Dynamics of concentration fluctuations for polydimethylsiloxane—diethyl carbonate

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The scaled decay rate Γ^* $[=\Gamma^c/\bar{R}k_B Tk^3/\eta(T)]$ of the system polydimethylsiloxane—diethyl carbonate, where $\eta(T)$ is the shear viscosity, k the transfer wave vector, and $\bar{R}$ a universal constant, is in agreement with the mode-coupling theory in the range of $0.2 \leq k\xi \leq 3$, and in disagreement with the renormalization-group calculation of critical dynamics with $\bar{R} = 1.2(6\pi)^{-1}$. The nonlinear shear viscosity due to shear gradients is in agreement with the theoretical prediction by Oxtoby.

I. INTRODUCTION

The critical dynamics of pure fluids and binary fluid mixtures have been investigated with great interest.[1] The mode-coupling approach by Kadanoff and Swift[2] and Kawasaki[3] and the decoupled-mode expression by Perl and Ferrell[4] are remarkably successful in describing the experimental results of dynamic critical phenomena. Oxtoby and Gelbart[5] have included the background Rayleigh linewidth in the scheme of the mode-coupling theory. Their prediction has been found to be in good agreement with experimental data for pure fluids. The renormalization-group approach is of great advantage in the derivation of the scaling relation and of the scaling function and in the calculation of the critical exponent.[6] Recent experiments of the critical dynamics by Burstyn and Sengers[7] and Güttinger and Cannell[8] support the mode-coupling theory, in contrast with those of Sorensen *et al.*[9]

The decay rate Γ associated with the order-parameter fluctuations is asymptotically represented by $\Gamma \propto k^z$ in the limit $\lim_{T \to T_c} \xi^{-1} = 0$, with ξ being the correlation length. The exponent z is the dynamical scaling exponent for the order-parameter relaxation rate and is related to η and x_λ by $z = 4 - \eta + x_\lambda$, where η is the exponent indicating deviation from the Ornstein-Zernike (OZ) theory and x_λ the characteristic exponent for the concentration conductivity. The scaled decay rate Γ^* for the critical part Γ^c, subtracted the background contribution Γ^B from Γ, can be represented by[1,5]

$$\Gamma^* = \Gamma^c/\bar{R}k_B Tk^3/\eta(T) , \tag{1}$$

where $\eta(T)$ is the macroscopic shear viscosity and k the transfer wave vector. The numerical constant $\bar{R}$ has the value $(6\pi)^{-1}$ in the original mode-coupling theory and subsequently its value is corrected by Lo and Kawasaki,[10] while the renormalization-group calculation yields $\bar{R} = 1.2(6\pi)^{-1}$. Then, the theoretical

prediction[5] for the scaled decay rate has the form

$$\Gamma^* = R(k, \xi)\Gamma_K^* . \tag{2}$$

$R(k, \xi)$ is a weakly nonuniversal function and Γ_K^* a universal function given by $K_0(k\xi)/(k\xi)^3$, with

$$K_0(x) = \tfrac{3}{4}[1 + x^2 + (x^3 - x^{-1})\arctan x] .$$

The shear viscosity can be represented by

$$\eta(T) = \eta^B(q_D \xi)^{x_\eta} = \eta^B(q_D \xi_0)^{x_\eta}\epsilon^{-\phi} , \tag{3}$$

where η^B is the background viscosity, q_D a microscopic cut-off wave number, $\xi = \xi_0\epsilon^{-\nu}$ the correlation length, $\epsilon = T/T_c - 1$ the reduced temperature difference, $\phi = x_\eta\nu$ the critical viscosity exponent. The exponent x_η is 0.054 (Ref. 11) and 0.070 (Ref. 12) in the mode-coupling theory, and 0.053 in an ϵ expansion to first order and 0.065 in an ϵ expansion to second order by the renormalization-group calculation.[13]

The effect of multiple scattering and of gravity on the correlation range and Rayleigh linewidth measurements[14,15] can be greatly reduced by selecting a mixture. In this work we report the decay rate of critical fluctuations and the shear viscosity for a critical mixture of polydimethylsiloxane in diethyl carbonate, which is isopycnic and almost isorefractive.[16]

II. EXPERIMENTAL

Polydimethylsiloxane ($M_w = 8.0 \times 10^4$, $M_w/M_n < 1.02$ with M_w and M_n being the weight- and the number-average molecular weight, respectively) in diethyl carbonate was used in the present work. Sample preparation and the critical mixing point ($T_c = 34.42$ °C, $w_c = 12.1(0)$ wt.%) have been fully described elsewhere.[16] The scattered light was detected by a Hamamatsu TV R464 photomultiplier or an EMI 9863 photomultiplier. The phototube signal was analyzed by a 48-channel, single-clipped auto-

correlator (Malvern K7023). The temperature of a silicone oil thermostat for the sample cell was controlled to within 1 mK and was monitored with a calibrated Hewlett-Packard 2804A quartz thermometer. Careful precautions were taken against the laser heating effect,[9] reflection, stray light, and use of dust-free silicone oil. The optical alignment of the photometer and the test of the correlator were achieved using a centrifuged colloidal silica solution and a polystyrene latex solution,[17] respectively.

The scattered light intensity was measured over the angular range of $25° \leqslant \theta \leqslant 135°$ in the temperature range of $1.63 \times 10^{-5} \leq \epsilon \leq 1.81 \times 10^{-3}$ and the autocorrelation function at $\theta = 35°$, $45°$, $60°$, $90°$, and $120°$ in the range of $1.63 \times 10^{-5} \leq \epsilon \leq 1.40 \times 10^{-3}$ and at $\theta = 45°$, $60°$, $75°$, and $90°$ in the range of $2.98 \times 10^{-3} \leq \epsilon \leq 3.12 \times 10^{-2}$. Besides, we measured the scattered light intensity at the fixed angle of $\theta = 90°$ over the range of $3.25 \times 10^{-6} \leq \epsilon \leq 2.1 \times 10^{-2}$. The background contribution for the measured intensity was approximately 1.3% at $\epsilon \simeq 3.22 \times 10^{-4}$ and 1.1% at $\epsilon \simeq 3.25 \times 10^{-6}$. The dark counts were approximately 0.4 counts/sec and negligibly small for the measured counts during a run.

The shear viscosity for the same sample was measured by a modified Ubbelohde-type viscometer over the temperature range $3.25 \times 10^{-6} \leq \epsilon \leq 4.64 \times 10^{-2}$. The viscometer made of Pyrex glass was flame sealed under vacuum immediately after filtering the dust-free critical mixture. We paid particular attention to avoid moisture in air, impurities, and dust particles.

III. RESULTS AND DISCUSSION

In order to obtain the critical parameters γ, ν, and ξ_0 we have analyzed the intensity data after performing the usual corrections[18] by taking the correlation scaling function[19]

$$[g(k\xi)]^{-1} = 1 + \Sigma_2 k^2 \xi^2 - \Sigma_4 k^4 \xi^4 \ ,$$

where Σ_2 and Σ_4 are set to unity and zero in the OZ theory. The results are represented by

$$I_s^{-1} = \{[1.1(5) \pm 0.19] \times 10^{-1}\} B \epsilon^{1.24 \pm 0.02} [g(k\xi)]^{-1}$$

with

$$\xi = \{[7.1(3) \pm 1.71] \times 10^{-8}\} \epsilon^{-0.62(5) \pm 0.015} \ \text{cm} \ ,$$

where B is nearly independent of temperature in the experimental range of ϵ. As the critical temperature is approached within $\epsilon \leq 2.93 \times 10^{-5}$, the intensity measured as a function of ϵ at the fixed $k = 1.95 \times 10^5$ cm^{-1} approximately levels off to a constant as expected by $I \propto \epsilon^{-\gamma}(k\xi)^{-2+\eta} \propto \epsilon^{-\gamma+(2-\eta)\nu}$. The $g(k\xi)$ calculated with $\gamma = 1.24$ varies from 1.10×10^{-2} to 7.47×10^{-4} in the range of $3.25 \times 10^{-6} \leq \epsilon \leq 2.93 \times 10^{-5}$ or of $9.47 \leq k\xi \leq 37.4$ and yields $g(k\xi) \propto (k\xi)^{-2+\eta}$ with $\eta = 0.03(7)$ ± 0.010. The attenua-

tion correction for the 6-mm cylindrical cell used in the present study is approximately 2% at $\epsilon = 3.25 \times 10^6$. Then, multiple scattering should be negligibly small. The present results of $\gamma = 1.24 \pm 0.02$, $\nu = 0.62(5) \pm 0.015$, and $\eta = 0.03(7) \pm 0.010$ are in good agreement with the recent work for the system 3-methylpentane—nitroethane[20] and with the theoretical values for the same universality class of fluids.

The shear viscosity has been analyzed in conformity with Eq. (3). The background viscosity evaluated in the temperature range of $1.77 \times 10^{-2} \leq \epsilon \leq 4.64 \times 10^{-2}$ is represented by $\eta^B = A \exp(B/T)$ P, with $A = [8.7(3) \pm 0.09] \times 10^{-4}$ and $B = 1160.(3) \pm 3.3$. The result yields $\phi = 0.028 \pm 0.001$ and $x_\eta \simeq 0.04(5)$ in the limited temperature region of $3.45 \times 10^{-4} \leq \epsilon \leq 1.77 \times 10^{-3}$. As the critical temperature is approached within $\epsilon \leq 3.45 \times 10^{-4}$ the shear viscosity asymptotically levels off to a constant. The dependence of the shear viscosity on shear gradient indicated by Oxtoby[21] is given by the quantity $\Delta(\lambda) = [\eta(0) - \eta(\lambda)]/\eta(0)$, which is a universal function of $\lambda = \eta\xi^3 S/k_B T$, with S being the magnitude of shear gradient. On the other hand, Onuki et al.[22] have found a lowering of the critical temperature $T_c(S)$ in the presence of shear flow, which has been observed on the experiment for the critical mixture aniline-cyclohexane.[23] For the present system $\Delta T = T_c(S_{\text{eff}}) - T_c(0)$, in which S_{eff} is the effective average value in terms of the experimentally known S_{max},[21] is estimated as -0.022 K in an ϵ expansion to the second order. The nonlinear shear viscosity $\Delta(\lambda_{\text{eff}})$ is shown as a function of λ^{eff} in Fig. 1. The solid curve represents the theoretical prediction by Oxtoby, the open circle the nonlinear shear-gradient effect, and the closed circle the nonlinear shear-gradient effect taken into consideration $T_c(S_{\text{eff}})$. It should be noted
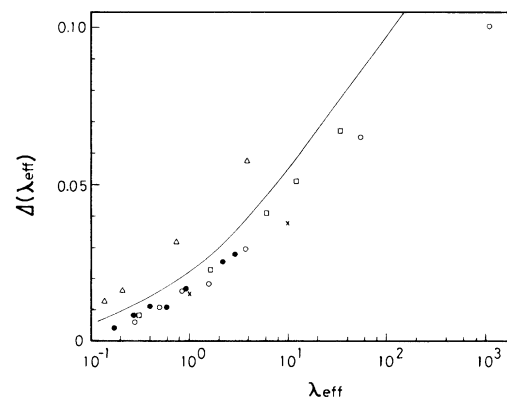

FIG. 1. Shear-gradient dependence of the viscosity. The solid line represents the theoretical prediction by Oxtoby; O, our original data; ●, our data corrected for a lowering of the critical temperature; △ , isobutyric acid—water (Ref. 24); □, aniline-cyclohexane (Ref. 25); ×, 3-methylpentane—nitroethane (Refs. 24, 26), respectively.

that the shear-gradient dependence of the viscosity corrected for $T_c(S_{eff})$ is in reasonable agreement with the theoretical prediction.[24-26] The viscosity corrected for $\Delta(\lambda_{eff})$ and $T_c(S_{eff})$ is represented by $\phi = 0.033 \pm 0.001$ and $x_\eta \simeq 0.05(3)$ to be in good agreement with $\phi = 0.034$ and $x_\eta = 0.054$ in the mode-coupling theory,[11] but in disagreement with $\phi = 0.04$ and $x_\eta = 0.065$ to the second order.

The experimental autocorrelation data have been fitted to an exponential decay law and the decay rate of the concentration fluctuations Γ has been obtained as a function of temperature at five different scattering angles, $35°$, $45°$, $60°$, $90°$, and $120°$. To estimate the critical exponent z, we have examined the Γ as a function of k at each temperature and obtained, for example, $z_{eff} \simeq 2.9(9)$ at $T - T_c = 5$ mK, $\simeq 3.0(4)$ at 31 mK, $\simeq 2.6(3)$ at 0.22 K, and $\simeq 2.1(5)$ at 4.25 K. The asymptotic value $z = \lim_{T \to T_c} z_{eff}$ evaluated from the z_{eff} in the range of $1.63 \times 10^{-5} \le \epsilon \le 1.40 \times 10^{-3}$ is 3.04 ± 0.03, which almost satisfies the dynamic scaling relation $z = 3 + x_\eta$. For comparison of the theory with the experiment over the wide temperature range, the background linewidth Γ^B must be subtracted from the measured Γ. By forming an estimate of an adjustable parameter q_D from the behavior of the shear viscosity and of the background diffusion coefficient D^B from the measured Γ at temperatures not close to T_c, we have evaluated the background part Γ^B to the critical part Γ^c in conformity with the prediction by Oxtoby and Gelbart.[5] The q_D in the Perl-Ferrell theory can be approximately given by $q_D = Ck_BT/8\pi\eta^BD_0^B\xi_0^2$, with C and D_0^B being a constant and the background diffusion amplitude, respectively. The background diffusion contribution D^B extracted from discrepancy of the measured Γ with the prediction by the original mode-coupling theory in the temperature region not close to $T_c(\epsilon \ge 3.0 \times 10^{-3})$ yields $D^B \simeq 6.3(0) \times 10^{-6} \epsilon^\gamma$ cm^2/sec with $\gamma \simeq 1.24$. As a result, the relative background linewidth to the critical linewidth can be represented by $\Gamma^B/\Gamma^c = (3C/4q_D\xi_0)\epsilon^\nu$, with $C = 0.36$ and $q_D = 5.0(6) \times 10^5$ cm^{-1}. The temperature-dependent Γ^B/Γ^c is evaluated 4.9% at $\epsilon \simeq 3.22 \times 10^{-4}$ and 0.6% at $\epsilon \simeq 9.75 \times 10^{-6}$. The value of $q_D\xi_0$ for the present system is, for example, about eight and one-half times smaller than that for the system 3-methylpentane—nitroethane.[7] Our value of $q_D\xi_0 = [3.6(1) \pm 0.28] \times 10^{-2}$ is taken to be reasonable for a variety of the $q_D\xi_0$ over 4.3×10^{-2} to 1.4×10^{-1} from substance to substance.[1] A weakly nonuniversal function $R(k, \xi)$, the ratio of the scaled decay rate Γ^* with the shear viscosity corrected for the nonlinear shear-gradient effect to Γ^*_K, is shown as a function of $k\xi$ in Fig. 2, where the solid curve represents the wave-vector-dependence correction and the dotted curve represents the wave-vector- and
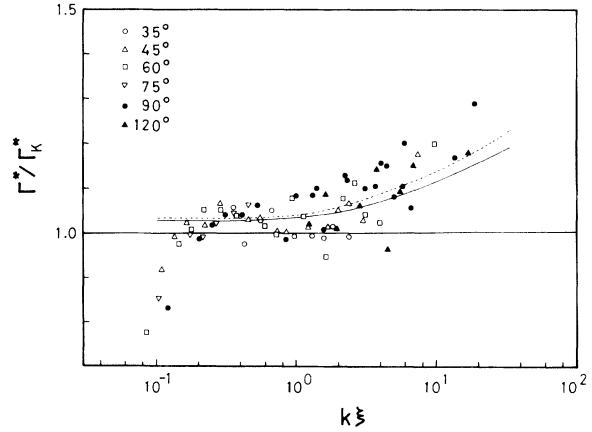

FIG. 2. The ratio of Γ^* to Γ^*_K as a function of $k\xi$, where $\Gamma^*_K = K_0(k\xi)/(k\xi)^3$ with

$$K_0(x) = \frac{3}{4}[1 + x^2 + (x^3 - x^{-1})\arctan x] .$$

The solid curve represents the wave-vector-dependence correction and the dotted curve represents the wave-vector- and frequency-dependence corrections.

frequency-dependence corrections. We used the linewidth function corrected by a factor of 2.[5,12] The present result is in good agreement with the mode-coupling theory over the range of $0.2 \le k\xi \le 3$, but in disagreement with the prediction of the renormalization-group calculation with the value of $\bar{R} = 1.2(6\pi)^{-1}$. Our result is consistent with those of the recent experiments carried out for the system 3-methylpentane—nitroethane[7] and for xenon.[8]

We have extracted the critical part Γ^c from the measured Γ over the temperature range of our experiment using the parameters C and $q_D\xi_0$, experimentally evaluated. The scaled decay rate Γ^* to Γ^*_K is in good agreement with the wave-vector-dependence correction over the range of $0.2 \le k\xi \le 3$. We feel, however, further work is still necessary for the interpretation of the dynamic properties of critical fluctuations, especially the dynamic properties in the large $k\xi$ region in terms of the critical-point universality. To our knowledge, a polymer system would be a good candidate for the work in the large-$k\xi$ region because of the large amplitude of correlation length, which is approximately three times larger than that in the ordinary critical binary mixtures.

ACKNOWLEDGMENT

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