Viscosity of a Phase-Separating Critical Mixture[1]

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Onuki has predicted the existence of a significant enhancement of the viscosity of a liquid mixture in the course of spinodal decomposition. We discuss a method to measure this effect in a critical mixture of isobutyric acid and water in which spinodal decomposition is induced by a pressure-quench technique. In addition, by varying the static pressure in the homogeneous phase, experimental information about the dynamic critical exponent for the viscosity is obtained.

KEY WORDS: critical phenomena; isobutyric acid and water; liquid mixtures; shear flow; spinodal decomposition; viscosity.

1. INTRODUCTON

When a liquid mixture near its critical point of mixing is suddenly brought into the unstable region, spinodal decomposition occurs by which the separation into two phases proceeds through the spontaneous appearance and growth of domains of different concentration [1–3]. Onuki has discussed a time-independent state that can result during spinodal decomposition in the presence of flow [4]. Domains that have grown to a certain size are then stretched and broken by shear forces. The work done against surface tension in stretching a domain is dissipated when it breaks and this new dissipative mechanism causes an enhancement $\Delta\eta$ of the viscosity over the viscosity η of the homogeneous phases at the same temperature. Onuki predicts that under certain conditions the relative enhancement $\Delta\eta/\eta$ could be as large as 50% or so. We have initiated an attempt to observe this

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effect experimentally and it is the purpose of this paper to present some preliminary results.

The experiments are performed with a mixture of isobutyric acid and water, and spinodal decomposition is induced by the pressure-quench technique [5–7]. Furthermore, by varying the static pressure in the homogeneous region we obtain additional information about the asymptotic critical behavior of the viscosity.

2. EXPERIMENTAL

The measurements are made with an oscillating-disk viscometer designed by Kestin and co-workers [8] and previously used in our laboratory to measure the viscosity of liquid toluene [9]. In the present experiments this viscometer is located inside an insulated box whose air temperature is controlled by a feedback controller. The large heat capacity of the viscometer contributes to a good temperature stability of a few millikelvins per day.

The disk used in the present experiments has a radius of about 25 mm and a thickness of about 11 mm. The two fixed plates above and below the oscillating disk were placed at the fairly large distance of about 7 mm from the surfaces of the disk, thereby guarding against convection without affecting the fluid velocity around the disk. To ensure an adequate number of oscillations during the spinodal decomposition process, the torsional strand from which the disk is suspended was chosen so as to obtain an oscillating period of about 4 s.

The viscosity is deduced from the decay rate of the oscillations with the aid of the working equations for a free thick disk [10–13]. Test measurements with water showed that these working equations yield the viscosity with an absolute accuracy of about 1 %. It is possible to obtain an accuracy of a few tenths of a percent by calibrating with a reference fluid [14]. The precision of the measurements is better than 0.1 %. For our present purpose we needed to measure only changes of the viscosity and further calibration was not necessary.

The critical mixture of 38.8 wt % isobutyric acid and water was prepared gravimetrically. Isobutyric acid was used as received from the supplier without further purification. However, care was taken to ensure that only inert gases came into contact with the mixture during its preparation and transfer into the viscometer.

The critical temperature T_c of isobutyric acid and water varies with the pressure P as [15]

$$dT_c/dP = -54 \text{ mK/bar} \tag{1}$$

Spinodal decomposition is induced by sudden depressurization which brings the critical temperature T_c above the actual temperature T. A given pressure change corresponds to an equivalent change of the value of $[T - T_c]$ [5]. The difference $P - P_c$, where $P_c(T)$ is the pressure at which the critical temperature equals the temperature of the liquid, is an alternative measure of the distance from the critical point. The design of the viscometer does not allow a direct visual observation of the critical point. Instead each experimental run begins with a series of measurements of the viscosity in the homogeneous phase as a function of pressure to determine P_c as described in the next section. Then the pressure is quenched to a value below P_c, after which the pressure is brought back to a high value above P_c. The time the system spends in the quenched state is about 1 min. We have found that the viscosity in the homogeneous phase is not completely reproduced after this cycle, but it assumes values that are typically about 1 % lower than before the quench. Therefore, we remix the sample after a few quenching cycles. This remixing requires that the viscometer be heated to a temperature well above the critical temperature and that the mixture be transferred to a stirring bottle. This process is somewhat tedious and slows the pace of the measurements.

The initial amplitude of the disk oscillations is about 1 rad. The shear rate S of the fluid is not uniform in our apparatus, but averaged over a cycle and over the disk's surface, it is about $5 \, \text{s}^{-1}$. This shear rate is to be compared with the relaxation time of the fluctuations in the homogeneous phase $\tau_\xi \simeq 6\pi\eta\xi^3/k_B T$, where ξ is the correlation length and k_B is Boltzmann's constant. For quenches corresponding to 10 mK or more we estimate $\tau_\xi \leqslant 0.02$ s, so that we operate in the low-shear regime of Onuki's theory with $S\tau_\xi \ll 1$. In a typical measurement we observe about 12 oscillations of the disk, while the amplitude is reduced by a factor $1/e$ in about 8 oscillations. The period and damping of the disk oscillations are determined by measuring the time intervals between successive detections of a laser beam reflected from a mirror suspended from the disk.

3. VISCOSITY IN THE HOMOGENEOUS PHASE

In each experimental run the pressure was varied at a constant temperature. Figure 1 shows the viscosity of the isobutyric acid and water mixture at 27.037°C obtained in the homogeneous phase as a function of $P - P_0$, where P_0 corresponds to atmospheric pressure. For a critical mixture at constant pressure the viscosity is expected to vary as [16]

$$\eta(T) = Y_T[(T - T_c)/T_c]^{-y} \tag{2}$$
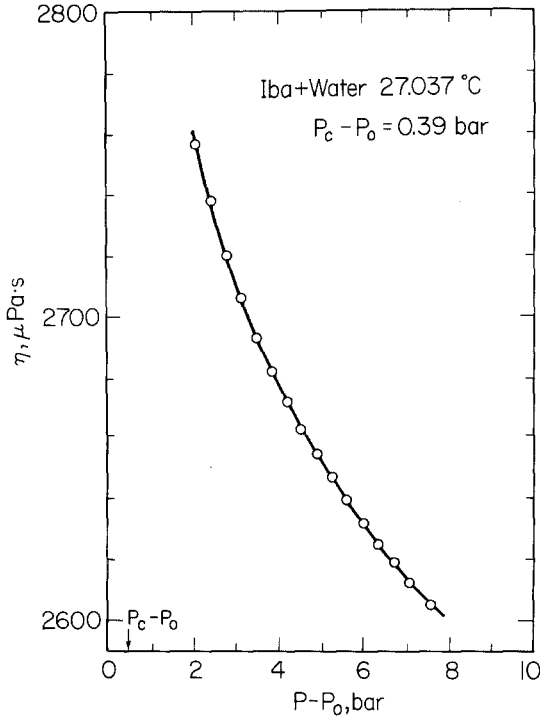
Fig. 1. The viscosity of a critical mixture of isobutyric acid and water as a function of $P - P_0$, where P_0 is atmospheric pressure.

with $y = vz$. Here $v = 0.63$ is the critical exponent of the correlation length and z is a universal dynamic critical exponent. The most recent theoretical prediction [17] suggests $z \simeq 0.05$, but experiments seem to yield slightly larger values for this exponent [18, 19]. The amplitude Y_T in Eq. (2) is proportional to the so-called background viscosity $\bar{\eta}$, which is a viscosity without the effect of critical fluctuations and which is itself a function of temperature [16]. In practice, $\bar{\eta}$ is represented by an empirical function of temperature that contains another adjustable parameter. In the pressure range under consideration T_c is expected to vary linearly with pressure [20]. Hence at a constant temperature, we expect the viscosity to vary as

$$\eta(P) = Y_p [(P - P_c)/P_c]^{-y} \tag{3}$$

The amplitude Y_p will again be proportional to the background viscosity $\bar{\eta}$ but at a constant temperature the dependence of $\bar{\eta}$ on P is negligibly small. Hence, in fitting our data to Eq. (3) we can treat Y_p as a constant.

Figure 2 shows the percentage deviations of the viscosity data when fitted to Eq. (3) with $y = 0.035$, $y = 0.040$, and $y = 0.045$ and with Y_p and P_c as two adjustable constants. With $y = 0.040$ an excellent representation is obtained as is evident from Fig. 2b; in this figure we have also indicated the equivalent reduced temperature $\varepsilon = (T - T_c)/T_c$. The critical pressure $P - P_0$ at 27.037°C is 0.39×10^5 Pa, which implies a critical temperature at atmospheric pressure $T_c(P_0) = 27.058$°C. On the other hand, with $y = 0.035$ and $y = 0.045$ pronounced systematic deviations are observed as shown in Figs. 2a and 2c. From an analysis of the standard deviation σ as a function of y and estimating the error as the range that doubles the standard deviation, we find
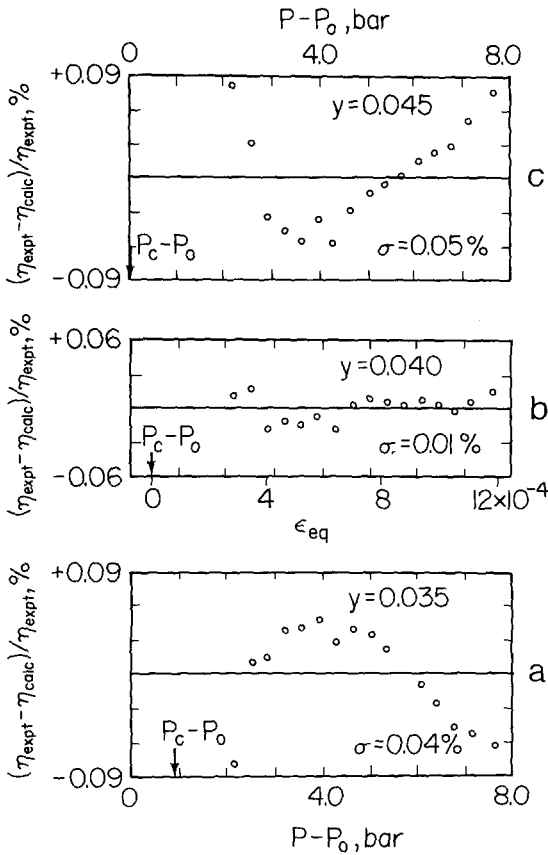
$$y = 0.039 \pm 0.002 \tag{4}$$

Fig. 2. Relative differences between the experimental viscosities η_{expt} and the values η_{calc} calculated from Eq. (3) with $y = 0.035$ (a), $y = 0.040$ (b), and $y = 0.045$ (c).

which corresponds to $z = 0.062 \pm 0.003$, in agreement with other experimental results recently reported [18, 19]. While we intend to obtain additional measurements, our preliminary results shows that measuring the viscosity as a function of pressure at constant temperature yields an accurate method for determining z. In principle, corrections need to be considered for shear-rate and frequency effects [19], but these effects can be shown to be negligible in the range where our data were obtained.

It should be remarked that we were not able to measure the viscosity at pressures closer than 1.7 bar from the critical pressure, which corresponds to an equivalent temperature difference $T - T_c$ of about 90 mK. Closer to the critical point we would observe a slow steady upward drift in the viscosity of about 0.2% per hour. We attribute this effect to incipient phase separation in a lower and cooler part of the apparatus. The height of the viscometer is rather large [8] and we are unable to avoid a small temperature gradient along the vertical direction of the viscometer.

4. VISCOSITY DURING SPINODAL DECOMPOSITION

In each experimental run, we first measure the viscosity in the homogeneous phase above P_c as a function of the pressure at a given temperature. The critical pressure P_c associated with each run is obtained by fitting these data to Eq. (3) with the exponent y fixed at 0.040.

Quench measurements begin in the one-phase region at an initial pressure P_i about 2 bar above P_c. Prior to the quench an oscillation is started and the oscillations of the disk are allowed to proceed for some time, usually 8 cycles or 32 s. Then a valve is opened and the pressure drops to a predetermined value P_f, typically about 0.5 bar below P_c. The motion of the disk is monitored for another 10–12 oscillations, whereafter the pressure is raised again to a value above P_c. To obtain the equivalent quench depth $Q = T_c - T$ in temperature, it should be noted that the depressurization also causes a slight drop of the actual temperature T due to adiabatic cooling. The behavior of the adiabatic thermal pressure coefficient $(\partial T/\partial P)_S$ of a liquid mixture near the critical point is rather complicated [7]. In practice, for adiabatic quenches into the unstable region we find a cooling of about 3 mK/bar, which is of the same order of magnitude as observed by Wong and Knobler [5]. This change in T adds to $T_c - T$.

In the measurements we observe successive time intervals τ needed for the reflected laser beam to sweep two stationary photodetectors, one of which is located at the position of zero deflection. From these time intervals one can deduce both the frequency ω and the damping constant Δ of the oscillations as described by Kestin and Khalifa [21]. If the viscosity η

remains constant during the experiment, $\ln(\sin \omega\tau)$ increases linearly with the time t as $\Delta\omega t$. Thus the function $\ln(\sin \omega\tau) - \Delta\omega t$, when plotted as a function of the time t, should be constant. However, in our quench experiments the viscosity will be different before and after the quench. If we still assign to the run a constant effective frequency $\bar{\omega}$ and a constant effective damping constant $\bar{\Delta}$, the function

$$f(\tau, t) = \ln(\sin \bar{\omega}\tau) - \overline{\Delta\omega}t \tag{5}$$

will no longer be independent of time. For times when $\Delta < \bar{\Delta}$ the function will decrease with time, and for times when $\Delta > \bar{\Delta}$ the function will increase with time, the damping constant Δ being approximately proportional to $\sqrt{\eta}$.

In Fig. 3 we have plotted the function $f(\tau, t)$ minus its time-averaged value $\langle f \rangle$ as a function of t for two quench experiments. These are the third and fourth in a series of seven quenches with an effective depth near 25 mK. The sample was remixed only at the beginning and the end of the
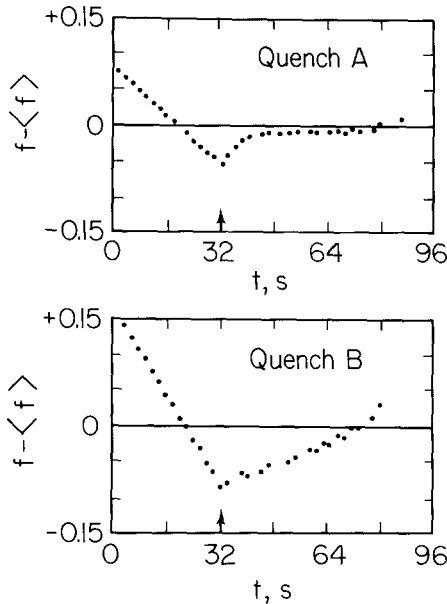
Fig. 3. Deviation of the function $f(\tau, t)$ from its average value $\langle f \rangle$ as a function of the time t. From $t = 0$ to $t = 32$ s the disk is oscillating in the homogeneous phase at constant $P \simeq P_c + 2$ bar. At $t = 32$ s the system is quenched into the unstable region.

series. The oscillations are started at $t = 0$, and from $t = 0$ to $t = 32$ s the mixture is in the homogeneous phase at $P = P_i$. During this time interval the function f has a negative slope corresponding to the lower viscosity of the fluid before the quench. After the quench at $t = 32$ s we observe an increase in f with time, indicating a larger viscosity. The detailed behavior observed in the two quenches differs a bit. In quench B the viscosity has a constant very high value from immediately after the quench until the end of the measurement. In quench A the viscosity falls, from a very high value immediately after the quench to a constant value of η close to the average effective value $\bar{\eta}$, which is still significantly larger than the viscosity before the quench. For quench B we find $\bar{\Delta} \simeq 0.026$ and $\bar{\omega} \simeq 1.54$ s^{-1}. The change in the damping constant caused by the quench is the change of slope indicated in Fig. 3 divided by $\bar{\omega}$. This change of the damping constant is about 0.006 or about 23%, which implies a viscosity increase of about 46%.

To obtain a quantitative measure of the change in viscosity upon spinodal decomposition we fit the pre- and postquench data separately. For quenches such as quench A the damping Δ after the quench depends on the time interval chosen. We have arbitrarily standardized our procedure by dropping from the postquench data the first two and the last two time intervals. This procedure favors the final constant viscosity section. We hope to explore further the details of the time dependence of the viscosity in future experiments.

Detailed information about the two quenches is presented in Table I. As a measure of the viscosity enhancement during spinodal decomposition we have compared it with the viscosity $\eta(Q)$ in the homogeneous region at a distance from the critical point equal the quench depth $|Q|$; the value of $\eta(Q)$ is calculated from Eq. (3) with the temperature interval $|Q|$ converted into the equivalent pressure difference $P - P_c$. We identify this measure with the enhancement $\Delta\eta/\eta$ of the theory. The viscosity enhancements

Table I. Some Experimental Results

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	Quench A	
$t = 26.557°C$	$P_i - P_0 = 5.52$ bar	$\eta = 3321 \ \mu Pa \cdot s$
$Q = 23$ mK	$P_f - P_0 = 3.04$ bar	$\eta(Q) = 2930 \ \mu Pa \cdot s$
	$P_c - P_0 = 3.33$ bar	$\Delta\eta/\eta = 0.13$
	Quench B	
$t = 26.556°C$	$P_i - P_0 = 5.53$ bar	$\eta = 4256 \ \mu Pa \cdot s$
$Q = 26$ mK	$P_f - P_0 = 2.87$ bar	$\eta(Q) = 2887 \ \mu Pa \cdot s$
	$P_c - P_0 = 3.21$ bar	$\Delta\eta/\eta = 0.47$

of the seven quenches in the run from which quenches A and B were taken are 6.8, 8.6, 13.3, 47.4, 50.8, 48.6, and 42.8%. The jump in the enhancements was not reflected in the behavior of the viscosity in the homogeneous phase, which continued to follow the power law given by Eq. (3) with $y = 0.040$ but with systematic different Y_p and P_c. The variation in the observed enhancement may be related to the change in the local composition of the mixture after repeated quenching cycles [22].

5. DISCUSSION

We have observed results of many quenches with depths from 20 to 150 mK. Most of these quenches have yielded enhancements of from 5 to 10%. Enhancements of 40 to 50%, such as that in quench B, have also been observed, but only after some repeated quenching cycles. It thus appears that the observation of these larger effects requires some shift in concentration of the mixture around the disk from that of the homogeneous freshly mixed sample. There is a qualitative difference between the large and the small enhancements in that the viscosity remains constant at a very high value when the enhancement is large but falls from a very high value to a somewhat lower constant value when the enhancement is small.

Quenches below the critical point of the mixture have an interesting effect on the period of oscillation of the disk. In a normal fluid an increase in the viscosity results in increased drag and an increase in the period. When the viscosity is increased by quenching below the critical point, this period increase is smaller than would be observed for the same change of viscosity in a normal fluid. In many cases the period actually decreases. From this we infer that the phase-separating mixture is viscoelastic: the deforming domains may exert a restoring force on the disk, resulting in a lower period. The size of this effect can be given quantitatively by calculating a complex viscosity with the aid of a second working equation [10–13] which links the viscosity and the period. The values of viscosity given in Table I were calculated from the first working equation only, and the period effect was ignored. When we solve the two equations simultaneously, the unknowns being the real and imaginary parts of the complex viscosity, we obtain a negative imaginary part with a magnitude of about one tenth of the real part.

Some discussion of the time and length scales in spinodal decomposition is relevant. Figure 4 shows the characteristic size of domains as a function of time for three quench depths during spinodal decomposition without shear. These curves were calculated from a scaling relation and a figure given by Wong and Knobler [5]. At times earlier than shown,
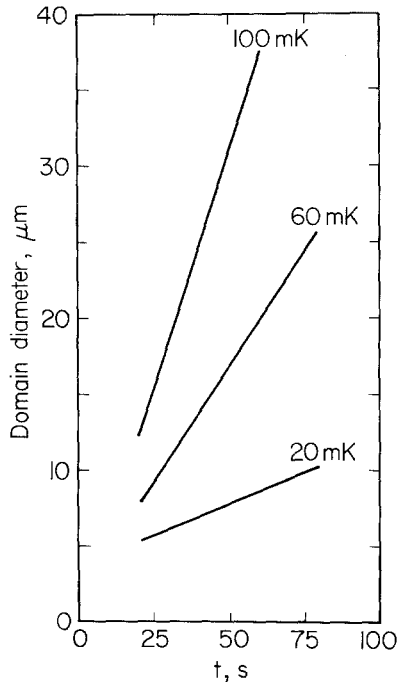
Fig. 4. Growth of the characteristic size of domains during spinodal decomposition for three quench depths according to Wong and Knobler [5] in the absence of shear flow.

domains grow like $t^{1/3}$. Gravity does not become important until the domain size becomes larger than the capillary length $(\sigma/g\,\varDelta\rho)^{1/2}$, where σ is the interfacial tension, g the gravitational acceleration constant, and $\varDelta\rho$ the density difference of the coexisting phases [4, 23]. Because $\varDelta\rho$ is small for the isobutyric acid and water system, gravity effects are small for several minutes. Our measurements are made in a time of about 1 min following the quench.

Onuki's estimate of the characteristic size of domains in the time-independent state where growth is balanced by shear is $R \sim \sigma/\eta S$. This gives, for quenches of depth 20, 60, and 100 mK, domain sizes of 12, 50, and 95 μm, when the average shear rate $S = 5\ \mathrm{s}^{-1}$ is used. Thus there is a rough agreement of the length and time scales, although domains growing freely in spinodal decomposition without shear would, with our average shear rate, not appear to have quite enough time to grow to the size given by Onuki's estimate in the 1-min time of our experiments.

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