

Phase separation in an unstable system polydimethylsiloxane-diethyl carbonate

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(Received 20 November 1981)

The effective growth rate of critical fluctuations in the unstable region of the system polydimethylsiloxane–diethyl carbonate was found to be time independent for an appreciable time and the negative composition diffusivity D^* to be represented by the power law of $D^* \propto \epsilon^{\nu^*}$ with $\nu^* \approx 0.62$, where $\epsilon = |(T - T_c)/T_c|$. The value of D^* was approximately three times larger than the positive composition diffusivity D at the same ϵ in the stable region.

I. INTRODUCTION

Recently the dynamics in the unstable region in critical mixtures has been of great interest.¹ When a homogeneous mixture with the critical composition is brought into the two-phase region, phase separation occurs by spinodal decomposition. The Cahn-Hilliard-Cook linearized theory² predicts spinodal decomposition to proceed only by the diffusionlike process with a spontaneous growth of fluctuations in the order parameter. The early stage of spinodal decomposition in fluids has been studied by taking into account hydrodynamic interactions among the order-parameter fluctuations by Kawasaki and Ohta.³ In most experiments, however, attention has been focused on time evolutions in rather the late stage than the early stage, especially the coalescing process, because of delicate experimental problems such as multiple-scattering and gravity effects and development of fluctuations with a rather fast rate even very close to a critical point. To study the growth rate of fluctuations in the early stage of phase separation we need at least a binary mixture with matched densities, approximately matched refractive indices, and a small value of diffusivity. A macromolecular solution used a well-fractionated polymer, which is characterized by $M_w/M_n < 1.02$ with M_w and M_n being the weight- and the number-average molecular weight, has been found to behave as if it were a binary mixture (i.e., the cloud-point curve and the precipitation threshold point coincide with the coexistence curve and the critical point, respectively).^{4,5} The amplitude of the correlation length in polymer systems has been found to be approximately three times larger in comparison with that in ordinary critical binary mixtures.⁵ Information concerning the negative diffusivity in the unstable region near the critical point by use of a polymer system,⁵ which belongs to the same universality class as the Ising model,⁶ should be applicable to fluids and alloys near their critical points. Our aim here is to reveal behaviors in the early stage of phase separation by

use of polydimethylsiloxane–diethyl carbonate, which is isopycnic, almost isorefractive, and highly viscous.

II. EXPERIMENTAL

Polydimethylsiloxane was fractionated into three fractions and then the middle-fraction polydimethylsiloxane was fractionated into 18 fractions by the fractional solution technique. The middle-fraction polydimethylsiloxane–ethyl formate solution at a concentration less than 0.01 wt. % was kept at a temperature a little below its phase separation temperature in a thermostated water bath whose temperature could be controlled to within ± 1 mK. After the phase equilibrium was attained the dilute-solution phase was separated from the other concentrated-solution phase of produce a fractionated polydimethylsiloxane of lower molecular weight. The concentrated phase was diluted by reagent-grade ethyl formate for further fractionations. In this work, the fraction characterized by $M_w = 8.0 \times 10^4$ and $M_w/M_n < 1.02$ was employed as a sample. Reagent-grade diethyl carbonate, dried thoroughly over anhydrous potassium carbonate, was fractionally distilled by use of a column of 140-cm length and 15-mm diameter packed with rasching rings. Preparation of solutions was performed in a dry box under dry nitrogen. We paid particular attention to avoid the moisture in air.

The critical mixing point ($T_c = 34.42^\circ\text{C}$, $w_c = 12.1_0$ wt. %) of the present system polydimethylsiloxane–diethyl carbonate was determined from the coexistence curve by use of a specially designed differential refractometer,⁵ which determines with a precision of $\pm 0.01\%$ in the weight fraction. The shape of the coexistence curve very near the critical point was asymptotically symmetric, namely, $B^+ = -B^-$ and $\beta^+ = \beta^-$.⁷ The critical point was confirmed to coincide well with the precipitation threshold point. A macromolecular solution used the present sample with the molecular weight distribution of $M_w/M_n < 1.02$ could be taken to behave as if it were

a binary mixture because of the symmetry features of the coexistence curve and the agreement of the precipitation threshold point with the critical point. Our experiments were carried out in the critical mixture ($w_c = 12.1_0$ wt. %) of polydimethylsiloxane and diethyl carbonate flame sealed under vacuum in a 0.5-ml rectangular quartz cell with 2.0-mm optical path length and 1.3-mm thickness. The sample was of critical composition, as evidenced by the volume equality of the two phases at ~ 2 mK below T_c .

A 0.05-mW laser beam of wavelength $\lambda_0 = 6328 \text{ \AA}$ was passed through the sample, which was positioned in a water bath with stability within 0.3 mK over 2 h. We allowed the beam passing through the sample and the forward scattered light to fall on a screen for observation of the pattern of illumination. This observation was very useful as a measure of temperature distance from the critical temperature. For $T - T_c \geq 0.2$ mK, we observed only a clear spot of the transmitted beam on the screen. In the temperature region of $T_c - T \leq 0.2$ mK, we could observe a ring of granular appearance, which is formed by the forward scattered light, increasing brightness and sharpness with lapse time around the spot of the transmitted beam. At $T \approx T_c$ a diffuse ring of granular appearance appeared and disappeared with time depending on temperature fluctuations in the water bath controlled to within 0.3 mK. Reproducibility of T_c was within 0.2 mK before and after each run. Over the three-month period in which the same sample was studied, its phase-separation temperature changed by 5 mK, there being no measurable change during a run. The bath temperature was stabilized at a temperature $T \approx T_c + 2.0$ mK and then quickly dropped to a desired temperature below its critical value $T_c = 34.42^\circ\text{C}$ using a lump of cooled copper. In less than 6 sec following the temperature quench the water bath was stabilized at the desired temperature. Temperature was monitored with a calibrated Hewlett-Packard quartz thermometer (HP 2804A, 18116A), which is located close to the sample. Intensities of the transmitted and the scattered light passed through an entrance slit (1 mm in diameter) were measured with a photomultiplier (Hamamatsu TV R446) and also registered by a chart recorder at seven angles $\theta = 0, 1.25, 1.50, 1.75, 2.00, 2.25, 2.50^\circ$. Angular measurements were corrected for attenuation, background, and refraction. Alternatively, the scattered light intensity was registered on photographic film. The wave number $k_m(t)$ at the maximum of the forward scattered light in the phase-separation process was measured with a microphotometer (Narumi NLM 201).

III. RESULTS AND DISCUSSION

The scaled scattered light intensity $\epsilon^{-2\beta}I(k, t)$ at $\theta = 1.5^\circ$ after corrections was plotted as a function of

the scaled time τ in double- and semilogarithmic plots in Fig. 1, where $\tau = Dt/\xi^2$ with D and ξ being the diffusion coefficient and the correlation length in the stable region.¹ The scattered light intensity is found to grow with the exponential-like growth rather than $\epsilon^{-2\beta}I(k, t) \propto \tau^a$ over the range of the early stage at each run, for example, over $0.7 \leq \tau \leq 1.6$ for $T = T_c - 1.0$ mK, $4.0 \leq \tau \leq 10.7$ for $T = T_c - 3.0$ mK, and $13.6 \leq \tau \leq 21.4$ for $T = T_c - 7.0$ mK. The scaling parameters were obtained by the scattered light intensity

$$I_s^{-1} = (1.15 \pm 0.19) \times 10^{-1} B \epsilon^{1.24 \pm 0.02} g(k\xi)$$

and

$$\xi = (7.13 \pm 1.71) \times 10^{-8} \epsilon^{-0.625 \pm 0.015} \text{ cm}$$

with the correlation scaling function⁸

$$g(k\xi) = 1 + \Sigma_2 k^2 \xi^2 - \Sigma_4 k^4 \xi^4 (k\xi \leq 6)$$

and by the relation¹⁰ $A = (\frac{3}{8})\pi D\xi$ and the experimental value of

$$A = \lim_{k\xi \rightarrow \infty} (\Gamma/k^3) = 7.02 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$$

within $k\xi > 1$ in the stable region.⁹ The parameter B includes $(\partial n/\partial C)_{p,T}^2$ and λ^{-4} in which n denotes the refractive index of the medium, C the concentration expressed in g/cm^3 , and λ the wavelength of light in medium, respectively, and Γ is the decay rate of the fluctuations of the order parameter in the

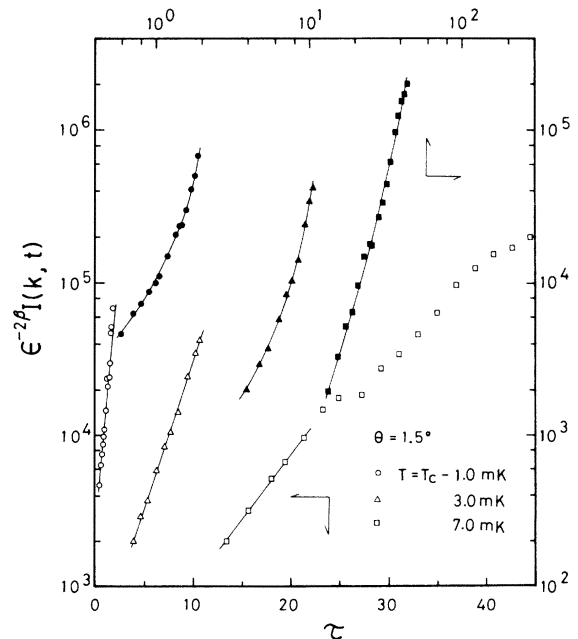


FIG. 1. Scaled scattered light intensity $\epsilon^{-2\beta}I(k, t)$ vs the scaled time τ at $\theta = 1.5^\circ$. Open and closed symbols are shown as plots of $\epsilon^{-2\beta}I(k, t)$ vs τ in semi- and double-logarithmics, respectively.

stable region. The wave number $k_m(t)$ and the scaled location $q_m(\tau) = k_m(t)\xi$ at $T \approx T_c - 1.5$ mK were plotted as a function of t and τ in comparison with recent theories^{3,11} in Fig. 2, respectively. Open circles stand for the early stage, at which the ring formed by the forward scattered light persists at its initial value of $q_m \approx 0.732$, increasing brightness and sharpness with lapse time; and closed circles stand for the late stage, at which the ring decreases in diameter with time. It is of particular interest that the ring of almost time-independent k_m or q_m in the early stage of phase separation exists over $86 \leq t \leq 173$ or $1.5 \leq \tau \leq 3.2$. Time-independent q_m was observed even for deep quenches and its temperature dependence is approximately represented by $q_m \propto \epsilon^{-0.36}$ over the range of $48.8 \times 10^{-6} \leq \epsilon \leq 3.25 \times 10^{-5}$ in the present work. On the other hand, it should be noted that the scaled location $q_m(\tau)$ in the late stage is in good agreement with the work of Kawasaki and Ohta, in which long-range hydrodynamic interactions are considered. The intensity as a function of time in the early stage with the exponential-like growth and almost time-independent wave number k_m suggests that the effect of thermal fluctuations introduced by Cook may give rise to little contributions in the present case of a small temperature jump from $T \approx T_c + 2.0$ mK at equilibrium state. We estimated the effective growth rate $\Gamma^*(k)$ in the unstable region over $1.36 \times 10^{-1} \leq k\xi \leq 1.15$ from the slope of a straight line in a semilogarithmic plot of intensity versus time.^{2,3} The values of $D^* = \lim_{k \rightarrow 0} [\Gamma^*(k)/k^2]$ was obtained from a plot of $\Gamma^*(k)/k^2$ as a function of k^2 . This plot shows a small curvature as reported by Huang, Goldberg, and Bjerkaas.¹² It is not clear

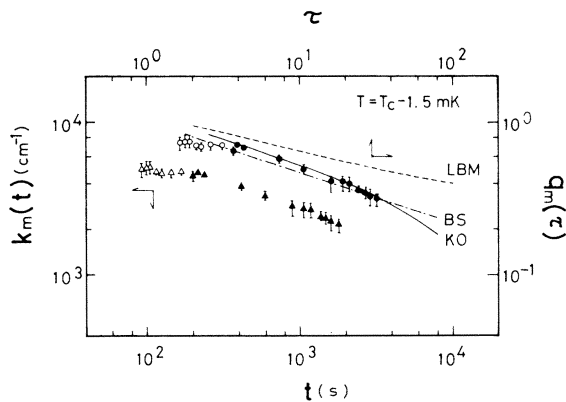


FIG. 2. Ring diameter $k_m(t)$ [symbol Δ] and the scaled location $q_m(\tau)$ [symbol \circ] vs time t and the scaled time τ , respectively, following a quench of $T \approx T_c - 1.5$ mK. The open symbol stands for the early stage and closed symbol for the late stage of spinodal decomposition. The solid, dashed, and dot-dashed lines represent the work of Kawasaki-Ohta, Langer-Bar-on-Miller, and Binder-Stauffer, respectively, in Ref. 3.

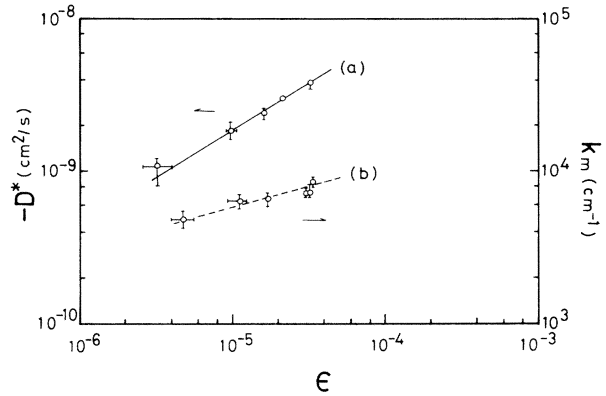


FIG. 3. (a) $D^* = \lim_{k \rightarrow 0} (\Gamma^*/k^2)$ vs ϵ . Here D^* is the negative diffusion constant. The solid line represents the simple power law $D^* \propto \epsilon^{\nu^*}$ with $\nu^* \approx 0.62$. (b) The ring diameter k_m vs ϵ . The dashed line represents the form $k_m \propto \epsilon^{0.27}$.

whether the small curvature is due to the effect of the wave-number dependence of the transport coefficient or not in the present study. Logarithmic plots of D^* and k_m vs ϵ are shown in Fig. 3. It should be noted that the negative diffusion constant in the unstable region was represented by the power law of $D^* \propto \epsilon^{\nu^*}$ with $\nu^* \approx 0.62$ as expected by the universal law of diffusion in critical phenomena. The value of D^* extracted within the approximation of the linearized theory is approximately three times larger than that at the same ϵ in the stable region and about one and a half times as much as that by taking account of $\xi/\xi' \approx 2$ with ξ' being the correlation length¹³ as the same ϵ in the two-phase equilibrium. The temperature dependence of k_m may suggest that spinodal decomposition first occurs through condensation of

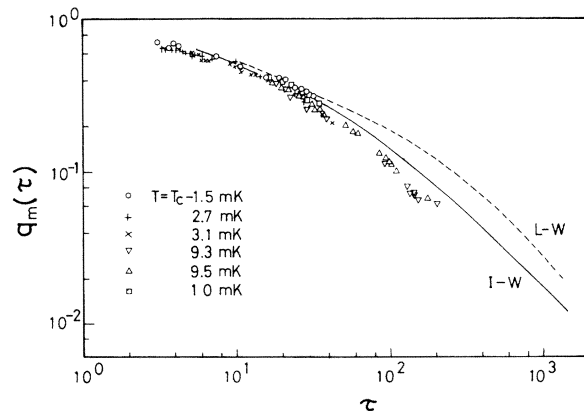


FIG. 4. Scaled location $q_m(\tau)$ vs τ for the late stage of spinodal decomposition. The solid and the dashed lines stand for the system isobutyric acid-water and the system 2, 6-lutidine-water, respectively, in Ref. 15.

fluctuations with the size of $k_m^{-1} \propto \epsilon^{-0.27}$. Finally, the scaled location $q_m(\tau)$ in the late stage of phase separation was plotted as a function of τ in Fig. 4. The present curve of $q_m(\tau)$ is in agreement with that of the system isobutyric acid–water (*I-W*) or the system 2, 6-lutidine–water (*L-W*)¹ in the range of $\tau \leq 30$, though a discrepancy appears among the three systems in the range of larger τ .

In summary, we have studied diffusive properties in an unstable state near the critical point and obtained the evidence of a break in time dependence into the early stage and the late stage in the spinodal decomposition process. For the polydimethylsilox-

ane–diethyl carbonate system, the simple power-law expression for diffusivity remains almost valid, even in the unstable region, if diffusivity is observed in the early stage. The scaling for the ring diameter in the late stage is valid for even a polymer system in which the two components differ greatly in molecular size.

ACKNOWLEDGMENT

The authors wish to thank the Ministry of Education in Japan for supporting this work with grant-in-aid for scientific research.

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⁷According to the Wegner expansion the difference $w^{\pm} - w_c$ is fitted to the form

$$w^{\pm} - w_c = B^{\pm} \epsilon^{\beta^{\pm}} + B_1^{\pm} \epsilon^{\beta^{\pm} + \Delta} + \dots,$$

where w^+ and w^- refer to the concentration of the con-

centrated and the dilute phase, w_c the critical concentration.

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¹⁰By the photon-counting technique the angular distribution and the autocorrelation function of scattered light have been measured in the stable region over the range of $1.63 \times 10^{-5} \leq \epsilon \leq 1.81 \times 10^{-3}$ and of $0.5 \leq k\xi \leq 16.7$.

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