Capillary-Wave Relaxation for a Meniscus between Miscible Liquids

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We have measured autocorrelation functions for light scattered from capillary waves at the interface in a near-critical binary liquid mixture both at two-phase equilibrium and after abruptly raising the temperature to drive the system toward one-phase equilibrium. Use of the capillary-wave dispersion relation allows the extraction of an effective "surface tension." This surface tension represents a dynamical integrity of the nonequilibrium interface which may affect pattern formation when the interface is driven.

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An interface between two miscible liquids is a nonequilibrium phenomenon which is complex and not well understood. Under some circumstances the interface will diffuse away only very slowly with time and will be clearly indistinguishable for many hours. However, very few studies have been made on the physical integrity of such an interface and its ability to form patterns [1-4] when driven out of mechanical equilibrium. Some [2,3] of these few studies have assumed for calculational purposes that no surface tension exists at the interface between miscible liquids. However, as long as the interface remains visible, it contains a significant amount of energy due to its composition gradient. That is, an effective interfacial surface tension can be defined, in analogy with the surface tension for an equilibrium interface between immiscible liquids, to have the form [5,6]

$$\sigma \propto \int_z (dc/dz)^2 dz \,, \tag{1}$$

where c is the local composition (or any intensive property of the liquids which varies across the interface).

Recent papers by Joseph [7] and Davis [8] suggest that stresses can be induced by gradients of concentration, density, and possibly temperature when two miscible liquids slowly interdiffuse, and that these stresses can cause effects that mimic surface tension. One of Joseph's papers also surveys previous work reported on the mechanics of miscible-liquid interfaces, finding three experiments whose results directly suggest the existence of an effective surface tension. In one such paper [9], the deformation of a liquid drop falling in another fluid with which it is miscible is studied; the authors conclude that a small time-dependent interfacial tension across the drop may exist by comparing theoretically predicted rates of expansion of the drop with experimental results. The second experiment involved a Wilhelmy plate measurement [10]. The results were qualitatively convincing that an effective interfacial tension exists, but they were quantitatively irreproducible. The third experiment involved the dynamical shape of a falling drop and was even less able to provide quantitative results [11]. In this paper we present the results of a surface light-scattering experiment in which we have measured autocorrelation functions at a variety of wave numbers, using the relaxation rate of thermally excited capillary waves to determine the effective surface tension at an interface between miscible liquids.

We have used a mixture of isobutyric acid and water (IBW) at near-critical composition (62.1 vol% water). This binary liquid mixture has an upper critical temperature, $T_c = 26.310\,^\circ\mathrm{C}$, below which its two equilibrium phases act as immiscible liquids with an interfacial tension $\sigma = \sigma_0[(T_c - T)/T_c]^{1.23}$. If this system is initially at two-phase equilibrium and then has its temperature abruptly raised above T_c but is not mechanically disturbed, the interface will remain visible for many hours as diffusion can only mix the two phases very slowly. In our measurements, 632.8-nm light from a He-Ne laser was reflected from the interface at an angle of 80.9° from the normal. We used a photon-counting photodiode to observe light scattered at very small angles off the direction of specular reflection. Our wave-number range for capillary-wave scattering was $65 < q < 345\ \mathrm{cm}^{-1}$. The observed light-scattering signal was a heterodyne signal with the local oscillator supplied by the specularly reflected beam creating a flare as it exited the glass sample tube. This signal was superimposed on background scattering signals from the scattering of both the reflected beam and the transmitted (refracted) beam in the bulk liquid phases. For two-phase equilibrium at temperatures of 200 mK or more below T_c, the bulk scattering from equilibrium concentration fluctuations was too weak to be observed in the presence of the surface light scattering in our range of wave number. However, once the temperature had been raised into the one-phase region, the intensity of the surface light scattering became smaller and composition fluctuations in the bulk became larger (in our temperature range) and both effects make bulk scattering a significant part of the observed light-scattering signal. The bulk scattering from the transmitted beam corresponds to large wave numbers and thus shorter relaxation times than are involved in our typical surface scattering; correspondingly, the small-wave-number bulk scattering from the reflected beam involves much longer relaxation times than those of present interest so we were able to follow the capillary-wave relaxation times, typically for about 2 h after driving the system away from equilibrium, before the interfacial signal became too weak to be extracted from the bulk scattering signals.

We measured autocorrelation functions using a Brookhaven BI-2030AT correlator. As a calibration we made this measurement first at two-phase equilibrium about 225 mK below T_c (after stirring and waiting at least 18 h for equilibrium) to determine the initial equilibrium surface tension using the dispersion relation. Our calibration measurements give good agreement with the work of Knobler [12] for this system, yielding a mean value $\sigma_0 = 12.9 \pm 1.2$ dyn/cm, where Knobler reported $\sigma_0 = 11.6 \pm 1$ dyn/cm. Our equilibrium results are shown in the top section of Fig. 1.

After completing several equilibrium autocorrelation measurements at a given wave number, we would raise the system temperature to either 215 or 410 mK above T_c to drive the system toward one-phase equilibrium. The system typically reached the neighborhood (± 130 mK) of the final temperature in about 100 sec, but temperature fluctuations were not often brought under close control (± 1 mK) in less than 25 min. Convection rolls were set up in each bulk phase during the temperature change [13]. These were not sufficiently damped out to allow a surface light-scattering measurement in the lower bulk phase for about 20 min after the temperature change and were not completely gone until about 40 min had elapsed. For reasons we do not understand well, convective disturbances were evident for an even longer time when our measurement was made from the upper (more reflective) side of the interface, so all measurements reported herein involved scattering from the lower (less reflective) side of the interface. We were then able to measure the surface light-scattering autocorrelation functions at 5-min intervals for up to 2 h as the system tried to reach the new composition equilibrium. As was discussed above, this 2-h limit was imposed by the increasing difficulty of extracting the surface scattering signal in the presence of the bulk scattering; true composition equilibrium would not be reached in an unstirred sample for many hundreds of hours, a shiny interface was typically observable for many hours, and a fuzzy interface for many tens of hours. As a check on our results, a two-phase-to-two-phase transition was also measured where we raised the IBW temperature from approximately 225 mK below T_c to about 100 mK below T_c and measured the effective surface tension as a function of time; in this latter case the final equilibrium involves immiscible phases and a well-defined surface tension but should only be approached by diffusive processes. All surface-tension values presented below result from naively applying the capillary-wave dispersion relation [14–16] appropriate to an equilibrium interface between immiscible liquids as if departure from equilibrium could change only the surface tension as defined in Eq. (1). This is not unreasonable because the capillary waves are mechanical, not thermodynamic, in origin and because the average viscosities of the two phases are known not to change significantly between the initial and final temperatures.

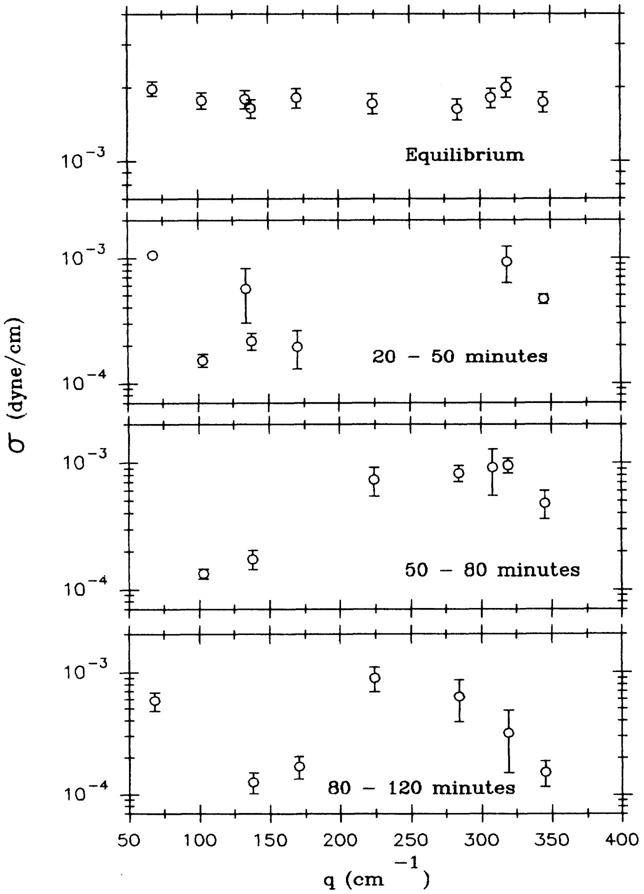

FIG. 1. Surface tension vs q at equilibrium and during three time intervals after the temperature change.

The IBW temperature in most of our measurements was abruptly changed from about 225 mK below T_c to either 215 or 410 mK above. The results were found not to be significantly different for the two final temperatures. The upper section of Fig. 2 illustrates how the measured surface tension (completely equivalent and approximately in inverse proportion to the measured relaxation time for any wave number) changed with time for a final temperature of 215 mK above T_c at a typical wave number. This example is qualitatively the same as was measured at all wave numbers and at both temperatures observed in the one-phase region. During approximately the first 5 min after the beginning of the temperature change, measured surface relaxation times and scattered light intensity increased greatly but then settled down before temperature equilibrium was reached (we do not understand this phenomenon but will ignore it since it ended before temperature equilibrium was attained). The average surface tensions were calculated during three time intervals after temperature equilibrium was reached, and were in general found to slowly decrease with time. These averaged surface tensions are shown for each of the time (after-

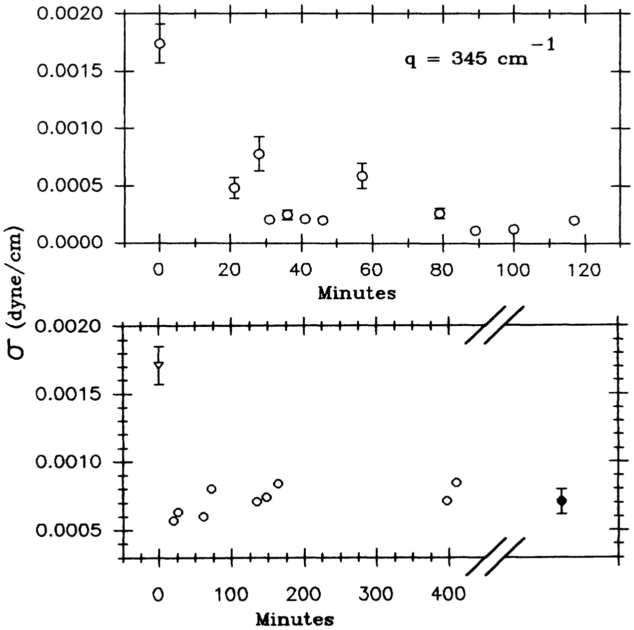

FIG. 2. Surface tension as a function of time after a temperature change from 225 mK below to (top) 215 mK above T_c and to (bottom) 100 mK below T_c. Surface tension at time 0.0 is the initial equilibrium value, and the solid circle at late time in the bottom plot is the final measured equilibrium value (and is the expected value).

temperature-change) intervals in the lower three frames of Fig. 1. Even after averaging many independent observations over relatively long time intervals the scatter in the effective surface tension is large and varies with wave number somewhat more than the measured standard deviation typical of any one wave number. We do not fully understand this apparent wave-number dependence, but particularly because it becomes somewhat less pronounced at later times, we ascribe it not to a real length-scale dependence of the effective interfacial tension but rather to systematic error associated with extracting our signal from the other background contributions discussed above while our heterodyning reference signal strength depends somewhat on wave number. While it would be desirable to explore the possibility of a length-scale dependence of the effective surface tension, we are convinced that we have reached the currently feasible limit of our experimental method in this case without resolving the issue. To proceed with our study of the integrity of the miscible-liquid interface, we average over all observed wave numbers the effective surface tension in a given time interval and present the time dependence of this average surface tension in Fig. 3. The results are for a final temperature 215 mK above T_c; the results for 410 mK above T_c are similar, with differences on the order of the experimental uncertainties.

The decrease in the effective surface tension obtained

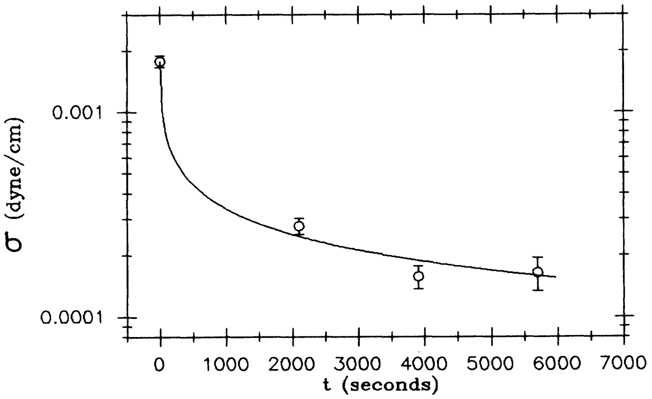

FIG. 3. Surface tension averaged over all wave numbers at equilibrium and during each time interval after the temperature change. The solid line shows the best fit to the data with the form in Eq. (2).

using the capillary-wave dispersion relation is very slow compared to what would be expected from naive use of the equilibrium diffusion constant. We estimate an effective interdiffusion constant using the approximation that the composition and index-of-refraction gradients vary linearly across the interface [15,16] ($dc/dz \propto 1/z$ and $dn/dz \propto 1/z$) and extend over a region from $z=0$ to $z=\xi_0+(D_{\text{eff}}t)^{1/2}$ assuming Fickean diffusion, where ξ_0 is the initial equilibrium correlation length at $T=26.085\,^\circ\text{C}$, D_{eff} is the effective diffusion constant, and t is the time. Using Eq. (1) for the surface tension we find that

$$\sigma(T,t)=F(T)/[\xi_0+(D_{\text{eff}}t)^{1/2}]\,, \tag{2}$$

where $F(T)$ is assumed to be approximately constant for the small range of temperatures we used. Using this admittedly simple model we obtained average best-fit D_{eff} values of $(4.1\pm1.2)\times10^{-14}$ and $(3.0\pm2.5)\times10^{-15}$ cm^2/sec for final temperatures of about 215 and 410 mK above T_c, respectively. The equilibrium one-phase diffusion constants at these temperatures in our IBW systems are several orders of magnitude larger, approximately 1.8×10^{-8} and 2.6×10^{-8} cm^2/sec, respectively, for the wave numbers used in our experiments. The curve drawn through the data in Fig. 3 results from inserting the best-fit diffusion constant into Eq. (2).

This anomalously slow dissolution of the interface probably results from gravitation stabilization. Rogers, Yeung, and Jasnow [17] report that in an Ising model simulation of the dissolution of a nonequilibrium interface, the dissolution proceeds at a rate consistent with the equilibrium diffusion constant when no external field is imposed on the system, but that the interface is effectively frozen when a stabilizing external field is applied. While we do not know how to relate the strength of the

Earth's gravity to that of the external field of Rogers, Yeung, and Jasnow, gravity is, in our case, stabilizing and plausibly causes the extremely slow dissolution of our interfaces. This slow dissolution gives the interface an integrity which may explain why many driven systems which involve miscible liquids develop interfacial patterns that are not very different from those formed at interfaces between similar but immiscible liquids [1,4].

As a final check on our understanding of our measurement and its interpretation, we have, as was mentioned above, done a series of measurements where we abruptly raised the system temperature to a final value which is still in the system's two-phase region. In this way we produce a system whose liquids are immiscible but whose final surface tension is lower and whose interface must transport molecules in each direction until diffusion succeeds in setting up the new equilibrium composition. When the IBW temperature was abruptly raised from about 225 to 100 mK below T_c the effective surface tension was found to relax to the new two-phase equilibrium value as quickly (about 20 min) as the temperature was brought to equilibrium. In the lower half of Fig. 2 we show (at wave number 174 cm^{-1}) the time dependence of the surface tension along with the average value measured after stirring and reaching equilibrium.

In summary, our experiments confirm, as do the reports [9-11] surveyed by Joseph [7], that an instantaneous effective surface tension exists between miscible liquids. This effective surface tension is available to possibly affect pattern formation at the interface [1-4]. Our surface light-scattering measurements provide the first quantitative measure of this surface tension through observing the relaxation of thermally excited capillary waves. The decrease of the surface tension with time is very slow compared to what would be expected from naive use of the one-phase equilibrium diffusion constant. This suggests that there is at least one stabilizing mechanism, gravity, acting on the system to greatly decrease the interdiffusion rate of the miscible liquids and provide the interface with an integrity which makes it an important feature of the nonequilibrium system for a very long time. Such an effect can explain some of the striking similarities [1,4] in pattern formation between immiscible systems and miscible ones and may be important technologically in the processing of materials.

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