Shear-Induced Critical Dynamics in a Nonionic Micellar Solution

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Shear-induced critical dynamics in a nonionic micellar solution has been investigated by measuring the viscosity η as a function of the shear rate S and a characteristic crossover temperature associated with S. The viscosity very close to T_c varies as $S^{-\omega}$ with $\omega = 0.021 \pm 0.003$ in excellent agreement with the expected value of $\omega = 0.021$. We also find a simple scaling relation between the temperature dependence and shear-rate dependence of η. In addition, we confirm the feasibility of observing phase-separation dynamics near the critical point by shear quenching.

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A system near a critical point exhibits large fluctuations in the order parameter associated with the phase transition. An interesting phenomenon is that critical fluctuations in fluids are affected by shear [1–3]. Near the critical temperature T_c the correlation length ξ of the fluctuations diverges as $\xi_0\epsilon^{-\nu}$ with $\epsilon = |T - T_c|/T_c$ and $\nu = 0.63$, while ξ_0 is a system-dependent amplitude [4]. The lifetime τ_ξ of these fluctuations is $6\pi\eta\xi^3/k_BT$, where η is the shear viscosity, k_B the Boltzmann constant, and T the temperature [5]. Since the viscosity diverges as $\eta \propto \xi^x$ with $x = 0.065$ [6,7], it follows that τ_ξ diverges as $\xi^z \propto \epsilon^{-\nu z}$ with $z = 3 + x = 3.065$. A shear rate S will affect the critical fluctuations when $S\tau_\xi$ becomes larger than unity. Since τ_ξ diverges strongly, this condition is encountered when the critical point is approached sufficiently close.

In this Letter we focus our attention on the shear-rate dependence of the viscosity η associated with the expected non-Newtonian behavior near the critical point. In the weak-shear regime, $S\tau_\xi \ll 1$, η will be independent of S, while in the strong-shear regime, $S\tau_\xi \gg 1$, η is expected to level off to a constant independent of ϵ [7,8]. For the moderate-shear regime, $S\tau_\xi \gtrsim 1$, Onuki and Kawasaki [9] have predicted that, in the limit $\epsilon \to 0$, η should vary with S as

$$\eta(S) = \eta^0 S^{-\omega}, \tag{1}$$

with $\omega = x/z = 0.021$. Since the viscosity exhibits only a weak critical enhancement and since the exponent ω in (1) is very small, an experimental verification of this shear-rate dependence is difficult. The trick is to find a liquid mixture that is much more sensitive to shear than the liquid mixtures that have conventionally been studied. We shall show that nonionic micellar solutions are suitable for quantitative experimental studies of shear-induced critical dynamics. In addition, the field of self-assembling microstructured fluids as exampled by a micellar solution is of paramount importance to an increasing number of industrial applications including engineering, physics, chemistry, biology, and medicine.

As originally pointed out by Corti and Degiorgio [10], aqueous solutions of nonionic amphiphiles often possess a lower critical solution temperature above which the system separates into a micelle-poor and a micelle-rich phase. After some initial confusion [11], it has been established that suitably chosen nonionic micellar solutions belong to the same static and dynamic universality class as ordinary nonionic liquid mixtures [12–15]. A specific example is an aqueous solution of *tetra*-ethylene glycol *n*-decylether ($C_{10}E_4$) [14,15]. This system has a correlation-length amplitude ξ_0 of about 11 Å [14]. We have measured in this system the viscosity η and have verified the shear-rate dependence of η as predicted by Onuki and Kawasaki [9]. We have also measured a characteristic crossover temperature $T_0(S)$ as a function of the shear rate S and have found a simple scaling relation between the shear-rate dependence of η at $\epsilon = 0$ and the temperature dependence of η at zero shear rate. Furthermore, the shear-rate effects are sufficiently large, so that we can observe the dynamics of this phase-separating micellar solution by shear quenching.

Measurements of various critical properties of the $C_{10}E_4$+water system have been presented in previous publications [14,15]. In the present study we continued to use a portion of the same $C_{10}E_4$ sample employed in our previous work. The viscosity was measured with a rotational viscometer of the Zimm-Crothers type [16]. In addition, a provision was made enabling us to observe simultaneously the light scattered by the micellar solution. The shear stress on the part of the solution located between the two coaxial cylinders was produced by driving the inner cylinder with an electrically induced magnetic field whose strength was varied continuously with the supply of an electric current [17]. The relevant diameters of the inner and outer cylinders are 10.00 ± 0.02 and 12.05 ± 0.04 mm yielding a gap with a thickness of 1 mm. The viscometer was calibrated against water as the calibration liquid. The shear rate S was calculated from the imposed angular velocity of the inner cylinder and the radii of the inner and outer cylinders. The viscosity and the shear rate were determined with an absolute accuracy of 3% and 2%, respectively. However, since all measurements were obtained under the same instrumental conditions, the relative errors in η and S are only 0.4% and 0.2%, respectively; these are the errors relevant for the analysis of the temperature and shear-rate dependence of η.

To observe the light scattered by the solution two He-Ne 633-nm light beams were passed through the viscometer, one at a level corresponding to the middle height of the inner cylinder and another at a level about 1 cm below the bottom of the inner cylinder. The first beam allowed us to observe the light scattering in the solution in the gap where it was subjected to shear, while the second beam enabled us to observe simultaneously the light scattering in the bulk solution at a position where the shear rate remained negligibly small. Upon raising the temperature with the inner cylinder at rest, both light beams would produce the appearance of a spinodal ring indicating phase separation at the same temperature within ±1 mK.

A double-logarithmic plot of the viscosity measured as a function of S is presented in Fig. 1. At $T_c - T = 1.22$ K and even at $T_c - T = 66$ mK, η appears to be independent of S, but at $T_c - T = 5$ mK, a shear-rate dependence of η is clearly observed. Since the application of shear raises the critical temperature $T_c(0)$ to a higher value $T_c(S)$ [1,7], it was also possible to measure η as a function of S at $T = T_c = T_c(0)$; these data are indicated by the black dots in Fig. 1 and cover the range $2.7\ \mathrm{s}^{-1} \le S \le 36\ \mathrm{s}^{-1}$. A fit of the data obtained at $T = T_c(0)$ with the power law (1) yields $\eta^0 = 3.22 \pm 0.02$ mPa s (with S measured in s^{-1}) and $\omega = 0.021 \pm 0.003$. We conclude that the observed value for the exponent ω is in excellent agreement with the value $\omega = x/z = 0.021$ expected on the basis of the theory of Onuki and Kawasaki [9].

In addition, we have observed the light scattering produced by the micellar solution as a function of temperature. We typically started at a temperature 2 K below $T_c(0)$ and then raised the temperature slowly with a rate of about 2 mK/min close to T_c. The light scattering at finite S would remain essentially unchanged at $T \ge T_c(0)$ until a temperature $T_0(S)$ was reached at which two spikes in the direction perpendicular to the flow would develop in the light-scattering pattern, similar to the spikes observed by Hashimoto, Takebe, and Suehiro for a dilute polymer solution [18]. We interpreted the temperature $T_0(S)$ at the onset of these spikes as the crossover temperature between the shear-unaffected to the shear-affected regime [1-3]. Since the enhancement $T_0(S) - T_c(0)$ due to shear is proportional to $T_0(S) - T_c(0)$, the observed crossover temperature $T_0(S)$ is expected to have the same dependence on S as T_c [1,2].

Since the scattering produced by the lower light beam enabled us to locate $T_c(0)$, we obtained accurate measurements of the relevant temperature difference $\epsilon_0(S) = [T_0(S) - T_c(0)]/T_c(0)$ in the range $2.67\ \mathrm{s}^{-1} \le S \le 35.8\ \mathrm{s}^{-1}$. A fit of these experimental data with a power law of the form

$$\epsilon_0(S) = [T_0(S) - T_c(0)]/T_c(0) = \epsilon_0^0 S^p \qquad (2)$$

yields $\epsilon_0^0 = (1.35 \pm 0.11) \times 10^{-5}$ and $p = 0.51 \pm 0.03$. This exponent p is in excellent agreement with the value $p = 1/\nu z = 0.52$ predicted by Onuki and Kawasaki [1] and with the earlier experimental values reported for liquid mixtures [2,3] and for a polymer mixture [18].

The viscosity of $C_{10}E_4$+water was previously measured as a function of temperature with another viscometer in the weak-shear limit $S \to 0$ [15]. The viscosity ratio η/η^B, where η^B is a background viscosity, could be represented by

$$\eta/\eta^B = A\epsilon^{-\phi} \quad (S = 0)\,, \qquad (3)$$

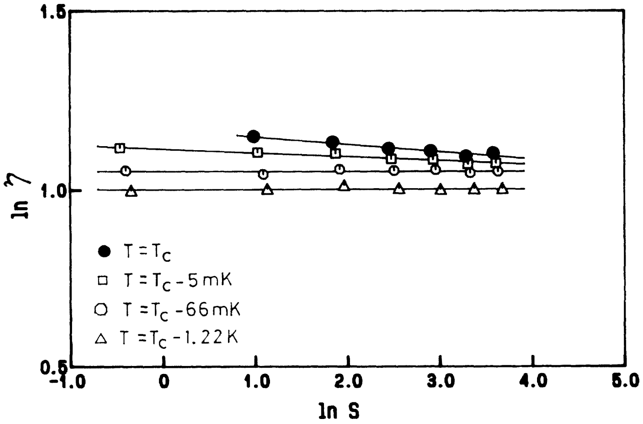

FIG. 1. Log-log plots of the viscosity η (mPa s) measured as a function of the shear rate S (s^{-1}).

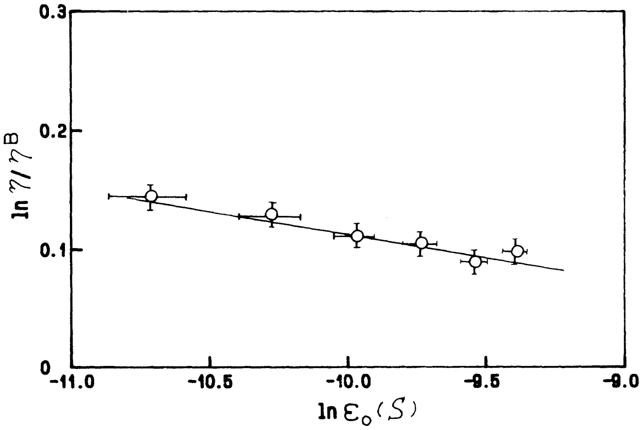

FIG. 2. Log-log plot of the viscosity ratio η/η^B obtained at $T = T_c(0)$ as a function of the reduced temperature shift $\epsilon_0(S) = [T_0(S) - T_c(0)]/T_c(0)$. The solid line represents the behavior of η/η^B at $S = 0$ as a function of $\epsilon = (T_c - T)/T_c$ [15].

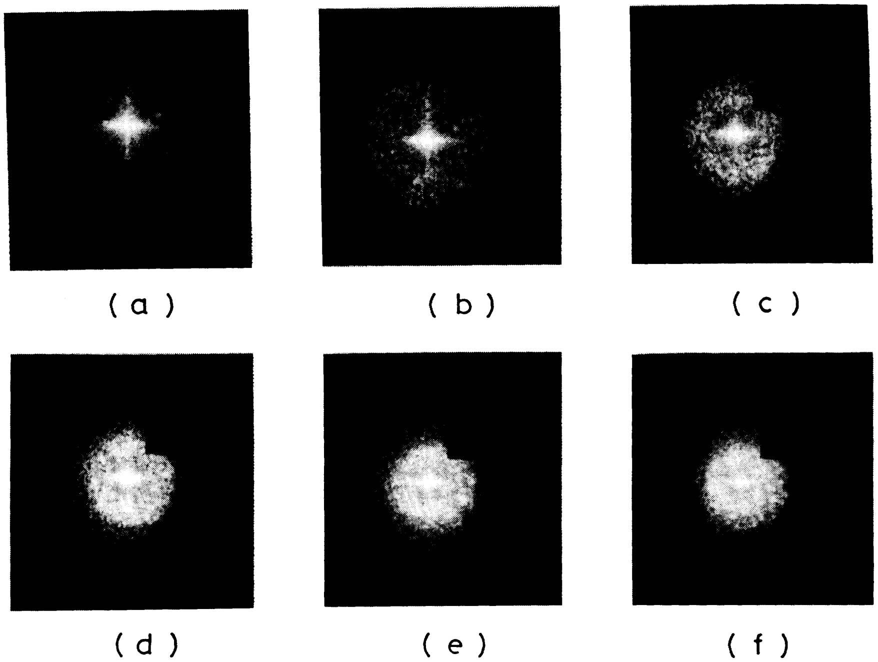

FIG. 3. Light-scattering patterns of the phase-separating critical mixture as a function of the time t after the application of a shear quench from $S=6.3$ to 0 s^{-1} at $T \simeq T_c(0)+10$ mK. (a) $t=0.3$ s, (b) $t=12$ s, (c) $t=22$ s, (d) $t=31$ s, (e) $t=45$ s, and (f) $t=58$ s.

with $A=0.74\pm0.03$ and $\phi=0.041\pm0.005$. This exponent ϕ is in excellent agreement with the value $\phi=\nu x$ found for ordinary liquid mixtures [6,7,19]. We now postulate that the shear-rate dependence of η at $T=T_c(0)$ can be obtained by replacing ϵ in (3) with $\epsilon_0(S)$ as given by (2):

$$\eta/\eta^B = A[\epsilon_s(S)]^{-\phi} \quad [T=T_c(0)]\,. \tag{4}$$

To test this scaling relation we show in Fig. 2 a double-logarithmic plot of the experimental viscosity ratio η/η^B as a function of the measured $\epsilon_s(S)$; for this purpose we have identified η^B with the viscosity measured at $T_c-T=1.22$ K. The solid line in Fig. 2 represents (4) with $A=0.75\pm0.04$ and $\phi=0.040\pm0.005$ in excellent agreement with the parameter values obtained for the power law (3) of η/η^B as a function of ϵ at $S=0$.

We were also able to measure the viscosity at temperatures above $T_c(0)$ and close to $T_0(S)$. A fit of the viscosity data obtained at $T \sim T_0(S)$ to (1) yields $\eta^0=3.26\pm0.03$ mPa s and $\omega=0.021\pm0.004$ which are within error equal to the values found at $T=T_c(0)$.

The dynamics of phase separation has been examined for a micellar solution by a shear quench, as applied by Beysens and Perot for simple liquid mixtures [20] and by Takebe and Hashimoto for a polymer solution [21]. We raised at a given S the temperature to $T_0(S)$ and then suddenly dropped the shear rate to zero. This method is equivalent to a temperature quench into the unstable region of $T_0(S)-T_c(0)$. In Fig. 3 we show the light-scattering patterns observed as a function of the time t after such a quench from $S=6.3$ to 0 s^{-1}. In the early stage after the shear quench the scattering pattern has a somewhat elliptical deformation with the major axis in the direction perpendicular to the flow [Figs. 4(b) and 4(c)], similar to the observations of Chan and co-workers in a phase-separating mixture at relatively low shear rates [20,22]. After this initial stage approximately isotropic

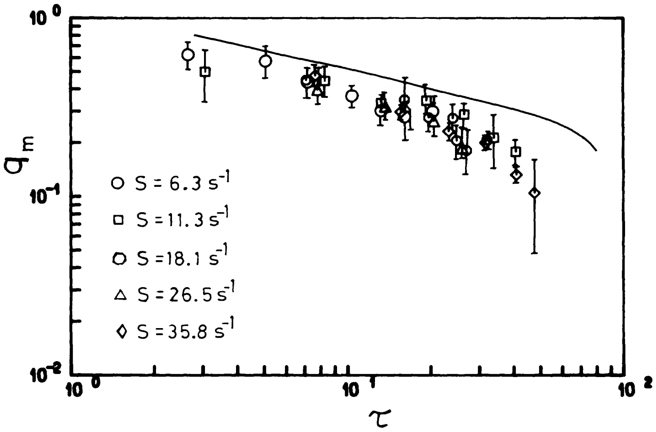

FIG. 4. Scaled wave number $q_m=k_m\xi$ of the spinodal ring observed as a function of the scaled time $\tau=t/\tau_\xi$ after applying a quench at $T \simeq T_0(S)$ from a shear rate S to a shear rate zero. The solid curve represents the theory of Kawasaki and Ohta [23].

spinodal rings were observed. This result suggests that after an initial anisotropic decay of the domains the shear stress is released. Excluding data in the initial anisotropic state we have determined the maximum wave number k_m of the light scattered in the flow direction as a function of t for shear quenches with initial shear rates S varying from $S=6.3$ to $35.8\ \mathrm{s}^{-1}$. A plot of the scaled wave number $q_m=k_m\xi$ as a function of the scaled time $\tau=t/\tau_\xi$ with ξ as determined previously [14], is presented in Fig. 4. The data do appear to have a tendency to follow the theoretical prediction of Kawasaki and Ohta as represented by the solid curve.

We conclude that we have verified the shear-rate dependence (1) of the viscosity predicted by Onuki and Kawasaki [9], that we have established a simple scaling relation between the shear-rate dependence of η at $T=T_c$ and the temperature dependence of η at $S=0$, and that we have demonstrated the feasibility of observing spinodal decomposition by shear quenching even for self-assembling microstructured fluids as exampled by a nonionic micellar solution.

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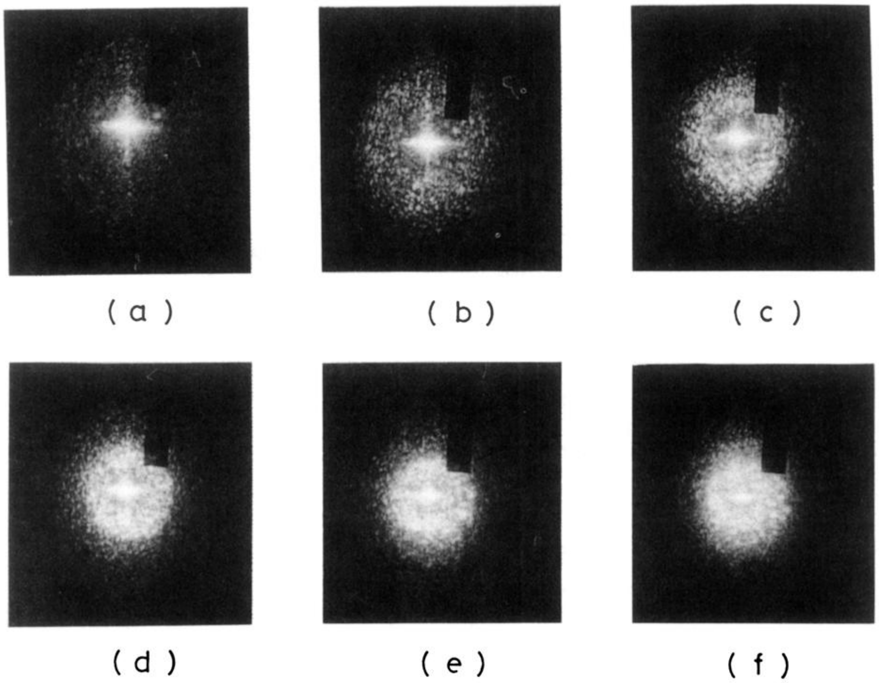

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