Capillary to bulk crossover of nonequilibrium fluctuations in the free diffusion of a near–critical binary liquid mixture.

Pietro Cicuta†, Alberto Vailati* and Marzio Giglio
Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materia, Università di Milano, via Celoria 16, 20133 Milano, Italy.
† *current address: Department of Physics, Cavendish Laboratory Madingley Road, Cambridge CB3 0HE, U.K.*
* *E-mail address: vailati@fisica.unimi.it*

We have studied the nonequilibrium fluctuations occurring at the interface between two miscible phases of a near-critical binary mixture during a free diffusion process. The small-angle static scattered intensity is the superposition of nonequilibrium contributions due to capillary waves and to bulk fluctuations. A linearized hydrodynamics description of the fluctuations allows us to isolate the two contributions, and to determine an effective surface tension for the nonequilibrium interface. As the diffuse interface thickness increases, we observe the cross-over of the capillary-wave contribution to the bulk one.

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I. INTRODUCTION

In this work we focus on the investigation of interface and bulk fluctuations in a near-critical binary liquid mixture undergoing a free-diffusion process. free-diffusion processes have been recently shown to give rise to giant nonequilibrium fluctuations [1,2]. However, it is still not well understood what happens in the very early stages of the diffusive remixing, when an effective surface tension should be detectable [3]. In this paper we use static light scattering to study the crossover between the capillary-waves at the interface and the bulk fluctuations, during the quick transient leading to the onset of giant nonequilibrium fluctuations. We show that the static light scattered from the diffusing sample is the superposition of a contribution due to interface fluctuations and one due to bulk fluctuations. By isolating the interface term we are able to recover the time evolution of the nonequilibrium surface tension. We show that the surface tension decreases very quickly, giving rise to a divergence of the amplitude of capillary-waves. However, as the interface thickness increases due to diffusion, a crossover from capillary to bulk fluctuations is observed: the interface layer becomes thicker than the length scales associated with the scattering wave vectors. Therefore, fluctuations do not displace this layer as a whole any more. Instead, they take place inside the layer, which behaves as a bulk phase. This prevents the divergence of the capillary-waves.

Similar free-diffusion experiments on critical fluids were performed on isobutyric acid-water (IBW) by May and Maher [4], and on cyclohexane-methanol (CM) and deuterated cyclohexane-methanol (CDM) by Vlad and Maher [5]. They used surface light scattering to recover the relaxation time of fluctuations at the diffusing interface, and they applied the capillary-waves dispersion relation to determine an effective surface tension. They derived the time evolution of what they assumed to be an effective surface tension of the interface. The time constant related to the relaxation of the surface tension led to a value of the diffusion coefficient which was many orders of magnitude smaller then the equilibrium one (2 order of magnitude for CM, 3-5 for CDM and 7-8 for IBW). These results were interpreted by assuming that gravity was responsible of the slow dissolution of the interface. However, Maher and coworkers did not take into account the presence of non-equilibrium bulk fluctuations at all. These fluctuations turn out to be much slower than the capillary ones and this might explain the slow relaxation time of the fluctuations they observed, without having to resort to a slow-diffusion hypothesis.

II. EXPERIMENT

Several authors have tried to detect an effective surface tension between two miscible fluids [3–8]. In particular, some experiments have been performed by injecting a fluid into the other one or by layering the fluid one on the top of each other [3,6,7]. However, it is very difficult to establish a flat interface without generating disturbances. The use of a critical binary liquid mixture has several advantages in this respect. A stable horizontal equilibrium interface between two phases can be obtained by bringing the mixture below its critical temperature. These two phases become completely miscible simply by raising the temperature above the critical one, without having to mechanically manipulate the sample. In this way disturbances in the formation of the interface can be avoided, provided that some precautions are taken to avoid convection. Moreover, working with a critical mixture allows one to tune the time scales of fluctuations by changing the distance from the critical point.

The experiment reported here has close connections with a previous experiment on the transient behavior of a nonequilibrium interface in a near critical binary mixture [9]. This experiment was performed by raising the temperature of a binary mixture from a value below T_c to a value still below it. In this way the system was separated into two phases at the beginning and again at the end of the experiment, and we investigated the transient behavior of the nonequilibrium interface and of the related surface tension. In the experiment described here the temperature is raised from below to above the critical one. In this way one starts with two phases and ends with an homogeneous phase. The two concerns are how does the interface evolve into a bulk phase and what happens to its surface tension.

The sample used is the binary mixture aniline-cyclohexane prepared at its critical aniline weight fraction concentration c=0.47. A horizontal, 4.5 mm thick, layer of the mixture is contained in a Rayleigh-Benard cell consisting of two massive sapphire plates in thermal contact with two Peltier elements controlled by a proportional-integral servo [1,10]. The sapphire windows act at the same time as thermal plates and as optical windows. The thermal stability of the cell is about 3 mK over one week , the temperature being uniform within 2 mK across the sample. The mixture is phase separated at 3 K below its critical temperature T_c, so that two macroscopic phases are formed, separated by a horizontal interface. The temperature is then suddenly increased to 1 K above T_c, so that the two phases become completely miscible. During the temperature jump the temperature of the upper plate is kept a few mK higher than that of the lower one, so as to discourage convection. This thermal conditioning of the sample has been thoroughly checked for spurious disturbances by using a very sensitive shadowgraph technique. Scattered intensity distributions are collected both during the initial equilibrium condition and during the temperature increase by using a unique ultra low-angle static light scattering machine described in detail elsewhere [11,12]. The heart of this machine consists of a unique solid state sensor which is able to collect light scattered within a two decades wave vector range, with a dynamic range of about 6 decades. This sensor is a monolithic array of 31 photodiodes, having the shape of a quarter of an annulus. Each photodiode collects the light scattered at a certain wave vector. The machine in the configuration used for this experiment is able to collect the light scattered in the wave vector range $80\,\mathrm{cm}^{-1} < q < 8000\,\mathrm{cm}^{-1}$ in a fraction of a second.

III. RESULTS AND DISCUSSION

Prior to the temperature increase most of the light is scattered by capillary-waves at the interface, the scattering due to the equilibrium bulk phases being negligible. The intensity scattered by equilibrium capillary-waves is well known to display the power-law behavior $I(q) \propto 1/(\sigma\, q^2)$ [13], where σ is the surface tension. The scattered intensity distribution in this condition is shown by the plusses in Fig. 1, together with the best fit to the power law. As soon as the temperature is raised, the scattered intensity increases at every wave vector and a typical length scale appears at intermediate wave vectors. The scattering data can be interpreted by following the guidelines outlined in Ref. [9] and summarized below. The concentration profile is assumed to be continuous across the sample. The sample is modeled as the superposition of an interface layer surrounded by two bulk layers. The character of a layer depends on whether the typical length scale associated with changes in the concentration gradient is respectively smaller or larger than that associated with a fluctuation of wave vector q. Therefore a certain layer of fluid can behave as an interface or as a bulk phase, depending on the wave vector of the fluctuation perturbing it. Landau's Fluctuating Hydrodynamics [14] can be used to describe the spectrum of the fluctuations. By using the approach outlined in [15], and extended to nonequilibrium interfaces in [9], one finds that the static contributions to the scattered intensities due to the interface and bulk fluctuations are

$$I_{\text{int}}(q) \propto \frac{\Delta c_{\text{int}}}{1 + (q/q_{\text{cap}})^2} \tag{1}$$

$$I_{\text{bulk}}(q) \propto \frac{\Delta c_{\text{bulk}}}{1 + (q/q_{\text{RO}})^4} \tag{2}$$

where

$$q_{\text{cap}} = \left(\frac{\rho\beta g \Delta c_{\text{int}}}{\sigma}\right)^{\frac{1}{2}} \tag{3}$$

and

$$q_{\text{RO}} = \left(\frac{\beta g \nabla c}{\nu D}\right)^{\frac{1}{4}} \tag{4}$$

In Eqs. (1-4) Δc_{int} and Δc_{bulk} represent the macroscopic concentration difference across the interface and bulk layers, respectively, g is the acceleration of gravity. We assume that the concentration difference across the sample is small, so that the fluid properties do not change much. Therefore, the mass density ρ, the kinematic viscosity ν, the diffusion coefficient D and $\beta = \rho^{-1}(\partial\rho/\partial c)$ represent suitable average values.

Equation (1) and (2) have basically the same form: a power law at large wave vectors, and a gravitationally induced saturation at smaller ones. Both capillary and bulk fluctuations are generated by concentration fluctuations induced by velocity fluctuations due to the presence of a macroscopic concentration gradient. Basically a parcel of fluid gets displaced due to a thermal velocity fluctuation. Whenever this displacement has a component parallel to a macroscopic concentration gradient, a concentration fluctuation arises, as the parcel of fluid is displaced into a region having a different concentration. The power-law behavior at large wave vectors characterizes these velocity-induced concentration fluctuations. In the case of an interface, the macroscopic concentration changes across a length scale much smaller than those associated with the scattering wave vectors. Therefore, a fluctuation displaces this region of sharp concentration variation as a whole, and relaxes back to equilibrium due to the capillary forces associated with the interfacial displacement. This leads to the power-law exponent -2 in Eq. (1). In the case of a bulk phase, the macroscopic concentration changes across a distance much larger than the length scales associated with the wave vectors. In this way the fluctuations take place 'inside' the concentration gradient and relax back to equilibrium due to diffusion. This mechanism leads to the exponent -4 of Eq. (2), typical of nonequilibrium fluctuations in a bulk phase [16–20,15,21–24,10,1].

The capillary and roll-off wave vectors q_{cap} and q_{RO} characterize the onset of the gravitational stabilization of the capillary and bulk fluctuations, respectively. As outlined above, the interface and bulk concentration fluctuations are brought about by the displacement of parcels of fluid due to velocity fluctuations parallel to the macroscopic gradient. As a consequence of the displacement, a buoyancy force acts on the parcel, as its density is now different from that of the surrounding fluid. Therefore gravity acts as a stabilizing mechanism against small wave vector velocity fluctuations. This saturation is apparent for the late time data in Fig. 1, while it falls outside the wave vector range for the early time data.

We assume that the interface and bulk phases scatter light independently, so that the scattered intensity is a superposition of their contributions:

$$I(q,t) = I_{\text{int}}(q,t) + I_{\text{bulk}}(q,t) \tag{5}$$

During a free-diffusion process the system is assumed to be infinite in the vertical direction, and the concentration difference across the sample height does not change in time. In practice the vertical extension of a diffusion cell is finite, and the assumption is met only at the beginning of a diffusion process, when the diffusive remixing involves the layers of fluid near the interface at the mid-height of the cell. The typical time for diffusion to occur across a cell of thickness s is $\tau_{\text{diff}} = s^2/(\pi^2 D)$. For times shorter than τ_{diff} the system can be assumed to be in a free-diffusion condition. Therefore, in the free-diffusion regime the concentration differences Δc_{int} and Δc_{bulk} are not independent, as their sum corresponds to the conserved concentration difference across the sample:

$$\Delta c(t) = \Delta c_{\text{int}}(t) + \Delta c_{\text{bulk}}(t) = \Delta c(t=0) \tag{6}$$

This conservation is apparent in the late scattered-intensity distributions of Fig. 1, collapsing onto the same curve at small wave vectors. According to our model, also the earlier data in Fig. 1 should collapse onto the same curve, but this occurs at wave vectors smaller than those accessible by our experimental setup.

As pointed out above, the initial data of Fig. 1 display the q^{-2} power-law behavior typical of capillary-waves. These data are not affected by bulk fluctuations, since their amplitude is very small at equilibrium. The q^{-2} dependence is also apparent at large wave vectors in the subsequent intensity distributions

This shows that an effective surface tension is present during the nonequilibrium diffusive remixing, in agreement with the suggestion by some authors that an effective surface tension should exist between miscible fluids in the presence of a composition gradient [3–8,25,26]. This surface tension is usually assumed to be related to the concentration gradient by the mean-field equilibrium Cahn-Hilliard relation [27]

$$\sigma \propto \int (\frac{dc}{dz})^2 dz \tag{7}$$

As soon as the diffusive process is started, the concentration gradient at the interface begins to drop. This determines the decrease of the effective surface tension defined by Eq.(7), and, according to Eq.(1), the increase of the intensity scattered at large wave vectors. After about 70 s the power-law exponent of the large wave vector scattered intensity gradually changes from 2 to 4. This corresponds to the capillary to bulk cross-over of the fluctuations at the interface. According to Eq. (7) , the effective surface tension vanishes due to the diffusive remixing, and this should determine a divergence of the light scattered from capillary-waves. However, diffusion also determines the increase of the typical length scale Λ_{int} associated with the concentration change at the interface: the concentration gradient at the interface gets smaller and the interface thicker. For a given scattering wave vector q, as soon as Λ_{int} gets larger than $2\pi/q$, the interface appears as a bulk phase and the power law exponent changes accordingly. Therefore diffusion prevents the divergence of capillary fluctuations as $\sigma \to 0$. Of course this is a q-dependent phenomenon: the first modes to undergo this transition are the highest wave vectors.We were not able to observe this transition at intermediate wave vectors, where the contribution of bulk fluctuations to the scattered intensity dominates.

By using Eqs. (1)-(6) we are in the unique position to fit the data in Fig. 1 to determine the time evolution of the nonequilibrium effective surface tension, together with the concentration difference at the interface. Best fits are represented by the continuous lines in Fig. 1. The time evolution of $\Delta c_{\rm int}$ and of the surface tension are shown in Fig. 2. The initial value of the surface tension derived from the equilibrium capillary-waves is a factor of two smaller than the reference data of Atack and Rice, obtained by the capillary-rise technique [28]. This is due to the smaller sensitivity of the static surface light scattering technique, whose measurements are affected by larger errors than the capillary rise ones. Our data show unambiguously that the surface tension decreases by roughly two orders of magnitude in about one minute. Results for the surface tension at times larger than 80 s are not presented, because after this time the capillary fluctuations cease to exist in our wave vector range, due to their crossover to bulk fluctuations, as seen in the abrupt change of the large wave vector power-law exponent in Fig. 1. The relaxation time of the surface tension is strongly coupled with the time needed to raise the temperature of the sample, which is of the order of 60 s. Therefore we have not attempted to relate it to a typical diffusive time, as it would be very difficult to isolate its contribution. Results for $\Delta c_{\rm int}$ show that the concentration difference gradually diminishes during the diffusion process. This is due to the fact that as the concentration gradient diminishes in layers of fluid at the boundary with the bulk phases, these layers cease to belong to the interface, because the length scale associated with variations in ∇c gets larger than those related with the scattering wave vectors. Therefore the diminishing of $\Delta c_{\rm int}$ is due to the gradual cross-over of the interface to a bulk phase.

Our results show unambiguously that the effective surface tension between two miscible phases of a near-critical binary mixture disappears very quickly during the diffusion process. Our results also show that after about 80 s the determination of the surface tension from the spectrum of scattered light is no longer feasible. This is due to the fact that the crossover from capillary to bulk fluctuations prevents the determination of the surface tension even at scattering angles as small as those achieved by our light scattering setup.

Maher and coworkers in their experiments [4,5] attempted to derive values of the surface tension during the free-diffusion in near critical binary mixtures for times as long as some hours. In view of the arguments above, we feel that they improperly applied the capillary-wave description to the bulk fluctuations in a diffuse interface, and this lead them to a puzzling discrepancy between equilibrium and nonequilibrium values of the diffusion coefficient. Their measurements were performed by means of surface quasi-elastic light scattering. By assuming that the dynamics of the fluctuations is controlled by capillary phenomena, one finds that the relaxation time constant is [29]

$$\tau_{\rm cap} = \frac{4\eta}{\sigma q} \tag{8}$$

where η is the shear viscosity. However, in the presence of a diffuse interface, the crossover from interface to bulk fluctuations occurs, and this leads to the dispersion relation [15]

$$\tau_{\rm bulk} = \frac{1}{Dq^2}\frac{1}{1+\left(\frac{q_{\rm RO}}{q}\right)^4} \tag{9}$$

Although these fluctuations have the same origin as capillary-waves, namely velocity fluctuations parallel to the concentration gradient, the transition from a sharp to a diffuse interface drastically modifies both the static and the dynamic structure factor of the fluctuations. We shall now compare the fluctuations time scales as measured by May and Maher with those of bulk fluctuations. From the nonequilibrium surface tension data from Ref. [4] we recover the order of magnitude of the relaxation time of the fluctuations observed by May and Maher. Data for the surface tension in Ref. 1 are scattered in the range $10^{-4} - 10^{-3}$ dyne/cm for wave vectors in the range $65\,{\rm cm}^{-1} < q < 345\,{\rm cm}^{-1}$. By using Eq. (8) we recover $\tau \approx 0.1\,{\rm s}{-}6\,{\rm s}$, where we have assumed $\eta \approx 10^{-2}$ poise. To compare these time scales with those associated with bulk nonequilibrium fluctuations it is essential to estimate the roll-off wave vector $q_{\rm RO}$ defined in Eq. (4). By assuming the diffusive behavior of the concentration gradient at the midheight of the cell $\nabla c = \Delta c/(4\pi Dt)^{1/2}$ and by using the reference values $\beta = 0.05$ ($\beta \approx [\rho_{\rm A} - \rho_{\rm I}]/\rho_{\rm A}$, where $\rho_{\rm A} = 1\,{\rm g/cm}^3$ is the density of pure water and $\rho_{\rm I} = 0.95\,{\rm g/cm}^3$ that of pure isobutyric acid), $\Delta c = 0.1$, $D = 1.8 \times 10^{-8}{\rm cm}^2/{\rm s}$ [4], we find $q_{\rm RO} \approx 900\,{\rm cm}^{-1} - 1100\,{\rm cm}^{-1}$ at times ranging from 20 minutes up to 120 minutes from the start of the diffusion process. Therefore, May and Maher have operated at wave vectors smaller that the roll off one. By using Eq. (9) for the time scale of nonequilibrium bulk fluctuations we recover $\tau_{\rm bulk} \approx 0.14\,{\rm s}{-}10\,{\rm s}$ in the wave vector range and time windows used by May and Maher. The agreement between the time scales observed by them and those predicted by our model is more than good, also considered that our description removes the puzzling discrepancy between equilibrium and nonequilibrium values of the diffusion coefficient reported by May and Maher.

The data presented in Ref. [5] are of better quality than those in Ref. [4], and are therefore suitable for a more quantitative check of the time scales. However the authors did not to report the wave vectors at which measurements were performed and therefore quantitative estimates are difficult.

IV. CONCLUSIONS

We have shown that the transient surface tension between two miscible phases of a binary liquid mixture decreases to vanishingly small values in a very short time. However the divergence of the associated capillary-waves is prevented due to their crossover to nonequilibrium bulk fluctuations as the interface gets thicker. We think that the fluctuations observed by May and Maher, and by Vlad and Maher, are not related to surface tension effects at all. The time scales of the fluctuations observed by them are fully compatible with those predicted for nonequilibrium fluctuations in a diffuse gradient. There is no ultra-slow macroscopic diffusion to speak of, and this could be checked by means of traditional interferometric techniques [30].

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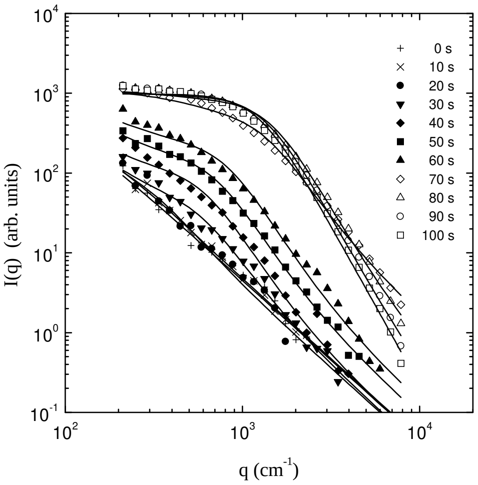

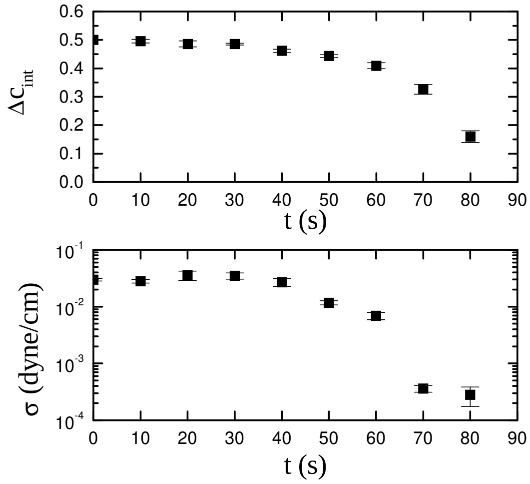

FIG. 1. Scattered intensity plotted vs. scattered wave vector q at different times. The initial dataset (+) is the intensity scattered by the initial equilibrium interface. Time is measured from the start of the remixing process. The figure shows the early stages of the remixing process, when the scattered intensity is increasing with time. The solid lines represent the best fit of the experimental data with Eqs. (1-6).

FIG. 2. Time evolution of the concentration difference across the interface, (a), and of the interfacial surface tension, (b).