

## Viscoelasticity of a Simple Liquid Mixture during Spinodal Decomposition

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We report measurements of the effective viscosity and elasticity of a critical mixture of isobutyric acid and water in the process of phase separation under shear. The viscoelasticity of the sheared sample is a consequence of capillary forces associated with domain interfaces that produce linear domain growth in quiescent samples. We find agreement with a theory recently proposed by Doi and Ohta and obtain an estimate of the interfacial area per unit volume during spinodal decomposition.

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Much theoretical and experimental effort has been devoted to the problem of the evolution toward a two-phase equilibrium state that results when an initially homogeneous mixture is "quenched" to conditions of partial miscibility, e.g., by applying an abrupt change of the temperature. A quench of the mixture with critical composition  $x_c$  through the critical temperature  $T_c$  leaves the uniform mixture in a state of maximum free energy unstable to infinitesimal concentration fluctuations, and the sample begins to unmix in a process called spinodal decomposition [1]. The appearance and growth of concentration inhomogeneities resulting from this thermodynamic instability is described by the Cahn-Hilliard-Cook (CHC) equation, a partial differential Langevin equation for the concentration field [2]. Solutions to this equation are quasiperiodic functions with a characteristic wavelength  $a(t)$  that increases in time according to  $a(t) \propto t^p$  with  $p \approx \frac{1}{3}$  at sufficiently long times. This result describes the coarsening of a structure of interconnected concentration domains [3].

If the coupling of the concentration field with other currents can be ignored, then the CHC equation by itself may fully describe the unmixing process. However, it is known that the coupling between the concentration and velocity fields is crucial in fluid systems and results in a much larger growth exponent  $p$ . An understanding of this behavior at a phenomenological level can be developed as follows [4]. In times that are typically short on the scale of an experiment, the concentration domains can attain a characteristic size  $a(t)$  of the order of  $10\xi$ , where  $\xi$  is the correlation length of the concentration fluctuations in the equilibrium phases. The boundaries between the domains then act like interfaces possessing an interfacial tension  $\Gamma$ . Rapid coarsening of the domain structure can then occur as the higher capillary pressure at regions of high interface curvature drives a flow of material from the necks to the bulges of the interconnected, tubelike domains. In this process, the interfacial area per unit volume  $q$  disappears from the system according to  $q^{-1}(t) \approx c(\Gamma/\eta_0)t$ , where  $\eta_0$  represents the viscosity of

the liquids in the interior of the domains, and  $c$  is a dimensionless constant. Since  $a(t) \propto q^{-1}(t)$ , this hydrodynamic instability results in domain growth with an exponent  $p=1$ . Linear domain growth has been reported in many light-scattering measurements performed on a variety of simple liquid mixtures [5,6]. More recently, it has been found in numerical solutions of the convectively coupled CHC and Navier-Stokes equations [7].

Since hydrodynamic effects are of paramount importance in the phase separation of liquid mixtures, it is natural to consider the effects of macroscopic flows. Up to now, most theoretical [8] and experimental [9] work on the spinodal decomposition of flowing liquid mixtures has dealt with the effect of an imposed shear flow on the shape and growth of the domains. Onuki has also considered the complementary question of how the deformation of the domains, by introducing new stresses, may affect the flow characteristics of the bulk liquid [10]. Light-scattering experiments have demonstrated the anisotropy of the domains' structure and growth [9], but a mechanical technique is required in order to measure the effect of these domain deformations on the state of stress in the fluid. It is this rheological information that would be needed, for example, to solve a boundary-value problem for the fluid-velocity field. We report the results of such rheological measurements. By observing the motion of a freely oscillating disk immersed in a binary liquid mixture undergoing spinodal decomposition, we deduce the effective stress-strain relation of the interconnected domains and their interfaces. We find that following a quench through  $T_c$ , a critical mixture of isobutyric acid and water (IBA+H<sub>2</sub>O) behaves like a viscoelastic material which possesses an enhanced viscosity  $\Delta\eta = \eta - \eta_0$  and an elastic shear modulus  $G$ . These quantities increase with increasing quench depth and decrease with time as the phase separation proceeds. We have analyzed our results in terms of a theory of the rheology of a system of interconnected coarsening interfaces recently proposed by Doi and Ohta [11]. This theory predicts the decay of  $\Delta\eta$  and  $G$  as a consequence of the decay of the sur-

face to volume ratio  $q$ . Consequently, in addition to the rheological information contained in  $\Delta\eta$  and  $G$ , our experiment allows the observation of the capillary-driven domain growth mechanism and a determination of the constant  $c$  by a purely mechanical technique.

We have described our apparatus and experimental procedures in an earlier paper, along with a few preliminary results [12]. Subsequent improvements in the handling of the mixture and in our understanding of our instrument's ability to yield both  $\eta$  and  $G$  have allowed us to obtain reproducible results and to compute the time-resolved values of these two rheological properties. A sample of IBA + H<sub>2</sub>O at the critical composition is contained within a pressure vessel. The temperature is kept constant and the well-established pressure-quench technique is used to initiate the phase separation [13]. A disk with radius  $R \approx 25$  mm and thickness  $2h \approx 10$  mm is suspended in the mixture from a torsion wire. Optical and time-interval measurements allow us to determine the equation of motion of the disk [14], which we write as

$$a(t) = A \exp(-\Delta\omega t) \sin(\omega t), \quad (1)$$

where  $a(t)$  is the disk's position angle,  $A$  is an amplitude,  $\Delta$  is the dimensionless decay rate, and  $\omega$  is the frequency of oscillation. Typical values are  $\Delta \approx 0.022$  and  $\omega \approx 1.58$  Hz which corresponds to an oscillation period of about 4 s. In the case now considered, where the fluid properties evolve during the process of phase separation,  $\Delta$  and  $\omega$  are functions of time. The drag of the fluid causes a decrease in the frequency  $\omega$  from its value *in vacuo*  $\omega_0$ . It is the measurement of two independent parameters characterizing the disk's motion, the damping  $\Delta$  and the frequency ratio  $\omega/\omega_0$ , that allows us to calculate two liquid properties, namely, the viscosity  $\eta$  and the elastic shear modulus  $G$ .

To give precise meaning to  $\eta$  and  $G$ , consider a shear flow  $\mathbf{v}$  of the form

$$v_x = S(t)y, \quad v_y = v_z = 0, \quad (2)$$

where  $S(t)$  is the time-dependent shear rate. Here  $\mathbf{v}$  represents the macroscopic velocity field that is observed on a length scale much larger than the characteristic size of the concentration domains. We define  $\eta$  and  $G$  by writing

$$\sigma_{xy}(t) = \eta S(t) + G \int_0^t S(t') dt', \quad (3)$$

where  $\sigma_{xy}$  is the shear component of the stress tensor. The first term of Eq. (3) represents ordinary viscous action. Since  $S(t)$  is the velocity gradient, its running time integral is the gradient of relative displacement, which we identify with the strain. Hence, the second term of Eq. (3) represents an elastic contribution due to the deformation of the underlying structure whose presence we ignore in writing the spatially smoothed velocity field in Eq. (2).

Working equations for oscillating-body rheometers can be found in the literature [15]. The expressions we use will appear in a future publication. They consist of a pair

of coupled equations in  $\eta$ ,  $G$ ,  $\Delta$ , and  $\omega/\omega_0$ . The values of  $\Delta$  and  $\omega/\omega_0$  that are possible for the disk oscillating in an ordinary viscous fluid, which has no elastic shear modulus, must be related in such a way as to yield  $G=0$ . In the limit  $\Delta \ll 1$ , this consistency relation is simply  $\omega/\omega_0 = 1 - \Delta$ . When  $G$  has a positive value, we find  $\omega/\omega_0 > 1 - \Delta$  in the same limit. Thus the elasticity of the liquid acts to increase the disk's oscillation frequency. This behavior is in accord with one's physical intuition about the effect of "springiness" in the liquid.

In a typical experiment, we begin with the sample in a one-phase state at such pressure as to place the sample at a distance above the critical point equivalent to a temperature difference of about 100 mK. The disk is set into motion, and after a few cycles the pressure is dropped so as to quench the sample to a point below the critical point by the quench depth  $Q$ , typically equivalent to a few tens of mK. We monitor the disk's motion during the spinodal decomposition process that follows for about ten cycles. Then the pressure is raised to a high value and the mixture is allowed to reequilibrate. We stir the sample whenever necessary to ensure a uniform concentration.

As a sensitive test of our apparatus and procedures, we perform runs in which the final pressure is chosen so that after the pressure drop the sample is still in an equilibrium one-phase state above the critical point. Because of the critical anomaly, the viscosity of the final state is higher than that of the initial state by 5% to 10%. We observe that, within experimental resolution, the measured viscosity becomes constant at the final expected value within one oscillation cycle. This shows that transient effects are negligible. Since during these tests the sample remains an ordinary viscous liquid, its elastic shear modulus must necessarily be zero at all times. In fact, we typically measure  $G = 0 \pm 0.01$  mPa. These deviations indicate the resolution of the elasticity measurements and can be attributed to the accuracy with which we can specify the frequency *in vacuo*  $\omega_0$ .

Figure 1 shows the results of a typical quench measurement in which the final pressure is equivalent to a temperature 19 mK below  $T_c$ . The indicated error bars represent the reproducibility we typically observe in repeated quenches of fixed quench depth. We obtain curves of similar shape after quenches with depths  $Q$  in the range  $10 \text{ mK} < Q < 70 \text{ mK}$  over which we make measurements. We find a systematic dependence of  $\eta$  and  $G$  on the quench depth: As the quench becomes deeper, the properties just after the quench start with higher and fall to lower values.

The general features of the behavior we observe can be understood in terms of the theories of Onuki [10] and Doi and Ohta [11]. The effective stress tensor of a flowing blend of immiscible liquids separated by an intricate interface may be written as

$$\sigma_{\alpha\beta} = \eta_0 \left( \frac{\partial v_\alpha}{\partial x_\beta} + \frac{\partial v_\beta}{\partial x_\alpha} \right) - \Gamma q_{\alpha\beta}, \quad (4)$$

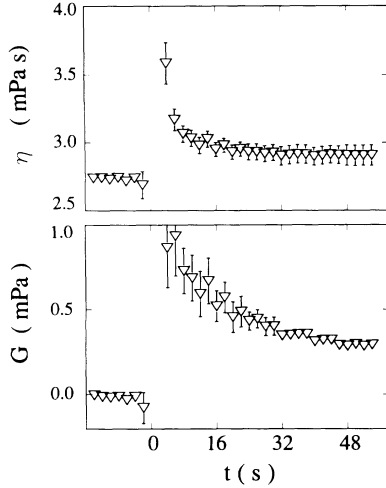


FIG. 1. Viscosity  $\eta$  and elastic shear modulus  $G$  as functions of the time  $t$  following a quench of depth 19 mK. The quench from an initial one-phase state occurs at time  $t=0$ .

where  $\Gamma$  is the interfacial tension and the interface tensor  $q_{\alpha\beta}$  is defined as

$$q_{\alpha\beta} = \frac{1}{V} \int ds (n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta}). \quad (5)$$

The first term of Eq. (4) represents the viscous stress associated with the macroscopic velocity field  $\mathbf{v}$ ; it is assumed that the two liquids have the same viscosity  $\eta_0$ . In Eq. (5),  $n_\alpha$  and  $n_\beta$  are components of the unit vector  $\hat{\mathbf{n}}$  normal to the interface. The integral is to be taken over all the interfacial surfaces within a volume  $V$  whose linear dimensions are large compared to the domain size but small compared to the length scale of the macroscopic flow.

Doi and Ohta have derived an equation of motion for the interface tensor  $q_{\alpha\beta}$ . In the case of the simple shear flow represented by Eq. (2), it takes the form

$$\dot{q}_{xy} = S(t)[q_{xy}^2/q - q_{xx} - q/3] - (c+k)(\Gamma/\eta_0)qq_{xy}, \quad (6)$$

$$\dot{q}_{xx} = S(t)[q_{xy}q_{xx}/q + \frac{2}{3}q_{xy}] - (c+k)(\Gamma/\eta_0)qq_{xx}, \quad (7)$$

$$\dot{q} = -S(t)q_{xy} - c(\Gamma/\eta_0)q^2, \quad (8)$$

where  $q$  is the interfacial area per unit volume. The terms on the right in Eqs. (6)–(8) describe free streaming of the interface in the macroscopic shear flow. The remaining terms force  $q_{xy}$ ,  $q_{xx}$ , and  $q$  to decay in the absence of a macroscopic flow. The decay of  $q$  is according to the capillary-driven coarsening mechanism, since the solution of Eq. (8) in the case  $S(t)=0$  is given by  $q^{-1}(t) = c(\Gamma/\eta_0)t + q_0^{-1}$ , where  $q=q_0$  at some initial time  $t=0$ . The second terms of Eqs. (6) and (7) describe the decay of the interface tensor according to the combined effects of the decay of the extent of the interface  $q$  and a tendency, measured by a phenomenological constant  $k$ , for the domain structure to become isotropic in

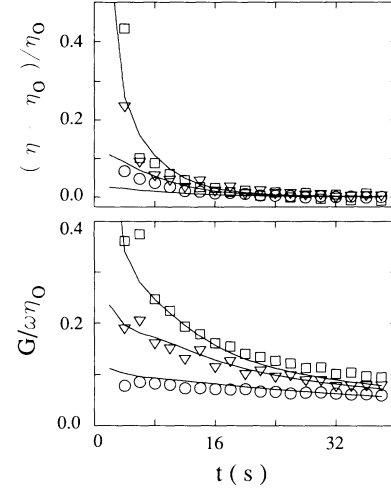


FIG. 2. Reduced viscosity  $(\eta - \eta_0)/\eta_0$  and elastic shear modulus  $G/\omega\eta_0$  as functions of the time  $t$ . The smooth curves have been calculated from the theory of Doi and Ohta. The symbols  $\circ$ ,  $\nabla$ , and  $\square$  correspond to quenches of depths 11, 19, and 64 mK, respectively. For clarity, error bars are omitted.

the absence of an imposed flow.

To apply the theory to our experiment, we solve Eqs. (6)–(8) numerically with  $S(t) = S_0 \exp(-\Delta\omega t) \cos(\omega t)$  with  $\Delta = 0.022$  and  $\omega = 1.58$  Hz; the shear-rate amplitude  $S_0 = 7.9 \text{ s}^{-1}$  is characteristic of our instrument. The predicted interfacial shear stress is then  $-\Gamma q_{xy}(t)$ . We then divide time into a series of intervals with length equal to the oscillation period. On each interval, we express  $-\Gamma q_{xy}(t)$  approximately as  $\Delta\eta S(t) + G \int S(t') dt'$  [see Eq. (3)], where the predicted interfacial viscosity  $\Delta\eta$  and elastic modulus  $G$  so obtained are constants on each interval.

When this calculation is carried out, it is found that after three or four oscillations the theoretical interfacial viscosities approach zero and the subsequent behavior of the interface is purely elastic. In the experiments we observe that the viscosity of the complete fluid system consisting of the domains' interfaces and liquid interiors approaches a constant value (see Fig. 1). We therefore identify the liquid viscosity  $\eta_0$  called for in the theory with the value at which the experimental viscosity becomes constant. In the case of the measurement shown in Fig. 1, we have  $\eta_0 = 2.91$  mPa s. Further inputs to the theory are the values of the phenomenological constants  $c$  and  $k$  and initial values for the quantities  $q_{xy}$ ,  $q_{xx}$ , and  $q$ . We take  $t=0$  as the instant of the quench and we assume  $q_{xy}(0)=0$ ,  $q_{xx}(0)=0$ , and  $q(0)=q_0$ . We fix  $q_0$  as a function of quench depth by putting  $q_0 = 1/b\xi$ , where  $b$  is a dimensionless constant, since we expect the initial length scale of the domains to be determined by the correlation length  $\xi = \xi_0(Q/T_c)^{-\nu}$ . We use  $\xi_0 = 0.362$  nm and  $\nu = 0.63$  for the correlation-length amplitude and exponent [16]. We treat  $c$ ,  $k$ , and  $b$  as free parameters

which we adjust to maximize the agreement between theory and experiment.

A comparison of the theory and data taken in three quench experiments is shown in Fig. 2. Reduced values of the interfacial viscosity  $(\eta - \eta_0)/\eta_0$  and elastic shear modulus  $G/\omega\eta_0$  are plotted as functions of time after the quench. The quench depths are 11, 19, and 64 mK and the corresponding values of  $\eta_0$  are 3.07, 2.91, and 2.72 mPas. The values chosen for the adjustable parameters are  $c = 0.038$ ,  $k = 0.0095 = c/4$ , and  $b = 27$ . The theory gives a good account of the observed time and quench-depth dependence of the measured rheological properties and a fair prediction of their values. Of interest are the implied values of the initial surface to volume ratio  $q_0 = 1/b\xi$ . In the case of the 19-mK quench, for example, we find  $q_0 = 2.32 \times 10^5 \text{ m}^{-1}$ , or  $2.32 \text{ cm}^2$  per cubic mm of fluid. The smallness of  $k$  in comparison to  $c$  indicates that the decay of the interface tensor  $q_{\alpha\beta}$  is primarily due to the decay of the extent of the interface itself. The relaxation of interfacial anisotropy is secondary.

We do not assign error bars to  $c$ ,  $k$ , and  $b$ , because the optimization of the agreement between theory and experiment has been somewhat subjective. In particular, we have favored the elasticity modulus. However, it is possible to compare  $c$  and  $b$  with quantities derived from light-scattering experiments performed on quiescent samples. For example, we have analyzed the data reported in Ref. [6] and find  $a(t) \approx c'(\Gamma/\eta_0)t$  with  $c' = 0.051$ , where we assume that the characteristic domain diameter  $a(t)$  is related to the wave vector of maximum scattering  $k_m(t)$  by  $a(t) = 2\pi/k_m(t)$ . At the time  $t_{\text{cr}}$  of the crossover to the regime of linear domain growth, we calculate  $a^{-1}(t_{\text{cr}}) \approx 1/b'\xi$  with  $b' = 37$ ;  $t_{\text{cr}}$  is about 5 s for a quench of depth 19 mK. The similarity of  $c$  to  $c'$  and  $b$  to  $b'$  is encouraging but requires further interpretation, because  $q^{-1}(t)$  and  $a(t)$  are not identical, but rather are related by an unknown dimensionless constant of the order 1.

In summary, we have measured the flow properties of a simple liquid mixture undergoing spinodal decomposition. Our results show that the interfacial effects which produce rapid domain growth in quiescent samples result in significant time-varying viscoelasticity in samples under

shear. The theory proposed by Doi and Ohta has been shown to apply. We conclude that information on the growth and morphology of the domains can be obtained from rheological measurements.

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