Spinodal decomposition in a critical isobutyric acid and water mixture

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Light scattering was used to study the time evolution of phase separation of a critical isobutyric acid and water mixture in the spinodal region. A shoulder is observed in the larger scattering-angle region of the main dominant peak in the structure factor, and the time dependence of the position of shoulder is well scaled by the same characteristic wave number and interdiffusion coefficient as those for the main peak. The tail in the large-scattering-angle region of the structure factor is well expressed by the Porod law in the intermediate and late stages of spinodal decomposition.

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Many theoretical and experimental studies have been presented about the kinetics of phase-separating systems that are quenched in the unstable two-phase region [1]. Phase separation in the unstable and demixing mixtures may proceed either by nucleation growth or by spinodal decomposition. The time evolution of spinodal decomposition in a system near the critical point has especially attracted much attention concerning the dynamics of ordering processes. The linearized theory [2] and the scaling concept [3] are very useful for analyzing the growth and time evolution of component fluctuation in such systems. The angular distribution of the scattering function has been of particular interest in the intermediate and late stages of spinodal decomposition, because a self-similar structure is formed, that reflects the scattering function especially in the late stage [4].

Recently, nonunimodal scattering functions have been observed experimentally [5] and theoretically [6], indicating the existence of a shoulder in the larger-scattering-angle region of the main dominant peak. We also found very recently, using the critical mixture of polydimethylsiloxane and diethyl carbonate, that a definite second peak appears and is scaled by the same scaling factors as those for the main peak [7]. The second peak grows with time and has a tendency to form a shoulder of the main peak in the late stage. Therefore, a detailed analysis of the scattering function is of great importance to understanding the kinetics of phase separation.

Here we report the measurement of time evolution of spinodal decomposition of the critical isobutyric acid and water mixture (IBAW) focusing on the time evolution of the structure factor in the process of the intermediate to the late stage. This mixture seems to be a standard system for the study near the critical point [8]. Wong and Knobler [9] and Chou and Goldburg [10] have previously studied this system in the spinodal region, but detailed analysis of the structure factor has not been done, although a preliminary and qualitative study was presented.

The experimental arrangement has been fully described elsewhere [7]. The most important feature is the use of a lens for increasing the signal-to-noise ratio which is particularly essential for small-angle light-scattering measurements as in the present case. Each scan over 512 channels of the photodiode array covering the range of wave number $K=(4\pi n/\lambda)\sin(\theta/2)$ of $\sim(1-16)\times10^3$

cm^{-1} is performed in every 3 s, thus the scattering functions from a relatively 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 ($w_c = 38.8$ wt.% of isobutyric acid) [11] is prepared using fractionally distilled isobutyric acid and water of liquid chromatographic grade. The quench into the spinodal region was achieved by the pressure-jump method in order to attain quick and accurate quenches [9]. Only a slight pressure elevation is needed for an mK-order quench because the pressure dependence of the critical temperature T_c is evaluated to be 55 mK/atm. The temperature was controlled with the accuracy of ±0.2 mK. The scattering functions of quench depths of 1.4, 2.2, 3.8, 5.0, and 9.5 mK below T_c were examined. The corrections for background and attenuation were carried out. The scattering function is proportional to the structure factor without multiple scattering. The correlation length ξ and the diffusion coefficient D in the one-phase region that are needed to arrange the experimental result in the spinodal region have already been obtained by Chu, Schoenes, and Kao as a function of reduced temperature [11].

One of the typical scattering functions is shown in Fig. 1 for the quench depth of 3.8 mK. The striking feature is the appearance of a shoulder in the larger-scattering-angle region of the main (dominant) peak. The shoulder exists from the intermediate stage to the late stage, although its magnitude varies with quench depth. In the case of a polydimethylsiloxane and diethyl carbonate mixture, the second peak appears at the beginning of the intermediate state and has a tendency to form a shoulder in the late stage [7]. A clear second peak was not observed in our IBAW system. Since the IBAW system is a low-molecular-weight mixture and the progress of fluctuation growth is fairly fast, the measurable time range is restricted from the intermediate stage. The scaling concept for the kinetics of phase separation gives a power-law relation for the time dependence of length scale or wave number K_m characterizing the distribution of component fluctuation as $K_m \sim t^{-a}$ with K_m and t being the wave number of the most dominant peak that has the maximum scattered intensity and the time of lapse after the quench, respectively. K_m and t can be scaled with the characteristic scal-
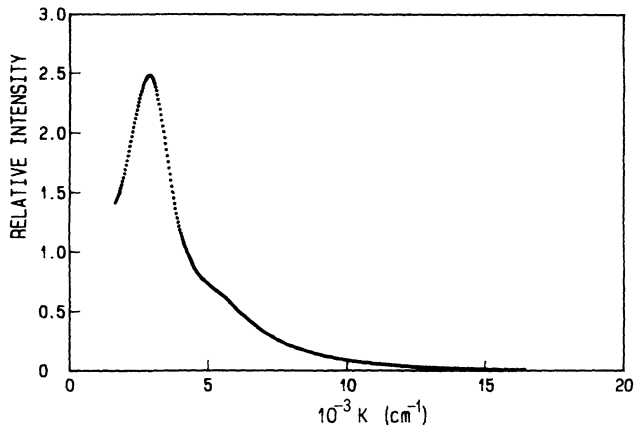
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K. KUBOTA, N. KUWAHARA, H. EDA, AND M. SAKAZUME

FIG. 1. A typical result of angular dependence of the scattered-light intensity. The quench depth is 3.8 mK and $\tau = 180$.

ing factors of ξ and D as $Q_m = K_m \xi$ and $\tau = (D/\xi^2)t$ using the relevant quantities in the one-phase region. So, the relation between the scaled wave number and time is expressed as $Q_m \sim \tau^{-a}$. This scaled relation should give a master curve characterizing the time evolution of phase separation, and has been confirmed for the main peak of the IBAW system previously [9,10]. Such a relation is reconfirmed for the main peak in the present measurement. In addition, the time dependence of the wave number of the shoulder through the scaling relation is studied. The wave number of the shoulder was determined as the wave number that gives the maximum intensity increase from the extrapolated value of the main peak in the scattering function. The scaled relation for both the main peak and the shoulder is illustrated in Fig. 2 as a function of scaled time. Superposition is very good. The behavior of the main peak is, of course, almost the same at that ob-

tained by Wong and Knobler and Chou and Goldburg. It should be noted that Q_m of the shoulder is also well scaled by the same scaling factors as those for the main peak. This means that the shoulder reflects an essential behavior in the time evolution of phase separation and the distribution of fluctuation modes governed by the same single-length scale as the dominant mode. The structure factor of IBAW was analyzed with respect to the appearance of the shoulder. From the viewpoint of the dynamic scaling concept, Furukawa recently proposed a simple form for the structure factor $S(x) \sim x^\delta/(\gamma/\delta + x^{\gamma+\delta})$ with $x = K/K_m$ [12]. This form suggests that $S(x) \sim x^\delta$ for $x \ll 1$ and $S(x) \sim x^{-\gamma}$ for $x \gg 1$. In the late stage of phase separation it is well known that the tail of the structure factor (in the large-scattering-angle region) behaves as K^{-4} for the three-dimensional system, the Porod law, indicating the formation of a sharp interface and $\gamma = 4$. For the conservative system $\delta = 4$ is predicted [13]. Furukawa's old form is expressed as $S(x) \sim x^2(3 + x^8)$ [14]. The difference for the behavior at $x \ll 1$ is related to the contribution of thermal noise [12]. There is an essential difference for the behavior at $x \gg 1$. The scaling of the structure factor suggests the existence of the single-length parameter describing the structure in the phase-separating system and the formation of self-similar structute [14]. These simple forms for the structure factor should be related with the wave-number dependence of
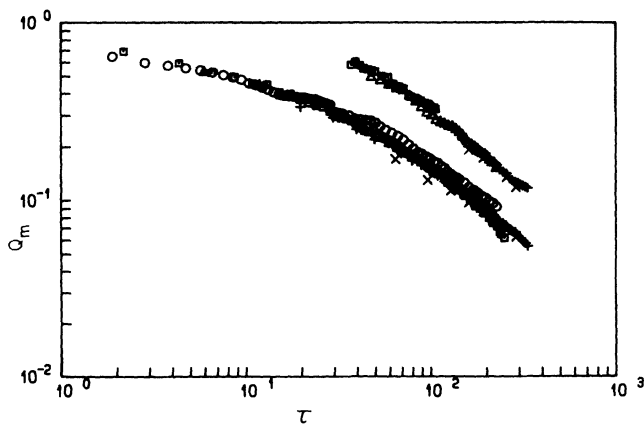

FIG. 2. Double logarithmic plot of the scaled wave number of the main peak and the shoulder as a function of scaled time. The symbols denote the quench depths 1.4 mK (o), 2.2 mK (□), 3.8 mK (△), 5.0 mK (+), and 9.5 mK (×), respectively. The lower and upper curves stand for the main peak and the shoulder, respectively.
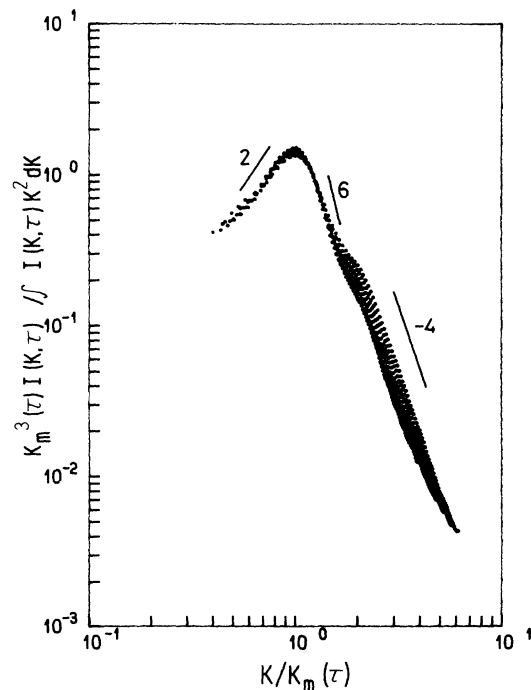

FIG. 3 Double logarithmic plot of the scaled structure function vs the normalized wave number for a 2.2-mK quench depth. The number denotes the slope of each line. The scaled time for each dotted curve is 52.0, 62.9, 73.7 84.5, 95.4, 106, and 117, from the bottom to the top, respectively. The lower and upper bounds of the integral that normalize the scaled structure function are $K/K_m = 0.5$ and 1.5, respectively. The peak height is ~ 1.4 in good agreement with Furukawa's theory.

the dominant peak or the fluctuation mode; however, they may be valid for describing the global structure in the system. The asymptotic behavior of Furukawa's theoretical structure factor for $x > 1$ appears at relatively low x, say, $x > 1.6$. Indeed, the value of $\gamma \sim 6$ is observed in several systems [15]. The normalized scaled structure factors for the present sample of a quench depth of 2.2 mK are shown in Fig. 3 as a function of the normalized wave number K/K_m at various scaled time. The normalization of the structure factor is done by introducing the integral term as shown in the ordinate of the figure in order to do a close comparison with theoretical predictions [16]. The time region of Fig. 3 corresponds to the intermediate stage to the (early) late stage ($\tau = 50$–120). Though the overall profile is a little broader than that obtained by Chou and Goldburg, several features are obtained from this figure: (1) the normalized structure factor is well scaled in this time range especially for the main peak, (2) the shoulder appears at $K/K_m \sim 2$–3, (3) the tail of the main peak (at $K/K_m \sim 1.5$) is rather well expressed by a K^{-6} dependence, (4) the tail at $K/K_m \gg 1$ has a K^{-4} dependence, (5) the (scaled) intensity at the shoulder increases with time without changing the shape of the tail and/or the width of distribution of the main peak increases with time, and (6) in the small-angle region a K^{-2} dependence seems to hold, though the angular range is restricted for a relatively large K/K_m. Because light-scattering measurements at a very-small-angle region is extremely difficult, a K dependence at $K/K_m \ll 1$ was not obtained. Feature (1)

indicates that the global structure evolves already with a self-similar manner in this time region. Feature (2) is in good agreement with other results [5,6]. Feature (3) should be related with the Furukawa's prediction of $\gamma \sim 6$, and it seems that Furukawa's form of the structure function is appropriate to describe the dominant fluctuation mode. Feature (4) corresponds to the Porod law and suggests that the interface is formed in this time region. This K^{-4} dependence is also observed in the middle of the intermediate stage, thus the formation of the interface should start in the intermediate stage. The tendency of feature (5) is in accordance with the recent theoretical prediction [6] and it could be related to the growth of the interface. Since the contribution of thermal noise in low-molecular-weight mixtures could be small compared with, for example, the polymer-polymer mixture and the gravitational effect does not come into play in the present system as shown by Chou and Goldburg, a K^{-2} dependence at $K < 1$ like feature (6) may not result from the thermal noise effect. The effect of multiple scattering might be probable especially at the late stage. It might be a characteristic of low-molecular-weight mixtures or result from another effect, e.g., the effect of interfacial tension, and it seems to be correlated with the relatively broad distribution of the main peak [17].

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