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Early-stage behavior of spinodal decomposition in a binary liquid mixture

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Time-resolved light scattering was used to study the time evolution of phase separation in a critical mixture of 2,5-hexanediol and benzene in the spinodal region. The early-stage behavior of spinodal decomposition is observed. The existence of the time region where the linearized theory of spinodal decomposition is valid is ascertained for the simple binary liquid mixture.

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A number of theoretical and experimental works have been presented about the kinetics of phase-separating systems that are quenched into an unstable two-phase region [1]. Phase separation in the unstable and unmixing mixture may proceed either by nucleation growth or by spinodal decomposition. The time evolution of spinodal decomposition in a system near the critical point especially has attracted much attention concerning the dynamics of ordering processes. The linearized theory [2] and the scaling concept [3] have given a great contribution to the study of the growth and time evolution of component fluctuation in such systems. Although the existence of the early stage of spinodal decomposition described by the linearized theory of Cahn-Hillard has been observed for polymer-polymer mixtures [4], such an existence has not been reported so far for systems that show three-dimensional Ising-model behavior in the stable one-phase region. Recently early-stage behavior of spinodal decomposition and the symmetric law of critical-point universality have been ascertained by the authors using a polymer solution system (polydimethylsiloxane-diethyl carbonate), taking advantage of very slow kinetics of phase separation due to polymer effect [5]. However, such a polymer solution system intrinsically has a large asymmetry in molecular size, shape, and mobility, and a small interfacial tension due to high molecular weight. In some cases, it is even considered that the early stage of spinodal decomposition does not exist in simple binary liquid mixtures. Therefore, it is of great interest to study early-stage behavior in simple binary liquid mixtures. Such a study is important from the viewpoint of confirming the validity of the universal master curve for the time evolution of the structure factor (scattering function) in detail and the dynamical scaling concept of phase separation in the absolutely unstable region.

Here we report the measurement of the time evolution of phase separation of a critical mixture of 2,5-hexanediol and benzene, focusing on the time evolution of a structure factor in the early stage of spinodal decomposition. This mixture has slightly lower turbidity than isobutyric acid and water mixture at the same reduced temperature ($\epsilon=|T-T_c|/T_c$, T_c being the critical temperature) [6]. The critical-point behaviors in the one-phase stable region have been reported elsewhere and the three-dimensional Ising-model values for the critical exponents have been obtained (for example, $\beta=0.323\pm0.007$ for the reduced temperature dependence of the concentration difference of two coexisting phases) [7]. The phase diagram is shown in Fig. 1. The critical concentration (C_c) and temperature are 33.02 wt.% and 35.132 °C, respectively. The experimental arrangement using a photo-diode array has been fully described elsewhere [8]. Each scan over 512 channels of a photo-diode array covering the range of wave number $K=(4\pi n/\lambda)\sin(\theta/2)$ of ca. $(1-16)\times10^3$ cm^{-1} is performed every 3 s, thus the scattering functions for fairly early time were measured. Here, n, λ, and θ are the refractive index of the sample, the wavelength of the incident beam (632.8 nm) in vacuum, and the scattering angle, respectively. A mixture of the critical concentration is prepared using thoroughly purified 2,5-hexanediol and benzene by the fractional distillation. The quench into the spinodal region was achieved by the pressure jump method in order to attain a quick and accurate quench. Only a slight pressure elevation is needed for an mK-order quench depth because the pressure dependence of the critical temperature T_c is evaluated to be 11.0 mK/atm. The temperature was controlled with an accuracy of ±0.2 mK. The scattering functions of quench depths ΔT of 0.9 and 1.2 mK below T_c were studied. The corrections for the background and attenuation were carried out. The scattering function is proportional to the structure factor without multiple scattering in the present system.

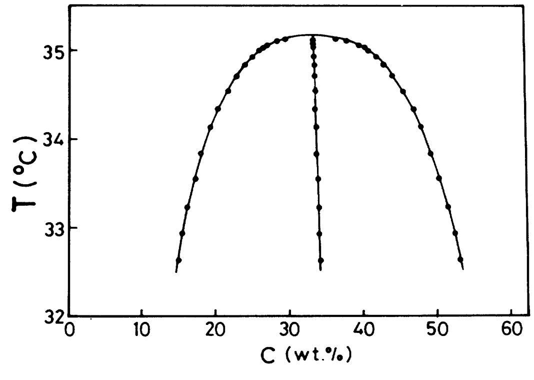

FIG. 1. The coexistence curve for 2,5-hexanediol and benzene mixture. Solid circles denote the diameter associated with the shape of the coexistence curve. T_c is 35.132 °C and C_c is 33.02 wt.%.

The scattering functions of $\Delta T = 0.9$ mK are shown in Fig. 2. It is observed that the scattered intensity increases with time and with almost no change of the wave number at the maximum intensity, indicating early-stage behavior expected by the linearized theory of Cahn-Hillard [2]. The linearized theory including the thermal noise effect has been introduced by Cook and recently modified by Sato and Han [9]. The following 1/3-power plot by Sato and Han was used to obtain an accurate growth rate, R, of the scattering function, $I(K,t)$, by

$$I(K,t) = I_x(K) + [I_0 - I_x(K)]\exp(2Rt)\,, \tag{1}$$

$$\{t/[I(K,t) - I(K,0)]\}^{1/3} = \{2R[I(K,0) - I_x(K)]\}^{-1/3}[1 - (\tfrac{1}{3})Rt + (\tfrac{1}{81})(Rt)^3 + \cdots]\,, \tag{2}$$

where $I_x(K)$ is the virtual structure factor arising from the thermal noise and I_0 is the intensity at time $t = 0$, the elapsed time after the quench. As the second-order term in t is absent in Eq. (2), this equation is able to be well approximated by a linear equation over the range of relatively wide time compared with the usual semilogarithmic plot. This plot for $\Delta T = 0.9$ mK is shown in Fig. 3. Although a little wiggling exists due to the remaining speckles, a good linear relation is observed. The growth rate R is related to the diffusion mobility, M, the composition susceptibility, χ, and the interdiffusion coefficient, D^*, by

$$\begin{aligned} R &= -MK^2(\chi^{-1} + 2\kappa K^2) \\ &= D^* K^2(1 - K^2/2K_m{}^2)\,, \end{aligned} \tag{3}$$

where κ is the constant related to the contribution of interfacial free energy and K_m defined by $\frac{1}{2}(D^*/M\kappa)^{1/2}$ is the wave number where the growth rate has a maximum value and should coincide with the wave number corresponding to the peak intensity, $K_m(t)$, at $t = 0$. The R values obtained from the slope and intercept in Fig. 3 at various scattering wave numbers are plotted as a function of K^2 in Fig. 4(a). The values of R/K^2 are also shown as a function of K^2 in Fig. 4(b). The relationship of R vs K^2 has a parabolic shape and of R/K^2 vs K^2 is well represented by a linear relation. The intercept of the abscissa gives $2^{1/2}K_m$ and that of the ordinate gives D^*. The value of K_m thus obtained agrees well with the maximum position of R [Fig. 4(a)] and that of the scattering function (Fig. 2) against K. These suggest that the early stage of spinodal decomposition exists and the linearized theory is confirmed to be valid. Similar behaviors are also obtained for $\Delta T = 1.2$ mK, though the linear range of time is shorter. The resultant values of $K_m(0)$ and D^* are 7.02×10^3 cm^{-1} and 1.02×10^{-9} cm^2/s for $\Delta T = 0.9$ mK and 8.67×10^3 cm^{-1} and 1.24×10^{-9} cm^2/s for $\Delta T = 1.2$ mK, respectively. The inverse of $K_m(0)$ and of $D^*[K_m(0)]^2$ are regarded as the characteristic length, ξ^*, and the characteristic time, t^*, which characterizes the time evolution of the structure in the process of spinodal decomposition and ξ^* at $\Delta T = 0.9$ and 1.2 mK are 1.42×10^{-4} and 1.15×10^{-4} cm, respectively. The correlation lengths in the stable one-phase region, ξ_+, at the same reduced temperature are estimated to be ca. 5×10^{-5} and 4×10^{-5} cm [7], thus ξ^* is about 2.8 times larger than ξ_+. This value of 2.8 is comparable with the one obtained for the critical mixture of polydimethylsiloxane and diethyl carbonate, 3.6 [5]. These values of ξ^* and D^* give $A = \frac{3}{8}\pi D^*\xi^*$ to be ca. 1.7×10^{-13} cm^3/s. The corresponding value in the one-phase region is evaluated to be ca. 1.3×10^{-13} cm^3/s

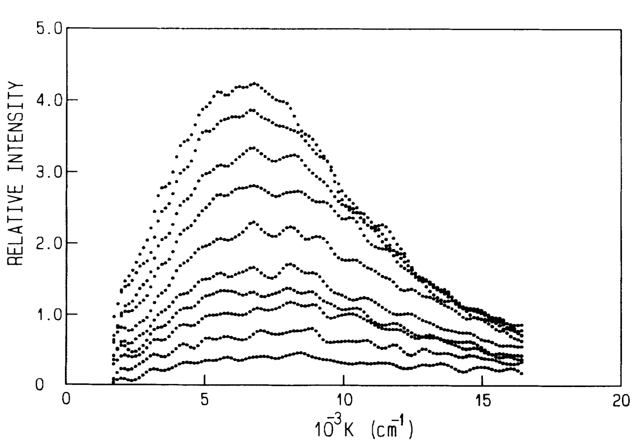

FIG. 2. Time evolution of the scattering functions of $\Delta T = 0.9$ mK. The elapsed time from the start of phase separation is 6, 9, 12, 15, 18, 21, 24, 27, 30, and 33 s from the bottom to the top.

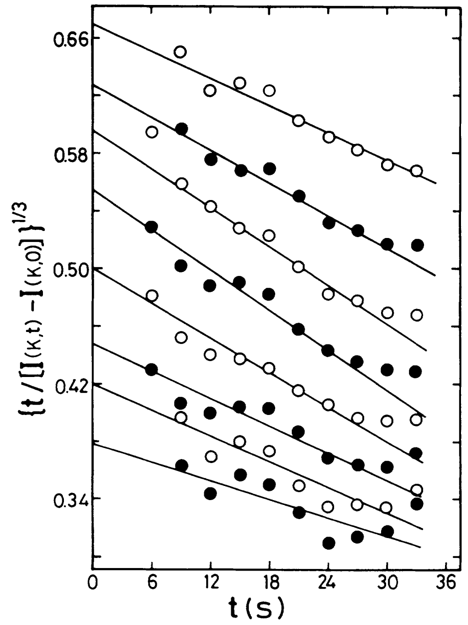

FIG. 3. The 1/3-power plot for $\Delta T = 0.9$ mK; t denotes the elapsed time. Each data set except for the fourth one from the top is shifted vertically to avoid cluttering. The wave number and the amount of shift for each data set are from the top to the bottom 4630 cm^{-1}, 0.12; 5300 cm^{-1}, 0.08; 6290 cm^{-1}, 0.04; 7020 cm^{-1}, 0; 7940 cm^{-1}, −0.04; 8610 cm^{-1}, −0.08; 9270 cm^{-1}, −0.12; and 9930 cm^{-1}, −0.16.

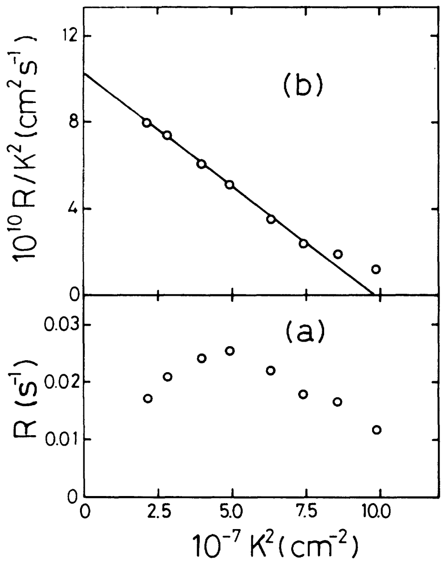

FIG. 4. The growth rate (a) R and (b) R/K^2 as a function of K^2. The values of R are determined from Fig. 2.

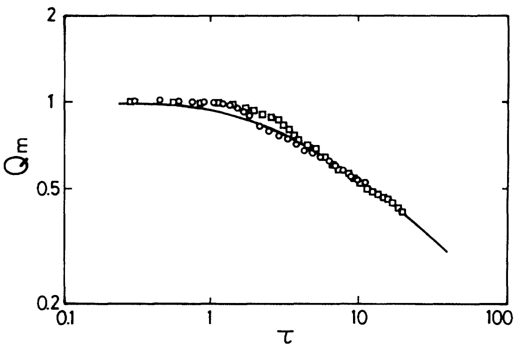

FIG. 5. The scaled time evolution of the scaled wave number at the maximum intensity of the scattering functions for $\Delta T = 0.9$ mK (○) and $\Delta T = 1.2$ mK (□). The solid curve denotes the theoretical prediction by the Furukawa theory with $A = 0.1$ and $B = 0.035$.

according to Kawasaki's mode-mode coupling theory [10]. It should be noted that ξ^* is not the correlation length, ξ_-, defined for the spontaneous fluctuation in the coexisting (stable) concentrated and/or dilute phase below T_c and that $\xi_+/\xi_- \sim 2$ according to the scaling theory of the critical phenomena [11].

The scaling behavior of the peak wave number, $K_m(t)$, versus time was also examined, though the experimental time range was a little restricted. The scaled peak wave number, $Q_m(\tau)$, and scaled time, τ, are defined as $Q_m(\tau) = K_m(t)/K_m(0) = K_m(t)\xi^*$ and $\tau = D^*[K_m(0)]^2 t = t/t^*$, respectively. According to the dynamic scaling concept this scaled relation should give a universal master curve characterizing the time evolution of phase separation. Such a relation is shown in Fig. 5 and a good superposition is obtained for the results of $\Delta T = 0.9$ and 1.2 mK without any adjusting parameters. It should be noted that there is a time region, $\tau < 1$, where $Q_m(\tau)$ is independent of τ and is almost unity. This indicates again the existence of the early stage of spinodal decomposition. The time dependence of $Q_m(\tau)$ in the region $1 \lesssim \tau \lesssim 10$ is well expressed by $Q_m(\tau) \sim \tau^{-1/3}$ corresponding to the intermediate stage of spinodal decomposition. This time dependence is in good agreement with our previous result for a polymer solution [5]. If ξ_+ or ξ_- are used as the scaling parameters for $Q_m(\tau)$, the portion that is almost independent of (scaled) time has an unreasonably low value of $Q_m(\tau)$.

Since the scaled relations around $\tau = 1$ have not been reported for other simple binary liquid mixtures (the time range is fairly higher, $\tau \gtrsim 20$) [6,12], Furukawa's theoretical form for the universal curve of the critical fluid mixtures is used for the comparison as [13]

$$Q_m(\tau)^{-1} - 1 - ((A/B)^{1/2}[\tan^{-1}\{Q_m(\tau)^{-1}(B/A)^{1/2}\} - \tan^{-1}\{(B/A)^{1/2}\}]) = B\tau , \qquad (4)$$

where A and B are the adjustable parameters and A is set as 0.1 to recover the prediction of Kawasaki and Ohta [14]. This equation is known to reproduce quite well the experimental master curve by using $B = 0.045$ for isobutyric acid-water [6] and $B = 0.022$ and/or 0.07 for cyclohexane-methanol [11]. The solid curve in Fig. 5 is drawn using $B = 0.035$. The agreement between the experimental and theoretical curves is good and the value of B is quite comparable with other simple binary liquid mixtures. Therefore, it is confirmed that the determined values of $K_m(0)$ and D^* are suitable in describing the time evolution of phase separation and the linearized theory is valid for early-stage behavior of spinodal decomposition not only for polymer solutions [5] but also for simple binary liquid mixtures.

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[1] For example, J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8; T. Hashimoto, Phase Transitions **12**, 47 (1988), and references cited therein.

[2] J. W. Cahn and J. E. Hillard, J. Chem. Phys. **28**, 258 (1958).

[3] K. Binder and D. Stauffer, Phys. Rev. Lett. **33**, 1006 (1974).

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

[5] K. Kubota and N. Kuwahara, Phys. Rev. Lett. **68**, 197 (1992).

[6] N. C. Wong and C. M. Knobler, J. Chem. Phys. **69**, 725 (1978); Y. C. Chou and W. I. Goldburg, Phys. Rev. A **20**, 2105 (1979); **23**, 858 (1981).

[7] T. Koike, Masters thesis, Gunma University, 1985.
[8] K. Kubota and N. Kuwahara (unpublished).
[9] T. Sato and C. C. Han, J. Chem. Phys. **88**, 2057 (1988).
[10] K. Kawasaki, Ann. Phys. (N.Y.) **61**, 1 (1970).
[11] N. Kuwahara, J. Kojima, and M. Kaneko, Phys. Rev. A **12**, 2606 (1975).
[12] P. Guenoun, R. Gastaud, F. Perrot, and D. Beysens, Phys. Rev. A **36**, 4876 (1987); D. Beysens, P. Guenoun, and F. Perrot, *ibid.* **38**, 4173 (1988).
[13] H. Furukawa, Adv. Phys. **34**, 703 (1985).
[14] K. Kawasaki and T. Ohta, Prog. Theor. Phys. **59**, 362 (1978).