

CHAPTER II

LITERATURE REVIEW

In this chapter, the literature on the description of spinodal decomposition theory on the experiment results are presented.

Hashimoto, T., Kumaki, J., and Kawai, H. [1983] investigated the dynamics of liquid-liquid phase separation of a polymer blend of polystyrene and poly(vinyl methyl ether) by time-resolved elastic light scattering techniques in both the nucleation-growth (NG) and spinodal decomposition (SD) regimes. It was found that in the early stage of SD the scattered intensity at a given momentum transfer, $q = (4\pi/\lambda) \sin(\theta/2)$, which increases exponentially with time after the initiation of the isothermal phase separation involved by a temperature jump from the temperature well below the binodal point. The relaxation rate $2R(q)$ of the intensity increase as a function of q such that $R(q)/q^2$ linearly decreases with q^2 , in accordance with the linear theories of SD originally proposed by Cahn for small molecules and extended by de Gennes for polymers. The spinodal temperature was obtained from the dynamics measured as a function of temperature in the linear SD regime. In the later stage of SD, the intensity increase with time starts to deviate from exponential behavior and the scattering maximum shifts to smaller q , corresponding to the onset of the coarsening process. The higher the superheating, the earlier the stage where the coarsening starts. In NG regime the intensity increases nonexponentially with time.

Snyder, H.S. and Meakin, P. [1983] investigated the time development of structure in polystyrene/poly(vinyl methyl ether) blends using conventional light scattering techniques. They showed that by utilizing the light scattering invariant and the angular dependence of scattering, one may quantitatively describe the

early stages of phase separation within the framework of the linearized Cahn-Hilliard expression. By extrapolating the measured diffusion constant to where it undergoes a sign change, one may also determine the spinodal curve.

Izumitan, T. and Hashimoto, T. [1985] investigated isothermal demixing process of binary polymer mixtures of SBR (styrene-butadiene random copolymer) and polybutadiene at deep quench depths by time-resolved light scattering technique. The results indicated that the systems undergo extremely slow spinodal decomposition of the type as adequately characterized by Cahn's linearized theory in the early stage and in the small q regime ($q \leq q_{\max} \approx 10^5 \text{ cm}^{-1}$) covered in this experiment where q is wave number of growing fluctuations and q_{\max} is the q value having maximum growth rate. The spinodal decomposition studied in this work was that in the diffusion-control regime, and in the slowest case of the decomposition, the early stage was found to extend up to about 80 min, corresponding to the reduced time about 2.7. The shortest reduced time achieved in this experiment is about 0.03.

Hashimoto, T., Itakura, M., and Shimidzu, N. [1986] investigated the early-to-late stage of the spinodal decomposition (SD) of the critical mixtures of polystyrene and poly(vinyl methyl ether) by the time-resolved light scattering technique. The early stage SD where the time evolution of the fluctuations can be described, at least with a good approximation, by the linearized theory of Cahn. The later stage unmixing processes were found to give the scaling laws on the reduced wave number of the dominant scales. In the intermediate stage, indicating that both the wavelength and amplitude of the dominant mode of fluctuations grow with time. In the late stage, the scaling relation was found and dynamical scaling relation was found on the scattering function, indicating that it exists the self-similarity between the structures developed at different times, and the unmixing kinetics is scaled with a single length parameter. The experimental

behavior of q_m was compared with those predicted by some theoretical models, and some unique features of unmixing kinetics of polymer were suggested to arise from entanglements of the long chain time.

Elder, K.R., Rogers, T.M., and Desai, R.C. [1988] studied early stages of spinodal decomposition by computer simulation using discretized space and time to examine the early stages of phase separation as described by the Cahn-Hilliard-Cook equation (CHCE). The relative simplicity of this simulation provides a direct test of various mathematical treatments of the nonlinear term in the CHCE. In particular, the numerical results are used to ascertain the validity of the approximations inherent in the perturbative expansions of Grant, San Miguel, Vinals, and Gunton, and of Langer, Bar-on, and Miller. The time of validity of all approximations is shown to be logarithmically related to the strength of the thermal fluctuations. In addition, the effect of the initial state on the dynamical evolution of the order parameter is examined.

Toral, R., Chakrabari, A., and Gunton, J.D. [1988] studied the results of the Cahn-Hilliard equation in three dimensions. They studied the asymptotic time dependence of the characteristic domain size $R(t)$, as well as the scaling of the pair correlation function and the structure function. The results indicate that dynamics scaling holds at sufficiently late times and that the data for $R(t)$ are consistent with a Lifshitz-Slyozov growth law $R(t) \sim t^{1/3}$

Sato, T., and Han, C.C.[1988] studied the dynamics of concentration fluctuation in a deuterated polystyrene/ poly(vinylmethylether) blend system by the temperature jump and also by the reverse quench light scattering techniques. The growth or decay rate $R(q)$ in Cahn-Hilliard-Cook's equation is almost proportional to the square of scattering wave vector. This indicates that the interracial free energy contribution to the concentration fluctuation dynamics in the wavelength range

examined is very small. The interdiffusion coefficient D which has been obtained as a function of temperature, is continuous at the phase separation boundary. The mobility M , which can be extracted from D by combining the results of both statics and kinetics has an Arrhenius type of temperature dependence on both sides of the phase boundary.

Gur, Y. S., Malone, M.F., Bhatia, Q.S., Reynolds, G., Karasz, F.E., Hanson, A.R., and Riseman, E.M. [1989] demonstrated the use of computer vision techniques and optical microscopy to follow the kinetics and microstructure during spinodal decomposition of a polymer blend. Among other features, the mean of the population of the local maximum of the gradients in each image is computed; this global feature is shown to co-develop with the phase separation of the blend. An algorithms were presented which employed the gradient magnitude technique to analyze optical images of spinodally decomposing polymer blends. This algorithm has been used to extract the Cahn-Hilliard spinodal growth rates for a binary blend of polystyrene with poly(vinyl methyl ether). They show that the spinodal temperature can be found from the temperature dependence of this growth rate. They also show how additional shape features such as compactness might be used to study the same binary blend.

Chakrabari, A., Toral, R., Gunton, J.D., and Muthukumar, M. [1989] studied of spinodal decomposition in polymer mixture in three dimensions for Flory-Huggins-de Gennes free energy, numerically integrating the time-evolution equations for the conserved order parameter. They studied the time dependence of the domain size as well as the pair correlation function and structure factors for several quench temperatures. The results indicate that the growth law for the characteristic domain size is independence of the final quench temperature in contradiction with the recent experiments on model polymer systems. As well, it is shown that dynamical scaling is valid at sufficiently late times.

P. Cifra, P., Karasz, F.E., and MacKnight, W.J.[1989] studied the isothermal remixing after an instantaneous quench to below the spinodal of a binary polymer mixture by using computer-simulation methods. Short-range fluctuations, corresponding to a large wavenumber (q), were followed during the demixing. The results obtained provide a useful supplement to those based on a linearized version of Cahn's theory of spinodal decomposition (SD). The latter theory applies to small q regimes and to scattering experiments that cover a range of fluctuation wavelengths typically larger than the size of the polymer coils. However, fluctuations in wavelength on the order of the interaction range, i.e., the nearest-neighbor distance in the mixture, are not adequately described by the linearized theory; deviations are observed at very early stages of phase decomposition. In this regime thermodynamic, rather than diffusional, factors are paramount. In the present study spinodal decomposition for mixtures on a three-dimensional cubic lattice were simulated, and the corresponding kinetics were evaluated for a range of quench depths.

Wang, Z., Konno, M., and Saito, S. [1991] studied the computational method for the spinodal decomposition that combines the Langer, Bar-on, and Miller (LBM) theory with Suzuki's general scaling theory for transient phenomena. The results were compared with experimental observations for a typical polymer-blend system with respect to the experimentally accessible quantities with as the structure factor and the single-point distribution function. The main features observed in scattering experiments of phase separation were reproduced by this method. The numerical analyses when fitting the power-law relations expressed by $q_m \propto t^{-\alpha}$ and $S_m \propto t^{\beta}$ to the time variations of the dominant Fourier component of concentration fluctuations q_m and the corresponding structure factor S_m . It is shown that the LBM theory can be used to describe the phase-separation behavior up to intermediate stages.

Wang, Z., Konno, M., and Saito, S. [1993] applied Suzuki's scaling theory for transient phenomena to the calculations of the kinetics of phase separation in the early-to-intermediate stage based on a nonlinear theory proposed by Langer, Bar-on, and Miller (LBM). Calculated results were compared with experimental data on light scattering from the polymer blend system. Deviations from predictions of Cahn's linearized theory in the early time range of phase separation can be explained well by the proposed method of calculation. Nonlinear effects are found to play an essential role in characterizing the light scattering behavior of phase separation in the intermediate stage. Time evolutions of the single-point distribution function of composition are calculated, and the results are in good agreement with those reported in digital imaging analysis experiments and computer simulations of the time-dependent Ginzburg-Landau equation. The influence of asymmetry of free energy on the single-point distribution function was also investigated in this study.

Xie, Y., Ludwig, K.F., Bansil, R., Gallagher, P.D., Kodak, C., and Morales, G. [1996] found the strong nonlinearities in the kinetics. A linear theory analysis could fit the evolution of the structure factor at short times and low wavenumbers. Nonlinearities become significant earlier at higher wavenumbers, which is consistent with recent computer simulation studies. From the linear theory analysis, the exponential relaxation rate of the structure factor $R(q)$ was found to be linear in q^2 in the low-wavenumber region of the experiments, in agreement with mean-field theory for spinodal decomposition in polymer solutions. The wavenumber-dependent Onsager transport coefficient $A(q)$, which is the Fourier transform of the nonlocal mobility in a polymer system, was determined to scale as q^{-4} . This q dependence, which is stronger than that predicted by existing theory, may be related to entanglement effects.

Merkle, G., Bauer, B.J., Han, C.C. [1996] studied the relaxation of the structure factor from a smaller to a larger fluctuation state after a temperature jump within the one-phase region of a miscible polymer blend by Small Angle Neutron Scattering (SANS). The blend studied is a 60/40 by weight mixture of a hydrogen bonded polymer blend which consists of hydroxy modified deuterated polystyrene and poly(butylmethacrylate). A peak clearly evolved during the transition from the initial state at T_1 to the final state at T_f as predicted by linear as well as nonlinear theories. This relaxation process, which took more than 10 h, could be represented reasonably well by a simple linear approximation of the Cahn-Hilliard-Cook (CHC) theory without involving nonlinear calculations for the evolution of the dynamic structure factor. The measurement offers an alternative method for estimating the order parameter relaxation rate in the one-phase region. Also, this demonstrates experimentally the correct relaxation (to a higher fluctuation state) mechanism predicted by the linear theory of CHC type.

Ribbe, A.E., Hashimoto, T. [1997] studied the morphological evolution during spinodal decomposition (SD) of a binary polymer blend of poly(styrene-ran-butadiene) and polybutadiene with near critical composition by Transmission Electron Microscopy (TEM) and Laser Scanning Confocal Microscopy (LSCM). The mechanically homogenized samples were exposed to a temperature jump, and the time evolution of the characteristic wavenumber $q(m)$ was recorded by time-resolved light scattering. TEM and LSCM micrographs at various stages are also presented to clarify the growing bicontinuous morphology. A real space analysis of the early stage of the spinodal decomposition is presented for the first time. Two-dimensional Fourier transformation was applied to the real space images to obtain information about the characteristic wavenumber, and the results were compared to the predictions obtained by Cahn's linearized theory.

Muller, G., Schwahn, D., Eckerlebe H., Rieger, J., and Springer, T. [1997] studied the early stage of spinodal decomposition by small-angle neutron scattering in the critical mixture of the isotopic blend deuterio-polystyrene/polystyrene (d-PS/PS) of equal molecular volume of $1.42 \times 10^6 \text{ cm}^3/\text{mol}$. The time evolution of this process is described by the dynamical structure factor. The observed time evolution of the fluctuation modes is non-exponential. The analysis of the data has shown that the non-exponential behavior was attributed to a time-dependent increase of the "range" of the Onsager coefficient.

Paizel, N., Kempkes, F., Cirman, C., Picot, C., and Weill G. [1998] studied time and a resolved light scattering and nuclear magnetic resonance spin-lattice relaxation time on polystyrene/poly(vinyl methyl ether) blends during the early stage of the spinodal decomposition. The two techniques are used to determine the apparent diffusion coefficient at two different temperatures. A satisfying agreement is found between the results of T_1 n.m.r. measurements and those from light scattering. Otherwise, it has been shown that n.m.r. spin-lattice relaxation measurements, during the decomposition time, permits discrimination between spinodal decomposition and nucleation and growth. $T_{1\rho}$ experiments indicate that the homogeneous phase as well as the phase-separated quenched blend contain short scale inhomogeneities but it is not clear whether they compete with the larger scale spinodal decomposition process.