Statics and Dynamics of a Critical Binary Fluid in a Porous Medium

S. B. Dierker
The Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan 48109-1120

P. Wiltzius
AT&T Bell Laboratories, Murray Hill, New Jersey 07974-2070

(Received 6 December 1990)

We present small-angle neutron-scattering measurements of the static structure factor $S(q)$ of the binary fluid water-lutidine mixture imbibed into the porous glass Vycor as a function of temperature and composition. $S(q)$ changes from a Lorentzian in the one-phase region to a Lorentzian squared at the random-field transition. We relate the correlation lengths ($9\ \text{Å} \lesssim \xi \lesssim 52\ \text{Å}$) to the previously measured relaxation times and find finite-size and random-field effects.

PACS numbers: 64.60.Cn, 61.20.Qg, 64.60.Ht, 66.20.+d

There has been widespread interest in the behavior of fluids imbibed into porous media.[1-8] The phase transition of imbibed binary fluids is particularly anomalous due to finite-size, wetting, and random-field effects. Order-parameter fluctuations probed with quasielastic light scattering (QELS) show a transition from diffusive to activated behavior at a random-field transition.[7] In the diffusive regime the autocorrelation functions are exponentials with a single decay rate, Γ. Evidence for a random-field transition to a frozen domain state is provided by the observation of strongly nonexponential autocorrelation functions whose characteristic relaxation time increases very strongly at the random-field transition temperature, T_{rf}.

The temperature dependence of Γ is qualitatively different from that in a bulk mixture.[7] In bulk mixtures and in the long-wavelength limit, the relaxation time Γ^{-1} diverges at the critical point with the same exponent as the static correlation length ξ. This remarkable relationship between static and dynamic behavior has been theoretically explained[9] by the mode-coupling treatment of model H. Agreement between experiments and dynamic scaling predictions is excellent.[10] Elastic light-scattering (ELS) measurements[8] on binary fluid mixtures imbibed into porous Vycor showed that ξ is too small to be measured with visible light. From these studies it was concluded that ξ never becomes very large compared to the pore radius r_p.

In this paper, we report small-angle neutron-scattering (SANS) experiments from which we directly determine both ξ and $S(q)$. We confirm that ξ is comparable in size to r_p and report its detailed temperature dependence. We find that $S(q)$ does crossover from Lorentzian to Lorentzian squared upon approaching the random-field transition as theoretically predicted[11] and as has been observed to occur in randomly diluted antiferromagnets.[12] The similar behavior of systems as seemingly different as random fluids and random magnets suggests that the effects of disorder may indeed be universal.

Currently, very little is known about the relationship between the hydrodynamics of composition fluctuations in fluids confined to random porous media and the length scale of the fluid mixture.[6] We relate the static correlation lengths reported here to be the relaxation times Γ^{-1} of this system which we reported previously.[7] We find that at low temperatures Γ^{-1} is approximately proportional to ξ, similar to the bulk behavior, but the effective viscosity is 2–3 times higher inside the porous glass.

The system studied here is the same one for which we previously reported QELS and ELS measurements: the binary fluid mixture water and 2,6-lutidine imbibed into porous Vycor glass.[7,8] The bulk mixture has an inverted coexistence curve, being in the one-phase region at room temperature and entering the two-phase region upon heating above $\sim 33\,^\circ\text{C}$ at the critical lutidine volume fraction $\phi_{\text{lut}} = 30\%$. Upon warming a piece of Vycor with a critical fluid mixture imbibed into it, the fluid does not phase separate macroscopically as it does in bulk but instead phase separates mesoscopically and undergoes a random-field transition to a frozen domain state. We previously characterized the structure of the porous network of Vycor using SANS.[13] The dominant feature in $S(q)$ is a pronounced maximum at $q_m \sim 0.023\ \text{Å}^{-1}$ corresponding to a length scale $2\pi/q_m \sim 270\ \text{Å}$, which can be interpreted as the mean spacing between pores (average pore radius, $r_p \sim 30\ \text{Å}$). It is important to note that the glass structure is rigid and does not exhibit any dynamics of its own when imbibed with a critical binary fluid, unlike, for example, gels or polymers.[3,4]

SANS is uniquely suited for studying the structure of this system. In addition to allowing access to the interesting length scales, neutrons provide the crucial ability to use contrast-variation techniques effectively to mask out the scattering from the glass-fluid interface, which is quite large for Vycor ($\sim 160\ \text{m}^2/\text{cm}^3$). By imbibing various mixtures of H_2O and D_2O into Vycor, we measured the scattering density of Vycor to be ρ_{Vycor}

$=3.6\times10^{10}$ cm^2. $S(q)$ for index-matched Vycor shows only very weak incoherent background scattering from the hydrogen. We thus studied binary fluid mixtures composed of lutidine, water, and heavy water for which on average $\rho_{\rm mixture}=\rho_{\rm Vycor}$. Samples with $\phi_{\rm lut}=30\%$, 40%, and 50% are denoted samples 3, 4, and 5 in this paper.

The results for $S(q)$ as a function of temperature between 10 and 80 °C for sample 4 are shown in Fig. 1. At low temperature $S(q)$ has a Lorentzian line shape (limiting slope of -2 at large q), which is very similar to what is observed in the one-phase region in a bulk mixture. As the temperature increases, the line shape changes from a Lorentzian to a Lorentzian squared (limiting slope of -4 at large q). In addition to these main features, there is also a small peak in $S(q)$ at $q\sim0.05$ Å^{-1}.

The structure of the critical mixture inside the porous glass is complex, consisting of a combination of fluid composition fluctuations, microphase- or mesophase-separated domains, and wetting layers, or composition gradients, next to the glass walls. An analytic formalism for interpreting the measurements in terms of such types of physical structure in the mixture is nonexistent. One major difficulty is that because the Fourier transform of the pair-correlation function of the fluid fluctuations is restricted to the random void space of the porous glass, the structure of the latter influences the shape of the measured structure factor, even in index-matched samples. Attempts to treat these difficulties analytically have had limited success.[14]

We have found that $S(q)$ is well fitted (χ^2 between 1 and 2 for all data) by the expression

$$S(q)=\frac{A_{\rm LOR}}{1+q^2\xi^2}+\frac{A_{\rm LSQ}}{(1+q^2\xi^2)^2}+A_0+A_p e^{-[(q-q_p)/\mu]^2}. \tag{1}$$

This equation models the evolution from Lorentzian to Lorentzian squared with temperature-dependent amplitudes, $A_{\rm LOR}$ and $A_{\rm LSQ}$, respectively, contains a small constant term, A_0, to account for the background incoherent scattering, and a Gaussian term with a small amplitude A_p which is used to describe the peak at $q_p\sim0.05$ Å^{-1}. Note that Eq. (1) fits our data very well with the same value of ξ in both the Lorentzian and the Lorentzian squared, as theoretically predicted.[11] This is in contrast to the case of binary liquids in gels, where a reasonable fit required very different values for ξ in the two terms.[3,4]

The temperature dependence of $A_{\rm LOR}$ and $A_{\rm LSQ}$ for samples 3, 4, and 5 are shown in Figs. 2(a) and 2(b), respectively. For $T\lesssim30$ °C, in the one-phase region, the line shape is purely Lorentzian for all concentrations. $A_{\rm LOR}$ shows a weak pretransitional increase upon approaching the bulk transition temperatures which are between 31 and 35 °C. This increase is qualitatively similar to the behavior of a bulk liquid mixture, although

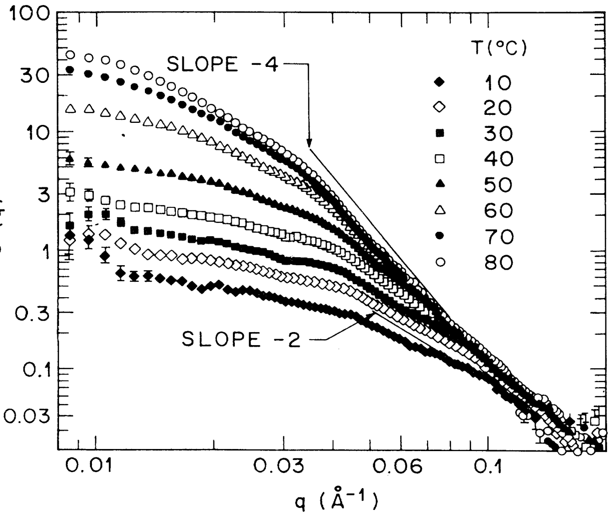

FIG. 1. The structure factor $S(q)$ of a mixture of 40% lutidine $+60\%$ (H_2O+D_2O) imbibed into Vycor as a function of temperature. The limiting slopes of -2 and -4 clearly illustrate the evolution from Lorentzian in the one-phase region to Lorentzian squared in the frozen domain state. $S(q)$ is in absolute units of cm^{-1}.

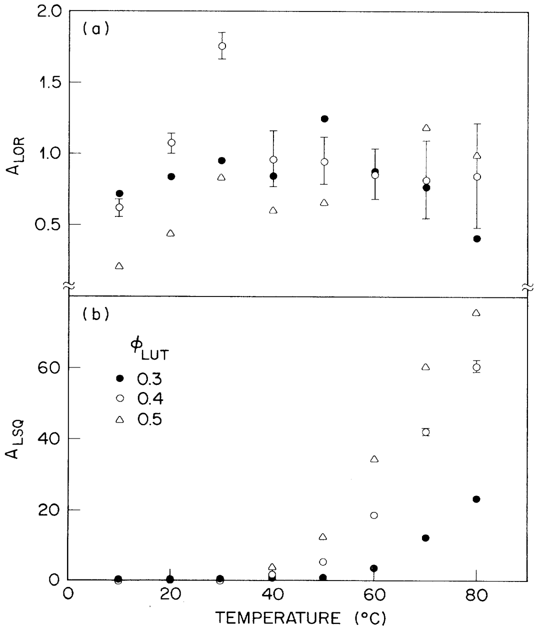

FIG. 2. The temperature dependence of the amplitudes of the (a) Lorentzian and (b) Lorentzian-squared components of $S(q)$ for samples with $\phi_{\rm lut}=30\%$, 40%, and 50%. $A_{\rm LOR}$ and $A_{\rm LSQ}$ are in absolute units of cm^{-1}. Error bars for the 30% and 50% samples are similar to those for the 40% sample.

A_{LOR} does not diverge.

For $T \gtrsim 30\,^{\circ}\mathrm{C}$, A_{LSQ} increases strongly with increasing temperature. At a given temperature, A_{LSQ} also increases as the lutidine concentration increases. This behavior is qualitatively similar to the behavior of the static light-scattering intensity which we reported earlier.[8] Because of the long wavelength of visible light we were only able to measure $S(q \approx 0)$, which corresponds to the sum of $A_{\mathrm{LOR}}+A_{\mathrm{LSQ}}$. With the current SANS measurements, we are able to separately determine A_{LOR} and A_{LSQ} and establish the crossover.

The measured correlation length for the imbibed fluid is shown in Fig. 3. It increases modestly as the temperature is raised from 10 to 80 °C, without showing any signs of divergence between 31 and 35 °C where it would diverge in the corresponding bulk mixtures.

For $T \lesssim 30\,^{\circ}\mathrm{C}$, the temperature dependence of ξ depends strongly on composition. Samples 4 and 5 show an increasing ξ which interestingly never exceeds the more or less constant values of sample 3, $\xi \approx 33$ Å, or about half the pore diameter. We note that A_{LOR} is roughly proportional to ξ^2, similar to what has been established experimentally and theoretically for bulk critical fluctuations. The picture emerging for this temperature range is one of composition fluctuations of correlation length ξ which at a given temperature is smaller at high lutidine concentrations because those samples are further away from a critical point. As the critical point is approached ξ increases but is bound due to finite-size effects. This physical picture loses its validity as the qualitative shape of $S(q)$ changes from Lorentzian to Lorentzian squared.

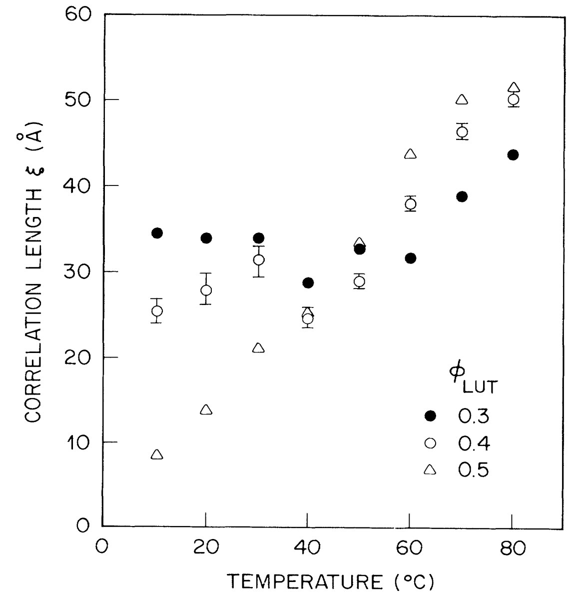

FIG. 3. The temperature dependence of the correlation length ξ for samples with $\phi_{\mathrm{lut}}=30\%$, 40%, and 50%. Error bars for the 30% and 50% samples are similar to those for the 40% sample.

For $T \gtrsim 50\,^{\circ}\mathrm{C}$, ξ has a similar temperature dependence for all three samples. The Lorentzian-squared line shape is theoretically expected for a random-field transition. A similar line shape is expected for scattering from water-rich and lutidine-rich domains separated by "sharp" interfaces filling the pore space. If we associate ξ with the size of the domains, we expect ξ to be proportional to ϕ_{lut}, which is in semiquantitative agreement with the observed composition dependence of ξ. A Lorentzian squared is a reasonable envelope for the form factor of a sphere of radius $R \approx 1.7\xi$. The size of the domains thus seems to be 2–3 times the size of a pore at 60 °C. This was previously expressed as a precondition for a random-field transition.[7] In a bulk mixture, interfacial surface tension between lutidine-rich and water-rich domains would make it energetically favorable for them to strongly increase in size. The observation that their size increases only slightly is evidence that the free energy of the system is dominated by effects other than fluid-fluid interfacial surface tension. The domains spanning several geometrically and chemically random pores each have a local energy barrier to overcome in order to establish long-range order.

We find that A_{LSQ} is proportional to $\xi^{4.4}$. The theoretical prediction[15] based on scaling arguments for random-field systems is $A_{\mathrm{LSQ}} \sim \xi^3$ in three dimensions. The difference between these exponents most likely indicates that the domains not only grow in size, but that their difference in composition, and hence contrast, also increases with increasing temperature.

We previously used QELS to probe temporal fluctuations in the composition of this system.[7] In a bulk fluid mixture, the time-autocorrelation function of these fluctuations is a single exponential. The characteristic reduced relaxation rate is given by[9,10,16]

$$\Gamma^* = 6\pi\eta\Gamma/k_B T q^3 \qquad (2)$$

$$= 1/q\xi, \quad q\xi \lesssim 1\,, \qquad (3)$$

where η is the shear viscosity. In general, due to the tortuous paths available for transport combined with nonslip boundary conditions on the velocity field at the pore surfaces, we expect that the effective viscosity of the imbibed mixture will be greater than that of a bulk mixture. By combining our measurements of Γ and ξ with Eqs. (2) and (3), we deduce the ratio, shown in Fig. 4, of the effective viscosity for the fluid in Vycor to the viscosity of a bulk mixture. The effective viscosity is greater than the bulk viscosity and the ratio is strongly temperature dependent, increasing from ~2 at 10 °C to ~6 at 60 °C. The ratio is composition dependent as well.

The transition from a modest temperature dependence for $T \lesssim 40\,^{\circ}\mathrm{C}$ to a very rapid rise at high temperatures is consistent with the prediction by Huse[6] that the characteristic time should grow like $\exp(b\xi^{\psi}/T)$ at the ap-

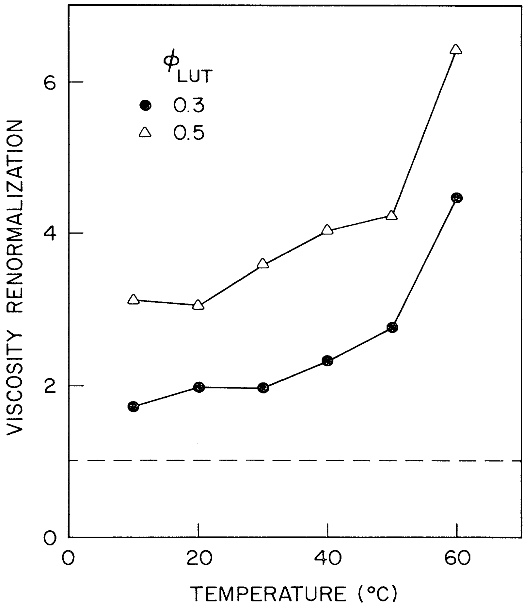

FIG. 4. The ratio of the effective viscosity of the imbibed fluid to that of the bulk fluid for $\phi_{\mathrm{lut}}=30\%$ and 50%. The dashed line represents the bulk.

proach to the ordering transition in a random-field system with a conserved order parameter. We do not have an explanation for the difference between sample 3 and sample 5 at low temperatures. Naively, one might expect the viscosity enhancement to be smaller for sample 5, since the correlation lengths are smaller, thus diminishing the effect of reduced dimensionality.

Work in progress is aimed at further understanding to what extent our findings can be universally applied to binary fluids in porous media. We are investigating this by studying mixtures both imbibed into a number of porous glasses with different pore sizes and into porous materials with different pore geometries. The latter is particularly interesting in light of a recent theoretical study of wetting in uniform cylindrical pores by Liu *et al.*[17] Metastable effects with time scales comparable to those measured[7] by QELS have been proposed without randomness in such a system. Experiments separating the effects due to randomness from those due to confined geometry are thus highly desirable.

We would like to thank Brian Dennis for assistance with sample preparation. It is a pleasure to acknowledge Phil Seeger and Rex Hjelm for assistance in conducting the SANS measurements on the Low-Q Diffractometer at Los Alamos. This work has benefited from the use of facilities at the Los Alamos Neutron Scattering Center, a national user facility funded as such by the DOE, Office of Basic Energy Sciences.

---

[1] P. G. de Gennes, J. Phys. Chem. **88**, 6469 (1984).

[2] D. Andelman and J. F. Joanny, in *Scaling Phenomena in Disordered Systems,* edited by R. Pynn and A. Skjeltorp (Plenum, New York, 1985).

[3] S. K. Sinha, J. Huang, and S. K. Satija, in *Scaling Phenomena in Disordered Systems* (Ref. 2).

[4] J. V. Maher, W. I. Goldburg, D. W. Pohl, and M. Lanz, Phys. Rev. Lett. **53**, 60 (1984); K.-Q. Xia and J. V. Maher, Phys. Rev. A **36**, 2432 (1987); **37**, 3626 (1988).

[5] M. C. Goh, W. I. Goldburg, and C. M. Knobler, Phys. Rev. Lett. **58**, 1008 (1987).

[6] D. A. Huse, Phys. Rev. B **36**, 5383 (1987).

[7] S. B. Dierker and P. Wiltzius, Phys. Rev. Lett. **58**, 1865 (1987).

[8] P. Wiltzius, S. B. Dierker, and B. S. Dennis, Phys. Rev. Lett. **62**, 804 (1989).

[9] K. Kawasaki, Ann. Phys. (N.Y.) **61**, 1 (1970).

[10] H. L. Swinney and D. L. Henry, Phys. Rev. A **8**, 2586 (1973).

[11] E. Pytte, Y. Imry, and D. Mukamel, Phys. Rev. Lett. **43**, 808 (1979).

[12] R. J. Birgeneau, Y. Shapiro, G. Shirane, R. A. Cowley, and H. Yoshizawa, Physica (Amsterdam) **137B**, 83 (1986), and references therein; D. P. Belanger, A. R. King, and V. Jaccarino, Phys. Rev. Lett. **54**, 577 (1985).

[13] P. Wiltzius, F. Bates, S. B. Dierker, and G. D. Wignall, Phys. Rev. A **36**, 2991 (1987).

[14] N. F. Berk, Phys. Rev. Lett. **58**, 2718 (1987).

[15] D. Mukamel and E. Pytte, Phys. Rev. B **25**, 4779 (1982); A. Aharony and E. Pytte, Phys. Rev. B **27**, 5872 (1983).

[16] A noncritical background contribution to Γ, observed to be negligibly small in bulk fluid mixtures, has been neglected here.

[17] A. J. Liu, D. J. Durian, E. Herbolzheimer, and S. A. Safran, Phys. Rev. Lett. **65**, 1897 (1990).