# Spinodal Decomposition in a Binary Mixture

K. Kubota and N. Kuwahara

*Department of Biological and Chemical Engineering, Faculty of Technology, Gunma University, Kiryu, Gunma 376, Japan*

(Received 25 July 1991)

The spinodal decomposition in a critical mixture of polydimethylsiloxane and diethyl carbonate was investigated by a time-resolved light-scattering technique focusing especially on the early and intermediate stages of phase separation. A second peak in addition to the main peak was found in the higher-scattering-angle region of the spectrum characteristic of the intermediate stage.

PACS numbers: 64.70.−p, 64.90.+b, 82.70.−y

Phase separation in unstable and unmixing mixtures may proceed either by nucleation and growth or by spinodal decomposition. The mechanism of spinodal decomposition has been an attractive object for physicists and has been studied recently by many groups [1]. It has been observed that the time evolution of phase separation can be divided into three stages, namely, the early, intermediate, and late stages, characterizing the behavior of phase separation and the scattering profile. In the early stage, the behavior is described by Cahn's linearized theory and the concentration fluctuation, having some characteristic wave number, evolves dominantly with an exponential time dependence without a change in its wave number [2]. In the intermediate stage, both the wavelength and amplitude of the concentration fluctuation increase but do not reach the final equilibrium values. In the late stage, the amplitude of the concentration fluctuation reaches the value of the equilibrium state and the fluctuation grows while maintaining self-similarity. In most of the works so far, attention has been focused on the intermediate to the late stage [3]. The early stage of binary liquid mixtures has been less investigated because of delicate experimental problems. Furthermore, the meaning and the importance of the intermediate stage have not been understood well, and it is considered only as the crossover from the early to the late stage in some cases.

Here, a detailed analysis of the scattering profile in the time evolution of spinodal decomposition of the critical mixture of polydimethylsiloxane (PDMS) and diethyl carbonate (DC) is reported. It has been ascertained that this system belongs to the same critical universality class as simple binary liquid mixtures [4]. The use of a polymer as one of the components makes it possible to observe the early-stage behavior of spinodal decomposition. PDMS was the well fractionated sample which has been used before in the study of critical phenomena in our laboratory [4]. The molecular weight is $8.0\times 10^4$ and $M_w/M_n < 1.02$, $M_w$ and $M_n$ being the weight- and number-averaged molecular weights, respectively. The critical mixture ($T_c = 34.42\,°\mathrm{C}$ and $w_c = 12.1_0$ wt%) determined from the coexistence curve was used. The details of sample preparation have been described elsewhere [5]. The most essential features of this system are that the multiple-scattering and the gravity effects are considerably reduced: $\Delta n \sim 0.021$ and $\Delta\rho \sim 0.0005$ g/cm$^3$ at 25 °C, where $\Delta n$ and $\Delta\rho$ are the differences of refractive index and density between PDMS and DC, respectively. Therefore, the progress of macroscopic phase separation into two coexisting phases is greatly slowed down. These greatly reduce the problem of stability of the sample arising from macroscopic phase separation during the time period of spinodal decomposition. The quench into the unstable region was achieved by the pressure jump method (the pressure dependence of the critical temperature is 8.85 mK/atm) to attain a quick and accurate response and to avoid unnecessary turbulence to the sample solution by the temperature jump method [3]. The essentially adiabatic pressure decrease causes a temperature decrease. This adiabatic temperature change decays sufficiently within 10 s after the pressure jump. Here we report the results of measurements with two quench depths, $\Delta T = 3.5$ and 6.5 mK.

The experimental arrangement is shown in Fig. 1. See the caption for details. A measurement of the scattering profile over 512 channels takes less than 3 s for data processing and averaging.

The time evolutions of the scattering profiles for quench depths of $\Delta T = 3.5$ and 6.5 mK are shown in Figs. 2 and 3. The scattered light before the pressure jump is subtracted to correct for the background contribution. The background contains a contribution from spontaneous composition fluctuations, but it was negligibly small compared to the scattered light intensity from the phase-separating mixture, as observed and noted by Goldburg *et al.* [3]. The central transmitted light is not shown and only every fourth point is shown to avoid cluttering in the figures. In the last scan of the measurements in Figs. 2 and 3, the transmitted light decreases by only about 5% from the initial value, and so multiple-scattering effects should be very small and the system should still be homogeneous enough. It is clearly seen that a second peak in addition to the main peak, which is normally observed and analyzed in the time evolution of spinodal decomposition, appears in the higher-scattering-angle region, though the intensity is considerably less than that of the main peak. The appearance of the second peak does not result from a ghost of the main peak, because the width of this peak is not as broad as is expected from the posi-

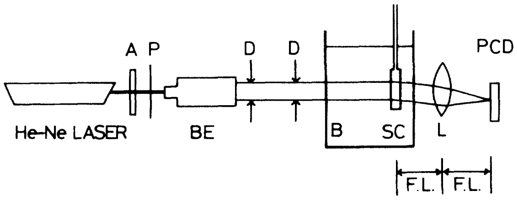

FIG. 1. Experimental arrangement of the measurement of spinodal decomposition. The sample cell (SC) (optical path length of 2 mm, and 10 mm×20 mm width and height) is located in a temperature-regulated silicon oil bath (B) and its temperature monitored by a quartz thermometer. The incident He-Ne laser beam, with a wavelength of 632.8 nm in vacuum, is attenuated (up to less than 0.1 mW) by a neutral-density filter (A) to avoid unnecessary local heating, and passes through the pinhole (P). The beam diameter is expanded to 10 times by a laser beam expander (BE); the expanded beam passes through diaphragms (D) to limit the beam diameter (8 mm) and illuminates the sample. The scattered light is collected by the Fourier-transform lens (L) (diameter = 12 cm) with a focal length (F.L.) of 15 cm on the photodiode array (PCD) (512 channels with 50 $\mu$m width for each channel; S2301-512Q, Hamamatsu Photonics). The use of the Fourier-transform lens greatly reduces the effect of speckles due to high coherency of the incident beam especially at very low scattering angles. The optical rays are shown to help in understanding the role of the lens. The uncertainty of $q$ is estimated to be $\leq 60\ \mathrm{cm}^{-1}$.

tions of both peaks. This second peak was not observed in the early stage but appears at the intermediate stage. The intensity of both the main and second peaks increases and the peak position shifts towards lower scattering angle with the progress of spinodal decomposition. As the time proceeds further, the second peak seems to form a shoulder on the main peak. The early stage of spinodal decomposition is clearly observed in Figs. 2(a) and 3(a).

A $\frac{1}{3}$-power plot was employed to obtain the growth rate $R(q)$ of the scattering structure factor $I(q,t)$ according to Sato and Han [6]:

$$I(q,t) = I_\infty + (I_0 - I_\infty)\exp[2R(q)t]\,, \tag{1}$$

where $I_\infty$ is the virtual structure factor arising from thermal noise and $I_0$ is the intensity at time $t=0$. The momentum transfer vector $q$ is

$$q = (4\pi/\lambda)\sin(\theta/2)\,, \tag{2}$$

where $\lambda$ is the wavelength in the medium and $\theta$ is the scattering angle. From the relation of $R(q)$ vs $q^2$ obtained by this method, the interdiffusion coefficient $D^*$ and $q_m(t=0)$ were determined based on Cahn's linearized theory, where $q_m(t=0)$ denotes the magnitude of the momentum transfer vector when the (main) peak of scattered light intensity appears at time $t=0$. In both Figs. 2 and 3, the linearized theory works well. Figure 4 shows the scaled relationship between the dimensionless parameters $Q_m(\tau)$ and $\tau$ defined by the scaling relations

$$Q_m(\tau) = q_m(t)/q_m(t=0)\,, \tag{3}$$

$$\tau = D^* q_m(t=0)^2 t\,. \tag{4}$$

The lower curve denotes the relationship for the dominant

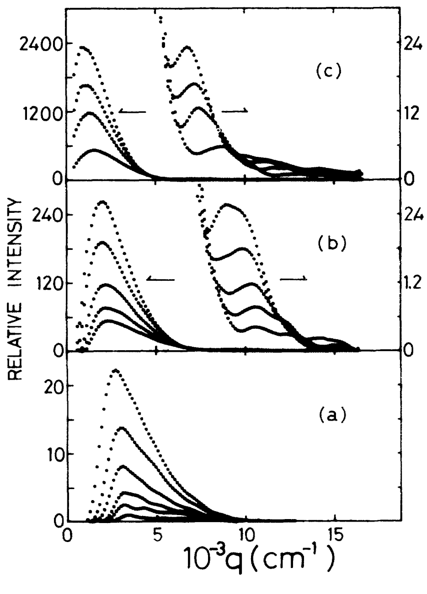

FIG. 2. Time evolution of the scattering profiles for $\Delta T = 3.5$ mK for the critical mixture of PDMS-DC. The elapsed time from the start of phase separation is (a) 30, 100, 170, 270, 370, and 470 s; (b) 770, 970, 1170, 1370, and 1550 s; and (c) 1920, 2670, 3420, and 4170 s from the bottom to the top, respectively. The arrows indicate the scale of intensity for the main peak and the second peak.

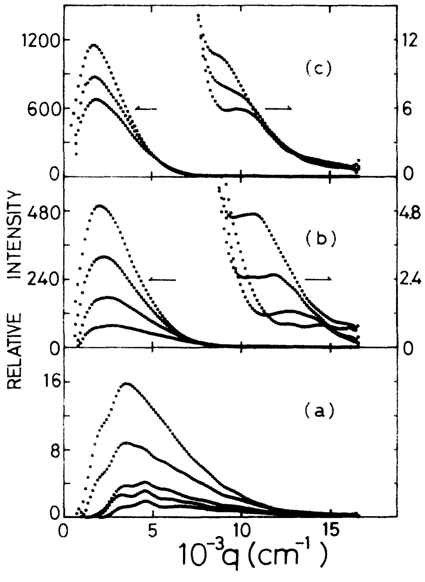

FIG. 3. Time evolution of scattering profiles for $\Delta T = 6.5$ mK for the critical mixture of PDMS-DC. The elapsed time from the start of phase separation is (a) 50, 80, 110, 150, and 210 s; (b) 450, 650, 850, and 1050 s; and (c) 1250, 1450, and 1750 s from bottom to top, respectively. At the last time, the second peak becomes a shoulder.

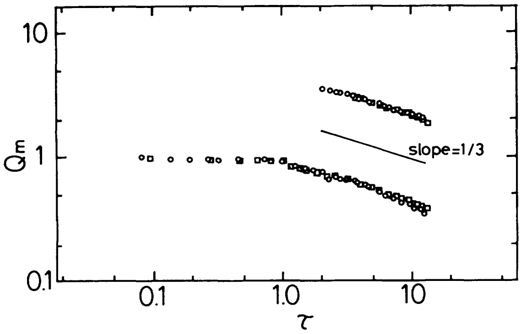

FIG. 4. Scaled time evolution of the scaled wave vector of the peak position for the main and the second peaks using $q_m(t=0)$ of the main peak determined from the linearized theory for the early stage. ○ and □ denote the results for $\Delta T=3.5$ and 6.5 mK, respectively. The slope of the solid line is $\frac{1}{3}$. It should be noted that there are no adjustable parameters, but the curves are absolutely determined using the values obtained from the relation of $R(q)$ vs $q$.

main peak and the upper curve denotes that for the second peak. Both are well superposed and each master curve is obtained. We used $q_m(t=0)$ and $D^*$ determined experimentally in the early stage for the scaling factors instead of $\xi$ and $D$ in the one-phase region, because the analysis of the early-stage behavior determines the characteristic length and time intrinsic to the system as $1/q_m(t=0)$ and $1/D^* q_m(t=0)^2$ [7]. Indeed, if the latter set is used for the scaling, the curve shifts translationally and the first portion of $Q_m(\tau)$, being independent of $\tau$, is unreasonably located at $Q_m(\tau)<1$ even for $\tau>10$ because $q_m(t=0)\xi$ is not unity but is evaluated to be about 0.28. The early stage where $Q_m(\tau)$ is essentially independent of time corresponds to $\tau<1$, in good agreement with the result of Hashimoto, Itakura, and Shimidzu [7]. $Q_m(\tau)$ of the second peak is about 5 times as large as that of the main peak. This seems to be the reason why the second peak has not been observed before. Because $Q_m(\tau)$ decreases with an increase of $\tau$, as has been observed before in many works in the intermediate stage, the appearance of the second peak should be essentially related to the intermediate stage. Regarding this point, it is worth noting that Wiltzius and Cumming recently observed the existence of two modes in a polymer mixture undergoing spinodal decomposition and attributed those modes to bulk and surface modes, the latter of which originates from the wetting effect [8]. In addition to this, Guenoun, Beysens, and Robert [9] observed behavior similar to the result of Wiltzius and Cumming. Both are quite interesting results for understanding the progress of spinodal decomposition, and their bulk mode corresponds to our main peak. In the present case, such a surface mode was not observed, and the reason for this is not clear at present. However, it should be noted that their time region ($50<\tau<1000$ [8] and $\tau>1000$ [9]) corresponds to the late stage and is much larger than our experimental time range ($\tau<10$).

The power-law behavior of $Q_m(\tau)$ against $\tau$ obtains well for both peaks and the exponent $a$ of $Q_m(\tau)\sim\tau^{-a}$ is evaluated as approximately $\frac{1}{3}$. Because our system has the critical concentration, which was previously ascertained experimentally in measurements of the coexistence curve and the critical phenomena in the one-phase region, the value of $\frac{1}{3}$ is not due to the off-critical quench effect. Though the theoretical predictions for the behavior of an unmixing mixture in the intermediate stage are not well established, comparable values for this exponent of $\sim\frac{1}{3}$ have been obtained in other systems too [3,7]. The superposed curve of $Q_m(\tau)$ vs $\tau$ locates slightly below the curve for isobutyric acid and water [3], for example, though the overall behavior is essentially the same, and shows the tendency to have a steeper $\tau$ dependence for larger $\tau$. When the second peak forms a shoulder of the main peak, the $q$ dependence of the tail of such a shoulder in the scattering function seems to be expressed by a $q^{-4}$ relation (Porod law) asymptotically, in contrast to the $q$ dependence of the tail of the main peak which is expressed approximately by a $q^{-6}$ dependence [10]. Takenaka, Hashimoto, and Jinnai analyzed their result for the late stage and related such a $q^{-4}$ dependence of the tail with the growth of local structure (development of the interface) where (semi)macroscopic phase separation already occurs ($\tau>60$) [11]. However, our result indicates that such a $q$ dependence results from the appearance of the second peak and the formation of a shoulder of the main peak. Therefore, it is strongly suggested that the behavior of the tail of the scattering function mentioned by Takenaka, Hashimoto, and Jinnai originates in the second peak, and the major factor in the formation of the local structure is a fluctuation mode of higher wave number, the second peak, which appears in addition to the main fluctuation mode of smaller wave number. The existence of the second peak means that the mechanism of phase separation cannot be understood only by the monotonous kinetics of the single fluctuation mode corresponding to the main peak, as has been considered so far in the intermediate stage, but should include another fluctuation mode having higher wave number, which results in the fine structure.

---

[1] J. W. Cahn, J. Chem. Phys. **42**, 93 (1965); J. S. Langer, M. Bar-on, and H. D. Miller, Phys. Rev. A **11**, 1417 (1975); K. Kawasaki and T. Ohta, Prog. Theor. Phys. **59**, 362 (1978); K. Binder and D. Stauffer, Phys. Rev. Lett. **33**, 1006 (1974); I. M. Lifshitz and V. V. Slyozov, J. Phys. Chem. Solids **19**, 35 (1961).

[2] J. W. Cahn and J. E. Hillard, J. Chem. Phys. **28**, 258 (1958); H. E. Cook, Acta Metall. **18**, 297 (1970).

[3] For example, W. I. Goldburg, C.-H. Shaw, J. S. Huang, and M. S. Pilant, J. Chem. Phys. **68**, 484 (1978); N.-C. Wong and C. M. Knobler, J. Chem. Phys. **69**, 725

(1978); T. Hashimoto, M. Itakura, and H. Hasegawa, J. Chem. Phys. **85**, 6118 (1986).

[4] K. Hamano, T. Nomura, T. Kawazura, and N. Kuwahara, Phys. Rev. A **26**, 1153 (1982).

[5] N. Kuwahara, M. Tachikawa, K. Hamano, and Y. Kenmochi, Phys. Rev. A **25**, 3449 (1982).

[6] T. Sato and C. C. Han, J. Chem. Phys. **88**, 2057 (1988).

[7] T. Hashimoto, M. Itakura, and N. Shimidzu, J. Chem. Phys. **85**, 6773 (1986).

[8] P. Wiltzius and A. Cumming, Phys. Rev. Lett. **66**, 3000 (1991).

[9] P. Guenoun, D. Beysens, and M. Robert, Phys. Rev. Lett. **65**, 2406 (1990).

[10] H. Furukawa, Adv. Phys. **34**, 703 (1985).

[11] M. Takenaka, T. Hashimoto, and H. Jinnai (private communications).