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Concentration fluctuations of a binary liquid mixture in a macroporous glass

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We performed static and dynamic light scattering measurements for the binary liquid mixture, carbon disulfide–nitromethane, imbedded in a 1000-Å porous glass. The system exhibits strong spatial but weak temporal fluctuations, giving rise to interesting nonergodic behavior. A reasonably sharp transition was detected at a temperature ~ 1 K below the bulk T_C, with the system showing critical slowing-down on both sides of the transition. Despite the large pore size (in comparison with the correlation length), the intensity-intensity autocorrelation function is nonexponential with a characteristic relaxation time that does not diverge even at low temperatures, $T \ll T_C$. Our observations cannot be explained by the random-field model.

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The effect of disorder, either due to geometrical or chemical inhomogeneities, on concentration fluctuations of critical binary liquid mixtures has brought about a great deal of controversy over the past years. The question at heart is whether the disorder behaves like a random field [1, 2] that strongly influences the thermodynamic (order-disorder) phase transition, or merely introduces a wetting effect for which the disorder plays no significant role [3, 4]. Experiments using Vycor glasses [5] and silica gels [6] lend support to the random-field picture. A more recent experiment [7] using tenuous silica gels indicates that the dynamics is consistent with the random-field model, whereas a spontaneous ordering at a temperature slightly above the bulk critical temperature is not accounted for by the random-field model.

Should the concentration fluctuations behave like a bulk system if the pore size ($\bar{L}$) is much greater than the correlation length (ξ) of the fluid? This question led us to an experiment in which a binary liquid mixture saturates a macroporous glass having an average pore size ~ 1000 Å. In accordance with our expectation, we did find a reasonably sharp phase transition at a temperature ~ 1 K below the bulk critical point T_C(bulk). However, the intensity autocorrelation is strongly nonexponential, even for temperatures as high as 10 K above T_C(bulk). Furthermore, the characteristic decay rate $\Gamma(q)$ has a significant deviation from the usual q^2 dependence that is expected for concentration fluctuations that relax diffusively. The random-field model [1, 2], which requires $\xi \gg \bar{L}$, is not applicable to our system. The wetting theory [3, 4] has been done so far only for $T < T_C$ and therefore cannot be compared with our experiment.

The critical binary liquid mixture carbon disulfide (CS_2) and nitromethane (CH_3NO_2) was used in the experiment. The mixture contains $\phi = 60.1\%$ volume fraction of CS_2 and has a bulk critical temperature T_C(bulk) $\simeq 63.4\,^\circ$C. A unique feature of this mixture is that in the single-phase regime, the refractive index of the mixture (1.485) is nearly matched to that of porous glass (1.470), while the contrast between the two pure fluid components is large, with $\Delta n_0 \simeq 0.2$. Previous experiments have shown that for a clean glass surface (hydroxylated), the nitromethane-rich phase wets the surface [8]. The correlation length for the bulk fluid has also been measured, with $\xi = \xi_0[T/T_C(\text{bulk})-1]^{-\nu}$, where $\xi_0 = 1.8$ Å and $\nu = 0.63$. For a temperature difference $[T - T_C(\text{bulk})]$ as small as 10 mK, ξ is only ~ 1000 Å, which is comparable to the pore size of the glass. In our experiment ξ varied from ~ 10 to 300 Å, assuming that ξ varied with T in the same way for the free and the entrained mixtures.

The host medium in this experiment is a porous glass which was produced by the same procedure as commercial Vycor glass, except that the pore size is significantly greater. Small-angle x-ray scattering [9] indicates that the pores have an average size of 1000 Å and the porosity is $\sim 40\%$. On small length scales (or large q wave vectors) the structure factor $S(q)$ obeys Porod's law, indicating that the surface of the pores is smooth. Before the sample was filled, the porous glass was baked for several hours at 500 °C in a vacuum. The binary liquid mixture was introduced into the porous glass, 0.4 cm (diam)×3 cm (height), in the atmosphere and the sample was then flame sealed. The light scattering was performed in a thermal bath, which had a temperature stability of ±2 mK over several hours. The light-scattering source was a 5-mW He-Ne laser.

The elastic light scattering $I(q)$ and the transmitted intensity I_T were simultaneously measured as a function of temperature in this experiment. In the measurement of $I(q)$, the scattering angle was 90°, which corresponds to $q \simeq 2 \times 10^5$ cm^{-1}. Figure 1 shows both $I(q)$ and I_T at a constant cooling rate $\dot{T} \simeq -20$ mK/s. In the high-temperature regime $I(q)$ is seen to increase gradually with decreasing T, while I_T decreases as the temperature is lowered toward 62 °C. This behavior is qualitatively the same as in a bulk fluid, suggesting that the concentration fluctuations grow in size and in amplitude as the sample is cooled. In the low-temperature regime,

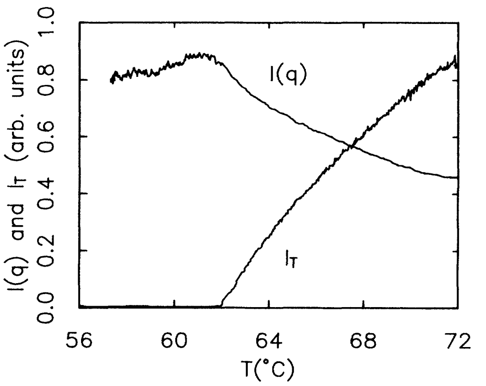

FIG. 1. Static light scattering (90°) and transmission vs temperature. The transition temperature in the porous glass is identified to be T_C(pore)$\sim$ 62.2 °C.

$T < 62$ °C, both $I(q)$ and I_T become insensitive to the temperature change. When $T \simeq 62$ °C, the sample becomes uniformly cloudy and scatters light strongly. Even though the input laser beam is still visible at this temperature, it is likely that $I(q)$ is contaminated by low-order multiple scattering events. The above behavior appears to be thermally reversible and does not change with time, even if the temperature is held at a fixed value for as long as several days.

The leveling off of $I(q)$ and I_T suggests that below $T \simeq 62$ °C, the binary liquid mixture experiences phase separation. The emerging domains cannot grow indefinitely in size due to the pinning of interfaces by the disordered medium. A further indication of phase separation comes from the slow intensity fluctuations in $I(q)$ that are seen in Fig. 1. At high temperatures the fluctuations in $I(q)$ are too rapid to be observed in this slow temperature scan. If the temperature sweep is stopped at $T < 62$ °C, slow fluctuations in $I(q)$ die out in a few minutes to hours, giving rise to anomalous noise in $I(q)$. It seems that domains rearrange themselves whenever the temperature is changed and the relaxation time associated with the rearrangement is slow. The above observations, together with the dynamic light-scattering data to be discussed later, suggest that the critical temperature in the pore is T_C(pore)$\simeq 62\,°$C. A clear phase transition of a binary liquid mixture in small pores (200 Å or less) has not been previously observed by static light intensity measurements [7, 5]. However, a phase transition was identified in 500-Å porous glasses [10], where the T_C was suppressed by several degrees. Due to the relatively large pore size in our sample, the shift in T_C is only ~ 1 K.

Having identified the phase transition in the macroporous glass, we turned our attention to study the dynamics of the concentration fluctuations. In the dynamic light-scattering experiment, one measures the intensity-intensity autocorrelation function $g_2(t) = \langle I(t)I(0)\rangle/\langle I(0)\rangle^2$. For scattered light that obeys Gaussian statistics, the homodyne signal $G_2(t) \equiv [g_2(t) -1]/f(A)$ is the square of the electric field autocorrelation function $G_1(t)$, which measures directly the order-parameter correlation function $G_1(t) \sim \frac{\langle c_q(t')c_q^*(t'+t)\rangle_{t'}}{\langle |c_q(t')|^2\rangle_{t'}}$. Here $f(A)$ is a contrast factor that determines the signal-to-noise ratio, and $c_q(t)$ is the qth Fourier component of local concentration $c(\mathbf{r},t)$. In the porous medium various factors, such as the variation of the index of refraction between the liquid-solid interfaces, spatially constrained concentration fluctuations, and frozen domains in low temperatures, all conspire to make $G_2(t)$ not decay at long times. In this case the quasistatic part of $I(t)$ is said to be nonergodic [11], and one must extract the ensemble averaged intensity fluctuations from the measured time variation of the scattered intensity.

Two procedures were used to obtain the requisite ensemble averaged $\langle G_2(t)\rangle_E$. One can physically move the sample or the photodetector while measuring the intensity correlation function, thereby assuring that the measurement spans an ensemble of pores [12]. Alternatively, one can extract the desired correlation function from a measurement of the time averaged $g_2(t)$, together with a measurement of the ensemble average of the intensity $\langle I(t)\rangle_E$ [11]. The latter quantity was obtained by slowly scanning the sample over several mm^2 areas. Both procedures were used and gave essentially the same $\langle G_2(t)\rangle_E$.

When the contrast factor $f(A)$ is small, as in our experiments, $\langle G_2(t)\rangle_E$ is proportional to $\langle G_1(t)\rangle_E$ rather than its square, and the proportionality constant is given by Pusey and van Megen [11]. Figure 2 is a plot of $\langle G_2(t)\rangle_E$, measured at $T - T_C$(pore)= 1.2 K. Note that the horizontal axis spans eight decades of time t. Four curves are superimposed in the plot. They correspond to the photodetector placed at very slightly different angles, but where the mean scattered intensity (the brightness of a speckle) was very different. All curves should yield the same value of $\langle G_2(t)\rangle_E$, and to a good approximation they do. The measurements in this figure were for a sample that was saturated with the critical mixture but with a trace amount of the bulk mixture surrounding it.

The most notable feature of the curves in Fig. 2 is that

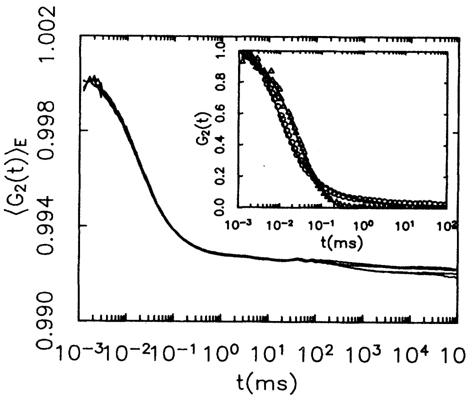

FIG. 2. Ensemble-averaged time-average autocorrelation function $\langle G_2(t)\rangle_E$. The measurements were performed at a 90° scattering angle and at the temperature $T - T_C$(pore)= 1.2 K. Autocorrelation functions were measured at four different speckles with intensity ranging from 90 to 700 kHz. The inset shows two measurements for an isolated sample (circles) and a sample in contact with a reservoir (triangles). The lines are the fitting curves.

$\langle G_2(t)\rangle_E$ does not decay exponentially. An exponentially decaying function in this semilog plot is a curve with zero slope for both large and small values of t, but which relaxes in a fraction of a decade centered on the decay time τ of the function $e^{-t/\tau}$. In a free critical binary mixture, Γ ($\equiv 1/\tau$) $= Dq^2$, where $D = k_BT/6\pi\eta\xi$ is the composition diffusivity, k_B is the Boltzmann constant, and η is the viscosity of the mixture. It was not possible to fit the curves in this figure with a single exponential, a sum of two exponentials, a power-law fit, or with other functional forms that have been proposed for $\langle G_2(t)\rangle_E$ [7, 5]. It is clear, however, that $\langle G_2(t)\rangle_E$ consists of a spectrum of relaxation times ranging from 10^{-6} up to 10^2 s or perhaps even longer [14].

Whereas the measurements shown in Fig. 2 were performed on an isolated sample, the measurements appearing in the inset of this figure were made to determine the effect of having the porous sample in contact with a large reservoir of the critical mixture. The upper curve (triangles) is made under this condition and at a temperature $T - T_C(\text{pore}) \simeq 1.8$ K. Many measurements of this type, spanning a range of compositions ($5\% \le \phi \le 95\%$), established that $G_2(t)$ is always well fitted by the sum of two exponentials: $G_2(t) = Ae^{-t/\tau_1} + (1-A)e^{-t/\tau_2}$. For the data in the inset $A \simeq 1/2$, $\tau_1 \simeq 0.02$ ms, and $\tau_2 \simeq 0.08$ ms. Thus the slowly decaying tail of $G_2(t)$ disappears when the sample is in contact with a reservoir.

For purposes of comparison, we also show in the inset of Fig. 2 a measurement of $G_2(t)$ for an isolated sample (circles) at a temperature $T - T_C(\text{pore}) \simeq 0.5$ K. As in the main figure, the slowly decaying tail of $G_2(t)$ is present. A function that fits this measurement well, but that has no physical basis [15], is $G_2(t) = \frac{1}{1+x^3}$, where $x = \log_{10}(t/\tau_0)/\log_{10}(\tau/\tau_0)$ with $\tau_0 \simeq 1$ μs being the shortest relaxation time of the system. The solid line through the data points is the best fit to this function, for which $\tau = 0.014$ ms. Thus, the decay time for the isolated sample is roughly equal to the shorter decay time of the sample in contact with the reservoir, though the functional form of $G_2(t)$ is very different for the two cases.

It is perhaps not surprising that $G_2(t)$ can have a different form for the isolated sample, as compared with the sample surrounded by a reservoir of the same composition. In the latter case, the porous sample can absorb an additional amount of the wetting component, whereas, for the the isolated sample, the composition is fixed. With this constraint, the surrounding and the entrained mixtures are held to the same chemical potential, rather than the same composition [16]. To examine the behavior of the system under this constraint, $G_2(t)$ and I_T were measured in a series of samples that were surrounded by mixtures of concentration that differed from the bulk critical value. The measurements showed that the phase separation temperature T^* was lower in these samples than in the isolated sample containing a mixture of bulk critical composition. Furthermore, in these samples $G_2(t)$ exhibited the type of two-exponential decay that was seen in the sample surrounded by a mixture of bulk critical composition. From these observations we infer that (a) the critical composition (c_c) shift of the mixture in the porous sample is small, and (b) the two-exponential decay of $G_2(t)$ is characteristic of the presence of a bulk reservoir.

Figure 3 shows the decay time τ as a function of T. Two different scattering angles $\theta = 90°$ (inset) and $\theta = 15°$ (main) were measured. They correspond to $1/q \simeq 500$ and 3000 Å, respectively. Since the average pore diameter is $\bar{L} \sim 1000$ Å, the two measurements probe concentration fluctuations within and between the pores. At 90° ($1/q < \bar{L}$), τ shows a cusp near $T_C(\text{pore})$, indicating the existence of critical slowing-down on both sides of the transition. Here two sets of data are included, with circles referring to the isolated sample and triangles referring to the sample surrounded by a reservoir. In the latter case, only the short time τ_1 has been shown. Note that even though the two measurements follow different thermodynamic paths, and the correlation functions have different forms, the decay times are nevertheless comparable. Our measurements are in quantitative agreement (within a factor of 2) with the mode-coupling theory for the bulk fluid [13, 17], as shown by the solid line in the inset. A remarkable difference occurs, however, when the measurements are performed at small angles. Though the effect of critical slowing-down is still observable at 15° ($1/q \gg \bar{L}$), the measured τ is a factor of 20 faster than that predicted by the mode-coupling theory. It seems that for small-angle scattering, the decay time is almost independent of q. It is generally expected that if the concentration fluctuations relax diffusively, the relaxation rate should be proportional to q^2. The q^2 dependence, robust for bulk systems, appears to break down in the porous sample.

Certain features that we observed can be qualitatively explained in terms of restricted Brownian motion in a one-dimensional box of size $\bar{L}$. The mode-coupling theory ensures that concentration fluctuations can be treated as diffusion of particles with radius ξ [13]. Assuming small $\xi(\ll \bar{L})$ and reflecting walls, the probability density that a Brownian particle moves from x to x' during time t is given by

$$g(x, x'; t) = \frac{1}{\bar{L}} + \frac{2}{\bar{L}} \sum_{p=1}^{\infty} \cos\frac{p\pi x}{\bar{L}} \cos\frac{p\pi x'}{\bar{L}} \times \exp\left(-\frac{p^2\pi^2}{\bar{L}^2} Dt\right),$$

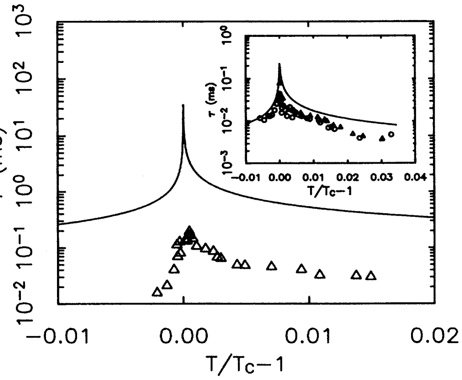

FIG. 3. Decay time τ vs reduced temperature. The τ at $\theta = 15°$ (triangles) was 20 times faster than that of a free system (solid line). Inset is a similar plot for $\theta = 90°$.

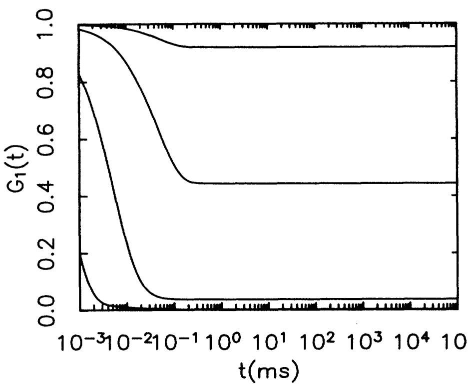

FIG. 4. Calculated $G_1(t)$. From top to bottom, $G_1(t)$ is calculated for $q\bar{L} = 1$, 3, 10, and 30, respectively.

where $D = \frac{k_B T}{6\pi\eta\xi}$ is the diffusion constant. The autocorrelation function $G_1(t)$ is obtained by a Fourier transformation of $g(x, x'; t)$:

$$G_1(t) = \frac{2(1-\cos q\bar{L})}{q^2\bar{L}^2} + \sum_{p=1}^{\infty} \frac{4q^2\bar{L}^2}{(p^2\pi^2 - q^2\bar{L}^2)^2}[1-(-1)^p \cos q\bar{L}] \times \exp\left(-\frac{p^2\pi^2}{\bar{L}^2}Dt\right).$$

The summation has been carried out numerically, and the results appear in Fig. 4. This simple model captures several important features of our measurements. The decay rate Γ depends on q^2 for $q\bar{L} \gg 1$ and loses its q dependence for $q\bar{L} \ll 1$. Furthermore, for $q\bar{L} \sim 1$, $G_1(t)$ decays less than 10%, in striking similarity to the data shown in Fig. 2. It is surprising that this simple model also predicts $G_1(t)$ to be nonexponential for a wide range of $q\bar{L}$. However, the functional form is qualitatively different from our measurements in that the decay of $G_1(t)$ to its asymptotic value is rapid rather than logarithmic, as seen in our experiment.

In summary, we have studied concentration fluctuations of a binary liquid mixture contained in porous glass having a pore size much greater than the correlation length. At small q the fluctuations do not decay diffusively, and at all q there appears a very broad spectrum of relaxation times. Since the logarithmic decay is observed when $\xi \ll \bar{L}$, random-field theory is inapplicable to our system. It is surprising, however, that the simple model of constrained Brownian motion accounts for two salient features of our measurements, the anomalous q dependence and the nondecaying part of $G_2(t)$. The slow dynamics still remains unexplained.

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[14] The extremely slow relaxation seen in the porous glass makes it impossible to determine the base line of the correlation function without performing the ensemble average.

[15] Even though the fitting function is conspicuously similar to the one suggested for activated dynamic processes, the use of this functional form is only for experimental convenience. The function appears to mimic the experimental data reasonably well and allows us to extract the characteristic decay time at early times.

[16] It is well known that different thermodynamic paths can have a profound influence on the bulk phase transitions as well as on the preferential adsorption and wetting on flat surfaces. However, it is not entirely clear how the different thermodynamic paths manifest themselves in small confined geometries with disorder and large interfacial curvature.

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