CHAPTER III

THEORY

3.1 Kinetics of Phase Separation

3.1.1 Phase Separation Mechanism

Phase separation will occur if the system can reduce its Gibb's free energy by proceeding the free energy down towards its lowest points [Thongyai, 1990]. The schematic diagram of Gibbs free energy and phase separation boundary can be seen in Fig.3.1.

From Fig.3.1, this system undergoes phase separation when temperature changes from T_O to T_2. The Gibbs free energy curve of the phase separated condition is concave upward in the middle part. This results in instability. Considering the free energy curve at T equal T_1 and T_2, the composition at free energy A, C is unstable and will phase separate into two compositions down to the tangent line at free energy B, D. At B, D, the chemical potential of the two compositions will be the same. These results in two stable phases at different composition regardless of the original composition within the tangent line.

Connecting the tangent point at different temperatures, the phase is found. The phase diagram is the map of compositions at different temperatures and constant pressure. Within the phase separation line, the system's composition will become unstable and phase separate into two stable compositions at the phase separation line.
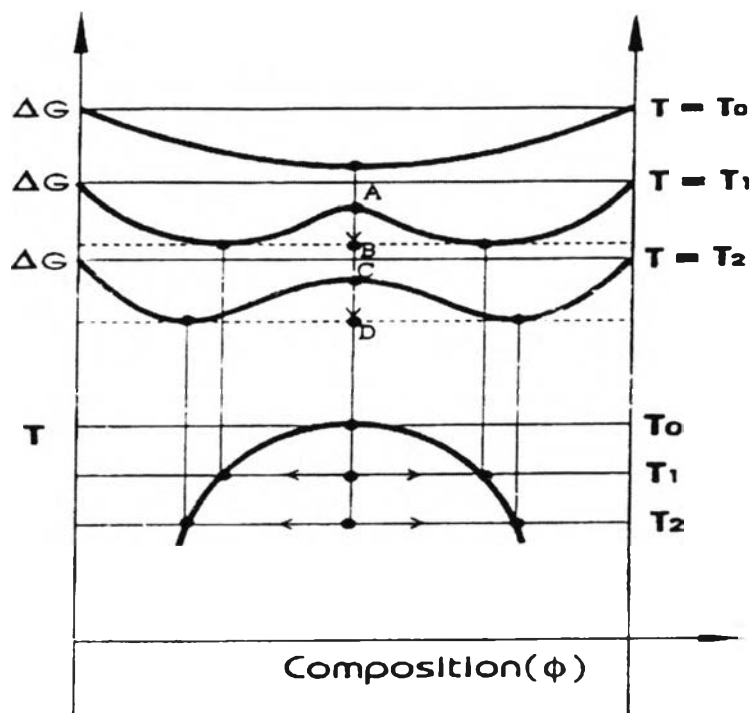
Fig.3.1 Gibb's free energy and phase diagram.[Thongyai, 1994]

3.1.2 Nucleation and Growth

Nucleation is the process of generating within a metastable mother phase the initial fragments of a new and more stable phase. This initial fragment is called a nucleus and its formation requires an increase in the free energy as illustrated in Fig.3.2. In Fig.3.2, any small perturbation in composition about C_0 that results in the appearance of two phases also results in higher free energy. The composition change must be rather large in the right-hand direction before phase separation is accompanied by a free energy reduction. Thus, phase C_0 is metastable and the minimum increase in free energy needed to render the system unstable is defined as its activation energy. This is generally the basis of the nucleation theory. The limit of metastability is the lowest free energy represented by the tie-line C_a-C_a', and it defined as the binodal. Nucleation is the system decomposes with a decrease in free energy, and nuclei grow. This growth process as well as the

corresponding phase structure can be represented by Fig. 3.3.

3.1.3 Binodal and Spinodal

Within the phase diagram, there are two separated regions called binodal and spinodal. The difference between the two regions affects the progress of change in Gibb's free energy to phase separate the system. A binodal system has to increase Gibb's free energy before it can lower the free energy to a stable condition. A spinodal system will automatically lower down the free energy to the stable condition. These phenomena are shown in Fig. 3.4.

From Fig.3.4a, binodal characteristics can be seen. The free energy of the system, at A, has to increase through B, C before it can reduce by itself to D. Fig.3.4b shows spinodal characteristics. The free energy of the system, at A, will decrease spontaneously through B, C and D. The boundary between binodal and spinodal is the point that the slope changes from plus to minus or vice versa. It can be shown graphically or numerically that the boundary is the point that the second order derivative of Gibb's files energy (G'') is equal to zero. Connecting the boundaries at different temperatures, and add another line to the phase diagram as shown in Fig.3.5.

The new line is called the spinodal limit. Within this limit, the system will spontaneously phase separate. The region between the phase separation line and the spinodal limit is called the binodal region. Within this region, the system needs some energy to overcome the barrier before phase separating. In small molecule system this energy may be small, but in the polymer systems this energy becomes larger, so the systems may need an initiator. The initiator may come from the composition fluctuation or from an impurity. It is called a nucleating site.
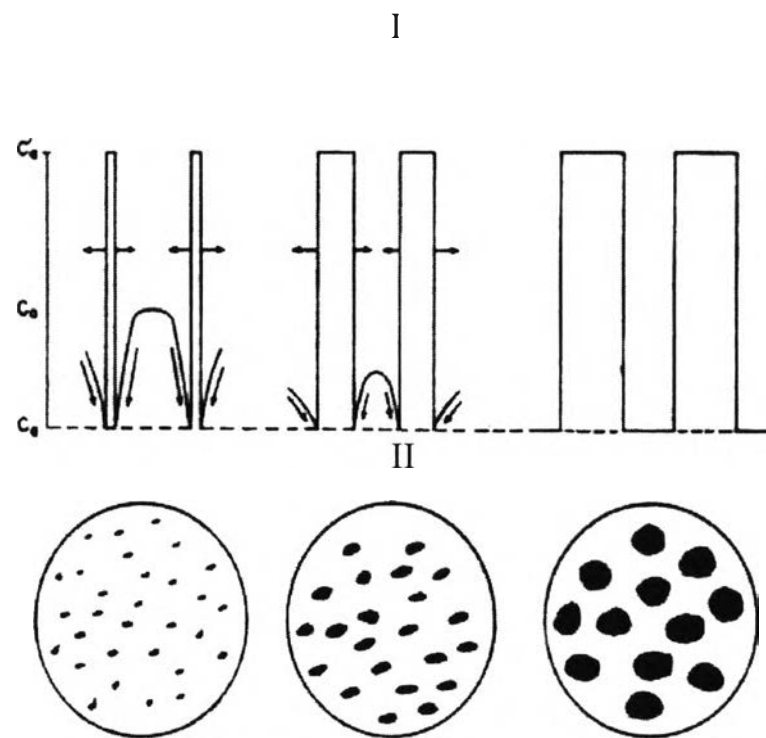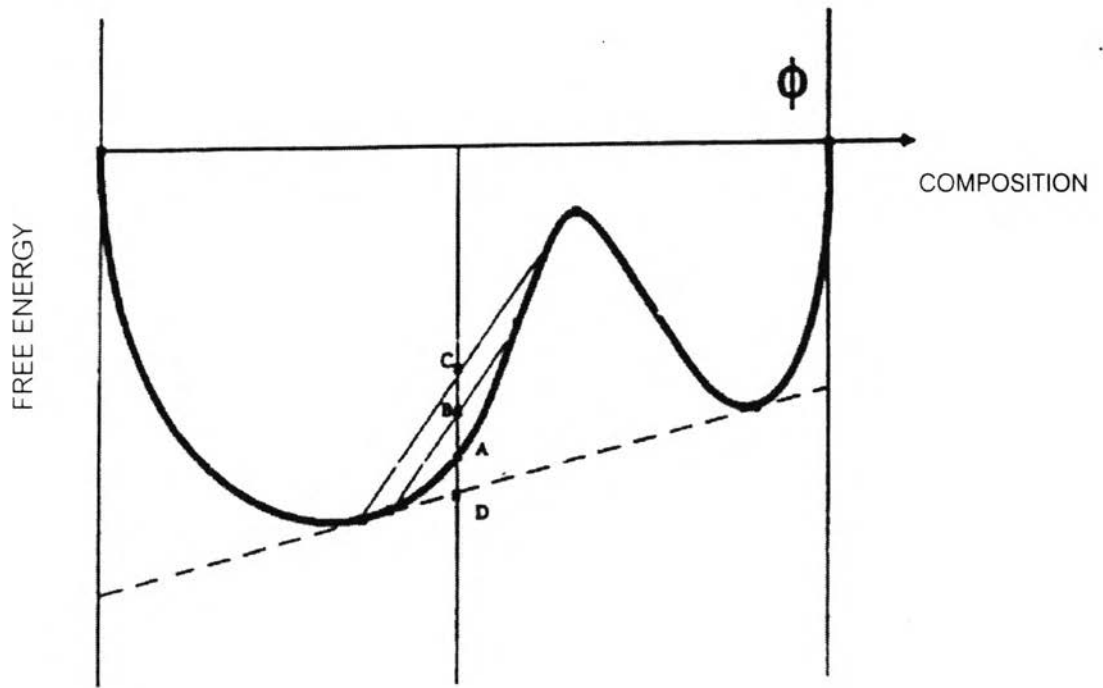
Fig.3.2 Schematic illustration of the free energy-composition diagram for a metastable phase.[Olabisi, 1979]
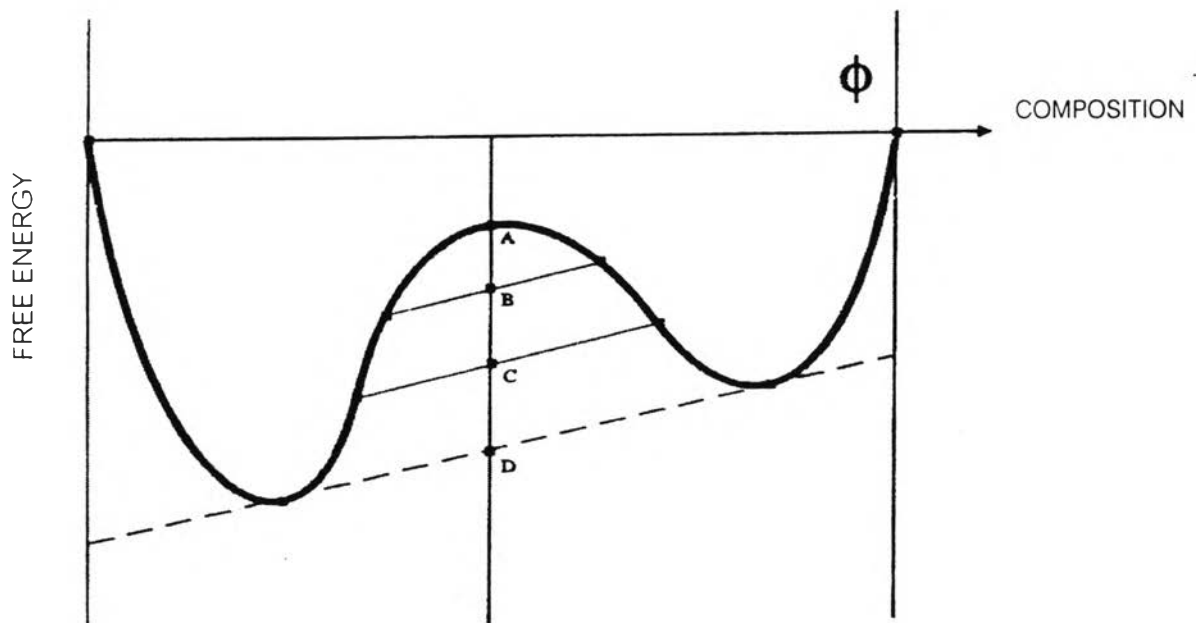
Fig.3.3 Schematic illustration of phase separation by the nucleation and growth mechanism (I) one-dimensional evolution of concentration profiles;(II) two-dimensional picture of the resultant phase structure.[Olabisi, 1979]

a) Binodal

b) Spinodal

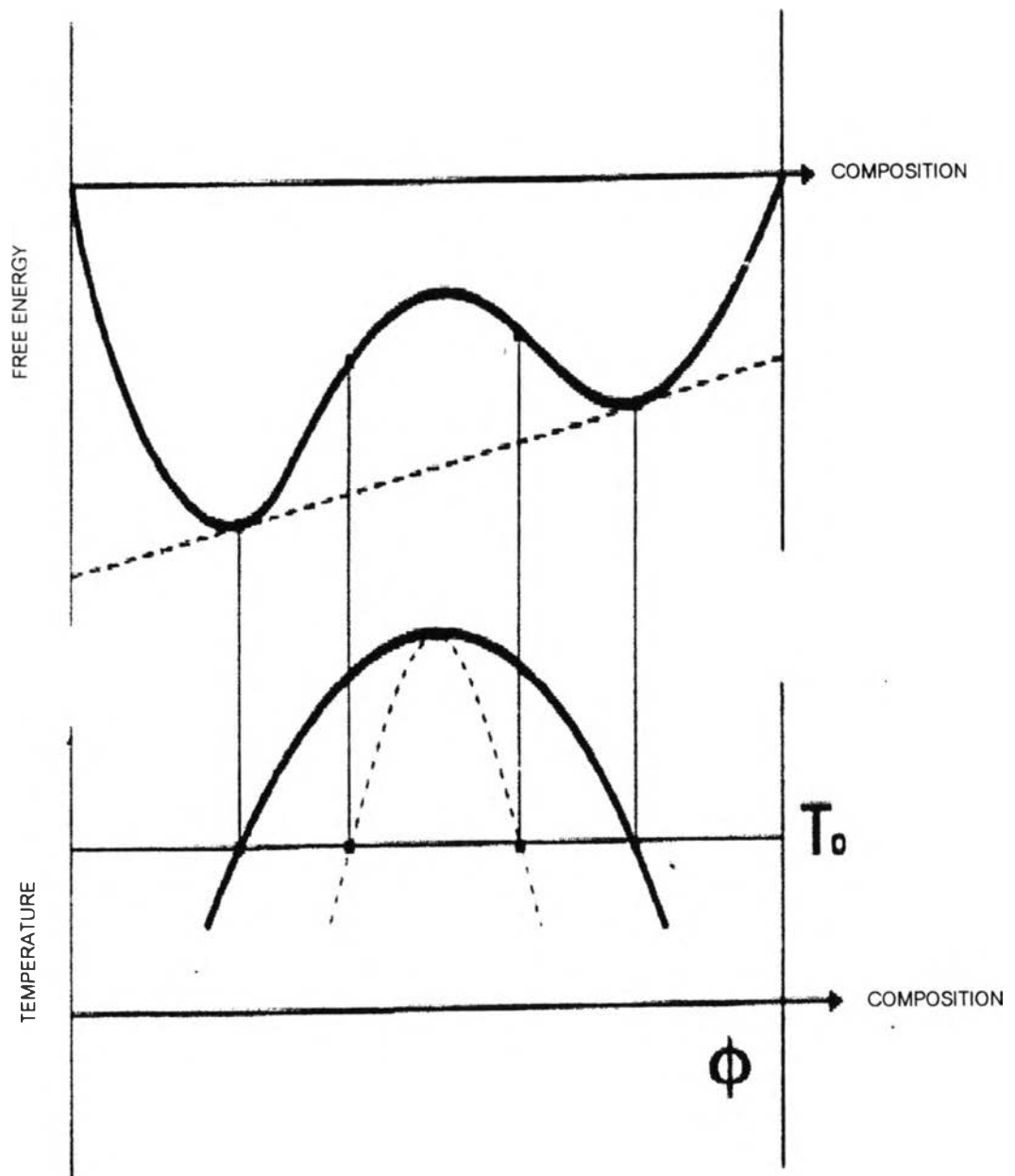**Fig.3.4** Binodal and Spinodal [Thongyai, 1994]

Fig.3.5 Spinodal line and phase diagram.[Thongyai, 1994]

3.1.4 Concentration Fluctuation and Phase Separation

The differences between binodal and spinodal are not only the paths of free energy but also the characteristics of the concentration fluctuations. Two types of the concentration fluctuation can be seen in Fig. 3.6.

From this figure, it is apparent that there are two different types of concentration fluctuation downhill diffusion and uphill diffusion. Binodal concentration fluctuation is downhill diffusion. The high concentration component diffuses to the low concentration boundary and expands the high concentration domain. Spinodal concentration fluctuation is uphill diffusion. The low concentration diffuses into the high concentration domain which continuously grows. This phenomenon is contradictory to the normal diffusion law which says that the difference in the concentration drives the diffusion. In other words, spinodal diffusion is driven by the difference in the chemical potential. The mathematical modelling of spinodal diffusion will be explained in the next section.

Spinodal decomposition is a very interesting phenomenon because it can produce controlled morphology which might result in new or better properties materials, Spinodal decomposition comprises three stages which differ in characteristics of the concentration fluctuations. A schematic diagram of the these three stages is shown in Fig. 3.7.

In the early stage, the amplitude of concentration fluctuations increase with time while the wavelength of concentration fluctuations is kept constant. In the intermediate stage, both the amplitude and wavelength of concentration fluctuation increase with time. In the late stage, the amplitude of concentration fluctuation reaches equilibrium but the wavelength of concentration still grows with time. These three stages describe the simple conceptions of the study of spinodal

decomposition.

In the early stage, the concentration fluctuations can be explained by linearized theory of spinodal decomposition which will be dealt with in the next section. The intermediate and late stage concentration fluctuations can be explained by late stage theory of Furukawa.
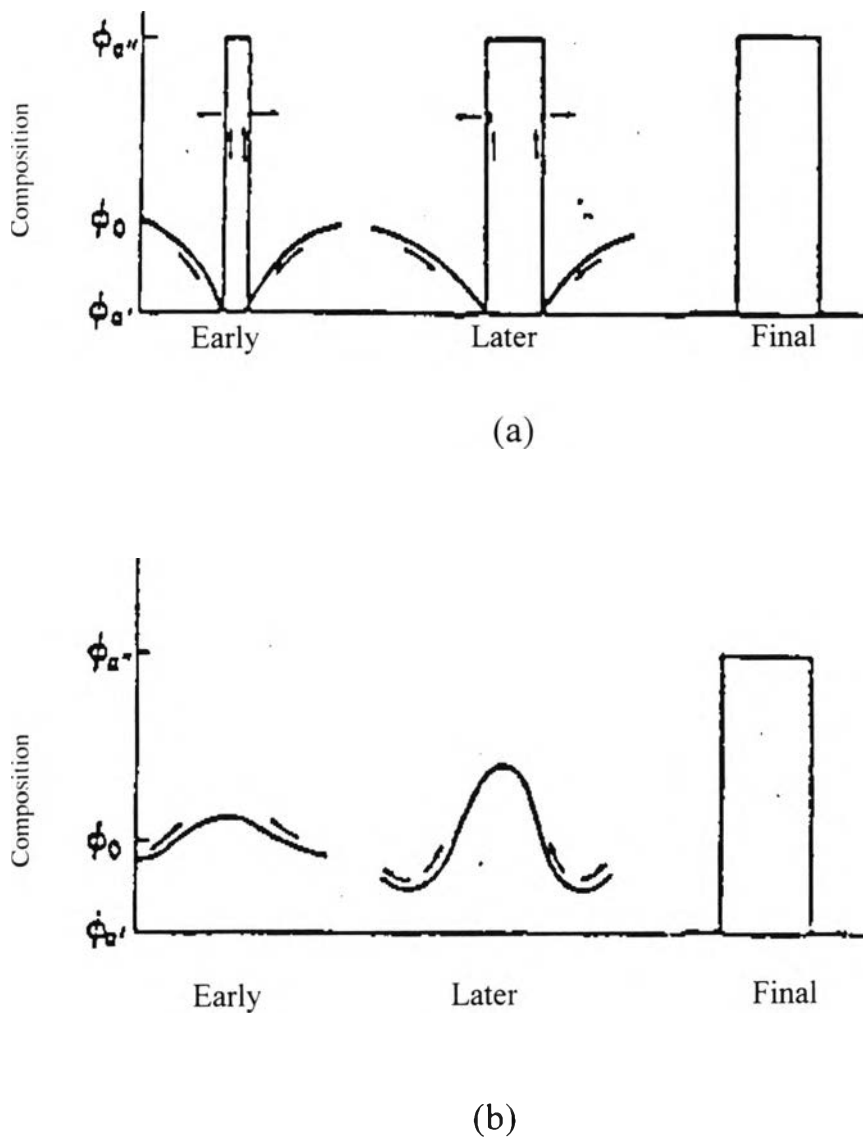

(a)

(b)

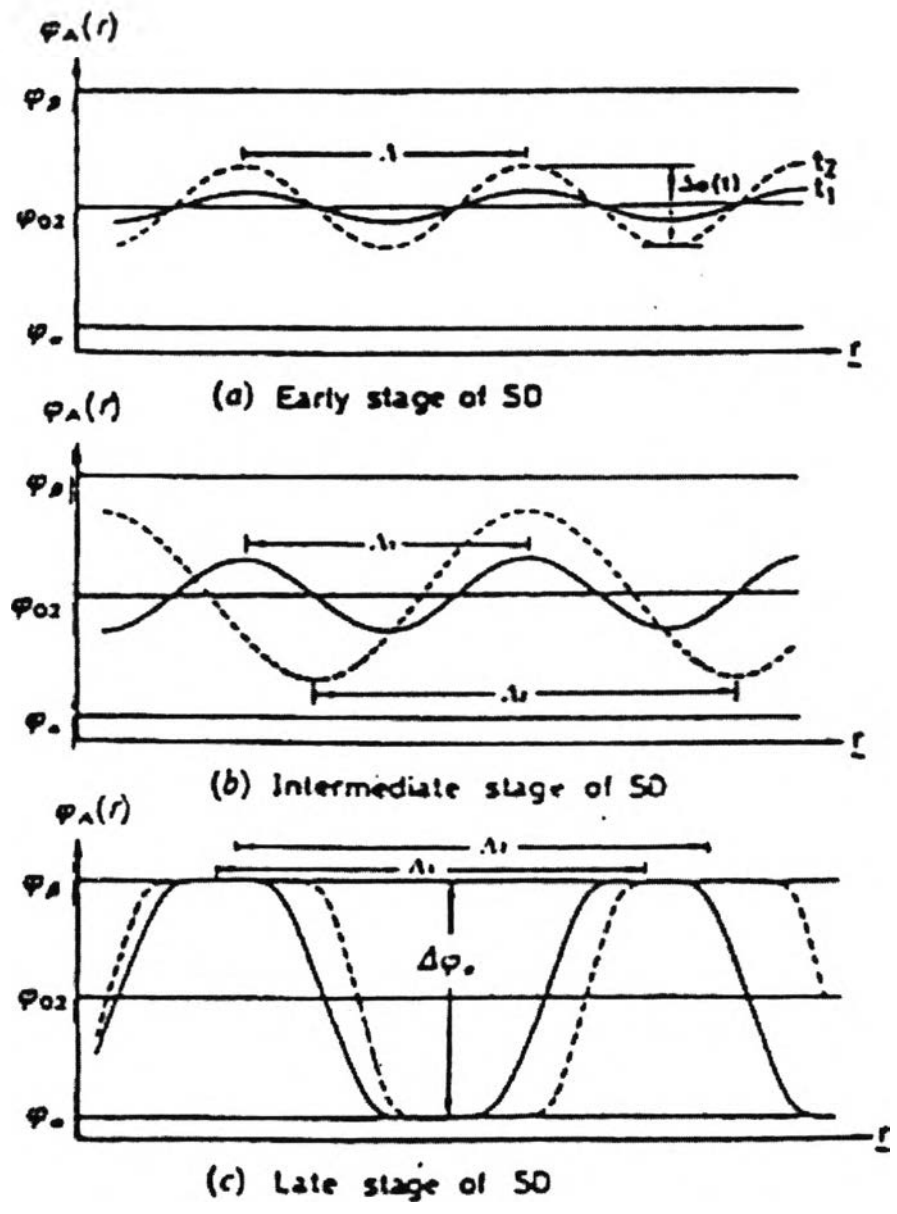**Fig.3.6** (a) Binodal and (b) Concentration Fluctuation.[Thongyai, 1994]

Fig.3.7 Spinodal decomposition concentration fluctuation.[Thongyai, 1994]

3.2 Linearized Theory of Spinodal

In this section, linearized theory of spinodal decomposition of Cahn and Hilliard will be explained. All equations in this section will be given in one dimension to avoid complexity.

3.2.1 Structure Function

Considering a two-component blend system with concentration of the fit component in distance x at time t, (c(x, t)), and average concentration (c_0), the difference in concentration (c(x, t)) can be defined as c_1(x, t)-co. The Fourier transform of c(x, t) into c(q ,t) is as follows,

$$c(q,t) = \int c(x,t) e^{(iqx)} dx \tag{3.2.1}$$

From this equation, the structure function (S(q, t)) is defined as,

$$S(q.t) = \left\langle \left| c(q,t) \right|^2 \right\rangle = \left\langle c(q,t) c(-q,t) \right\rangle \tag{3.2.2}$$

The structure function is important because it can relate the concentration fluctuations with the experiment. In the scattering experiment, the structure function can relate to the scattering cross section per unit solid angle ($d\Sigma/d\Omega$(q, t)) by equation (3.2.3).

$$\frac{d\Sigma}{d\Omega}(q,t) = A.S(q,t) \tag{3.2.3}$$

Where A is an apparatus constant and q is the Fourier transform parameter, can directly relate to angle of scattering. From this equation, for example, in Small Angle Light Scattering (SALS) experiment, the intensity at different angles can be

related to the structure function. So the theory, that describe the concentration fluctuations, can be tested by scattering experiments and the variation of intensity with angle light scattering or value of q, because of q can be calculated from,

$$q = \frac{4\pi n \sin(\theta/2)}{\lambda}$$ (3.2.4)

Where n is the refraction index of the blend, θ is the angle of the diode ,and λ is the wave length of the laser.

3.2.2 Equation of Motion

The driving force for the spinodal decomposition of the system is the chemical potential, which can be defined as,

$$\mu(x,t) = \frac{\partial G(x,t)}{\partial c(x,t)}$$ (3.2.5)

From the difference in the chemical potential, the total flux (J(x, t)) is obtained. The relation between the chemical potential and the total flux can be written as,

$$J(x,t) = -M \frac{\partial \mu(x,t)}{\partial x}$$ (3.2.6)

The mobility (M) is the diffusion constant that relates the chemical potential with the total flux. The equation of motion that explains the concentration fluctuation can be shown below,

$$\frac{\partial c(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x} = M \frac{\partial^2 \mu(x,t)}{\partial x^2}$$ (3.2.7)

3.2.3 Chemical Potential

When the system phase separates, many interfaces will be formed and the free energy of the system is balanced by the free energy of the formed interfaced. In order to estimate the interfacial free energy term, Cahn-Hilliard assume that the Helmholtz free energy (f) of a non homogeneous system could be expressed by a multivariable Taylor's expansion as in the following equations.

$$f = f(c) + L\left(\frac{dc}{dx}\right) + K_1\left(\frac{d^2c}{dx^2}\right) + K_2\left(\frac{d^2c}{dx^2}\right) + \dots \tag{3.2.8}$$

Where

$$L = \frac{\partial f}{\partial\left(\frac{dc}{dx}\right)} \tag{3.2.9}$$

$$K_1 = \frac{\partial f}{\partial\left(\frac{d^2c}{dx^2}\right)} \tag{3.2.10}$$

$$K_2 = \frac{1}{2}\frac{\partial^2 f}{\partial\left(\frac{d^2c}{dx^2}\right)^2} \tag{3.2.11}$$

It is assumed that the system is symmetrical, the L will be equal to zero because the free energy will be invariant with respect to a change in sign of the axis (x). Neglecting the higher order term of equation (3.2.8) (third and higher-order terms), the total free energy of the system of cross-sectional area A (G) can be written as,

$$G = A\int\left[f(c) + K_1\left(\frac{d^2c}{dx^2}\right) + K_2\left(\frac{dc}{dx}\right)^2\right]dx \tag{3.2.12}$$

Integrating the second term by parts, it results,

$$\int K_1 \left(\frac{d^2c}{dx^2} \right) dx = \left[K_1 \left(\frac{dc}{dx} \right) \right]_s - \int \left(\frac{dK_1}{dc} \right) \left(\frac{dc}{dx} \right)^2 dx \tag{3.2.13}$$

The system is assumed to be homogeneous at the surface, the first term on the right-hand side then vanishes. The equation for total free energy which include the interfacial free energy can be written as,

$$G = A \int \left[f(c) + K \left(\frac{dc}{dx} \right)^2 \right] dx \tag{3.2.14}$$

$$K = K_2 - \left(\frac{dK_1}{dc} \right) \tag{3.2.15}$$

From this point, in order to model the chemical potential, equation (3.2.14) is modified when the system reaches equilibrium, i.e., the total free energy becomes minimum and equals to a constant. To find the minimum point of the integral of total free energy, the system must satisfy the Euler equation in this way, which results in the chemical potential as,

$$\mu = \frac{df}{dc} - 2K \left(\frac{dc}{dx} \right)^2 \tag{3.2.16}$$

So, from equation (3.2.7) and (3.2.16), the equation of motion can be written as.

$$\frac{\partial c}{\partial t} = M \frac{\partial^2 \left[\left(\frac{df}{dc} \right) - 2K \left(\frac{d^2c}{dx^2} \right) \right]}{\partial x^2} \tag{3.2.17}$$

3.2.4 Linearized Theory

In order to solve the equation of motion in equation (3.2.17), Cahn and Hilliard linearized df/dc around the mean value (c_o) by Taylor expansion as follows,

$$\left(\frac{\partial f}{\partial c}\right) = \left(\frac{\partial f}{\partial c}\right)_{c_0} + \left(\frac{\partial^2 f}{\partial c^2}\right)_{c_0} c + \sum_{n=3}^{\infty} \frac{1}{n-1}\left(\frac{\partial^n f}{\partial c^n}\right)_{c_0} c^{n-1} \qquad (3.2.18)$$

From this equation, Omitting the third and higher-order term, the equation becomes linearized in c. Since the first term on the right-hand side is a constant, inserting it under the derivative lead to be zero. Therefore inserting equation (3.2.18) into the equation (3.2.17). There exists only the second term on the right hand side of equation (3.2.18) as shown below,

$$\frac{\partial c(x,t)}{\partial t} = M \frac{\partial^2}{\partial x^2}\left[\left(\frac{\partial^2 f}{\partial c^2}\right)_{c_o} - 2K \frac{\partial^2}{\partial x^2}\right]c(x,t) \qquad (3.2.19)$$

This is the linearized equation of Cahn-Hilliard. This equation can be modified by Fourier transform to relate it with the structure function. The Fourier transformation of equation (3.2.19) can be written as,

$$\frac{\partial c(q,t)}{\partial t} = -Mq^2\left[\left(\frac{\partial^2 f}{\partial c^2}\right)_{c_o} + 2Kq^2\right]c(q,t) \qquad (3.2.20)$$

3.2.5 Structure Equation

The structure function $(S(q, t))$ is differentiated to relate the dc/dt. By the definition of the structure function in equation (3.2.2), the differentiation of the structure function can be shown as below.

$$\frac{\partial S(q,t)}{\partial t} = c(-q,t)\frac{\partial c(q,t)}{\partial t} + c(q,t)\frac{\partial c(-q,t)}{\partial t} \qquad (3.2.21)$$

Fortunately, the equation of motion (equation 3.2.20)) does not depend on the sign of q or the dc(q, t)/dt as same as dc(-q, t)/dt. So the structure equation can be written as,

$$\frac{\partial S(q,t)}{\partial t} = -2Mq^2\left[\left(\frac{\partial^2 f}{\partial c^2}\right)_{c_o} + 2Kq^2\right]S(q,t) \qquad (3.2.22)$$

This equation can be solved mathematically by integrating both sides of the equation as follows,

$$\ln(S(q,t)) - \ln(S(q,0)) = -2Mq^2\left[\left(\frac{\partial^2 f}{\partial c^2}\right)_{c_o} + 2Kq^2\right]t \qquad (3.2.23)$$

This equation is the basic equation for scattering experiments. The intensity measured at different angle (I(q, t)) is proportional to the structure function (S(q, t)). Thus this theory can be tested by light scattering experiments. However, this equation does not take account of the thermal fluctuation which can occur at shallow quench depths.

The basic equation of Cahn-Hilliard can be rewritten in other form as,

$$\frac{R(q)}{q^2} = MG'' - 2MKq^2 \qquad (3.2.24)$$

$$R(q) = -q^2 M.S_x^{-1}(q) \qquad (3.2.25)$$

$$S_x(q) = \frac{1}{\left(\left(\frac{\partial^2 f}{\partial c^2}\right)_{c_o} + 2Kq^2\right)} \qquad (3.2.26)$$

Where G" is $\partial^2 f / \partial c^2$. So equation (3.2.23) can be written as,

$$\ln(S(q,t)) - \ln(S(q,0)) = 2R(q)t \qquad (3.2.27)$$

3.3 Spinodal Decomposion of Langer, Bar-on, and Miller's Theory

The basic theory of spinodal decomposition has been developed, primarily from a metallurgical point of view by Cahn, Hilliard and Cook. Cahn developed a more general linearized theory of the spinodal instability. The role of thermal fluctuations was later described by Cook, still within the linear approximation. Cahn pointed out the essential role played by nonlinear effects in determining the nature of the instability and thus in limiting its growth, but Cahn did not attempt to formulate a statistical theory based on his nonlinear equation.

A new computation technique is described. Each of these previous methods had serious limitations that there are largely overcome by a new technique. A quatitative theory of spinodal decomposition is developed which will be sufficiently accurate to be used with confidence in the analysis of experiments

It is assumed that the systems can be described by a single scalar order parameter c(r), it can be visualized as the average concentration of one of the components of a binary solution in some region around the position r. In terms of c (r), Helmholtz free energy can be written in the Ginzburg-Landau form as,

$$F(c) = \int dr \left[\frac{1}{2} \kappa (\nabla c)^2 + f(c) \right] \qquad (3.3.1)$$

The kinetics of this system can be described by use the continuity equation in form

$$\frac{\partial c}{\partial t} = -\nabla \cdot j \qquad (3.3.2)$$

where j is a current density which describes to the interdiffusion of atomic species and is given by

$$j(x) = -M\nabla \frac{\delta F}{\delta c(x)} = -M\nabla\left(-\kappa\nabla^2 c + \frac{\partial f}{\partial c}\right) \qquad (3.3.3)$$

Here, M is a mobility and assumed to be constant, independent of c(x). In order to construct a statistical theory based on the equations of motion (3.3.2) and (3.3.3). A master equation can be derived for the distribution-functional $\rho(c)$ defined on the space of functions c(x). This master equation the form of a functional continuity equation shown as below.

$$\frac{\partial \rho(c)}{\partial t} = -dx \frac{\delta J(x)}{\delta c(x)} \qquad (3.3.4)$$

Where the probability current J(x) is given by

$$J(x) = -M\nabla^2\left(\frac{\delta F}{\delta c(x)}\rho + k_B T \frac{\delta \rho}{\delta c(x)}\right) \qquad (3.3.5)$$

The equation (3.3.4) and (3.3.5) constitute a mathematically complete statement of the model upon which all of our subsequent analysis will be based.

The structure factor S(q) can be calculated, which is the Fourier transform of the two-point correlation function S(x). S(q) is directly proportional to the x-ray scattering intensity at wave-vector transfer (q). Let c_c denotes the fluctuation variable c(x, t) to be

$$c(x,t) = c_1(x,t) - c_o \tag{3.3.6}$$

Then

$$S([x - x_o], t) = \langle c(x,t) c(x_o, t) \rangle \tag{3.3.7}$$

and

$$S(q,t) = \int dx S(x,t) e^{iqx} \tag{3.3.8}$$

Here, the angular brackets denote averages with respect to the distribution functional ρ, and it is assumed translational symmetry after averaging.

The equation of motion for S is obtained by multiplying the master equation by $c(x)c(x_i)$ and integrating over the space of functions c. The resulting equation is best written in the Fourier representation, where it takes the form

$$\frac{\partial S(q,t)}{\partial t} = -2Mq^2 \left[\left(\kappa q^2 + \frac{\partial^2 f}{\partial^2 c} \right)_{c_o} S(q,t) + \left(\frac{1}{2} \frac{\partial^3 f}{\partial c^3} \right)_{c_o} S_3(q) + \left(\frac{1}{6} \frac{\partial^4 f}{\partial c^4} \right)_{c_o} S_4(q,t) + ... \right] \tag{3.3.9}$$

The quantities S_n is denoted by the Fourier transforms of the higher order two-point correlation functions:

$$S_n(|x - x_o|) = \langle u^{n-1}(x) u(x_o) \rangle \tag{3.3.10}$$

From the equation (3.3.9) and (3.3.10), it shows that each of the higher-order correlation functions that it involves only two spatial positions, x and x_o. Thus, a knowledge of the two-point distribution function, $\rho[c(x), c(x_o)]$, would be sufficient to

determine the right-hand side of (3.3.9). By ρ_2, the normalized distribution function obtained from the full functional $\rho\{c\}$ by integrating over c space while holding the values of c fixed at points x and x_o. Of course, an attempt to write exact equations of motion for ρ would lead to a hierarchy of ρ_n equations even less tractable than the correlation-function hierarchy.

Let $\rho_1(c)$ be the single-point distribution function, and write as,

$$\rho[c(x), c(x_o)] \cong \rho_1[c(x)]\rho_1[c(x_o)] \times \{1 + \gamma(|x - x_o|)c(x)c(x_o)\} \quad (3.3.11)$$

The quantity in curly brackets as the first two terms in a power series expansion in the two variables $c(x)$ and $c(x_o)$.

The function $\rho_1(c)$ must be normalized in such a way that

$$\int_{-\infty}^{\infty} \rho_1(c)dc = 1 \quad (3.3.12)$$

and

$$\int_{-\infty}^{\infty} \rho_1(c)cdc = 0 \quad (3.3.13)$$

The second of these conditions follows from the definition of the variable c in equation (3.3.6). From equation (3.3.12) and (3.3.13), it follows that ρ_2 is automatically normalized, it can be written as,

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho_2(c,c_o)dcdc_o = 1 \quad (3.3.14)$$

Where

$$\rho_1(c) = \int_{-\infty}^{\infty} \rho_2(c,c_o)\,dc_o \qquad (3.3.15)$$

The correlation function is

$$S(x) = \left\langle c^2 \right\rangle^2 \gamma(\gamma) \qquad (3.3.16)$$

By using equation (3.3.16) to identify the function $\gamma(\gamma)$ in (3.3.11), The $S_n(x)$ can be written as,

$$S_n(x) \cong \frac{\left\langle c^n \right\rangle}{\left\langle c^2 \right\rangle} S(x) \qquad (3.3.17)$$

Therefore, within the approximation suggested here, the higher-order correlation functions of the form (3.3.10) all have the same x dependence S. The resulting form of equation (3.3.9) as,

$$\frac{\partial S(q,t)}{\partial t} = -2Mq^2 \left[\left(Kq^2 + \left(\frac{\partial^2 f}{\partial c^2} \right)_{c_o} \right) S(q,t) + \sum_{n=3}^{\infty} \frac{1}{(n-1)!} \left(\frac{\partial^n f}{\partial c^n} \right)_{c_o} S_n(q,t) \right] \qquad (3.3.18)$$

In the above equation, the $S_n(q, t)$ term is the Fourier transformation of the higher-order correlation function. Langer et.al. approximated the last term on the right hand side of equation (3.3.18) by the following equation.

$$A(t) = \sum_{n=2}^{\infty} \frac{1}{(n-1)!} \left(\frac{\partial^n f}{\partial c^n} \right)_{c_o} \frac{\left\langle c^n \right\rangle}{\left\langle c^2 \right\rangle} = \sum_{n=2}^{\infty} \frac{1}{(n-1)!} \left(\frac{\partial^n f}{\partial c^n} \right)_{c_o} \frac{S_n(q,t)}{S(q,t)} \qquad (3.3.19)$$

Equation (3.3.19) can be rewritten as,

$$A(t)S(q,t) = \sum_{n=2}^{\infty} \frac{1}{(n-1)!} \left(\frac{\partial^n f}{\partial c^n} \right)_{c_o} S_n(q,t) \qquad (3.3.20)$$

Substitution of equation (3.3.20) in equation 3.3.18, one can obtain,

$$\frac{\partial S(q,t)}{\partial t} = -2Mq^2 \left[Kq^2 + A(t) \right] S(q,t) \qquad (3.3.21)$$

3.4 Spinodal Decomposition of Akcasu's Theory

This theory approach is essentially the same as the one developed by Langer, Bar-on, and Miller. There are however differences in the way the fluctuations are included in the nonlinear theory, and in the details of the calculations arising from the chain connectivity (polymer effect) in the case of polymer blends. In addition, the variation of the scattering intensity as a function of time at various wave numbers is studied not only during the spinodal decomposition but also during dissolution. The formalism is also applicable to transients in I(q, t) following step temperature changes within the single phase region.

Considering a melt of two homopolymer species A and B. The volume fractions of monomers at a point r and time a denoted by $\phi_A(r, t)$ and $\phi_B(r, t)$. The mixture is assumed to be incompressible so that the local volume fractions satisfy $\phi_A(r,t)+\phi_B(r, t)$ equal 1. When the mixture is in a homogeneous equilibrium state, the volume fractions are uniform and denoted by $\phi_A =\phi_0$ and $\phi_B = 1-\phi_0$. The incremental volume fraction of the component is defined as $\varphi(r, t) = \phi_A(r, t)-\phi_0$. The monomeric volumes V_A and V_B of the species are allowed to be different.

The intensity I(q, t) of the scattering beam in a scattering experiment is related to the Fourier transform of φ (r, t).

$$I(q,t) = \left\langle |\varphi_q(t)|^2 \right\rangle \tag{3.4.1}$$

Where q is the momentum transfer vector, and $\varphi_q(t)$ denotes the discrete Fourier transform of φ (r,t),

$$\varphi_q(t) = \frac{1}{V} \int d^3 r e^{iq \cdot r} \varphi(r,t) \tag{3.4.2}$$

In which V is the volume of the system. It notes that both φ(r, t) and $\varphi_q(t)$ are dimensionless. When the mixture is an equilibrium state, I(q, t) is independent of time. and is given by $I_{eq}(q) = (V_0/V)S(q)$, where V_0 is a reference volume to be specified later, and S(q) is the static structure factor, calculated by de Genes in the small q limit approximation as

$$\frac{1}{S(q)} = 2\left\{ \chi_s - \chi + \frac{q^2}{36}\left[\frac{\sigma_A^2}{z_A \phi_o} + \frac{\sigma_B^2}{z_B(1-\phi_o)} \right] \right\} \tag{3.4.3}$$

Where χ_s denotes the value of the interaction parameter on spinodal,

$$\chi_s = \frac{1}{2}\left[\frac{1}{z_A N_A \phi_o} + \frac{1}{z_B N_B(1-\phi_o)} \right] \tag{3.4.4}$$

In which χ is the Flory interaction parameter, and N_α is the number of monomer, and $z_\alpha = V_\alpha/V_0$ denotes the normalized monomeric volumes relative to the reference volume V_0, a chain kind α = A, B. In equation (3), σ_α denotes the statistical segment lengths of an α chain.

Following Binder, the free energy excess for a binary mixture of A and B homopolymers can be written as,

$$\frac{\Delta F}{k_B T} = \int d^3 r \frac{1}{v_o} \left\{ f[\phi(r)] + \frac{1}{36} \left[\frac{\sigma_A^2}{z_A \phi(r)} + \frac{\sigma_B^2}{z_B(1-\phi(r))} \right] |\nabla \phi(r)|^2 \right\} \qquad \text{(3.4.5 a)}$$

Where $\phi(r) = \phi_A(r)$, $k_B T$ is the temperature in energy units, and

$$f(\phi) = \frac{\phi}{z_A N_A} \ln \phi + \frac{(1-\phi)}{z_B N_B} \ln(1-\phi) + \chi\phi(1-\phi) \qquad \text{(3.4.5 b)}$$

The functional derivation of ΔF with respect to $\phi_A(r)$ yields the the local chemical potential difference $\mu(r)$, and when $V_A = V_B = V_o$ and V_o is set equal to unity, this equation can be written as

$$\mu(r) = \frac{k_B T}{v_o} \left\{ \begin{array}{l} \dfrac{1}{z_A N_A}[1 + \ln\phi_A] - \dfrac{1}{z_B N_B}[1 + \ln\phi_B] + \chi(1 - 2\phi_A) - \\ \dfrac{1}{18}\left[\dfrac{\sigma_A^2}{z_A \phi_A} + \dfrac{\sigma_B^2}{z_B \phi_B}\right]\nabla^2\phi_A + \dfrac{1}{36}\left[\dfrac{\sigma_A^2}{z_A \phi_A^2} - \dfrac{\sigma_B^2}{z_B \phi_B^2}\right]|\nabla\phi_A|^2 \end{array} \right\} \qquad \text{(3.4.6)}$$

When $V_A = V_B = V_c$ and V_c is set equal to unity, equation (3.4.6) can be written as

$$\mu(r) = k_B T \left\{ \begin{array}{l} \left[\dfrac{\ln\phi_A + 1}{N_A}\right] - \left[\dfrac{\ln(1-\phi_A) + 1}{N_B}\right] + \chi(1 - 2\phi_A) - \\ \dfrac{1}{18}\left[\dfrac{\sigma_A^2}{\phi_A} + \dfrac{\sigma_B^2}{1-\phi_A}\right]\nabla^2\phi_A + \dfrac{1}{36}\left[\dfrac{\sigma_A^2}{\phi_A^2} - \dfrac{\sigma_B^2}{(1-\phi_A)^2}\right]|\nabla\phi_A|^2 \end{array} \right\} \qquad \text{(3.4.7)}$$

The $\phi_q(t)$ satisfies the following nonlinear stochastic diffusion equation:

$$\frac{\partial \varphi_q(t)}{\partial t} = -q^2 V \frac{\Lambda_q}{k_B T} \mu_q(t) + \eta_q(t) \tag{3.4.8}$$

Where Λ_q is the q-dependent Onsager coefficient, with the discrete Fourier transform of the nonlocal Onsager coefficient chemical potential $\Lambda[r]$, $\mu_q(t)$ is the discrete Fourier transform of the local chemical potential difference given in equation(3.4.7) and $\eta_q(t)$ is the random force accounting for thermal fluctuations, the statistical properties is assumed to be a delta correlated random process with autocovariance C(q) as

$$\langle \eta_q(t)\varphi_{-q}(t)\rangle + \langle \varphi_q(t)\eta_{-q}(t)\rangle = C(q) \tag{3.4.9}$$

The factor V denoting the volume of the system comes from the discrete Fourier transform of the convolution. In order to obtain an equation for $\varphi_q(t)$, on substitutes $\phi(r, t) = \phi_o + \varphi(r, t)$ in equation (3.4.7). It can be written as

$$\mu(r) = k_B T \cdot \begin{bmatrix} \frac{\ln(\phi_o + \varphi(r,t))}{N_A} - \frac{\ln[1-(\phi_o + \varphi(r,t))]}{N_B} + \chi[1 - 2(\phi_o + \varphi(r,t))] - \\ \frac{1}{18}\left[\frac{\sigma_A^2}{\phi_o + \varphi(r,t)} + \frac{\sigma_B^2}{1-(\phi_o + \varphi(r,t))}\right]\nabla^2(\phi_o + \varphi(r,t)) + \\ \frac{1}{36}\left[\frac{\sigma_A^2}{[\phi_o + \varphi(r,t)]^2} - \frac{\sigma_B^2}{[1-(\phi_o + \varphi(r,t))]^2}\right]|\nabla(\phi_o + \varphi(r,t))|^2 \end{bmatrix} \tag{3.4.10}$$

From equation (3.4.8), (3.4.9) and (3.4.10), expands $\mu(r, t)$ into a power series in power of $\varphi(r,t)$, and then perform discrete Fourier transform. After lengthy but straightforward calculations one obtains,

$$\frac{\partial \varphi_q(t)}{\partial t} = -R(q) \left\{ \begin{array}{l} \varphi_q(t) + S(q) \sum_{q1,q2} \Gamma_2(q,q_1,q_2) \delta(q,q_1 + q_2) \varphi_{q1}(t) \varphi_{q2}(t) + \\ S(q) \sum_{q1,q2,q_3} \Gamma_3(q,q_1,q_2,q_3) \delta(q,q_1 + q_2 + q_3) \varphi_{q1}(t) \varphi_{q2}(t) \varphi_{q3}(t) \end{array} \right\} + \eta_q(t)$$

(3.4.11)

Where the relaxation frequency R(q) *is* found as

$$R(q) = \frac{q^2 \Lambda(q)}{S(q)}$$

(3.4.12)

In which S(q) is given in equation (3.4.3). In the small-q limit, The R(q) value can be expressed as,

$$R(q) = 2q^2 \Lambda(q) \left\{ \chi_s - \chi + \frac{q^2}{36} \left[\frac{\sigma_A^2}{z_A \phi_o} + \frac{\sigma_B^2}{z_B(1-\phi_o)} \right] \right\}$$

(3.4.13)

It shows this equation includes only the coupling among the concentration modes arising from the nonlinearity of equation (3.4.8), but does not include the coupling between the modes representing the concentration and the momentum fluctuations. Terms arising from fourth and higher order nonlinear are neglected. In equation (3.4.12) and (3.4.13), the $\Lambda_q(V/V_o)$ term is replaced by $\Lambda(q)$ by redefining the Onsager coefficient. The vertex function $\Gamma_2(q, q_1, q_2)$ in equation (3.4.11) is obtained as follows,

$$\Gamma_2(q,q_1,q_2) = U_1 - U_2 \frac{1}{2} \left(q^2 + q_1^2 + q_2^2 \right)$$

(3.4.14 a)

with

$$U_1 = \frac{1}{2} \left[\frac{1}{z_B N_B (1-\phi_o)^2} - \frac{1}{z_A N_A \phi_o^2} \right]$$

(3.4.14 b)

$$U_2 = \frac{1}{36}\left[\frac{\sigma_A^2}{z_A \phi_o^2} - \frac{\sigma_B^2}{z_B(1-\phi_o)^2}\right]$$

(3.4.14 c)

In obtaining equation (3.4.14 a), the second term in equation (3.4.11) is symmetrized by interchanging q_1 and q_2, adding the resulting equations and dividing by 2. It is to be noted that $\Gamma_2(q, q_1, q_2)$ vanishs in the case of a symmetric mixture in which the molecules of the two species are identical to each other so that $N_A = N_B$, $z_A = z_B$, $\sigma_A = \sigma_B$, and their volume fractions are equal. In the present application the mixture is not symmetric, an hence $\Gamma_2(q, q_1, q_2) \neq 0$.

The vertex function $\Gamma_3(q, q_1, q_2, q_3)$ is calculated as

$$\Gamma_3(q, q_1, q_2, q_3) = Z_1 + \frac{Z_2}{6}\left(q^2 + q_1^2 + q_2^2 + q_3^2\right)$$

(3.4.15 a)

with

$$Z_1 = \frac{1}{3}\left[\frac{1}{z_A N_A \phi_o^3} + \frac{1}{z_B N_B (1-\phi_o)^3}\right]$$

(3.4.15 b)

$$Z_2 = \frac{1}{18}\left[\frac{\sigma_A^2}{z_A \phi_o^3} + \frac{\sigma_B^2}{z_B(1-\phi_o)^3}\right]$$

(3.4.15 c)

In equation (3.4.11), inserting the expansion of $\mu(r, t)$ in power $\varphi(r, t)$ after the cubic term.

The equation for intensity is obtained from $I(q, t) = <|\varphi_q(t)|^2>$ using the above stochastic nonlinear description of the mixture. For this purpose, the equation (3.4.11) is multiplied by $\varphi_{-q}(t)$, and its complex conjugated by $\varphi_q(t)$, and add them up, and make use of equation (3.4.9), obtaining

$$\frac{dI(q,t)}{\partial t} = -2R(q)\left[\begin{array}{l} I(q,t) + S(q)\sum_{q1,q2}\Gamma_2(q,q_1,q_2)\delta(q,q_1+q_2)\langle\varphi_{q1}(t)\varphi_{q2}(t)\varphi_{-q}(t)\rangle + \\ S(q)\sum_{q1,q2,q3}\Gamma_3(q,q_1,q_2,q_3)\delta(q,q_1+q_2+q_3)\langle\varphi_{q1}(t)\varphi_{q2}(t)\varphi_{q3}(t)\varphi_{-q}(t)\rangle \end{array} \right] + C(q)$$

(3.4.16)

In the linear theory, equation (3.4.16) is approximated by

$$\frac{dI(q,t)}{dt} = -2R(q)I(q,t) + C(q)$$

(3.4.17)

In the nonlinear theory, one has to introduce approximations to express the third and fourth order correlation functions in equation (3.4.16), in terms of I(q, t). It is assumed that $\varphi_q(t)$ for different values of q are Gaussian random variables with zero mean, then it can be written as,

$$\langle\varphi_{q1}(t)\varphi_{q2}(t)\varphi_{-q}(t)\rangle = 0$$

(3.4.18)

$$\langle\varphi_{q1}(t)\varphi_{q2}(t)\varphi_{q3}(t)\varphi_{-q}(t)\rangle = 3I(q,t)I(q,t)\sigma(q_1-q)\sigma(q_2+q3)$$

(3.4.19)

Substitution of equation (3.4.18) and (3.4.19) into equation (3.4.16) yields

$$\frac{dI(q,t)}{dt} = -2R(q)I(q,t)[1 + Z(q,t)] + C(q)$$

(3.4.20)

Where

$$Z(q,t) = \sum_q \gamma(q,q')I(q',t)$$

(3.4.21)

In equation (3.4.21), the $\gamma(q, q')$ term can be expressed as,

$$\gamma(q,q') = 3\Gamma_3(q,-q,q',-q')S(q) \qquad (3.4.22)$$

Where Γ_3(q,-q, q',-q') is to be obtained from equation (3.4.15 a), and S(q) is given equation(3.4.3), in small limit, The γ(q, q') value can be written as

$$\gamma(q,q') = \frac{3}{2}\left\{ \frac{Z_1 + (Z_2/3)(q^2 + q'^2)}{\chi_s - \chi + (q^2/36)[\sigma_A^2/z_A\phi_o + \sigma_B^2/z_B(1-\phi_o)]} \right\} \qquad (3.4.23)$$

Where Z_1 and Z_2 are defined in equation (3.4.15 b) and (3.4.15 c).

3.5 Spinodal Decomposition of Nauman's Theory

Starting from Gibbs 'free energy of many given by Landau-Ginzburg, the equation can be written as,

$$G_{total} = \iiint G dv = \iiint \left[g + \frac{\kappa}{2}(\nabla a)^2 \right] dv \qquad (3.5.1)$$

Where, $a = a(x,y,z)$ is the mole fraction of component A, and G=g+(1/2κ)x $(\nabla a)^2$ is the free energy of mixing per unit volume. The concentration gradient term,$1/2\kappa(\nabla a)^2$, is similar to the density gradient term used by Van der Waals but its appearance in the modern literature was established by Cahn and Hilliard. For the sake of simplicity, temperature and pressure are assumed to be constant, and number of moles of each component are fixed in this work.

3.5.1 A Generalized Chemical Potential

Considering a multicomponent generalization of equation (3.5.1). It is supposed there are just three components, A, B and C. The Gibbs' free energy then can be written as,

$$G_{total} = \iiint G(a,b,c,\nabla a,\nabla b,\nabla c)dv \qquad (3.5.2)$$

Where a,b,c are the mole fractions of components A, B, C respectively so that $a+b+c=1$. It is defined by a new thermodynamic property, the variational free energy, Γ, using the following differential relationships,

$$\left(\frac{\partial \Gamma}{\partial a}\right)_{b,c} = \left(\frac{\delta G_{total}}{\delta a}\right)_{b,c} \qquad (3.5.3)$$

With similar expressions holding for $\partial\Gamma/\partial b$ and $\partial\Gamma/\partial c$. It can be seen that $\delta G_{total}/\delta a$ is the variational partial derivative defined as,

$$\left(\frac{\delta G_{total}}{\partial a}\right)_{b,c} = \left(\frac{\partial G}{\partial a}\right)_{b,c} - \nabla.\left(\frac{\partial G}{\partial(\nabla a)}\right)_{b,c} \qquad (3.5.4)$$

It should be noted that the definition can be extended to situations where G depends on higher derivatives such as $\nabla^2 a$, yet the above formulation suffices for present applications.

The generalized chemical potentials is the partial molar property of the variational free energy Γ, just as the chemical potential is the partial molar property of the free energy g. The chemical potential is defined as,

$$\mu_A = \Gamma + (b+c)\left(\frac{\partial\Gamma}{\partial a}\right)_{b,c} - b\left(\frac{\partial\Gamma}{\partial b}\right)_{a,c} - c\left(\frac{\partial\Gamma}{\partial c}\right)_{a,b} \qquad (3.5.5)$$

μ_B and μ_C have similar equations. This definition of chemical potential reduces to the ordinary form when G_{total} depends only on a,b,c and not the composition gradients. It satisfies Euler's theorem in the form,

$$\Gamma = a\mu_A + b\mu_B + c\mu_C \tag{3.5.6}$$

The Gibbs-Duhem equation can be shown as,

$$a\nabla\mu_A + b\nabla\mu_B + c\nabla\mu_C = o \tag{3.5.7}$$

The above definitions allow chemical potentials to be calculated for each of the n components in a multicomponent system.

Considering of the minimization of equation (3.5.2), which is subject to the material balance constraints,

$$\frac{1}{V}\iiint a\,dv = \bar{a};\frac{1}{V}\iiint b\,dv = \bar{b};\frac{1}{V}\iiint c\,dv = \bar{c} \tag{3.5.8}$$

The two composition variables are independent and will apply the calculus of variations as though all three were independent. This gives a partial differential form of the Euler-Lagrange equation as,

$$\left(\frac{\delta G_{total}}{\delta a}\right)_{b,c} = \gamma_A = cons\tan t \tag{3.5.9}$$

From equation (3.5.3), it therefore appears that $\partial\Gamma/\partial a$ is constant. Similarly, $\partial\Gamma/\partial b$ and $\partial\Gamma/\partial c$ are constant. Thus,

$$\Gamma = \gamma_A a + \gamma_B b + \gamma_C c \tag{3.5.10}$$

It is assumed in this work that the constant of integration is zero. Inserting Γ into equation (3.5.5) gives

$$\mu_A = \gamma_A \qquad \mu_B = \gamma_B \qquad \mu_C = \gamma_C \qquad (3.5.11)$$

This is Gibbs' condition of equilibrium applied to the case of generalized chemical potentials.

The case of two component with $G = g + 1/2\ \kappa(\nu a)^2$ as given by the Landau-Ginzburg function. Equation (3.5.3) gives $\partial\Gamma/\partial a$ and $\partial\Gamma/\partial b$ which are integrated to give

$$\Gamma = g + \frac{1}{2}\kappa(\nabla a)^2 \qquad (3.5.12)$$

So that $\Gamma + G = 2g$. By using equation (3.5.5) to find μ_A and μ_B, and the equilibrium condition equation (3.5.11), It is can be written as,

$$\mu_A = g - \frac{1}{2}\kappa(\nabla a)^2 + (1-a)\left(g' - \kappa\nabla^2 a\right) = \gamma_A \qquad (3.5.13)$$

$$\mu_B = g - \frac{1}{2}\kappa(\nabla a)^2 - a\left(g' - \kappa\nabla^2 a\right) = \gamma_B \qquad (3.5.14)$$

3.5.2 Approach To Equilibrium By Diffusion

As mentioned earlier, there are many mechanisms by which real systems can approach equilibrium. Diffusion is to be considered here. Novick-Cohen and Segal followed Cahn and Hilliard in developing the following equation for the net molar diffusion flux of component A.

$$J_A = -M\nabla(\mu_A - \mu_B) = -M\nabla\left(g' - \kappa\nabla^2 a\right) \qquad (3.5.15)$$

This flux assumes equal molar counterdiffusion relative to any possible bulk motion of the mixture. The condition that $J_A=0$ at equilibrium seemed consistent with the Euler-Lagrange condition that $g'-\kappa\nabla 2 a=$ constant. However, for $\kappa = 0$, equation (3.5.13) predicts the unphysical result that diffusion will be zero for the three-phase mixture contemplated by Novick-Cohen and Segel. Also, equation (3.5.13) does not reduce to Fick' s law in the case of an ideal mixture. The reason for these problems is that the driving force for diffusion assumed by equation (3.5.13) is subtly wrong. The modern literature (Bird et.al.,1960; Ghai et.al.,1973; Cussler, 1984) bases the driving force directly on $\nabla\mu_A$ and not on $\nabla(\mu_A-\nabla\mu_B)$. A pregradient mole fraction is also included in conformity with the Gibbs-Duhem relationship. Thus

$$J = J_A = -D_{AB}a\nabla\mu_A = -D_{AB}a\nabla a(d\mu_A / da) = -J_B = +D_{AB}b\nabla\mu_B \quad (3.5.16)$$

Equation (3.5.14) reduces to Fick' s law with constant D_{AB} for an ideal solution, It is assumed that $\nabla\mu_A=\nabla\mu_B = 0$ for $J = 0$. This gives $\mu_A = \gamma_A$ and $\mu_B = \gamma_B$ at equilibrium.

It is assumed that equation (3.5.14) remains valid for the present situation where chemical potential depends on gradients energy. Thus the net diffusion flux of component A is

$$J = J_A = -D_{AB}a\nabla\left[g - \frac{\kappa}{2}(\nabla a)^2 + (1-a)\left(g'-\kappa\nabla^2 a\right)\right] \qquad (3.5.17\ a)$$

$$J = -D_{AB}a(1-a)\nabla\left(g'-\kappa\nabla^2 a\right) \qquad (3.5.17\ b)$$

$$J = -D_{AB}a(1-a)\left(g''-\kappa\nabla^3 a\right) \qquad (3.5.17\ c)$$

The corresponding continuity equation is

$$\frac{\partial a}{\partial t} = D_{AB}\nabla a(1-a)\nabla\left(g'-\kappa\nabla^2 a\right) = D_{AB}\nabla a(1-a)\left(g''-\kappa\nabla^3 a\right) \qquad (3.5.18)$$

This result differs from that of Cahn and Hilliard by a factor of $a(1-a)$.