# Random-Field Transition of a Binary Liquid in a Porous Medium

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(Received 29 January 1987)

We have used quasielastic light scattering to study a binary-liquid critical mixture in a porous medium, which undergoes a random-field transition upon warming to a history-dependent frozen-domain state. Finite-size effects and a crossover to activated dynamics with nonexponential relaxations are observed. The relaxation time is found to increase very rapidly at the random-field transition, in agreement with recent theories of activated dynamics in disordered systems.

PACS numbers: 64.60.−i, 05.40.+j, 47.55.Mh, 64.60.Ht

Confinement of fluids within random porous media can lead to dramatic and complex changes in their physical behavior. An especially interesting situation arises when the porous medium confines a critical binary fluid which would undergo a bulk demixing phase transition at a critical temperature, $T_c$, and when one of the fluid components preferentially wets the pore surfaces. When the binary-fluid correlation length, $\xi$, is smaller than the pore radius, $r_p$, one has a system for studying finite-size effects in the presence of a surface field.[1] When $\xi > r_p$, the random porous medium can exert a random field,[2-5] resulting in a new model system for the study of random-field effects.

Recently theoretical work[6,7] has emphasized that novel ordering dynamics is one of the most important aspects of random-field Ising systems. A new kind of activated dynamic scaling[7] has been proposed to describe these systems in which the natural scaling variable is $\ln(t)$ rather than $t$, where $t$ is the time. The characteristic time for ordering, $\tau$, is predicted to diverge exponentially[6,7] upon approach to the random-field transition, implying that systems will fall out of equilibrium on experimental time scales. This scenario provides an appealing explanation for many aspects of the frozen-domain states and history-dependent effects seen in random-field magnets.[8] Nonexponential dynamic correlations which scale as a function of $(\ln t)/\ln\tau$ have been confirmed in recent Monte Carlo simulations[9] in the strong random-field regime but have not been observed experimentally.

A random-field fluid system has the additional richness that its dynamics are constrained by order-parameter conservation. Huse[10] recently considered this and predicted that as $q\xi$ increases the dynamics should cross over from nonactivated to activated at $(q\xi)_x \lesssim 1$, where $q$ is the wave vector and $\xi$ is the correlation length.

We have studied the binary-liquid mixture[11] 2,6-lutidine plus water, which has an inverted coexistence curve with a $T_c$ of 33.3 °C, in the rigid random porous glass Vycor. We find that the system enters a history-dependent frozen-domain state upon warming through a random-field transition at $T_{\mathrm{rf}}$. Using quasielastic light scattering, we are able to study in detail the microscopic hydrodynamic critical behavior of the confined mixture. In the homogeneous phase, the dynamics show a complex temperature dependence due to finite-size effects. At the random-field transition, we observe the predicted crossover[10] from nonactivated to activated dynamics, with nonexponential correlations which scale[7] with $(\ln t)/\ln\tau$ rather than $t/\tau$. The activated relaxation time increases very rapidly upon approach to the frozen-domain state at $T_{\mathrm{rf}}$. We also show that the character of the relaxations changes from nonactivated to activated in inverse proportion to the length scale probed. Our results are the first experimental study of the dynamic critical behavior of a random-field system with a conserved order parameter and provide evidence in support of the activated-dynamic-scaling theory[7] of disordered systems.

Porous Vycor[12] glass is made by acid leaching of the boron-rich phase of a spinodally decomposed borosilicate glass. The resulting pore space forms a three-dimensional highly interconnected structure with a pore-radius distribution sharply peaked at 30 Å and a porosity of 28%. Neutron-scattering measurements[13] reveal a broad peak in the structure factor corresponding to a length of 190 Å and a surface-to-volume ratio of 180 $\mathrm{m^2/cm^3}$.

A precleaned 12-mm-diam by 12-mm-high cylinder of Vycor was sealed in a closely fitting sample tube on the sides and bottom with a transparent chemically inert, UV-crosslinked polymer. The tube was then filled with a mixture of the bulk critical composition which was imbibed into the Vycor. The liquid composition within the Vycor was determined by Raman scattering[14] to be within a few percent of the surrounding bulk composition at a temperature of 21 °C. Constant composition was insured by our then removing the reservoir of excess bulk fluid from the tube and having only a thin layer of mixture above the Vycor.

Intensity autocorrelation functions were measured with a typical dynamic light-scattering apparatus[15] (temperature stability $\lesssim 1$ mK) at a range of scattering angles, $\theta$, from 30° to 162°. Our measurements thus probe diffusion over length scales ranging from 118 to 31 times the average pore diameter.

Upon warming, the Vycor sample develops a uniform cloudiness which is first visible at ~45 °C and gradually increases up to ~60 °C. From 60 °C to as high as 110 °C, the scattering intensity is roughly temperature independent and persists unchanged for as long as two weeks. This behavior is reversible upon cooling. We interpret these observations as evidence for the formation of phase-separated domains which are frozen in size above ~60 °C because of the pinning by the random field. The domains are presumably smaller than a few tens of microns since they are not observable under a 40× microscope.

Macroscopic evidence for a transition at ~60 °C comes from the study of the stability of an artificially created domain wall within the Vycor. When a Vycor sample saturated with lutidine is submerged in a reservoir of water, water diffuses into its outer region and an interface appears within the Vycor separating the differing outer and inner compositions. Below ~60 °C, this interface is diffuse and in a day disappears into the center of the sample, indicating that a homogeneous composition is attained. Above ~60 °C, however, the interface is sharp and after penetrating into the Vycor several millimeters slows to a virtual stop, staying in position for several days. Our observations thus reveal that the state of the system above $T_{\rm rf} \sim 60\,^\circ{\rm C}$ is history dependent and suggest that a frustrated transition into a frozen-domain state occurs at $T_{\rm rf}$ upon field heating. Note that $T_{\rm rf}$ is strongly shifted upward from the pure mixture's $T_c$ by ~27 °C, as expected for random-field effects in a system with an inverted coexistence curve.

We are able to provide insight into the microscopic nature of the history-dependent metastability effects we observe by studying the dynamics of our system. Dynamic correlations of equilibrium order-parameter fluctuations in fluid mixtures have universally been observed to decay as a single exponential, $e^{-\Gamma t}$.[16] According to nonactivated-dynamic-scaling theory,[17] the reduced decay rate

$$\Gamma^* \equiv 6\pi\eta\Gamma/k_{\rm B}Tq^3 \qquad (1)$$

is a universal function for pure binary liquids equal to $1/q\xi$ for $q\xi \lesssim 1$. $\eta$ is the shear viscosity and $q$ is the scattering wave vector.

The results for $\Gamma^*$ for data acquired at $q^{-1} = 1120$ Å (a scattering angle of 30°) are presented in Fig. 1.[18] Far below the bulk mixture's $T_c$, where $\xi$ is significantly smaller than $r_p$, $\Gamma^*$ is decreasing with increasing temperature but is ~6 times smaller than predicted[17] and measured[16] for bulk mixtures. By 20 °C, where the bulk $\xi$ would be $\sim r_p/2$, $\Gamma^*$ begins to saturate. $\Gamma^*$ then decreases only very slowly until ~40 °C, where it begins decreasing more rapidly again, finally going through a minimum just below $T_{\rm rf}$ before increasing once more.

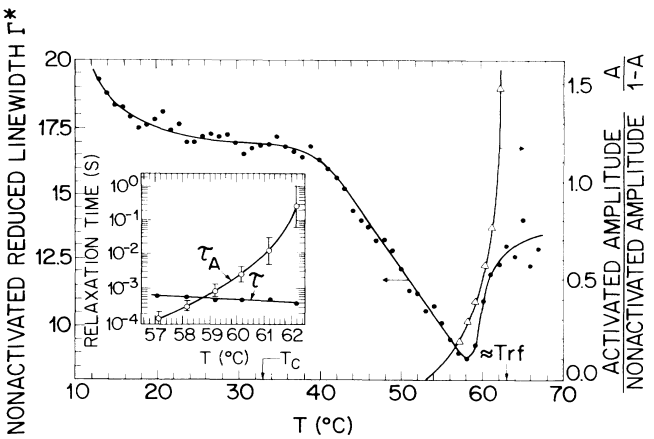

FIG. 1. Temperature dependence of the nonactivated reduced relaxation rate, $\Gamma^*$, and the relative weight of activated to nonactivated relaxations $A/(1-A)$. Inset: Temperature dependence of the nonactivated and activated relaxation times, $\tau$ and $\tau_A$. Solid lines are a guide to the eye. The bulk mixture's $T_c$ is indicated as well as the approximate vicinity of the random-field transition, $T_{\rm rf}$, as estimated from $\tau_A$. $q = 8.85 \times 10^4$ cm$^{-1}$.

We find that the correlations are well described by a single-exponential line shape for temperatures below the minimum in $\Gamma^*$ at 58 °C, but become strongly nonexponential at higher temperatures.

The behavior of the dynamic correlations is dramatically different from that previously observed for binary liquids. A complete theory of this anomalous behavior will need to address at least four crossover effects which we outline here in the order in which they are encountered as $\xi/r_p$ increases from $<1$ to $>1$.

The first involves the viscous damping of the porous medium.[2] $\Gamma^*$ is proportional to the ratio of the composition transport coefficient, $\lambda$, to the static susceptibility, $\chi$. A fluid in the restricted geometry of a porous medium is not translationally invariant and the tortuous paths available for transport will suppress $\lambda$. Nonslip boundary conditions on the velocity field at the pore surfaces will also suppress $\lambda$.[19] We believe that these effects are responsible for the factor of 6 suppression of $\Gamma^*$ below ~20 °C.

The saturation in $\Gamma^*$ occurring near 20 °C can be understood as a correlation-length finite-size effect. In a closed system with a conserved order parameter, preferential wetting at the pore surfaces will induce an opposite composition shift near the pore centers.[20] Although initially diverging toward $T_c$ with pure Ising exponents, the local composition shifts pull the system away from the critical point, inducing a finite-size saturation of $\xi \sim r_p$ and hence also the observed saturation of $\Gamma^*$. A small effect of this type was recently observed[1] in thin (2 μm) planar fluid films within 1 mK of $T_c$. In contrast, as a result of our 330 times smaller pores, we observe a large effect 15 °C below $T_c$.

As the temperature increases, the repulsive interaction between the two components of the mixture will eventually dominate. $\xi$ will then extend over larger blocks of the pore network. It is likely that this is responsible for the decrease of $\Gamma^*$ above 40 °C. These blocks will encompass varying numbers of pores of various sizes, which exert a random field on the fluid. The random field induces a shift in the critical point from $T_c$ to $T_{\mathrm{rf}}$ and a crossover to random-field Ising critical behavior.

As $\xi$ increases, order-parameter fluctuations will experience barriers to relaxation which grow as $(\xi/l_0)^\psi$, where $\psi$ is a barrier exponent expected[7] to be $\sim 1.5$ and $l_0$ is a microscopic length scale. The activated relaxation time for hopping over these barriers will increase very rapidly[6,7] as $\tau_A \sim t_0 \exp[(\xi/l_0)^\psi]$. Huse[10] finds that because of the dynamic constraints of order-parameter conservation, fluctuations on sufficiently long length scales $q^{-1} \gg \xi$ will continue to relax in a nonactivated fashion. For shorter length scales, however, there will be a fourth crossover to activated relaxation of the fluctuations. The activated-dynamic-scaling theory of Fisher[7] predicts that the dynamic correlations will then be nonexponential and will scale as functions of $(\ln t)/\ln \tau_A$.

An example of the complex nonexponential line shape near $T_{\mathrm{rf}}$ is shown in Fig. 2. We find that the dynamic correlations near $T_{\mathrm{rf}}$ are well described as a sum of relaxation processes,

$$g(t) = [1 + A(T)]e^{(-\Gamma t)} + A(T)\exp\{-[\ln(t/t_0)/\ln(\tau_A/t_0)]^3\}. \qquad (2)$$

The first term corresponds to standard nonactivated relaxation.[17] The second term scales as a function of $\ln(t/t_0)/\ln(\tau_A/t_0)$, as expected from the activated-dynamic-scaling theory,[7] and successfully fitted Monte Carlo simulations[9] of random-field magnets. $t_0$ is a microscopic time scale. The concept of two separate relaxations, with temperature-dependent relative weights, is a simple *Ansatz* for the crossover from nonactivated to activated dynamics.

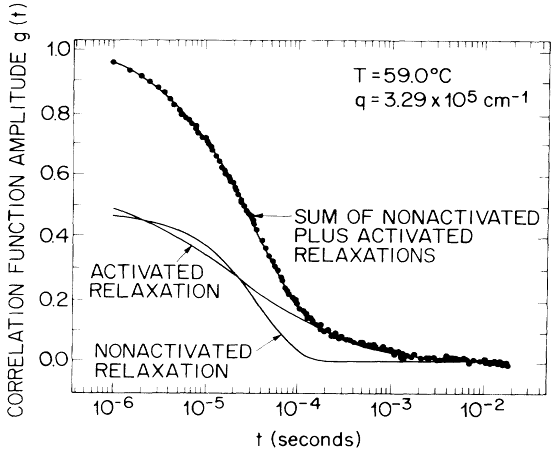

FIG. 2. An example of the nonexponential line shape of the dynamic correlation functions near $T_{\mathrm{rf}}$. A fit by Eq. (2), with nonactivated and activated components, is shown.

The results for $\Gamma^*$ above 57 °C, derived from the first term of Eq. (2), and the relative weight of activated to nonactivated relaxations, $A/(1-A)$, are shown in Fig. 1. Fits of temperature-dependent and also $q$-dependent data (discussed below) all yielded similar $t_0$ values, and so we fixed $t_0$ at $3.5 \times 10^{-8}$ s. The fitted values of the activated relaxation time, $\tau_A$, and the nonactivated relaxation time, $\tau = 1/\Gamma$, are shown in the inset of Fig. 1. We see that $\Gamma^*$ begins increasing, $\tau_A$ increases rapidly, and the relaxations become increasingly activated, upon approach to $T_{\mathrm{rf}}$. We interpret the increase of $\Gamma^*$ as a signal of the formation of phase-separated domains. Dynamic fluctuations of these domains relax in an activated fashion with a relaxation time, $\tau_A$, which increases very rapidly. These changes coincide with the onset of metastability effects as evidenced by the strong slowing down of interface motion and saturation of static intensity discussed earlier. Our observations thus strongly support recent theories[6,7] which attribute metastability effects to activated dynamics.

Two types of energy barriers can be identified. One is the variation in interfacial energy as a domain wall sweeps through a pore of varying cross-sectional area. From the surface tension of a 2,6-lutidine–water interface,[21] we estimate this to be $\sim 7T_{\mathrm{rf}}$. A second type is the variation of preferential wetting energy with pore surface area. Using data for the interface between 2,6-lutidine + water and Pyrex glass,[21] we estimate this to be $\sim 200T_{\mathrm{rf}}$. The actual energy barriers will be smaller for partially phase-separated domains and smaller geometrical variations. Nevertheless, it is entirely plausible that domains in our system should encounter energy barriers to relaxation.

As $\tau_A$ increases and the activated relaxations become broader[7,9] than the measured time range ($10^{-6}$ to $2 \times 10^{-2}$ s), it becomes difficult to determine large values of $\tau_A$ precisely. Although $\tau_A$ clearly increases rapidly, we cannot say whether it actually diverges or instead attains a large, but finite, value in the frozen-domain state. According to the activated-dynamic-scaling theory,[7] our measured value of $t_0$ suggests that fluctuations with a correlation length of only $10 l_0$ would take 1 d to relax. Together with a reasonable estimate of $l_0 \sim 10$ Å this implies that our system falls out of equilibrium and develops frozen correlations on a length scale much smaller than $2\pi/q = 7040$ Å. This is consistent with the fact that we never observe a complete crossover to activated relaxations, which is not expected[10] to occur until $q\xi \gtrsim 1$.

We have also studied the $q$ dependence of the dynamic correlations at 59 °C, where both types of relaxation are prominent. As shown in Fig. 3, we find that both $\tau$ and $\tau_A$ scale like $1/q^2$ as expected for hydrodynamic

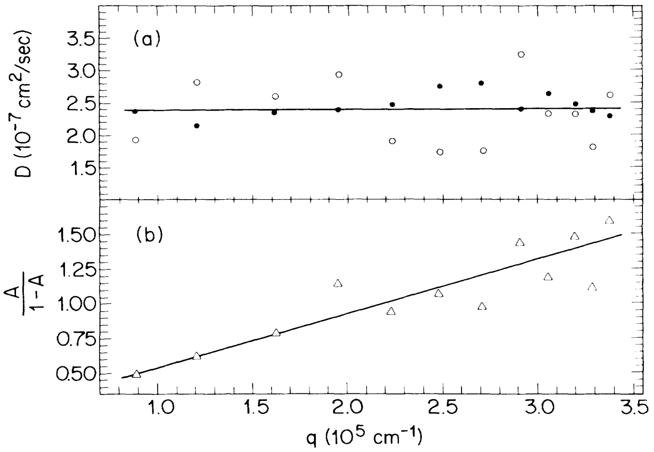

FIG. 3. Wave-vector dependence of (a) the nonactivated (filled circles) and activated (open circles) diffusion coefficients, $D=1/\tau q^2$ and $1/\tau_A q^2$, respectively, and (b) the relative weight of activated to nonactivated relaxations, $A/(1-A)$. $T=59\,^\circ\mathrm{C}$.

modes.[17] More importantly, we see that the character of the relaxations is more activated on short length scales than long length scales, giving further support to the theoretical prediction of Huse[10] of a crossover in the dynamics as $q$ increases.

In summary, we have found that binary-liquid critical mixtures in porous media display a number of novel finite-size effects and history-dependent metastability effects similar to those seen in random-field magnets. We are able to study the dynamics directly and we observe nonexponential dynamic correlations which scale as a function of $(\ln t)/\ln \tau_A$, which have characteristic relaxation times $\tau_A$, which increase very rapidly, and which become increasingly activated on short length scales and upon approaching $T_{\mathrm{rf}}$. This observed coincidence of metastability effects and activated dynamics supports recent theory[6,7,10] for the novel ordering dynamics of random-field systems.

It is a pleasure to thank F. S. Bates, R. J. Birgeneau, S. N. Coppersmith, D. S. Fisher, M. E. Fisher, C. Frank, P. C. Hohenberg, R. B. Meyer, J. Patel, and especially D. A. Huse for useful and stimulating discussions.

*Note added.*— Goh, Goldburg, and Knobler[22] recently reported *static* light-scattering measurements on the binary mixture $n$-$C_6H_{14}$+$n$-$C_6F_{14}$ in porous glass of 45-nm pore diameter. After receiving a preprint of our work, Goldburg[23] was able to confirm the observability of *dynamic* composition fluctuations.

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[1] Y. Tang, P. D. Beale, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. **56**, 480 (1986).

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

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

[4] J. V. Maher, W. I. Goldburg, D. W. Pohl, and M. Lanz, Phys. Rev. Lett. **53**, 60 (1984).

[5] R. Lipowsky and M. E. Fisher, Phys. Rev. Lett. **56**, 472 (1986).

[6] J. Villain, J. Phys. (Paris) **46**, 1843 (1985).

[7] D. S. Fisher, Phys. Rev. Lett. **56**, 416 (1986), and to be published.

[8] A. R. King, J. A. Mydosh, and V. Jaccarino, Phys. Rev. Lett. **56**, 2525 (1986); R. J. Birgeneau, R. A. Cowley, G. Shirane, and H. Yoshizawa, Phys. Rev. Lett. **54**, 2147 (1985).

[9] A. T. Ogielski and D. A. Huse, Phys. Rev. Lett. **56**, 1298 (1986).

[10] D. A. Huse, private communication, and to be published.

[11] E. Gulari, A. F. Collings, R. L. Schmidt, and C. J. Pings, J. Chem. Phys. **56**, 6169 (1972).

[12] Vycor brand 7930 glass from Corning Glass Works, Corning, NY.

[13] P. W. Wiltzius, F. S. Bates, S. B. Dierker, and G. D. Wignall, to be published.

[14] S. B. Dierker, P. W. Wiltzius, and B. S. Dennis, to be published.

[15] B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).

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

[17] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).

[18] $\eta$ is taken to be the temperature-dependent shear viscosity of the pure bulk mixture as reported in Ref. 11. For temperatures above the bulk mixture's $T_c$, we extrapolated the expression given in Ref. 11 which fitted $\eta$ below $T_c$.

[19] M. Calvo and R. Ferrell, Phys. Rev. A **31**, 2570 (1985); M. Calvo, Phys. Rev. A **31**, 2588 (1985).

[20] M. E. Fisher and H. Nakanishi, J. Chem. Phys. **75**, 5857 (1981); H. Nakanishi and M. E. Fisher, J. Chem. Phys. **78**, 3279 (1983).

[21] D. W. Pohl and W. I. Goldburg, Phys. Rev. Lett. **48**, 1111 (1982).

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

[23] W. Goldburg, private communication.