation of the initial homogeneous liquid crystal-polymer mixture. They can be used as light shutters, switchable windows, color projectors and so on. PDLC films have some advantages over conventional twisted nematic displays (also called 'TN cell') in that one can make large size and flexible displays since no polarizer is required and it is much easier to fabricate them.

In 1976 Hilsum patented a light shutter device in which micron-size soda glass spheres are dispersed in a nematic liquid crystal confined between two glass plates with transparent conducting electrodes [Hilsum, 1976]. The surface of the soda glass spheres orient the liquid crystal. The incident light is then scattered due to the mismatch between the refractive index of the liquid crystal and that of the soda glass spheres. Upon application of an electric field to the device the electric field aligns the nematic to match its refractive index with that of the soda glass spheres. Thus less light is scattered for normally incident light and the device becomes transparent.

In 1982 Craighead et al. at Bell Laboratories patented a device where the
micron-size pores in a microporous filter were filled with a nematic liquid crystal of positive dielectric anisotropy [Craighead et al., 1982]. This electro-optic device was also not developed further.

In 1983 Fergason developed a liquid crystal based electro-optic device formed by an encapsulation method [Fergason, 1985]. In this method, an emulsion is formed of liquid crystal in water and later a water soluble polymer, polyvinyl alchol (PVA) is added. As the water is evaporated, liquid crystal droplets are entrapped in the polymer. The material is referred to nematic curvilinearly aligned phase (NCAP) and commercialized by Taliq.

In 1984 researchers at the Liquid Crystal Institute of Kent State University developed phase separation methods to obtain a polymer dispersed liquid crystal (PDLC) material [Doane, 1986]. Phase separation procedures greatly improved the electro-optic display fabrication methods.

The PDLC film sandwiched between two conductive indium tin oxide (ITO) thin film coated glasses may be switched from an opaque scattering state to a clear transparent state by application of electric field because of the dielectric anisotropies of the film. The mismatch of the refractive indices between the liquid crystal droplets and the polymer induces the film to an opaque state (Fig. 4-a). The applied electric field can cause the symmetrical axes of liquid crystal molecules in the droplets to align parallel to the electric field, so that the ordinary refractive index of the nematic liquid crystal can be matched with that of the polymer and the film becomes transparent (Fig. 4-b). The refractive indices typically for the nematic liquid crystal E7 are known to be $n_o=1.521$ and $n_e=1.746$. The refractive index for epoxy polymer is 1.55.
Fig. 4. Schematic illustration of opto-electric response of a PDLC film.
1.3 Binary mixtures

Mixtures consist of different chemical species. Let us consider a binary system which has two components with the total number of $N_1$ and $N_2$ particles, respectively. The free energy density, $\sigma = u - T s$, of the binary system has two contributions: the energy and the entropy. These contributions arise when the system is mixed. The average energy density of the mixture, $u$, may be larger or smaller than for the separated constituents. The energy difference is called the energy of mixing. The entropy of the mixture also changes when two different species interchange their positions. The change is called the entropy of mixing.

Usually, the same species of molecules prefer to interact. If the entropy term in the free energy density is negligible, as at $T=0$, the mixture is not stable because of the excessive mixing energy. Such a mixture will then separate into two phases. But at a finite temperature the $-T s$ term in the free energy of the homogeneous mixture always tends to lower the free energy.

If the entropy term dominates, the system remains a homogeneous single phase. If, however, the energy term dominates, the system phase separates. In general, competition between the energy and the entropy always exist.

The simple statistical model of the binary mixture called the 'regular solution model' was proposed by Becker [1938]. The free energy density of the mixture, based on the model, is expressed in terms of the volume fraction $\phi$ and the molecular volume $v$ of each constituent as

$$f = \frac{\phi_1}{v_1} \varepsilon_1 + \frac{\phi_2}{v_2} \varepsilon_2 + k_B T (\frac{\phi_1}{v_1} \ln \frac{\phi_1}{\phi_2} + \frac{\phi_2}{v_2} \ln \frac{\phi_2}{\phi_1})$$

(1.22)
Here the system has two different species respectively with $N_1$ and $N_2$ particles and $\varepsilon_i$ is the average energy, the total volume of the system is $V$, and $\phi_i = \frac{N_i V_i}{V}$.

If we quench the homogeneous system into lower temperature, the effect of entropy is reduced and the mixture phase separates. The entropy can also be reduced by polymerization, which leads to phase separation. Eq. (1.22) and the entropy decrease by polymerization will be derived and discussed in detail in Chapter II.

1.4 Studies of phase separation

Phase separation kinetics has been the subject of vivid theoretical and experimental investigation in various fields, such as metallic alloys and binary fluid mixtures [Gunton et al., 1983]. The phase separation of polymer blends has also become the subject of recent studies [Nishi et al., 1975; de Gennes, 1980; Pincus, 1981; Hashimoto et al., 1983; Snyder and Meakin, 1983]. Phase separation provides us with the characteristic PDLC materials of current interest for optical device application. Three mechanisms have been known to form PDLC materials; thermal quenching induced phase separation (TIPS), polymerization induced phase separation (PIPS), and solvent evaporation induced phase separation (SIPS). Most of the work has been mainly on thermal quench induced phase separation. However, little work has been done to date on the kinetics of phase separation due to polymerization [Kim and Palfy-Muhoray, 1991; Visconti and Marchessault, 1974; Kim and Kim, 1991].

Phase separation by polymerization in PDLC systems is usually achieved by either a condensation reaction or photo initiated polymerization. An example
for the former case is a solution formed by a thermoset epoxy Epon 828 mixed with the eutectic liquid crystal mixture E7 and the curing agent Capcure 3-800 in a 1:1:1 ratio by weight. An ultraviolet-curable polymer (e.g., Norland optical adhesive) mixed with the liquid crystal E7 can be the latter case.

The solution of a thermoplastic epoxy (e.g., Polymethyl methacrylate with an average molecular weight 12,000 by Aldrich Chemical Co., Inc.) mixed with the liquid crystal E7 can form a PDLC material by the thermal quench induced phase separation. It is usually mixed at a temperature higher than the melting temperature of the thermoplastics and cooled into the miscibility gap of the system, which causes phase separation of the liquid crystal. The droplet size distribution may be controlled by the rate of cooling.

A homogeneous solution in the solvent evaporation induced phase separation is formed in a common solvent. As the solvent is evaporated, the system is induced into the miscibility gap and the liquid crystal phase separated. The droplet size distribution depends on the rate of solvent removal.

The application of the PDLC materials to a display is in need of understanding the kinetics of phase separation of the liquid crystal-polymer mixtures since its characteristic electro-optic properties are affected by the droplet morphology. The focus of this dissertation is on the kinetics of phase separation.

The studies associated with phase separation have been carried out in the following areas.

- simple fluids (gas-liquid transitions)
- binary fluids
- binary alloys
- superfluids and superconductors
- physisorption and chemisorption
- polymer blends
- gels
- chemically reacting systems
- glasses and crystalline ceramics
Chapter II

Phase Separation

2.1 Overview

Let us consider a binary mixture which is composed of two different species of molecules. When the individual molecules are indistinguishable, the total configurational partition function is given in the mean field approximations as

\[ Q_i = \frac{q_i^{N_i}}{N_i!}, \quad i = 1, 2 \]  

(2.1)

where \( i \) indicates one of the molecular species, \( q_i \) is the partition function of one molecule, and \( N_i \) is the total number of one of the components of molecules. We assume that

\[ q_i = \int e^{-\beta \mathcal{V} \ d^3r} \ c_i e^{-\beta \epsilon_i} \ V \]  

(2.2)

where \( \mathcal{V} \) is the potential energy for the \( i^{th} \) molecule, \( \epsilon_i \) the average energy, \( V \) the volume of the system, and \( c_i \) the integral constant. From the relationships of

\[ F = -k_B T \ln Q, \quad Q = Q_1 \cdot Q_2, \quad \text{and Stirling's formula} \ (\ln N! \simeq N \ln N - N), \]  

the free energy of the system is

\[ F = \epsilon_1 N_1 + \epsilon_2 N_2 + k_B T \left\{ N_1 \ln N_1 + N_2 \ln N_2 - (N_1 + N_2) - (N_1 \ln c_1 V + N_2 \ln c_2 V) \right\}. \]  

(2.3)
The free energy density is then

\[ f = F/V \]

\[ = \varepsilon_1 \rho_1 + \varepsilon_2 \rho_2 + k_B T (\rho_1 \ln \rho_1 + \rho_2 \ln \rho_2) - k_B T (\rho_1 \ln c_1 + \rho_2 \ln c_2 + \rho) \]  

(2.4)

where \( \rho_i = \frac{N_i}{V} \) is the number density of species \( i \), \( \rho = \rho_1 + \rho_2 \), and \( \rho = \frac{N}{V} \).

In the model,

\[ -\varepsilon_1 = \rho_1 \gamma_{11} + \rho_2 \gamma_{12} \]

and

\[ -\varepsilon_2 = \rho_2 \gamma_{22} + \rho_1 \gamma_{21} \]  

(2.5)

where \( \gamma_{ij} \) is the strength of interaction between molecules. Assuming the geometric-mean interaction between constituents which is valid for London-van der Waals interaction between spherical molecules,

\[ \gamma_{12} = \gamma_{21} = \sqrt{\gamma_{11} \gamma_{22}}. \]  

(2.6)

By substituting Eqs. (2.5) and (2.6) into Eq. (2.4), the free energy density of the mixture can then be rewritten as

\[ f = - (\rho_1 \sqrt{\gamma_{11}} + \rho_2 \sqrt{\gamma_{22}})^2 + k_B T (\rho_1 \ln \rho_1 + \rho_2 \ln \rho_2) - k_B T (\rho_1 C_1 + \rho_2 C_2) \]  

(2.7)

where \( C_1 = \ln c_1 + 1 \) and \( C_2 = \ln c_2 + 1 \).
When we put

\[ V = N_1 v_1 + N_2 v_2 \]  \hspace{1cm} (2.8)

and

\[
\begin{align*}
\nu_1 \rho_1 &= \frac{v_1 N_1}{V} = \phi_1 \\
\nu_2 \rho_2 &= \frac{v_2 N_2}{V} = \phi_2
\end{align*}
\]  \hspace{1cm} (2.9)

where \( N_i \) and \( v_i \) are respectively the number of molecules of species \( i \) and the molecular volume and \( \phi_i \) is the volume fraction of each species, the free energy density is given by

\[
f = -\left\{ \frac{\phi_1}{V_1 (\gamma_{11} + \gamma_{22})} + \frac{\phi_2}{V_2 (\gamma_{22})} \right\}^2 + k_B T \left( \frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2 \right) - k_B T \left( \frac{\phi_1}{V_1} C_1 + \frac{\phi_2}{V_2} C_2 \right). \]  \hspace{1cm} (2.10)

Since the strength coupling constant \( \gamma_{ij} \) between molecules in the van der Waals interaction is proportional to the multiplication of each molecular polarizability, \( \alpha_i \alpha_j \) and the molecular polarizability is proportional to the molecular volume, i.e., \( \alpha_i \sim v_i \), we can write

\[
\gamma_{ij} \sim \alpha_i \alpha_j
\]

\[
=(a_i v_i) \cdot (a_j v_j). \]  \hspace{1cm} (2.11)

where \( a_i \) is the proportional constant. Terms in the free energy and linear in \( \phi_i \) do not contribute to making the free energy unstable and hence we neglect them.
Thus the free energy density can be rewritten as

\[ f = -(a_1 \phi_1 + a_2 \phi_2)^2 + k_B T \left( \frac{\phi_1}{v_1} \ln \frac{\phi_1}{v_1} + \frac{\phi_2}{v_2} \ln \frac{\phi_2}{v_2} \right) \] (2.12)

The free energy \( f \) and the phase diagram of the binary mixture are shown in Fig. 5. The free energy of the homogeneous mixture usually exhibits a double well form as a function of one of the constituents (e.g., component 2) at a temperature below the critical temperature, \( T_c \), of the system, which results in a miscibility gap. The points of common tangency to the top curve in Fig. 5 define the concentration of the coexisting phases at the temperature. The curve which consists of the locus of the points is called 'binodal'. The locus of two inflection points satisfying the condition of \( \frac{\partial^2 f}{\partial \phi^2} = 0 \) in the curve is termed 'spinodal'. Gibbs is recognized as the first to classify the two different regimes [Cahn, 1968].

When the system is quenched into the metastable region from a homogeneous single phase, the free energy change due to the concentration fluctuations, \( \phi - \phi_0 \), exists as shown in Fig. 6. We consider the change \( \Delta f \) in \( f \) for the system when one mole of concentration \( \phi \) is formed from the mixture of concentration \( \phi_0 \). We will assume that the amount of mixture is large enough so that its compositional change may be neglected. At the original mixture of concentration \( \phi_0 \), the partial molar free energy are \( f_1(\phi_0) \) and \( f_2(\phi_0) \). The free energy change arises from the transfer of \( \phi \) mole of component 2 from the original mixture of concentration \( \phi_0 \) and from the analogous transfer of component 1. The change is given by
Fig. 5. Free energy and corresponding phase diagram of a two component mixture.
\[ \Delta f = \left\{ f_2(\phi) - f_2(\phi_0) \right\} \phi + \left\{ f_1(\phi) - f_1(\phi_0) \right\} (1 - \phi) \]

\[ = f(\phi) - f(\phi_0) - \left( \frac{df}{d\phi} \right) \phi_0 (\phi - \phi_0) \]  \hspace{1cm} (2.13)

Suppose that there is an infinitesimal fluctuation \( \delta \phi = \phi - \phi_0 \). Expanding the free energy in a Taylor's series about \( \phi_0 \),

\[ f(\phi) = f(\phi_0) + (\phi - \phi_0) \left( \frac{\partial f}{\partial \phi} \right) \phi = \phi_0 + \frac{1}{2}(\phi - \phi_0)^2 \left( \frac{\partial^2 f}{\partial \phi^2} \right) \phi = \phi_0 + \cdots \]  \hspace{1cm} (2.14)

Substituting in Eq. (2.13) we get

\[ \Delta f = \frac{1}{2}(\phi - \phi_0)^2 \left( \frac{\partial^2 f}{\partial \phi^2} \right) \phi = \phi_0 + \cdots \]  \hspace{1cm} (2.15)

\( \left( \frac{\partial^2 f}{\partial \phi^2} \right) \phi = \phi_0 \) is positive in Fig. 6. When there is a small separation by thermal fluctuation, the free energy is increased and the system is therefore metastable. In the region, if the fluctuation is small, then it will spontaneously disappear (Fig. 7-a). In order to get the decrease in the free energy, the fluctuation should exceed \( \phi_a \). The fluctuation can then form tiny 'nuclei' of the minor phase (Fig. 7-b). These small 'nuclei' grow by attracting the same species of the component from the mixture (Fig. 7-c). The growing nuclei will finally reach two separate concentrations \( \phi_a \) and \( \phi_b \) (Fig. 7-d). This process is called nucleation and growth (NG).

As in Fig. 8, \( \left( \frac{\partial^2 f}{\partial \phi^2} \right) \phi = \phi_0 \) is negative which means that any small fluctuations
Fig. 6. The free energy changes during phase separation of a metastable phase of concentration $\phi_0$. 
Fig. 7. Spontaneous disappearance of concentration fluctuations and diffusion towards a nucleus in a system undergoing nucleation and growth.
Fig. 8. The free energy changes during phase separation of an unstable phase of concentration $\phi_0$. 
can decrease the free energy of the system spontaneously, as indicated by the successive lines, until the lowest free energy is achieved which is a two phase mixture. Thus the system is unstable. The system evolves through the nonlocalized fluctuations with characteristic wavelengths, which forms interconnected domains of the minor phase. In the initial state, the system has negative diffusion constant (D<0), which Cahn first called ‘uphill diffusion’ (Fig. 9-a). The state of D=0 is then followed by, where the two concentrations reach $\phi_{s1}$ and $\phi_{s2}$ (Fig. 9-b). Finally the system enters into metastable region (D>0) (Fig.9-c). This is termed spinodal decomposition (SD).

Although this classical model can be used to distinguish between metastable and unstable states, recent studies suggest that there is no sharp distinction between them. In addition, Langer [1974] has shown that the transition between the two mechanism is intrinsically smooth, i.e. that no sharp spinodal line exists. Experimental evidence of the transitional region was carried out by Tanaka et al. [1990].

To distinguish the qualitative features of the dynamical properties of metastable and unstable phases, microscopic observations may be used. Usually interconnected domains are observed in spinodal decompositions and droplet-like domains in nucleation and growth. However, it has been pointed out that morphology alone can not be used to determine whether the phase separation is driven by the process of spinodal decomposition or nucleation and growth. In fact, we can hardly distinguish in determining the difference at late stage—this stage will be discussed later.
Fig. 9. Temporal change in concentration profile in a system undergoing spinodal decomposition.
2.2 Phase separation in thermally quenched binary mixtures

2.2.1 Nucleation theories

Let us consider a simple situation in which a droplet with radius $R$ is formed from a mixture. The free energy densities of the mixture and the droplet are $\mathcal{F}_1$ and $\mathcal{F}_2$, respectively. The free energy density of the droplet can be represented as

$$ F = \frac{4}{3} \pi R^3 \mathcal{F}_2 + 4 \pi R^2 \sigma \quad (2.16) $$

The first term denotes the bulk free energy and the second the surface free energy. The free energy density before phase separation is originally

$$ F_0 = \frac{4}{3} \pi R^3 \mathcal{F}_1 \quad (2.17) $$

so that the energy excess is given as

$$ \Delta F = \frac{4}{3} \pi R^3 (\mathcal{F}_2 - \mathcal{F}_1) + 4 \pi R^2 \sigma \quad (2.18) $$

But it should be noticed that this would be true only for an open system in which substance could be exchanged with an external source reservoir.

The critical radius of the nucleus, $R_c = \frac{2\sigma}{\mathcal{F}_1 - \mathcal{F}_2}$, is obtained from the condition of $\frac{\partial \Delta \mathcal{F}}{\partial R} = 0$. In this case, the energy excess is

$$ \Delta F_c = \frac{4}{3} \pi R_c^2 \sigma. \quad (2.19) $$
If the radius $R$ of the nucleus is larger than the critical size, then the droplet will grow. Otherwise, the droplet shrinks and disappears. This is the basis of the nucleation theory.

2.2.2 Early stage theories of spinodal decomposition

(i) Cahn-Hilliard theory

The theory of Cahn and Hilliard describes the early stage of spinodal decomposition [Cahn and Hilliard, 1958 and 1959; Cahn, 1959]. It is based on the assumption that an inhomogeneous binary mixture (consisted of components 'A' and 'B') can be described by a free energy.

$$ F = \int \left[ f(\phi) + \kappa (\nabla \phi)^2 + \cdots \right] \text{d}r \tag{2.20} $$

where $f(\phi)$ is the Helmholz free energy density of the homogeneous system of concentration $\phi$ of one component (component 'A') and $\kappa (\nabla \phi)^2$ is the second term of the expansion of $f(\phi(x))$ in a Taylor series in $x$. The term is associated with the interfacial energy. When the variational derivative of Eq. (2.20) is taken, we obtain

$$ \frac{\delta F}{\delta \phi} = \frac{\partial f}{\partial \phi} - 2\kappa \nabla^2 \phi + \cdots = \mu \tag{2.21} $$

where $\mu$ is a chemical potential of component A. The interdiffusional flux ($J = J_A = -J_B$) is related to the gradient of chemical potential difference which is the thermodynamic driving force for the phase separation. That is,
\[ J = -M \nabla \mu \] (2.22)

where \( M \) is the mobility. By substituting Eq. (2.22) into the continuity equation
\[ \frac{\partial \phi}{\partial t} + \nabla \cdot J = 0, \]
the concentration diffusion is described by
\[ \frac{\partial \phi(\mathbf{r})}{\partial t} = M \nabla \cdot \left[ \nabla \{ \frac{\partial f}{\partial \phi} - 2\kappa \nabla^2 \phi(\mathbf{r}) \} \right] \] (2.23)

Cahn linearized this nonlinear equation about the concentration \( \phi_0 \), to obtain
\[ \frac{\partial \psi(\mathbf{r})}{\partial t} = M \nabla^2 \left[ \frac{\partial^2 f}{\partial \phi^2} \phi_0 - 2\kappa \nabla^2 \right] \psi(\mathbf{r}), \] (2.24)
where
\[ \psi(\mathbf{r}) = \phi(\mathbf{r}) - \phi_0. \] (2.25)

This theory based on the linearization approximation has been called linear theory. One would expect this linearization to be valid for the early time following a quench, since the concentration fluctuations should be small. The Fourier transform of Eq. (2.24) yields
\[ \frac{\partial \psi(q)}{\partial t} = -Mq^2 \left[ \frac{\partial^2 f}{\partial \phi^2} \phi_0 + 2\kappa q^2 \right] \psi(q). \] (2.26)

The scattered intensity \( I(q,t) \) is proportional to \( |\psi(q)|^2 \) and
\[ I(q,t) = I(q,0) e^{2\kappa(q)t} \] (2.27)

where
is the growth rate. Each sinusoidal component will grow or shrink exponentially in
time according to the corresponding value of \( R(q) \). As long as the effects of
multiple scattering are neglected, the scattered intensity is proportional to the
structure factor, which is called Rayleigh-Gans approximation [Van de Hulst,
1957]. In the spinodal decomposition region, \( \frac{\partial^2 f}{\partial \phi^2} \) is negative and \( R(q) \) thus can
be either positive or negative, since \( \kappa \) is positive. That is, it is positive for \( q \)
smaller than \( q_c \) and negative for \( q \) larger than \( q_c \). In the nucleation and growth
region, \( \frac{\partial^2 f}{\partial \phi^2} \) is positive leading to negative \( R(q) \) (Fig.10).

\[
q_{\text{max}}^2 = \frac{q_c^2}{2} = - \frac{1}{4\kappa} \left( \frac{\partial^2 f}{\partial \phi^2} \right).
\]  

(2.29)

As we mentioned above, this linear theory applies only to the early stage spinodal
decomposition.

(ii) Langer, Bar-on, and Miller (LBM) theory

The theory developed by Langer, Bar-on, and Miller for the spinodal
decomposition is the best of the various attempts made so far [Langer et al.,
1975]. The statistical model for the kinetics of spinodal decomposition starts with
the Helmholtz free energy functional as in Eq. (2.20). Before discussing the
theory, we need to understand how to establish the free energy functional. Here,
\( \phi(r) \) is constructed by dividing the system into small cells whose size is
comparable to the cube of the equilibrium correlation length \( \xi \), so that it can be
assumed to be a smooth function on the scale of the correlation length. The free
Fig. 10. The growth rate in the early stage predicted by the Cahn-Hilliard theory.
energy functional $F(\phi)$ constructed by the suitable choice of the cells is termed a ‘coarse-grained’ free energy functional of the system. Based on this functional $F(\phi)$, the phase transformation of the system can be interpreted.

The model is described by a continuity equation with a Langevin force term,

$$\frac{\partial \phi(r,t)}{\partial t} = -\nabla \cdot j + \zeta(r,t). \tag{2.30}$$

The mean value of the Langevin force term, $\langle \zeta(r,t) \rangle$, vanishes and its correlation

$$\langle \zeta(r,t)\zeta(r',t') \rangle = -2k_B T M \nabla^2 \delta(r-r') \delta(t-t') \tag{2.31}$$

satisfies the fluctuation-dissipation theorem. By considering the distribution function $\rho(\phi)$ defined on the space of $\phi(r)$, Langer et al. have derived a functional continuity equation:

$$\frac{\partial \rho(\phi)}{\partial t} = - \int d\tilde{r} \frac{\delta J(\tilde{r})}{\delta \phi(\tilde{r})} \tag{2.32}$$

and

$$J(r) = -M \nabla^2 \left( \frac{\delta F}{\delta \phi(r)} \rho + k_B T \frac{\delta \rho}{\delta \phi(r)} \right) \tag{2.33}$$

where $J(r)$ is the probability current. The complete statistical description of the binary system is described by eqs. (2.20), (2.32), and (2.33).

The theory involves an equation for the fluctuation correlation function,

$$S(|r-r_0|,t) = \langle u(r,t)u(r_0,t) \rangle, \tag{2.34}$$
where $u$ is the deviation of the concentration from $\phi_0$, i.e., $u(r)=\phi(r)-\phi_0$. The Fourier transform of Eq. (2.34) is

$$S(q,t)=\int e^{i\mathbf{q} \cdot \mathbf{r}} S(r,t) d\mathbf{r}$$

(2.35)

The equation of motion for $S$ obtained by Langer et al. is

$$\frac{\partial S(q)}{\partial t} = -2Mq^2 \left\{ (Kq^2 + \frac{1}{2}\frac{\partial^2 f}{\partial \phi_0^2})S(q) + \frac{1}{6}\frac{\partial^4 f}{\partial \phi_0^4}S_4(q) + \cdots \right\} + 2Mk_BTq^2$$

(2.36)

where the quantities $S_n$ are the Fourier transforms of the higher-order two-point correlation function:

$$S_n(|r-r_0|) \equiv \langle u^{n-1}(r)u(r_0) \rangle$$

(2.37)

Neglecting all the $S_n(q)$ ($n>2$) and the noise term $(2Mk_BTq^2)$, we obtain the Cahn-Hilliard theory.

When we assume that $\rho(\phi)$ is a Gaussian distribution on the function $u(r)$, centered at $u=0$, then all odd correlation functions vanish, and

$$S_4(q) \approx 3\langle u^2 \rangle S(q)$$

(2.38)

with

$$\langle u^2 \rangle = \frac{1}{(2\pi)^3} \int dq \ S(q)$$

(2.39)
The resulting equation of motion for $S(q)$ has the same form as that in the linear theory, but the previously constant quantity $\frac{\partial^2 f}{\partial \phi_0^2}$ is now replaced by the time-dependent expression

$$\frac{\partial^2 f}{\partial \phi_0^2} + \frac{1}{2\partial \phi_0^4} <u^2(t)>$$

Because $<u^2>$ is a positive, increasing function of time, the characteristic wave number $q_c$ must decrease. That is, the mean-square fluctuations, via the nonlinear part of $\frac{\partial f}{\partial \phi}$, cause a qualitatively correct coarsening of the precipitation pattern.

Binder [1977] has pointed out that the LBM theory is inconsistent with the Lifshitz-Slyozov $t^{1/3}$ law [Lifshitz and Slyozov, 1961] which will be discussed in the next section. The theory can not correctly describe the late stage coarsening. It is thus considered an early time theory.

2.2.3 Late stage growth theories

(i) Overview

As a quenched system evolves toward the stable equilibrium state, the average domain (or droplet) size becomes large and the interfacial thickness of domain boundary becomes vanishingly small compared with the average domain size $R$. This stage is usually known as the late stage of the phase separation. As one can see, Eqs. (2.27) and (2.28) predict that the concentration variations will continue to grow indefinitely at an ever increasing rate. This physically impossible result is due to the assumption of a constant $\frac{\partial^2 f}{\partial \phi_0^2}$ and the neglect
of the higher order derivatives in the Cahn-Hilliard theory. The system can thus apparently continue to decrease its free energy indefinitely. This implies that the linearized Cahn-Hilliard theory is not appropriate to explain the late stages of the phase separation. The stage may be further categorized into distinct regimes as follows.

Four different stages of the spinodal decomposition process was suggested by Hashimoto et al. [1986] and Bates and Wiltzius later [1989] while they analyzed their polymer binary mixtures; early, intermediate, transition, and final stages. The temporal development of the concentration undulations during each of these four distinct stages are shown in Fig. 11.

The early stage is dominantly characterized by the single wavelength $L_m(0)$ which leads to the development of a peak in the scattering structure factor at $q_m(0)$. It is noticed that in this stage, the amplitude of the concentration fluctuations increases with time and the position of $q_m$ does not change as shown in Fig. 11 (a). It is in this stage that the linearized Cahn-Hilliard theory may be applicable.

In the intermediate stage, the wavelength of fluctuations and the amplitude of the fluctuations grow with time as shown in Fig. 11 (b). Thus the linearized Cahn-Hilliard theory may not be applicable to the stage.

The transition stage begins when the amplitude of the concentration fluctuations profile reaches its equilibrium values. The stage is characterized by two time-dependent length scales as indicated in Fig. 11 (c). As the heterogeneity length $L_m(t)$ increases, the interfacial breadth $\Delta(t)$ decreases with increasing time, until the latter reaches its equilibrium value $\Delta \equiv \Delta(\infty)$. 
Fig. 11. Four different stages of spinodal decomposition.
A single time-dependent length scale $L_m(t) \gg \Delta$ exhibits the final stage which is depicted in Fig. 11 (d).

The experimental results based on the different stages will be discussed later. However, some stages may not be observed.

(ii) **Lifshitz-Slyozov coalescence**

Lifshitz and Slyozov [Lifshitz and Slyozov, 1961; Wagner, 1961] calculated the asymptotic behavior of the droplet distribution function $f(R,t)$ and the asymptotic growth of droplets of a minority phase in a small initial supersaturation. Since the growth occurs only after a nearly equilibrium volume fraction of the new phase of droplets has formed, the concentration gradients are very small. Therefore, we can assume that $\frac{\partial \phi}{\partial r} \approx 0$. The diffusional flux $j$ of one of the components into a droplet is given by

$$\frac{\partial \phi}{\partial t} + \nabla \cdot j = 0 \quad (2.41)$$

From $j = D \nabla \phi$ where $D$ is the diffusion coefficient and a steady state diffusional condition,

$$\frac{\partial \phi(r)}{\partial t} = D \nabla^2 \phi(r) = D \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \phi(r)}{\partial r} \right) = 0 \quad (2.42)$$

With the boundary conditions $\phi(r=R) = \phi_\alpha$ and $\phi(r=\infty) = \bar{\phi}$ (the overall composition of the system), we obtain

$$\phi(r) = \bar{\phi} - \frac{(\bar{\phi} - \phi_\alpha) R}{r} \quad (2.43)$$
On the surface of a droplet, \( j \sim \frac{1}{R^2} \) and \( \frac{dV}{dt} \sim j \cdot A \) where \( V \) and \( A \) denote the volume and the area of the droplet respectively. From the relationship,

\[
\frac{d\left(\frac{4}{3}\pi R^3\right)}{dt} \sim \frac{4\pi R^2}{R^3} = \text{constant},
\]

we obtain that \( R^3 \sim t \) which is one of the results of the Lifshitz-Slyozov calculations.

The basic mechanism of the theory is that diffusional flow due to the concentration gradient between two domains (or droplets) having different sizes cause the larger droplet to grow at the expense of the smaller one. This is explained by the Gibbs-Thomson effect [Appendix II]. At the curved surface of a domain (Eq. A.II.6),

\[
\phi_R = \phi_\infty \exp\left(2\sigma/k_B \Gamma R\right)
\]

\[
\sim \phi_\infty \left(1 + 2\sigma/k_B \Gamma R\right)
\]

(2.45)

where \( \phi_R \) is the matrix concentration in equilibrium with a droplet of radius \( R \) (or with a local radius of curvature \( R \)), i.e., the saturation concentration above a spherical droplet surface with radius \( R \), \( \phi_\infty \) the concentration of the saturated solution above a plane surface of the minority phase (that is, when \( R \rightarrow \infty \), \( v \) the molar volume of the minority phase, and \( \sigma \) the surface tension.

For two particles with radius \( r_1 \) and \( r_2 \) and from Eq. (2.45),
A concentration gradient existing in the matrix between two particles of different sizes will cause diffusion flow. Thus the larger droplet can grow at the expense of the smaller one.

(iii) Hydrodynamic effects and power laws

Siggia [1979] has focused on the late stages of spinodal decomposition in a binary fluid and analyzed them with several different mechanisms. These mechanisms depend on the volume fraction \( v \) occupied by the drops. One possible growth is the coalescence of spherical droplets of radius \( R \). The resulting growth law is given as

\[
R^3 = 12DR\nu t
\]  

(2.47)

Experimental observations of Siggia's theory were done in critical binary mixtures of isobutric acid-water and 2,6-lutidine-water by Chou and Goldburg [1979] and of isobutric acid-water Wong and Knobler [1981]. Wong and Knobler have interpreted their experimental light scattering results in terms of Siggia's theory. For this purpose they use the estimate \( R = q_m^{-1} \), where \( q_m \) denotes the wavenumber corresponding to the maximum in the intensity of the scattered light. In this case Eq. (2.47) can be written approximately as

\[
k_m^{-3} \simeq 12\nu r
\]  

(2.48)
where $k$ and $\tau$ are the scaled variables with the correlation length $\xi$ near the critical temperature $T_c$:

$$k_m = q_m \xi$$  \hspace{1cm} (2.49)

and

$$\tau = D \xi^2$$  \hspace{1cm} (2.50)

Hydrodynamic interactions between the drops modifies Eq. (2.48). Namely, as the drops diffuse toward each other, the intervening fluid must be squeezed out from between them. An estimate of this effect leads to

$$k_m^{-3} = \frac{16\pi \nu r}{\ln(0.55/k_m)}$$  \hspace{1cm} (2.51)

Another growth mechanism is due to evaporation and condensation. This occurs for small supersaturations, i.e., $\nu$ is small, and leads to the Lifshitz-Slyozov law

$$k_m^{-3} = 0.053D \xi \tau$$  \hspace{1cm} (2.52)

It should be noted that the amplitude of this $\tau^{1/3}$ growth law is independent of $\nu$, unlike Eq. (2.48) and Eq. (2.51).

Siggia also discussed several growth mechanisms, unique to fluids, which result from a critical quench. If the volume fraction exceeds the percolation limit whose estimated value is $\sim 15\%$, one has connected minority phase (droplets) and can have growth driven by surface tension. The basic idea of so-called a capillary
flow model is to imagine a long tube of fluid of radius $R$ with a radial undulation of wavelength $l \gg R$. The undulations lead to a pressure gradient $\sim \sigma / R l$ along the axis. The net effect of this gradient is to drive fluid from the necks to the bulges. An estimate of the growth rate leads to

$$k_m^{-1} = R \approx 0.1 \sigma t / \eta,$$  \hspace{1cm} (2.53)

where $\sigma$ and $\eta$ are the surface tension and the viscosity. This then leads to the approximate result

$$k_m^{-1} \approx 0.3 \tau$$ \hspace{1cm} (2.54)

[Wong and Knobler, 1981].

To summarize, for concentrated mixtures (critical mixtures) one should first observe diffusive growth, with $k_m \sim \tau^{-1/3}$, followed by a crossover to the $\tau^1$ behavior given by Eq. (2.54). However, the behavior of the dilute mixtures (off-critical mixtures) will be dependent on the relative quench $\Delta T_i / \Delta T_f$ (Fig. 5). When $\Delta T_i \leq 0.35 \Delta T_f$, the volume fraction exceeds the percolation limit and some region of $\tau^1$ may be exhibited. Quenches for which $0.35 \Delta T_f \leq \Delta T_i \leq 0.9 \Delta T_f$ should initially exhibit $\tau^{-1/3}$ growth with $v$. After the supersaturation has been reduced, a crossover to a $v$ independent Lifshitz-Slyozov growth can be observed. Only Lifshitz-Slyozov growth should be observed when $\Delta T_i \geq 0.9 \Delta T_f$.

For the late stage of SD, Langer et al. [1975], Binder and Stauffer [1974], and Siggia [1979] have considered power-law relationship between $q_{max}$ and $t$ and $I_{max}$ and $t$: 
Langer et al. predicted $\alpha=0.21$. Binder and Stauffer argued, based on cluster dynamics, that $\alpha=1/3, \beta=1$, and $\beta=3\alpha$. Siggia predicted for mixtures of the critical composition that the initial growth is diffusional where $\alpha=1/3$, and at long times the domain growth proceeds by coalescence due to surface tension where $\alpha=1$.

2.2.4 Scaling theories for structure factors

For the various systems in which phase separation is observed the structure factor is a fundamental measure of the nonequilibrium properties of the system. The structure factor $S$ of the decomposing seems to exhibit a simple scaling behavior analogous to the scaling behavior observed in critical phenomena. Although some theoretical work has been done to this nonequilibrium scaling, the subject is not yet well understood.

The basic idea of the scaling of $S(q,t)$ is that after some initial transient time following a quench, a time-dependent characteristic scaling length $R(t)$ is established. Various choices of choosing this length exist. Furukawa's approach calls for the use of $1/q_{\max}$ where $q_{\max}$ is the wavevector corresponding to the maximum of the intensity peak, whereas Lebowitz and coworkers choose $q_1$, the first moment of the structure factor. One can choose the length as $q_{\max}^{-1}(t)$, the position of the maximum in $S(q,t)$. The structure factor of the decomposing system, which is proportional to the scattering intensity, may be related to a scaled factor such that

$$q_{\max} \sim t^{-\alpha} \text{ and } I_{\max} \sim t^\beta$$

(2.55)
\[ S(q,t) = b(t) \cdot F(qR(t)) \] (2.56)

where \( F(qR(t)) \) is the time-independent scaling factor [Marro et al., 1979]. As the system reaches the equilibrium phases after quenching, the mean-square concentration fluctuation can be obtained from the requirement that

\[ \frac{1}{(2\pi)^3} \int S(q,t) \, dq = \langle \phi^2 \rangle - \langle \phi \rangle^2 \] (2.57)

which is independent of time. The normalized structure factor is given by

\[ \bar{S} = \frac{S(q,t)}{\int q^2 S(q,t) \, dq} \] (2.58)

From Eqs. (2.56) and (2.57), we must have

\[ \bar{S}(q,t) = R(t)^3 \cdot F(qR(t)). \] (2.59)

Theoretical and computer simulation approaches [Furukawa, 1984; Marro et al., 1979; Lebowitz et al. 1982] have been attempted to investigate the dynamical scaling behavior. It is known that \( F(qR(t)) \) depends on quenches and is weakly time-dependent. It was noticed by Wong and Knobler that the identification of \( R(t) = q_m^{-1} \) is not clear for their binary fluids.

Furukawa proposed a series of dynamical scaling expressions for \( F(x) \) for the late stage of SD [Furukawa, 1984]:
\[ F(x) = \frac{(1 + \frac{\gamma}{2}) x^2}{\gamma/2 + x^2 + \gamma} \]  

(2.60)

where \( F(x) \) is the scaled structure factor and \( x = q/q_{\text{max}} \). The constant \( \gamma = d + 1 \) for an off-critical mixture and \( \gamma = 2d \) for a critical mixture; \( d \) is the dimensionality.

For three dimensional growth, \( F(x) \sim x^2 \) for \( x < 1 \), and for \( x > 1 \) \( F(x) \sim x^{-6} \) for a critical mixture and \( F(x) \sim x^{-4} \) for an off-critical mixture. Furukawa [1986, 1989] subsequently also proposed the following modifications for the late stage of phase separation in three dimensions:

\[ F(x) \sim \frac{x^3}{2 + x^6} \]  

(2.61)

\[ F(x) \sim \frac{x^4}{2/3 + x^{10}} \]  

(2.62)

For large \( q \), Porod's law \( S(q) \sim q^{-4} \) is expected to hold, provided that the boundaries of the domains are sharp [Porod, 1982].

2.3 Polymerization induced phase separation

2.3.1 Flory-Huggins model – binary systems

We focus on the liquid crystal (component 1) and the polymer mixture (component 2). In fact, the system consists of three components which are the liquid crystal, the polymer, and the curing agent. We treat the polymer and the curing agent as one species and furthermore assume that the system is monodisperse, even though it consists of different sized n-mers. During polymerization, \( \phi_1, v_1 \), and \( \phi_2 = 1 - \phi_1 \) remain constants and \( v_2 = n_2 v_p \) increases where \( n_2 \) is called the 'degree of polymerization' of component 2 (the degree of
polymerization of the liquid crystal is 1, that is, \( n_1 = 1 \) and \( v_p \) is the monomer volume. If we neglect terms independent of \( \phi_i \) and linear in \( \phi_i \) which do not contribute to making the system unstable and assume that \( v_1 \approx v_p \), the normalized free energy density in terms of \( \phi_1 \), after some manipulation of Eq. (2.12), becomes

\[
\frac{\sigma}{k_B T} = \frac{f v_1}{k_B T} = \phi_1 \ln \phi_1 + \frac{(1 - \phi_1)}{n_2} \ln (1 - \phi_1) + \chi \phi_1 (1 - \phi_1).
\]  

(2.63)

This is the Flory-Huggins free energy [Flory, 1971]. \( \chi = \frac{v_1 (a_1 - a_2)^2}{k_B T} \) is the interaction parameter and favors separation.

Initially, \( n_2 = 1 \), the second derivative of the free energy with respect to composition,

\[
\frac{\partial^2 \sigma}{\partial \phi_1^2} = k_B T \left\{ \frac{1}{\phi_1} + \frac{1}{n_2 (1 - \phi_1)} - 2 \chi \right\},
\]  

(2.64)

is positive, and a homogeneous mixture is stable. As the polymerization proceeds, \( n_2 \) increases with time, the second derivative becomes negative at a certain time, and the free energy takes on a double well form which favors phase separation for certain concentrations.

2.3.2 Complex multicomponent systems

(i) Size distribution

The size of a linear polymer molecule can be expressed in terms of the degree of polymerization, i.e., the number of repeating units along the chain. In a
polymerizing system, the size distribution of the polymer molecules changes with time. To make the discussion simple, we consider only linear polymers which are long, flexible and have two active parts in the end of each monomer molecule.

Let \( \rho(n,t) \) represent the number of molecules of size \( n \) at time \( t \) and let \( N \) be the total number of the monomers [Rogers, 1977]. A change in the number of size \( n \) of the polymer molecules at time \( t \) is due to an increase of size \( n \) from the connection of size \( m \) and size \( n-m \) molecules and a decrease of size \( n \) from the connection of size \( n+m \) molecules where \( m=1, 2, 3, \ldots \).

\[
\frac{d\rho(n,t)}{dt} = \sum_{m=1}^{\infty} a_{n,m} \rho(m,t)\rho(n-m,t) - \rho(n,t) \sum_{m=1}^{\infty} a_{n,m} \rho(m,t) \tag{2.65}
\]

where \( n=1,2,3,\ldots \). If we assume that the rate constants \( a_{m,n-m} \) are the same, then with the substitutions \( a_{m,n-m}=a=\text{constant} \) and \( \tau=\frac{at}{2} \), Eq. (2.65) can be written as

\[
\frac{d\rho(n,\tau)}{d\tau} = \sum_{m=1}^{\infty} \rho(m,\tau)\rho(n-m,\tau) - 2\rho(n,\tau) \sum_{m=1}^{\infty} \rho(m,\tau). \tag{2.66}
\]

The solution of this equation is given in more detail in Appendix I and is

\[
\rho(n,\tau) = \frac{N(N\tau)^{n-1}}{(N\tau+1)^{n+1}} \tag{2.67}
\]

If we regard \( z=n/N \) as a continuous variable since \( N \) is very big number (typically, \( N>10^5 \)),

\[
P(z,\tau) = \frac{n}{N} \rho(n,\tau) = \frac{z\tau}{2} e^{-\frac{z}{\tau}}. \tag{2.68}
\]
As shown in Fig. 12, the function shows that only monomers initially exist. As time passes, the molecules react with each other and the size distribution becomes broader.

In an Epon-Capcure system, the Epon and the Capcure has respectively three and two reactive parts. Eq. (2.65) can be modified to the system as

\[
\frac{d\rho(n,\tau)}{d\tau} = \sum_{m=1} \left( 2m - 1 \right) \rho(m,\tau) \left( 2(n-m) - 1 \right) \rho(n-m,\tau)
\]

\[ - 2\rho(n,\tau) \sum_{m=1} \left( 2m - 1 \right) \rho(m,\tau). \]  \hspace{1cm} (2.69)

The weighted quantities \(2m-1\) and \(2(n-m)-1\) are associated with the number of the reactive part of the epoxy. However, the solution has not been achieved yet.

(ii) Free energy and stability

Let us consider a situation in which small phase separation in a local region is induced by the concentration fluctuations of the multicomponent system. When the two separated phases are represented by A and B, \(y_{iA}\) and \(y_{iB}\) denote the concentrations of size \(i\) in the phase separated mixture and \(y_{i0}\) is the average value. \(V_A\) and \(V_B\) are the volumes of the phases. We assume that in the system the total number of molecules, \(N=\sum_i N_i\), is consisted of the number of \(N_i\) of size \(i\) where \(i=1,2,3,\cdots\). The free energy density is then given by

\[
f = \frac{V_A}{V} f(\tilde{y}_A) + \frac{V_B}{V} f(\tilde{y}_B) \]  \hspace{1cm} (2.70)

where \(f(\tilde{y}_A) = f(y_{1A}, y_{2A}, y_{3A}, \cdots)\), \(f(\tilde{y}_B) = f(y_{1B}, y_{2B}, y_{3B}, \cdots)\) and \(V\) is the total
Fig. 12. n-mer distribution as function of time and size.

\[ P(x,t) = \frac{x}{t^2} e^{-\frac{x}{t}} \]
volume of the system. The following relationship holds between the different size molecules in two phases:

\[
\frac{V_A}{y_{iA}} + \frac{V_B}{y_{iB}} = \frac{N_i}{V} = y_{i0}
\]  

(2.71)

When we expand \( f(y_A) \) in Taylor's series around \( f(y_0) \),

\[
f(y_A) = f(y_0) + \sum_i \frac{\partial f}{\partial y_i} (y_{iA} - y_{i0}) + \frac{1}{2} \sum_i \sum_j \frac{\partial^2 f}{\partial y_i \partial y_j} (y_{iA} - y_{i0})(y_{jA} - y_{j0}) \]

(2.72)

where \( \tilde{y}_0 = (y_{10}, y_{20}, y_{30}, \ldots) \). It is noted that the same form holds for \( f(y_B) \). When we put \( \frac{V_A}{V} = x \) and \( \frac{V_B}{V} = 1 - x \),

\[
x = \frac{y_{i0} - y_{iB}}{y_{iA} - y_{iB}}
\]  

(2.73)

for any \( i \). The free energy of Eq. (2.70) is then given by

\[
f = f(\tilde{y}_0) + \sum_i \frac{\partial f}{\partial y_i} (y_{iB} - y_{i0}) + \frac{1}{2} \sum_i \sum_j \frac{\partial^2 f}{\partial y_i \partial y_j} (y_{iB} - y_{i0})(y_{jB} - y_{j0})
\]

\[
+ \left( \frac{y_{i0} - y_{iB}}{y_{iA} - y_{iB}} \right) \left( \sum_i \frac{\partial f}{\partial y_i} (y_{iA} - y_{iB}) + \frac{1}{2} \sum_i \sum_j \frac{\partial^2 f}{\partial y_i \partial y_j} ((y_{iA} - y_{i0})(y_{jA} - y_{j0})
\]

\[
- (y_{iB} - y_{i0})(y_{jB} - y_{j0}) \right) \right) \]  

(2.74)

When we put \( x_{iA} = y_{iA} - y_{i0} \) and after some calculation, we are end up with

\[
f = f(\tilde{y}_0) + \frac{1}{2} x (1 - x) \sum_i \sum_j \frac{\partial^2 f}{\partial y_i \partial y_j} (y_{iA} - y_{iB})(y_{jA} - y_{jB})
\]  

(2.75)
When we assume the geometric-mean interaction between different-size molecules, we can generalize the free energy \( f \) of Eq. (2.12) for two component system to the multicomponent system:

\[
f = -(\sum_{i=0}^{nA} a_i \phi_i)^2 + k_B T \sum_{i=0}^{nA} \phi_i \ln \phi_i
\]

(2.76)

where \( a_i = \frac{\sqrt{v_i}}{v_i} \) [Kehlen et al., 1986]. For the liquid crystal-polymer mixture, if we represents the concentration of the liquid crystal as \( \phi_0 \), considering that \( \sum_{i=1}^{i=nD} \phi_i = 1 \) and \( \phi_0 = 1 - \sum_{i=1}^{i=nD} \phi_i \), the free energy density is

\[
f = -\left\{ a_0 (1 - \sum_{i=1}^{i=nD} \phi_i) + \sum_{i=1}^{i=nD} a_i \phi_i \right\}^2 + k_B T \left( \frac{1 - {\sum_{i=1}^{i=nD} \phi_i}}{v_0} \right) \ln \left( \frac{1 - {\sum_{i=1}^{i=nD} \phi_i}}{v_0} \right) + k_B T \sum_{i=1}^{i=nD} \frac{\phi_i}{v_i} \ln \phi_i.
\]

(2.77)

The stability of the system can be investigated by finding the eigenvalues of the second derivative of the free energy:

\[
\frac{\partial^2 f}{\partial \phi_i \partial \phi_j} = -2(a_0 - a_i)(a_0 - a_j) + k_B T \left( \frac{1 - \sum_{i=1}^{i=nD} \phi_i}{v_0 \phi_0} \right) \ln \left( \frac{1 - \sum_{i=1}^{i=nD} \phi_i}{v_0 \phi_0} \right)
\]

(2.78)

If all the \( a_i \) for \( i=1, 2, 3, \ldots, n \) are assumed to be the same, i.e., \( a_i = a \), the second derivative can be represented in a matrix form as

\[
\frac{\partial^2 f}{\partial \phi_i \partial \phi_j} = \begin{bmatrix} b_1 & 0 & \cdots & 0 \\ 0 & b_2 & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & b_n \end{bmatrix} - \varepsilon \begin{bmatrix} 1 & 1 & \cdots & 1 \\ 1 & 1 & \ddots & \vdots \\ \vdots & \ddots & \ddots & 1 \\ 1 & \cdots & 1 & 1 \end{bmatrix}
\]

(2.79)

where both of the matrices are \( n \)-by-\( n \) orthogonal matrices, \( b_i = \frac{k_B T}{v_i \phi_i} \delta_{ij} \) and
\[ \varepsilon = 2(a_0 - a)^2 + \frac{k_B T}{\nu_0 \phi_0}. \]

The eigenvalue problem of the above type of a matrix is well known [Golub and Van Loan, 1989]. Suppose that the diagonal entries satisfy \( b_1 > \cdots > b_n \) and \( \varepsilon \neq 0 \). If the eigenvalues of the matrix is such that \( \lambda_1 \geq \cdots \geq \lambda_n \), then

(a) The \( \lambda_i \) are the zeros of \( f(\lambda) = 1 + \varepsilon \sum \frac{1}{\lambda - b_i} \).

(b) If \( \varepsilon > 0 \) then \( b_1 > \lambda_1 > b_2 > \cdots > b_n > \lambda_n \).

If \( \varepsilon < 0 \) then \( \lambda_1 > b_1 > \lambda_2 > \cdots > \lambda_n > b_n \). \hspace{1cm} (2.80)

In the liquid crystal-polymer system, the limit of stability of the system can be determined by the relationship:

\[ f(\lambda) = f(0) + f'(\lambda). \] \hspace{1cm} (2.81)

The smallest eigenvalue, \( \lambda_{\text{min}} \), is then proportional to

\[ -2(a_0 - a_p)^2 + k_B T \left( \frac{1}{\nu_0 \phi_0} + \frac{1}{\sum \nu_i \phi_i} \right) \] \hspace{1cm} (2.82)

where \( o \) and \( i \) indicate 'liquid crystal molecules' and 'polymer molecules with size \( i' \) respectively. As \( \sum \nu_i \phi_i \) increases due to polymerization, \( \lambda_{\text{min}} \) decreases and the system phase separates.

(iii) Cascade phenomena

In the beginning of the curing process of the liquid crystal-epon mixture under study, \( \frac{\partial^2 f}{\partial \phi_i \partial \phi_j} \) is assumed to be positive so that any small fluctuation increases the free energy of the system. As the curing process proceeds, the
number of size $i$ increases and hence so does $\phi_i$. Thus the second terms of Eq. (2.78) becomes smaller due to the term of $\phi_i v_i$. Finally, $\frac{\partial^2 f}{\partial \phi_i \partial \phi_j}$ becomes negative so that the system becomes unstable. The second derivative changes continuously with time. This continuing change of free energy beyond the limit of stability induces the system to a multiple phase separation. We term this phenomena 'cascade'. The phenomena will be discussed with optical micrographs.
Chapter III

Light Scattering

3.1 Light scattering theory

In a light scattering experiment, an incident electric field is scattered by induced dipoles. The scattered field at a point far from the scattering medium is the superposition of the scattered fields from scatterers in the medium. If the medium is homogeneous, there will be no scattered light except the forward direction because in other direction scattered light from a pair of scatterers is identical in amplitude but opposite in phase, and thus cancel each other. In condensed matter, light scattering originates from the inhomogeneity of the dielectric constant.

Let us consider a plane wave with polarization vector \( \mathbf{n} \),

\[
E_i(r) = n_i E_i e^{i \mathbf{k}_i \cdot \mathbf{r}}, \quad (3.1)
\]

incident upon a medium as shown in Fig. 13. The wave propagates through the scattering medium where \( E_i \) is the incident amplitude and \( \mathbf{k}_i \) is the incident wave vector. The scattered wave vector \( \mathbf{q} \) is defined as \( \mathbf{q} = \mathbf{k}_i - \mathbf{k}_f \). Considering the scattering geometry and assuming quasi-elastic scattering, that is, \( |\mathbf{k}_i| \approx |\mathbf{k}_f| \),

\[
q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right). \quad (3.2)
\]
Fig. 13. Schematic of the scattering geometry.
where $n$ is the refractive index of the medium, $\lambda$ the wavelength of the incident light and $\theta$ the scattered angle from the direction of the incident wave vector $k_i$. The scattered electric field with polarization vector $n_s$ at $r$ is approximately

$$E_s = \frac{k^2 E_i e^{ikr}}{4\pi} \int dr' e^{-ik_s \cdot r'} n_s \cdot \epsilon(r') \cdot n_i \quad (3.3)$$

where $\epsilon(r') = \epsilon_0 \delta_{ij} + \delta\epsilon(r')$ is the dielectric constant fluctuation tensor of the medium and the integral is carried out over the scattering volume [Jackson, 1975]. The equation can be expressed in terms of the spatial Fourier transform of the dielectric constant

$$E_s = \frac{k^2 E_i e^{ik \cdot r}}{4\pi} n_s \cdot \epsilon(q) \cdot n_i \quad (3.4)$$

PDLC materials during the curing process consist of the liquid crystal molecules, the Epon monomers, the Capcure monomers, and compounds of Epon and Capcure. This is a multicomponent system since the polymerization between the Epon and the Capcure creates many different size compound molecules. However, we consider this system as a pseudo-binary mixture. In other words, the system can be thought of as the binary mixture of the liquid crystal (A species) and the rest of components (B species), where polymerization between the latter components drives phase separation. The structure factor of the complex mixture may then be considered as the Fourier transform of the correlation function of the concentration of the liquid crystal (A species):

$$S(q,t) = \int <\phi(0,t)\phi(r,t)> e^{i\mathbf{q} \cdot \mathbf{r}} \, dr. \quad (3.5)$$
where $\phi$ is the concentration of the liquid crystal.

The scattered light intensity is proportional to the spatial Fourier transform of the correlation function of the dielectric constant of the pseudo-binary mixture:

$$I(q,t) \sim \int \langle \epsilon(0,t)\epsilon(r,t) \rangle e^{i \mathbf{q} \cdot \mathbf{r}} \, dr$$

(3.6)

Since $\epsilon \simeq \epsilon_A \phi + \epsilon_B (1 - \phi)$, the scattered intensity is proportional to the structure factor:

$$I(q,t) \sim S(q,t).$$

(3.7)

From light scattering measurements we can get the structure factor of the pseudo binary mixture during phase separation process.

3.2 Dynamic light scattering

3.2.1 Photon correlation

Correlation function is a measure of the degree of similarity or regularity between two signals in time or space. The mathematical expression for the time-correlation function between two periodic scattered light intensity $I_1(t)$ and $I_2(t + \tau)$ is given by

$$C_{12}(\tau) = \lim_{T \to \infty} \frac{1}{T} \int_{-T/2}^{+T/2} I_1(t)I_2(t + \tau) dt$$

(3.8)
where $C_{12}(\tau)$ refers to the cross-correlation function. The process of correlation between a signal and its delayed version, i.e., $C_{11}(\tau)$, is termed auto-correlation function. By using a correlator, we can get a correlation function which include dynamical information of the system.

### 3.2.2 Director fluctuation in PDLC films

Several different director configurations in nematic droplets of PDLC films are known [Golemme et al., 1988]. The molecules in spherical droplets typically exhibit the bipolar configuration in which the cylindrically symmetric axes of molecules are aligned parallel to the surface of the droplets except near two singular points. We define droplet director as the direction of average orientation of the symmetry axis of the molecules in the droplet. Assuming that the droplet is a prolate ellipsoid, the droplet director is represented by $\mathbf{N}_d$ and $\mathbf{L}$ is a unit vector along the symmetry axis of the ellipsoid (Fig. 14). An alternating electric field $\mathbf{E}$ is applied to a thin PDLC film layer perpendicular to the substrate planes, the droplet director oscillates according to the electric field. From the measurement of the correlation function of the scattered light we interpret the dynamics of director fluctuations.

By using a droplet order parameter and a film order parameter in PDLC film, Kelly and Palffy-Muhoray [1991] have established a simple model which can explain a variety of PDLC phenomena, such as optical transmittance and dielectric response. In this model, the free energy density of a nematic droplet under an applied electric field $\mathbf{E}$ can be written as

$$\mathcal{F} = -\frac{A}{2} (\mathbf{N}_d \cdot \mathbf{L})^2 - \frac{B}{2} (\mathbf{N}_d \cdot \mathbf{E})^2$$

(3.9)
Fig. 14. Illustration of the droplet director of an elongated cavity in the presence of an electric field.
where the first is the elastic energy term and the second term is due to the electric field. \( A \) and \( B \) are the proportional constants and \( K \) is the elastic constant. If \( \theta \) is the angle between \( \hat{N}_d \) and \( \hat{L} \) and \( \theta_0 \) between \( \mathbf{E} \) and \( \hat{L} \), the free energy is given by

\[
\mathcal{F} = -\frac{AK}{2}\cos^2 \theta - \frac{BE^2}{2}\cos^2(\theta - \theta_0) \tag{3.10}
\]

The equation of motion of the director is

\[
\gamma \dot{\theta} = -\frac{\partial \mathcal{F}}{\partial \theta} \\
= -AK \cos \theta \sin \theta - BE^2 \cos(\theta - \theta_0) \sin(\theta - \theta_0) \tag{3.11}
\]

where \( \gamma \) is the viscosity. When we assume that \( \theta \) and \( \theta_0 \) are small, i.e., \( \hat{N}_d \) and \( \mathbf{E} \) do not deviate from \( \hat{L} \), and Langevin force \( F(t) \) is involved, the equation of motion can be linearized in \( \theta \) and \( \theta_0 \):

\[
\gamma \dot{\theta}(t) = -AK\theta + BE^2 \cos \theta_0 \sin \theta_0 + F(t) \tag{3.12}
\]

where the electric field is given by \( E(t) = E_0 \cos(\omega_0 t) \).

Taking the Fourier transform of Eq. (3.12) in frequency space, we can transform \( F(t) \) into a constant, \( D \), in respect that the random force exhibits a white noise. Simple calculations show from the transform that

\[
\theta(\omega) = \frac{1}{i\omega \gamma + AK}\left\{D + 2b\delta(\omega) + b(\delta(2\omega_0 - \omega) + \delta(2\omega_0 + \omega)) \right\}. \tag{3.13}
\]
where \( b = \frac{1}{4}(BE^2 \cos \theta_0 \sin \theta_0) \) and \( \delta(\omega) \) is a delta function. Now, doing the reverse transform of \( \theta(\omega)\theta^*(\omega) = \delta(\omega)\theta(-\omega) \), the correlation function \( C(t) \) of the director fluctuation can be written as

\[
C(t) = \int \theta(\omega)\theta^*(\omega) e^{i\omega t} d\omega
\]

\[
= \frac{\pi D^2}{\gamma AK} e^{-t/(\gamma/\Delta K)} + \frac{4bD}{(2\omega_0\gamma)^2 + (AK)^2} \cos(2\omega_0 t) + \infty. \tag{3.14}
\]

The correlation function has three contributions. The first term is due to thermal fluctuation and the second the applied electric field. The infinity term is the contribution from the constant background field, which can be ignored. There is a competition between first two terms. This simple understanding of the director dynamics will be discussed with experimental results of the correlation function. The study for the director fluctuation has not been completed yet.
Chapter IV

Experimental Details and Results

4.1 Experimental details
4.1.1 Sample preparation

PDLC samples were prepared using the polymerization induced phase separation method. The materials used consisted of the nematic liquid crystal E7, the epoxy Epon 828, and the curing agent Capcure 3-800. The epoxy resin Epon 828 (from Miller Stephenson Company) is the reaction product of epichlorohydrin and bisphenol A. The curing agent Capcure 3-800 (from Miller Stephenson Company) is a trifunctional mercaptan. E7 (EM industries, Inc.) is a eutectic liquid crystal mixture of cyanobiphenyls and triphenyls. It is composed of 5 CB, 7 CB, 8 OCB, and 5 CT.

The molecular structure and components of E7 are given in Fig. 15. The structures of Epon 828 and Capcure 3-800 are shown in Fig. 16. The Epon 828 has two epoxide group which are the reactive groups. The Capcure has three reactive groups which are indicated as R in Fig. 16. Equal weights of Epon 828 and Capcure 3-800 result in almost exact mole fraction ratio of 3:2. The physical properties of E7 is shown in Table 1.

Typical samples studied were ternary mixtures with a 0.45 weight fraction of E7, 0.275 weight fraction of Epon, and 0.275 weight fraction of Capcure. The
Fig. 15. The chemical structures of the components of the nematic liquid crystal E7.
Fig. 16. Molecular structures of Epon 828 and Capcure 3-800.
**Table I.** Some physical properties of the liquid crystal mixture E7

<table>
<thead>
<tr>
<th>Properties</th>
<th>Physical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>-10 °C</td>
</tr>
<tr>
<td>Clearing point</td>
<td>60.5 °C</td>
</tr>
<tr>
<td>Kinematic viscosity</td>
<td>$39 \times 10^{-6}$ m$^2$/sec at 20 °C</td>
</tr>
<tr>
<td></td>
<td>$181 \times 10^{-6}$ m$^2$/sec at 0 °C</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>$\epsilon_\parallel = 19.0$</td>
</tr>
<tr>
<td></td>
<td>$\epsilon_\perp = 5.2$</td>
</tr>
<tr>
<td></td>
<td>$\Delta \epsilon = 13.8$ at 20 °C (1KHz)</td>
</tr>
<tr>
<td>Refractive indices</td>
<td>$n_\epsilon = 1.746$</td>
</tr>
<tr>
<td></td>
<td>$n_0 = 1.522$</td>
</tr>
<tr>
<td></td>
<td>$\Delta n = 0.224$ at 20 °C (589nm)</td>
</tr>
<tr>
<td>Elastic constants ratio (bend/splay)</td>
<td>$K_3/K_1 = 1.54$</td>
</tr>
<tr>
<td></td>
<td>at 20 °C</td>
</tr>
</tbody>
</table>
components – 200 mg of E7, 122.2 mg of Epon, and 122.2 mg of Capcure – were mixed and stirred mechanically to form a clear homogeneous solution from which dissolved air was removed by centrifuging. The solution was then placed between two glasses (2.54cm × 2.54cm × 1mm) with a transparent layer of conducting indium tin oxide (ITO). 30µm thick mylar spacers were put on the corners between the glasses.

The schematic variation of refractive indices of the nematic liquid crystal E7 and the polymer mixture with temperature are shown in Fig. 17.

4.1.2 Experimental setup

(i) Resistance and capacitance measurements

The polymerization induced phase separation process for epoxy PDLC materials begins with a homogeneous mixture of prepolymer, curing agent, and liquid crystal. As the prepolymer Epon and the curing agent Capcure react with each other and form the high molecular weight polymer, the liquid crystal becomes immiscible and phase separation takes place. In order to study the kinetics of the curing process both to determine the onset time of phase separation and to look at long term behavior, an electric circuit was designed to measure the sample resistance (Fig. 18). By increasing the gain of the circuit, the small change in the resistance of the sample during the long term can be detected and in that point an ohmmeter can not be used.

To protect the circuit from external noise, coaxial cables were used between the sample holder and other devices. The electric circuit and sample
Fig. 17. Refractive indices of the pure liquid crystal E7 and the pure polymer as function of temperature.
Fig. 18. Experimental setup for resistance measurement during curing process.
holder were housed in an aluminum box which are grounded. The power conditioner was also used as a surge protection. In the circuit of Fig. 18, the part ‘A’ is a follower which has unit gain and the part ‘B’ is an amplifier whose gain can be adjusted by the variable resistance ‘R’. The maximum value of the resistance is 10 Kohm so that the maximum gain through the amplifier can be 14.7 which is calculated from $G = \frac{R_{\text{max}}}{.679 \text{ Kohm}}$.

The output of the circuit is connected to the Keithly 197 autoranging multimeter which ultimately convert the input A.C. voltage to the output D.C. voltage which is proportional to the input. Finally, the D.C. output was recorded on the Soltec Chart Recorder. The temperature was kept at $62 \pm 0.02^\circ\text{C}$ by a temperature controller (Instec, Inc.).

The capacitance and resistance were also measured simultaneously during the curing process using a GenRad 1615-A capacitance bridge which is capable of capacitance measurements with $\sim 1 \times 10^{-3} \text{pF}$ accuracy. Fig. 19 shows the schematic diagram of the measurement. Changes in the environment and in the connections can vary the terminal capacitances, $C_G$. However, the direct capacitance, $C_X$, are not affected from the changes. An EG&G 5102 lock-in amplifier was used to detect the null. Measurements were made at 10KHz with 1.00 rms volt across the sample. A Tektronix 501A function generator was the signal generator for the bridge. The Instec temperature controller was used to keep at $62 \pm 0.02^\circ\text{C}$.

(ii) Light scattering

The preliminary light scattering experiment, (hereafter called I), was
Fig. 19. Capacitance and resistance measurement by a GenRad capacitance bridge.
carried with a setup as shown in Fig. 20. The homogeneous mixture was placed between two glasses separated by a 27 μm thick mylar spacer. The cell then immersed in glycerol in a thermostatted cylindrical cell housing. The refractive index of the glycerol used is 1.5 which is very close to that of glass so that we can avoid the experimental error due to the light deflection on the glass surface of the sample. The sample temperature was kept at 62°C, above the nematic-isotropic transition of the pure liquid crystal. An 8 mW He-Ne laser (Photochemical Research Associates Inc.) was used as the light source. The data was collected by using a photomultiplier tube (PMT). The detected light intensity was then read from AT&T PC 6300 computer.

In order to detect the scattered light during a short period of phase separation, the computer-controlled experimental setup was required as shown in Fig. 21. The scattered intensity was detected by a photomultiplier under V₀ polarization conditions. The output of the photomultiplier was converted to digital and stored in RAM of IBM personal computer. The scanning of the PMT is driven back and forth by a stepping motor which is monitored by the computer as well. The equipments in this part were used in conjunction with T. Kyu at the Institute of Polymer Engineering, The University of Akron. The scanning rate of the rotator was 5.5°/sec which can sample 17.45 data points/sec. The resolution angle of the photomultiplier was less than 2.2°. The temperature of the sample holder was kept at 62 ± 0.2°C by a temperature controller (Omega Engineering, Inc.), above the 58°C nematic-isotropic transition temperature of the liquid crystal E7. This experiment will be represented by II.
Fig. 20. Light scattering setup 1.

Sample spatial pin lens Pol. lens holder

Laser

Temp. Controller

Sample holder
diaphragm

neutral density filter

diaphragm

PMT

Computer
Fig. 21. Light scattering setup II.
(iii) **Morphology of PDLC materials**

Most of morphologies of the PDLC materials were investigated mainly by using a JEOL scanning electron microscope (SEM).

(iv) **Cascade phenomena**

Phase separation at 45°C below the nematic-isotropic phase transition temperature was investigated. At this temperature, phase separation was slower than that at higher temperatures so that we may expect to observe phase separation more precisely. The experiment was monitored by a color video camera and recorded by a videocassette recorder as shown in Fig. 22. Magnification of the Nikon microscope was 100 times.

(v) **Effect of shear measurement**

Fig. 23 shows the experimental arrangement. A Nikon microscope and a mechanical puller was used while the temperature was fixed at 62°C by a temperature controller (Instec, Inc.). The speed of the mechanical puller was \( \sim 3.4 \text{ mm/hr} \).

The sample was formed by mixing the liquid crystal E7, the epoxy Epon 828, and the curing agent Capcure 3-800 in a 1:1:1 ratio by weight.

(vi) **Director fluctuations**

The sample used was the same type as that made in light scattering measurement. That is, it consists of 0.45 weight fraction of E7, 0.275 weight fraction of Epon, 0.275 weight fraction of Capcure.
Fig. 22. Schematic of a microscope and a VCR arrangement to study phase separation.
Fig. 23. Schematic of the experimental arrangement to see the effect of shear during phase separation.
The autocorrelation function of the scattered intensity at a fixed angle was measured with an electric field applied to the sample from a Tektronix 501A function generator amplified by a Kepco BOP 72-5 operational amplifier. A schematic diagram of the experimental system is shown in Fig. 24.

A PRA (Photochemical Research Associates Inc.) He-Ne laser used has 8 mW maximum output. Hamamatsu R464 photomultiplier tube and C1050 photon count unit which contain a pre-amplifier, main amplifier, discriminator and waveform shaping circuit along with a photomultiplier tube socket, and power supply (Bertan Associates, Inc.) were used. The ±12V low power supply designed and built in the laboratory was also used for the preamplifier of the photo counting unit. A Malvern K7032 CE 8 bit digital correlator was used to determine the autocorrelation of light intensity. The correlator was used in conjunction with AT&T PC 6300 computer. The scattered light was detected at 30° from the direction of the incident light. A line filter (Oriel) used has the maximum transmittance of 62% for λ=634.05 nm with the half peak bandwidth of 10.1 nm.
Fig. 24. Experimental arrangement for detecting the fluctuating scattered light from the PDLC film.
4.2 Experimental results

4.2.1 Resistance and capacitance measurements

Resistance of the sample was measured over a long period. Results for about 40 hours are shown in Fig. 25. Fig. 26 shows the measurement for about 6 days. The gain of the circuit was 7.535 for both of Fig. 25 and Fig. 26. Even though the curing process is assumed to start right after the components are mixed, the phase separation takes place only after certain time which we call the 'induction time'. This is the elapsed time between the insertion of the mixture into the thermostat and the time when phase separation, as determined by both changes in resistance and light scattering measurements, begins. Further discussion will be given later with light scattering measurement. For the mixture of 0.45 weight fraction of E7, the induction time was usually 31 minutes (which corresponds to 3.449 on the horizontal axis of Fig. 26).

We see that the curing process persisted for a long time. Surprisingly, after about 7 hours, resistance curve exhibits a different trend as shown in both of Figs. 25 and 26. As shown in Fig. 26, the trend showed the second change after four and half days (106.7 hours).

In the measurements of capacitance and resistance at the same time, the capacitance of the sample decreases with time and the resistance increases as shown in Fig. 27. The size of the sample was 2.1cm $\times$ 1.7cm $\times$ 30$\mu$m. The applied frequency and voltage were respectively 10KHz and 1 volt.
Fig. 25. Resistance of a sample as a function of time during phase separation I.
Fig. 26. Resistance of a sample as a function of time during phase separation II.
Fig. 27. Capacitance and resistance during phase separation.
4.2.2 Light scattering

The time when the abrupt change in the scattered intensity occurs is recognized as the onset time of phase separation. Fig. 28 shows that the higher the curing temperature, the shorter the onset time of phase separation, \( t_c \). Fig. 29 shows the temporal evolution of the diffraction pattern; the elapsed time between photographs is 30 seconds. The decrease in the radius of the ring in the diffraction pattern indicates that \( q_{\text{max}} \) is decreasing with time. The structure factor can be more accurately determined by detailed measurements of the intensity of the scattered light as a function of angle. Fig. 30 shows typical scattered intensity at a fixed angle as function of time.

The scattered data was analyzed based on Eq. (2.20) and the assumption that the shape of the free energy changes with time during the polymerization process. The convexity of the free energy \( \frac{\partial^2 f}{\partial \phi^2} \), the mobility \( M \) of the liquid crystal and the coefficient \( \kappa \) are all expected to vary with time. On the basis of Eq. (2.21), we have extracted values of \( M \left( \frac{\partial^2 f}{\partial \phi^2} \right) \) and \( \kappa M \) as functions of time from the results of our light scattering measurements. Values of these quantities are shown in Fig. 31; the solid lines in the figure are merely to guide the eye. We expect that \( -\frac{\partial^2 f}{\partial \phi^2} \) and \( \kappa \) both increase with time as the degree of polymerization \( N_B \) increases. Assuming that the mobility \( M \) is a weak function of \( N_B \), this is consistent with our observations. The observed decrease of \( q_{\text{max}}^2 = \frac{1}{4\kappa \left( \frac{\partial^2 f}{\partial \phi^2} \right)} \) with time indicates that \( \kappa \) increases more rapidly than the curvature of the free energy.

In order to know the corresponding scattered angles, a diffraction grating was used which has three different ranges of spacings; 100 lines/mm, 300 lines/mm, and 600 lines/mm. Fig. 32 is a typical plot of the scattered intensity for a
Fig. 28. Onset time of phase separation as function of composition.
Fig. 29. Temporal evolution of the diffraction pattern.
Fig. 30. Scattered intensity as a function of angle and time.
Fig. 31. Variation of $-\frac{\partial^2 f}{\partial \phi^2}$ and $\kappa M$ with time.
Fig. 32. Typical scattered intensity from a diffraction grating.
diffraction grating in air. Distinct peaks in the scattered intensity were observed. There are 100 lines/mm in the diffraction grating, so that \( d = 10 \, \mu \text{m} \). Fig. 33 shows typical scattered intensity at a fixed angle as function of time. 3.449 on the time-axis in Fig. 33 corresponds to 31.5 minutes. The onset time is functions of the curing temperature and the liquid crystal concentration.

The scattered intensity profile \( I(q,t) \) is shown in Fig. 34 and Fig. 35 at different times. The scattered intensity is proportional to the structure factor of the sample which is isotropic with a broad peak at a wave vector \( q_{\text{max}} \). As time increases, the maximum scattered intensity increases while \( q_{\text{max}} \) shifts towards smaller \( q \). The peak position characterizes the wavelength of the spatial periodic concentration variation. The first point on the \( q \)-axis in Fig. 34 corresponds to the angle of 0.984° and the last one 31.6°.

Fig. 36 shows the plots of \( I_\text{nor} \cdot q_{\text{max}}^3 \) against \( q/q_{\text{max}} \). All the curves for various time scale are superposed suggesting that self-similarity has been attained. This observation is consistent with the results of other studies such as in polymer blends and alloys.

The exponent of the scaled vector \( x \) for \( x<1 \) in Fig. 37 takes on values between 2 and 4, in agreement with the prediction of Furukawa [Ohta and Nozaki, 1989]. The exponent for \( x>1 \) is -6 near \( \approx 1 \), and -4 for \( x>>1 \). The slope -4 is associated with Porod's law to the case of small angle x-ray scattering [G. Porod, 1982] where the law is valid not only for single particles, but also densely packed systems and for non-particulate structures provided that the boundaries of the domains of the systems are well defined or sharp. This is because only the structure near the surface is responsible for the slope of \( S(q) \). One can imagine
Fig. 33. Graph of intensity vs. time
Fig. 34. Scattered intensity vs. $q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$ at different times I.
Fig. 35. Scattered intensity vs. $q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$ at different times II.
Fig. 36. Plot of the scaled structure factor $I_{\text{nor}} \cdot q_{\text{max}}^3$ vs. the scaled wavevector $q/q_{\text{max}}$. 
Fig. 37. Log-log plot of the scaled structure factor \( F(q/q_{\text{max}}) \) vs. the scaled wavevector \( q/q_{\text{max}} \).

- \( \square = 38.1 \)
- \( \triangle = 38.7 \)
- \( \diamond = 39.3 \)
- \( \times = 40.4 \)
- \( * = 40.6 \)
- \( \circ = 41.2 \)
that the interfacial thickness becomes thinner in the final stage of the phase separation.

The slope $-6$ is typical for a critical quench in a thermally quenched binary system. In our system it may arise if, during the polymerization, the convex (unstable) point of the free energy occurs for compositions near the initial composition of the mixture. We have also observed a second maximum of the structure factor (Fig. 38), which has been previously observed in thermally quenched near critical binary system [Bates and Wiltzius, 1989], and in homogeneously nucleated systems [Cumming and Wiltzius, 1990]. We believe this to be a signature of long range structural periodicity.

Fig. 39 and Fig. 40 show the power law dependence of $q_{\text{max}}$ and $I_{\text{max}}$ on time $t$, respectively. For small $t-t_0$, the predicted exponent is $-\frac{1}{3}$, which is reasonably consistent with the results as shown in Fig. 39. However, in this regime, the exponent is sensitively dependent on the value of $t_0$, and thus more data is required for its unambiguous determination. Tanaka et al. [1990] have shown experimentally that there exists a crossover region between the metastable and unstable regions where the exponent $\alpha$ changes its value as a function of the quench depth. In the unstable region, they found that the exponent $\alpha$ was roughly equal to $\frac{1}{3}$, which is characteristic of the intermediate stage of phase separation in a system with conserved order parameter. In the metastable region, on the other hand, their exponent was very small ($\sim \frac{1}{10}$), reflecting very slow coarsening. In the transitional region, NG and SD can proceed simultaneously, which suggest both process can be thermally activated.

At later times, the exponent is clearly $-1$. Binder and Stauffer [1974]
Fig. 38. Log-log plot of the scaled structure factor $F(q/q_{\text{max}})$ vs. the scaled wavevector $q/q_{\text{max}}$. II.
Fig. 39. $\ln q_{\text{max}}$ vs. $\ln (t-t_0)$. 

45 wt% E7
62 °C
Fig. 40. ln $I_{\text{max}}$ vs. ln $(t - t_0)$.
predicted the exponent of +1 associated with the increase of \( I_{\text{max}} \); again, our observations in Fig. 40 are consistent with this, but again, our results here sensitively depend on \( t_0 \) and more data is needed. At later times, the exponent is +3 in agreement with Siggia. The increasing intensity for even later times corresponds to the slow change of resistance after the relatively rapid phase separation; we speculate that slow diffusive phase segregation, due to the dramatically decreased mobility, persists even at very long times.

4.2.3 Morphology of PDLC materials

Figs. 41 and 42 show scanning electron micrographs of typical cured PDLC (33% and 45% liquid crystal E7 by weight, respectively) material. Both of samples were cured at 62°C. The white bar in the micrographs corresponds to 1\( \mu \)m and 10\( \mu \)m, respectively. The droplet size is dependent on the curing temperature and the concentration of liquid crystal. In Fig. 42, some droplets are observed to be interconnected each other.

Smith and Vaz [Smith and Vaz, 1988] have found that the fraction of liquid crystal contained in a droplet decreased with increasing curing temperature, presumably as a result of greater liquid crystal solubility in the epoxy matrix at higher temperatures.
Fig. 41 Scanning electron micrograph (SEM) of the cured PDLC material. It consists of 33% liquid crystal E7 by weight.
Fig. 42 Scanning electron micrograph (SEM) of the cured PDLC material. It consists of 45% liquid crystal E7 by weight.
4.2.4 Cascade phenomena

The micrographs are shown in Fig. 43 (a)-(f). The picture were taken from the TV monitor. The elapsed time after mixing are shown on the pictures. After 2 hours and 14 minutes, a pattern with a characteristic wave length which has a periodic pattern occurs. The pattern starts from a region and spread out to other regions and grows. This early periodic pattern reminds us of the early stage spinodal decomposition in a mixture. The periodic pattern phase separates and keep growing (Fig. 43 (a)). It is thought that small domains are polymer-rich areas.

In Fig. 43 (b)-(c), we can observe the direct coalescence of the domains. The system still exhibits phase separation. This is a so-called later stage of spinodal decomposition which is different from the early process.

We can observe in Fig. 43 (d)-(e) that the second phase separation takes place in each regions. We also observe that smaller domains become smaller and finally dissappear and that larger ones become larger. That is, smaller domains diffuse and larger ones enlarge at the expense of smaller ones, which is similar to the Lifshitz-Slyozov mechanism usually observed in a solid alloys. These are due to the Gibbs-Thomson effect [Appendix II]. There is a concentration gradient which arises from the different curvatures of the domains between domains of different size (Fig. 44).

Finally, mobility of the system becomes small as the curing goes on. This prevents the domains from moving so that the mixture can not flow any more (Fig. 43 (f)). However, the curing process persists for a long time as shown in resistance measurement, especially about one week for the sample cured at 62°C.
Fig. 43-(a). Micrographs of cascade phenomena while curing at 45°C.
Fig. 43-(b). Micrographs of cascade phenomena while curing at 45°C.
Fig. 43-(c). Micrographs of cascade phenomena while curing at 45°C.
Fig. 43-(d). Micrographs of cascade phenomena while curing at 45°C.
Fig. 43-(e). Micrographs of cascade phenomena while curing at 45°C.
Fig. 43-(f). Micrographs of cascade phenomena while curing at 45°C.
Fig. 44. Illustration of Gibbs-Thomson effect.
4.2.5 Effect of shear during phase separation

The cured sample under shear is shown in Fig. 45. The shear was applied vertically in the picture. The shapes of droplets was elongated along the shear direction more or less. Even though the elongated shape is not clear, the sample showed clear birefringence through a microscope. It was shown by Wu et al. [1989] that the droplet shape can be a dominant factor, particularly for the relaxation time.
Fig. 45. SEM micrographs of the sample in the presence of shear during phase separation.
4.2.6 Director fluctuations

Without an applied electric field, the director fluctuation is due to thermal motion of the molecules in droplets. Figs. 46 and 47 show the autocorrelation functions of the scattered light at the scattering angle of 30° under $V_V$ and $V_H$ polarization conditions respectively. Here $V$ indicates vertical direction and $H$ horizontal direction. In figures, ST and ED indicate 'sample time' and 'experimental duration' of the correlator. The figures show the exponential decay of the function with $\sim 1\; \text{m second}$ of a correlation time.

When 10 r.m.s. volt with 1 KHz frequency is applied to the sample, the autocorrelation function shows two contributions due to the applied electric field and thermal fluctuation (Figs. 48 and 49). Specially, under $V_H$ polarization, the function showed the period function which has 1KHz and 2KHz components which is not observed under $V_V$ polarization. This is more clearly shown in Fig. 50 when the sample time and the experimental duration are increased.
Fig. 46. Autocorrelation function of the scattered light with time. The polarization is $V_y$ and no electric field was applied.
Fig. 47. Autocorrelation function of the scattered light with time. The polarization is $V_H$ and no electric field was applied.

$ST=40 \ \mu$Sec  
$ED=20 \ \text{Sec}$  
$V_{app}=0$ 
$V_H$
Fig. 48. Autocorrelation function of the scattered light with time. The polarization is $V_y$ and the applied electric field was 10 V with 1 KHz.
Fig. 49. Autocorrelation function of the scattered light with time. The polarization is $V_H$ and the applied electric field was 10 V with 1 KHz.
Fig. 50. Autocorrelation function of the scattered light with time. The polarization is $V_H$ and the applied electric field was 10 V with 1 KHz. Sample time and experimental duration are longer than those of Fig. 48.
Chapter V

Some Applications

5.1 Overview – Optical power limiting and bistability

It has been shown that the liquid-crystal droplets in PDLC films can undergo a transition to an elastically deformed state under the influence of static magnetic fields [Kelly et al., 1989] and optical fields [Palffy-Muhoray and West, 1988]. This transition was first observed in a nematic liquid crystal by Freedericksz and Zolina [1933].

Wang et al. [1987] studied the Freedericksz transition in a nematic cell with feedback. A cell with planar alignment at the cell walls was placed between crossed polarizers, and illuminated with a light source. The output voltage of the detector measuring the transmitted light intensity was used as the feedback signal which modulated the voltage applied to the cell. It was found that, for certain feedback parameters, the normally second-order transition became first order.

In this chapter, the behavior of a PDLC film with feedback is considered, where the voltage applied across the film depends on the intensity of light transmitted by the film. The effects of both positive and negative feedback were studied. Bistable and optical power limiting behavior was observed and these can be simply explained in terms of the optical transmittance characteristics of the film.
The mechanism of reorientation in PDLC films is similar to the Freedericksz transition in that it is the result of competition between the aligning effects of the applied fields and the restoring torques due to elastic and surface effects [Wu et al., 1989; Palffy-Muhoray et al., 1990]. The direction of average alignment of the liquid crystal in each droplet is determined by the elastic constants of the liquid crystal, the orientation and strength of the molecular anchoring at the droplet wall, external fields, and shape effects of the droplets. In general, the response of each droplet to an external field is similar to a Freedericksz transition in a planar cell with pretilt; and the random distribution of the effective "pretilt" angle (as well as polydispersity in size and shape anisotropy) makes the bulk optical response of the film to applied fields gradual rather than abrupt.

5.2 Experimental details

The PDLC films under study consist of the liquid crystal E7 dispersed in an epoxy matrix. The epoxy constituents are Epon 828, MK107, and Capcure 3-800. Approximately 25% of the film volume is occupied by the liquid crystal, dispersed in the form of droplets. The sample used was a 26-μm-thick PDLC film between 2.54cm × 2.54cm × 1mm glass slides coated with a transparent layer of indium tin oxide (ITO). A schematic diagram of the experimental system is shown in Fig. 51. The sample is illuminated by the attenuated beam of a 5 mW He-Ne laser. The intensity of the transmitted light is measured by a photodiode. The feedback circuit generates a voltage which is a linear function of the photodiode amplifier output, and this voltage is used to modulate the output of a signal generator. The 1KHz sinusoidal output of the signal generator is applied
Fig. 51. Schematic diagram of the experimental setup and the feedback circuit.
to the sample cell via a step-up transformer.

5.3 Experimental results

In the analysis of the planar nematic cell with feedback [Wang et al., 1987], an expression for the response of the cell to an applied voltage is obtained by minimizing a free energy, and keeping only the lowest-order term describing the distortion [Appendix III]. This description cannot be accurate for large distortions which occur, for example, if the transition is strongly first order. Although we have obtained closed form expressions for the orientational order and transmittance of PDLC films as a function of applied voltage from a free-energy minimization procedure, we find it more useful here to simply characterize the film by its experimentally determined response. In Fig. 52, the transmittance of the sample is shown at $\lambda=632.8$ nm as a function of the applied voltage $V_c$. Although there is some hysteresis, for these samples it is a small effect, and will not be considered further here.

The nonlinear dependence of the transmittance on the applied $V_c$ is responsible for the characteristic nonlinear response of the system in the presence of linear feedback. The power transmitted by the sample is

$$P_{out} = tP_{in}, \quad (4.1)$$

where $t$ is the transmittance and $P_{in}$ is the incident power. The output voltage of detector 2 is proportional to $P_{out}$, and the voltage across the cell is a linear function of the detector output so that
Fig. 52. Sample transmittances as a function of applied voltage.

\[ \lambda = 632.8 \text{ nm} \]
\[ T = 22^\circ\text{C} \]
\[ V_c = V_o + GdP_{in}, \]  

(4.2)

where \( V_o \) is the offset and \( G \) is the gain of the feedback circuit. The transmittance \( t \) is a function of \( V_c \), as indicated in Fig. 52. The response of the system with negative feedback \((G<0)\) is shown in Fig. 53. For low incident intensities, \( V_c \) decreases, reducing the transmittance and giving rise to optical power limiting behavior. By varying the feedback parameters, the characteristic of this behavior may be modified. For example, increasing \( V_o \) increases the range where \( P_{out} \) is proportional to \( P_{in} \), while changing \( G \) simply scales \( P_{in} \) and \( P_{out} \), leaving the response otherwise unchanged. The expected response of the system calculated by choosing a value of \( V_c \), obtaining the corresponding \( P_{in} \) and \( P_{out} \) is shown in Fig. 54.

For positive feedback \((G>0)\), the response of the system is shown in Fig. 55. At high incident intensities, \( V_c \) is large, \( t \) is essentially constant, and \( P_{out} \) is proportional to \( P_{in} \). As the incident power is decreased, \( V_c \) decreases, reducing the film transmittance which further reduces \( V_c \). This instability can lead to an abrupt change in \( P_{out} \) as the incident power is varied; however, the value of \( P_{in} \) where this jump takes place depends on whether the incident power is increasing or decreasing. This gives rise to hysteresis, and to the existence of two stable states with different transmittance for some range of incident power. Increasing the offset \( V_o \) causes the width of the hysteresis region to be reduced, and above a critical value of \( V_o \), no hysteresis can be observed. Changing the gain again simply scales the power. The expected response of the system calculated by choosing a value of \( V_c \), obtaining the corresponding \( P_{in} \) and \( P_{out} \) is shown in Fig.
Fig. 53. Measured response of the system with negative feedback.

\( G = -1040 \text{ V/mW} \)

\( V_o = 28.9 \text{ V} \)
Fig. 54. Calculated response of the system with negative feedback.

\[ G = -1040 \text{ V/mW} \]
\[ V_o = 28.9 \text{ V} \]
Fig. 55. Measured response of the system with positive feedback.
G = 198 V/mW

$V_0 = 5.23$ V

Fig. 56. Calculated response of the system with positive feedback.
The behavior of the system may be simply understood by rearranging Eq. (4.2) to read

\[ t = \frac{(V_c - V_o)}{GP_{in}}, \quad (4.3) \]

and noting that transmittance of the cell is given by the intersection of the cell response curve of Fig. 52 and the straight line through \( V_o \) with slope \( 1/(GP_{in}) \) given by Eq. (4.3), as illustrated in Fig. 57.

For \( G<0 \), there is only a single intersection, and hence there is no hysteresis or bistability. If, instead of the gradual increase in the cell transmittance with \( V_c \), the cell response was a step function at some voltage \( V_{step} \), then the output power \( P_{out} \) would be exactly proportional to \( P_{in} \) for \( P_{in} < (V_o - V_{step})/(-Gt) \), and have the constant value \( (V_o - V_{step})/(-G) \) for all values of \( P_{in} \) greater than this. In the case of linear feedback, therefore, ideal power limiting behavior is obtained if the cell response is a step function. It is worth noting that, by decreasing \( G \), the limiting value of the output power may be readily increased up to the (large) optical damage threshold of the PDLC material.

For \( G>0 \) and for sufficiently small values of \( V_o \), there may be three intersections of the straight line of Eq. (4.3) and the cell response curve for some range of incident power \( P_{in} \). The state of the system here is determined by its history; however, as \( P_{in} \) is varied, the intersection corresponding to the state of the system may be vanish, giving rise to a discontinuous jump in \( t \) and hence in
Fig. 57. Sketch showing the intersection of the sample transmittance and feedback response curves to determine the operating point.

slope = 1/(G P_{in})
In the regime where there are three intersections, the state corresponding to the intermediate one is unstable. That is, any perturbation in $V_c$ will grow, and take the system to one of the other states, which are both stable. Hysteresis and bistability exist in this regime. It is interesting to note that if the cell response is a step function, although a large multiple intersection regime exists, it is not possible to switch into more transparent state by varying $P_{in}$ only.

It is interesting to consider the behavior of a system where transmittance of the film as a function of applied voltage shows strong hysteresis. Here we expect bistability even in the case of negative feedback, and a broadening of the bistable region in the case of positive feedback.
Chapter VI

Conclusions

Phase separation in a liquid crystal and polymer mixture has been observed where the phase separation is induced by polymerization. The polymerization process observed by resistance and capacitance of the sample persists for long times compared to the onset time of the phase separation. The structure factors show that the behavior of this system is similar to thermally quenched binary system. However, the induction time is needed to initiate the phase separation which is not observed in thermally quenched binary system. Typically, the induction time is 31.5 minutes for the mixture of 0.45 liquid crystal weight fraction and it is a function of the curing temperature and the concentration of the liquid crystal. The scaling behavior of the structure factor of the late stage of spinodal decomposition is in reasonable agreement with Furukawa’s proposition. A second maximum at higher wavenumber was found in the scaled structure factor. The crossover of $q_{\text{max}}$ from $t^{-1/3}$ to $t^{-1}$ predicted by Siggia was observed.

It was observed that phase separation takes place twice at 45°C. This is due to the continuing change of the free energy of the system. After the second phase separation, no process can be observed because the increased viscosity due to polymerization prevents the system from further process.
The effect of shear during the polymerization process was investigated. The SEM picture of the sheared sample revealed the elongated shape of the nematic droplets.

The autocorrelation function observed from scattered light intensity gives useful information of director dynamics inside the droplets. Two contributions due to thermal fluctuation and external electric field were observed. The results were understood based on the simple model for the droplet director fluctuation. Quantitative explanation is an objective for future work.

The behavior of PDLC films with linear feedback was examined. Both optical power limiting and bistable behavior were observed and the experimental results showed good agreement with predicted values. These results suggest that PDLC films with feedback may be useful in optical protection and in optical memory applications.
Appendix I

The Size Distribution in Multicomponent Systems

We derive here the size distribution function of polymer molecules due to polymerization. The similar derivation was carried out by Rogers [1977] in his mathematical model of the phenomena of multiple clustering of like embryonic cells. Helpful discussion with R.G. Petschek is acknowledged in the derivation.

The distribution of the system consisted of initially linear monomers is characterized by Eq. (2.63):

$$
\frac{d\rho(n,\tau)}{d\tau} = \sum_{m=1}^{\infty} \rho(m,\tau)\rho(n-m,\tau) - 2\rho(n,\tau) \sum_{m=1}^{\infty} \rho(m,\tau). 
$$  \hspace{1cm} (A.I.1)

We define a new function as follows.

$$
\rho(z,\tau) = \sum_{m=1}^{\infty} \rho(m,\tau) z^{m-1}.
$$  \hspace{1cm} (A.I.2)

Substituting Eq. (A.I.2) into Eq. (A.I.1), we get

$$
\frac{d\rho(n,\tau)}{d\tau} z^{n-1} = \sum_{m=1}^{\infty} \rho(m,\tau) z^{n-1} \rho(n-m,\tau) - 2\rho(n,\tau) z^{n-1} \sum_{m=1}^{\infty} \rho(m,\tau). 
$$  \hspace{1cm} (A.I.3)

Summing Eq. (A.I.3) over a large number $n$ (we can choose it as an infinite
number),

\[
\sum_{n=1}^{\infty} \frac{d\rho(n,\tau)}{dr} z^{n-1} = z \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \rho(m,\tau) z^{m-1} \rho(n-m,\tau) z^{n-m-1} - 2 \sum_{n=1}^{\infty} \rho(n,\tau) z^{n-1} \sum_{m=1}^{\infty} \rho(m,\tau)
\]

(A.I.4)

This reduces to

\[
\frac{d\rho(z,\tau)}{dr} = z \rho^2(z,\tau) - 2 \rho(z,\tau) \rho(1,\tau)
\]

(A.I.5)

and we have

\[
\frac{d\rho(1,\tau)}{dr} = -\rho^2(1,\tau)
\]

(A.I.6)

The solution of Eq. (A.I.6) gives

\[
\rho(1,\tau) = \frac{1}{\tau + \tau_0}
\]

(A.I.7)

From Eqs. (A.I.6) and (A.I.7),

\[
\frac{d\rho(z,\tau)}{dr} = z \rho^2(z,\tau) - \frac{2 \rho(z,\tau)}{\tau + \tau_0}
\]

(A.I.8)

\[
\Leftrightarrow \quad -\frac{d}{dr} \rho(z,\tau) = z - \frac{2}{\rho(z,\tau)(\tau + \tau_0)}
\]

Let us define a new relationship and substitute it into Eq. (A.I.8):
\[
\frac{1}{\rho(z,\tau)} = u(\tau + \tau_0)^2
\]  
(A.I.9)

where \( u \) is a function of time. Substituting (A.I.9) into (A.I.8), we get

\[
-2u(\tau + \tau_0) - (\tau + \tau_0)^2 \frac{\partial u}{\partial \tau} = z - 2u(\tau + \tau_0)
\]

\[
u = \frac{z}{\tau + \tau_0} + c
\]

\[
\frac{1}{\rho(z,\tau)} = z(\tau + \tau_0) + c(\tau + \tau_0)^2
\]  
(A.I.10)

The constant \( c \) is calculated from the condition of \( \rho_0(1) = \frac{1}{\tau_0} \) at \( \tau = 0 \).

\[
c = \rho_0(1) \left\{ \frac{\rho_0(1)}{\rho_0(z)} - z \right\}
\]  
(A.I.11)

Therefore,

\[
\rho(z,\tau) = \frac{1}{z\left\{ \tau + \frac{1}{\rho_0(1)} \right\} + \rho_0(1)\left\{ \frac{\rho_0(1)}{\rho_0(z)} - z \right\}\left\{ \tau + \frac{1}{\rho_0(1)} \right\}^2}
\]  
(A.I.12)

If \( \rho(1) = N \) and \( \rho(n) = 0 \) at \( \tau = 0 \) where \( n \neq 0 \), \( \rho_0(z) = N \) and \( \rho_0(1) = N \). Thus,

\[
\rho(z,\tau) = \frac{1}{z(\tau + \frac{1}{N}) + N(1 - z)(\tau + \frac{1}{N})^2}
\]  
(A.I.13)

Considering the following relationship,

\[
\rho(z) = \rho(1) + \rho(2)z + \rho(3)z^2 + \cdots,
\]
\[ \rho(z) = \rho(1), \]
\[ \frac{\partial \rho(z)}{\partial z} = \rho(2), \]
and
\[ \frac{\partial^2 \rho(z)}{\partial z^2} = 2! \rho(3), \]
we have
\[ \rho(1) = \frac{1}{N(\tau + \frac{1}{N})^2} \] (A.I.14)
and
\[ \rho(n, \tau) = \frac{1}{(n-1)!} \frac{\partial^{n-1}}{\partial z^{n-1}} \rho(z, \tau). \] (A.I.15)

Now,
\[ \rho(z, \tau) = \frac{1}{N(\tau + \frac{1}{N})^2 + z\{\tau + \frac{1}{N} - N(\tau + \frac{1}{N})^2\}} \]
\[ = -\frac{1}{\tau(N\tau + 1)} \cdot \frac{1}{\{z - 1 - \frac{1}{N\tau}\}} \] (A.I.16)
and
\[ \frac{\partial^k \rho(z, \tau)}{\partial z^k}\bigg|_{k=0} = -\frac{1}{\tau(N\tau + 1)} \cdot \frac{(-1)^k k!}{\{-(1 + \frac{1}{N\tau})\}^{k+1}} = \frac{k!}{\tau(N\tau + 1)\{1 + \frac{1}{N\tau}\}^{k+1}}. \]
\[ \frac{1}{(n-1)!} \frac{\partial^{n-1}}{\partial z^{n-1}} \rho(z, \tau) = \frac{1}{\tau(N\tau + 1)\{1 + \frac{1}{N\tau}\}^n} \]
\[ \rho(n, \tau) = \frac{N}{N\tau(N\tau + 1)\{1 + \frac{1}{N\tau}\}^n} = \frac{N(N\tau)^{n-1}}{(N\tau + 1)^{n+1}} \] (A.I.17)

The final result is that
\[ P(n,r) = \frac{n\rho(n,r)}{N} = \frac{n(N\tau)^{n-1}}{(N\tau + 1)^{n+1}} \quad (A.I.18) \]

Since \( N \) is very large number, \( \frac{n}{N} \approx x \) can be regarded as a continuous variable. By the relationship between \( P(x,\tau) \) and \( P(n,r) \),

\[ P(x,\tau) \frac{dn}{N} = P(n,r) \, dn \quad (A.I.19) \]

and

\[ P(x,\tau) = N P(n,r) \]

\[ = \frac{nN(N\tau)^{n-1}}{(N\tau + 1)^{n+1}} \]

\[ = \frac{x}{\tau^2} \left( 1 + \frac{1}{N\tau} \right)^{n} \cdot \frac{n+1}{N} \quad (A.I.20) \]

Since \( \lim_{N \to \infty} (1 + \frac{x}{N})^N = e^x \),

\[ P(x,\tau) \approx \frac{x}{\tau^2} e^{-\frac{x}{\tau}} \quad (A.I.21) \]

Therefore, we have finally

\[ P(x,\tau) \approx \frac{x}{\tau^2} e^{-\frac{x}{\tau}} \quad (A.I.22) \]
Appendix II

The Gibbs-Thomson Relation

The Gibbs-Thomson equation expresses the effect of the curved interface between two phases on its solubility in an adjacent phase. As an example, we consider a solution in which there exist a precipitate particle with the radius \( R \) and thus two phases are separated by the curved interface. Imagine that \( dn \) molecules are brought into the particle from the surrounding phase. If \( \mu_R \) is the chemical potential of the particle and \( \mu \) is the corresponding quantity of the solution with a planar surface, the work \((\mu_R - \mu)dn\) in this process is done. This is the same as if \( dn \) molecules had been used in enlarging the surface of the drop. It is, in turn, equal to \( \sigma dA \), where \( \sigma \) is the surface tension and \( A \) the area of the surface of the particle:

\[
(\mu_R - \mu)dn = \sigma dA = 8\pi R \sigma dR
\]  

(A.II.1)

From the relationship of \( V = \frac{4}{3}\pi R^3 \), we obtain

\[
vdn = dV = 4\pi R^2 dR
\]  

(A.II.2)

By eliminating \( dn \) and \( dR \),
which is the general form of the Kelvin equation.

The chemical potential is respectively given for the two phases as

\[ \begin{align*}
\mu_R - \mu = & \frac{2\pi \nu}{R}, \\
\mu = & \mu_0 + k_B T \ln \phi \\
\mu_R = & \mu_0 + k_B T \ln \phi_R
\end{align*} \]  

(A.II.3)

where \( \phi \) is the concentration of dissolved material in the mixture in contact with a plane interface, and \( \phi_R \) that of the particle [Landau and Lifshitz, 1986]. From the above equation, we have

\[ \mu_R - \mu = k_B T \ln \left( \frac{\phi_R}{\phi} \right) \]  

(A.II.5)

From equations (A.II.4) and (A.II.5) one obtains

\[ \ln \left( \frac{\phi_R}{\phi} \right) = \frac{2\pi \nu}{k_B T R} \]  

(A.II.6)

This is the Gibbs-Thomson solubility relationship.
Appendix III

The First Order Freedericksz Transition with Linear Feedback

Let us consider a planar parallel-aligned nematic liquid crystal cell of thickness \( d \). The \( z \)-axis is perpendicular to the plates of the cell and the \( x \)-axis along the direction of the molecules at the surfaces. In the presence of an electric field, the molecules will be tilted by an angle \( \theta \) relative to the plates due to the dielectric anisotropy (Fig. A.1). The Frank free energy is

\[
F = \frac{1}{2} \int_0^d \left[ k_1 (\nabla \cdot \mathbf{n})^2 + k_2 (\mathbf{V} \cdot \mathbf{n})^2 + k_3 (\mathbf{n} \times \mathbf{n} \times \mathbf{n})^3 + \mathbf{D} \cdot \mathbf{E} \right] dz \tag{A.III.1}
\]

where \( \theta = \theta(z) \) and \( \hat{n} = (\cos \theta, 0, \sin \theta) \).

From the requirement that \( \nabla \cdot \mathbf{D} = 0 \), the \( z \) component is independent of \( z \) and

\[
\mathbf{D} \cdot \mathbf{E} = D_z E_z(z) = \frac{D_z^2}{\epsilon_{zz}} \tag{A.III.2}
\]

Let us assume that \( \epsilon_{zz} = \epsilon_{||} \sin^2 \theta + \epsilon_{\perp} \cos^2 \theta \) [Deuling, 1972 and 1974]. Then,

\[
\mathbf{D} \cdot \mathbf{E} = \frac{D_z^2}{\epsilon_{||} \sin^2 \theta + \epsilon_{\perp} \cos^2 \theta} \tag{A.III.3}
\]

Therefore,
Fig. A.1. Schematic of Freedericksz transition due to an electric field applied perpendicular to the cell.
\[ F = \frac{1}{2} \int_0^d \left( (k_1 \cos^2 \theta + k_3 \sin^2 \theta) \frac{d\theta}{dz} \right)^2 + \frac{D_z^2}{\epsilon_{||} \sin^2 \theta + \epsilon_{\perp} \cos^2 \theta} \right] dz \]  

(A.III.4)

By applying an Euler-Lagrange equation, we obtain

\[
(k_1 \cos^2 \theta + k_3 \sin^2 \theta) \left( \frac{d\theta}{dz} \right)^2 + (k_3 - k_1) \sin \theta \cdot \cos \theta \left( \frac{d\theta}{dz} \right)^2 + D_z^2 (\epsilon_{||} \sin \theta) \cdot \cos \theta (\epsilon_{||} \sin^2 \theta + \epsilon_{\perp} \cos^2 \theta)^2 = 0
\]

\[
\Rightarrow \quad \frac{d}{d\theta} \left[ (k_1 \cos^2 \theta + k_3 \sin^2 \theta) \left( \frac{d\theta}{dz} \right)^2 - \frac{D_z^2}{\epsilon_{||} \sin^2 \theta + \epsilon_{\perp} \cos^2 \theta} \right] = 0
\]

\[
\Rightarrow \quad (k_1 \cos^2 \theta + k_3 \sin^2 \theta) \left( \frac{d\theta}{dz} \right)^2 - \frac{D_z^2}{\epsilon_{||} \sin^2 \theta + \epsilon_{\perp} \cos^2 \theta} = \text{constant} \quad (A.III.5)
\]

Considering the boundary and symmetry condition, i.e., \( \frac{d\theta}{dz} \bigg|_{z=d/2} = 0 \) and \( \theta(z=d/2) = \theta_m \),

\[
\frac{d\theta}{dz} = D_z \left( \frac{\Delta}{\epsilon_{||} k_1 (1 + \Delta \sin^2 \theta_m)} \right)^{1/2} \left( \frac{\sin^2 \theta_m - \sin^2 \theta}{(1 + \Delta \sin^2 \theta)(1 + \kappa \sin^2 \theta)} \right)^{1/2} \quad (A.III.6)
\]

where \( \Delta = \frac{\epsilon_{||} - \epsilon_{\perp}}{\epsilon_{||}} \) and \( \kappa = \frac{k_3 - k_1}{k_1} \). Finally, the solution of (A.III.6) is

\[
z = \frac{1}{D_z} \left\{ \frac{\epsilon_{||} k_1 (1 + \Delta \sin^2 \theta_m)}{\Delta} \right\}^{1/2} \int_0^\theta \left\{ \frac{(1 + \Delta \sin^2 \theta)(1 + \kappa \sin^2 \theta)}{\sin^2 \theta_m - \sin^2 \theta} \right\}^{1/2} d\theta \quad (A.III.7)
\]

By using the above results, the potential applied across the cell is

\[
V = \int_0^d E_z dz = \int_0^d \frac{D_z}{\epsilon_{zz}} dz
\]
\[ = 2D_z \int_0^{\theta_m} \frac{d\theta}{\varepsilon_{zz}} \\frac{d\varepsilon_{zz}}{d\theta} \]

\[ = 2D_z \int_0^{\theta_m} \frac{d\theta}{\varepsilon_{zz}} \frac{d\varepsilon_{zz}}{d\theta} \]

\[ = 2D_z \int_0^{\theta_m} \frac{1}{D_z} \left[ \frac{1 + (\Delta \sin^2 \theta_m)}{1 + \Delta \sin^2 \theta_m} \right]^{1/2} \frac{d\theta}{\varepsilon_{zz}} \]

When we let \( \varepsilon_{zz} = \varepsilon_\parallel \sin^2 \theta + \varepsilon_\perp \cos^2 \theta = \varepsilon_\perp (1 + \Delta \sin^2 \theta) \) and \( \sin^2 \theta_m \cdot \sin^2 \alpha = \sin^2 \theta, \)

\[ V = 2 \int_0^{\theta_m} \frac{k(1 + \Delta \sin^2 \theta_m)}{\Delta} \frac{1 + \kappa \sin^2 \theta}{(\sin^2 \theta_m - \sin^2 \theta)(1 + \Delta \sin^2 \theta)}^{1/2} d\theta \]

\[ = 2 \int_0^{\theta_m} \frac{k(1 + \frac{\Delta}{2} \cdot \theta_m^2)}{(1 + \frac{\Delta}{2} \cdot \theta_m^2)(1 + \Delta \sin^2 \theta_m \cdot \sin^2 \alpha)(1 - \sin^2 \theta_m \cdot \sin^2 \alpha)}^{1/2} d\alpha \]

Approximately,

\[ V \approx \frac{k_1}{\varepsilon_\perp \Delta} \int_0^{\pi/2} (1 + \frac{\Delta}{2} \cdot \theta_m^2 \cdot \sin^2 \alpha - \frac{\Delta}{2} \cdot \theta_m^2 \cdot \sin^2 \alpha + \frac{1}{2} \cdot \theta_m \cdot \sin^2 \alpha) d\alpha \]

\[ = V_0 \cdot (1 + \frac{\Delta}{2} \cdot \theta_m^2 \cdot \sin^2 \alpha) \left[ 1 + \left( \frac{\kappa}{4} - \frac{\Delta}{4} + \frac{1}{4} \right) \theta_m^2 \right] \]

\[ = V_0 \cdot \left( 1 + \left( \frac{\kappa}{4} + \frac{\Delta}{4} + \frac{1}{4} \right) \theta_m^2 \right) \]

That is,

\[ \frac{V - V_0}{V_0} = \frac{1}{4} (1 + \kappa + \Delta) \theta_m^2 \]

We can also derive the voltage from the free energy.
\[ F = \frac{1}{2} \int_0^d \left\{ (k_1 \cos^2 \theta + k_2 \sin^2 \theta) \left( \frac{d\theta}{dz} \right)^2 + \frac{D^2}{\epsilon} \right\} dz \]

\[ = \frac{1}{2} \int_0^d \left\{ k_1 (1 + \kappa \theta^2) \left( \frac{d\theta}{dz} \right)^2 + \frac{D^2}{\epsilon} \left( 1 - \Delta \theta^2 + \Delta \theta^4 \right) \right\} dz \]

\[ = \frac{1}{2} \int_0^d \left\{ k_1 (1 + \kappa \theta^2) \cdot \sin^2 \left( \frac{\pi \theta}{d} \right) \cdot \frac{\pi^2}{d} \cdot \cos^2 \left( \frac{\pi \theta}{d} \right) \right. \]

\[ + \frac{D^2}{\epsilon} \left( 1 - \Delta \theta^2 \cdot \sin^2 \left( \frac{\pi \theta}{d} \right) + \Delta (\Delta + \frac{1}{3}) \theta^4 \cdot \sin^4 \left( \frac{\pi \theta}{d} \right) \right) \right\} dz \]  

(A.III.11)

By taking the derivative of the free energy,

\[ \frac{\partial F}{\partial \theta} = 0 = \frac{\pi^2 k_1}{d^2} (1 + \frac{1}{2} \kappa \theta^2) + \frac{D^2}{\epsilon} \left\{ - \Delta + \frac{3}{2} \Delta (\Delta + \frac{1}{3}) \theta^2 \right\} \]  

(A.III.12)

The applied voltage is

\[ V = D_z \int_0^d \frac{dz}{\epsilon \cdot \epsilon} \]

\[ = D_z \int_0^d \frac{dz}{\epsilon \cdot \epsilon \left( 1 + \Delta \sin^2 \theta \right)} \]

\[ = \frac{D_z}{\epsilon} \int_0^d dz \left( 1 - \Delta \theta^2 + \frac{\Delta \theta^4}{3} + \Delta^2 \theta^4 + \cdots \right) \]

\[ \simeq \frac{D_z}{\epsilon} \left\{ 1 - \frac{1}{2} \Delta \theta^2 \right\} \]  

(A.III.13)

Therefore,
When $\theta_m=0$, $V_0 = \frac{k_1}{\epsilon_\perp \Delta}$. That is,

$$\frac{V - V_0}{V_0} = \frac{1}{4}(1 + \kappa + \Delta)\theta_m^2$$

This is the same result as Eq. (A.III.10). This is different from Eq. (4) of Wang et al.’s paper [1987] and is believed to be the correct expression.
References


H.C. van de Hulst, *Light Scattering in Small Particles*, (republished by Dover...


