Phase Separation of a Binary Liquid Mixture in a Porous Medium

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The phase separation of a binary liquid mixture contained in a rigid porous medium has been investigated by study of the light scattered at 90° from a porous glass rod containing a critical mixture of n-C_6H_{14}+n-C_6F_{14}. Evidence is found for phase separation at a temperature markedly below the critical temperature of the bulk mixture. Temporal concentration fluctuations in the rod are not observed. The separated phases remain metastable at temperatures well above the bulk critical temperature. These phenomena are in part consistent with a description in terms of a random field.

In this paper we are concerned with the dynamics of phase separation of a critical binary liquid mixture contained within the interconnected domains of a porous medium. One of the two phases preferentially wets the medium. If the pores are large, one might expect the wetting to have little effect on critical behavior, and the mixture will separate as in the absence of the medium. On the other hand, if the pores are smaller than ξ, the thermal correlation length in the bulk liquid, the transition may be modified or perhaps suppressed.

If the wetting forces are not so strong as to destroy long-range order, the transition may change from continuous to first order, or its singular behavior may be modified. In the latter case one expects to encounter random-field behavior, a phenomenon that has been intensively studied in recent years.[1-3] For mixtures in porous media the analog of the random magnetic field is a random contribution to the chemical potential, whose source is the preference of the surface of the medium for one component over the other.[4] We may view this preference as wetting on a local scale.[5]

In our experiments we have measured the scattering of light from a critical mixture of hexane, n-C_6H_{14}, with perfluorohexane, n-C_6F_{14}, suffused through porous glass with a nominal pore size $d = 45$ nm. The bulk fluid mixture has a critical temperature[6] of 21.5 °C at a critical mole fraction of perfluorocarbon of 0.36. There is a large difference in density between the two components, and so phase separation in the bulk is very rapid. If the separated phases are heated above the critical temperature, they will mix only very slowly unless subjected to vigorous stirring. Contrary to our expectations, the porous medium strongly affects the dynamics of phase separation, even though the equilibrium correlation length is presumably much less than d. The most obvious effect of the medium was to induce strong history-dependent effects. The mixture exhibits metastability with characteristic relaxation times that vary from a fraction of an hour to a day. It is doubtful, in fact, that any of the measurements to be described were on fluid states of true thermal equilibrium.

Metastability is known to be a feature of domain growth in random-field magnetic systems,[1] and one would not be surprised to see it in wetting phenomena as well. We do not know whether the experiments reported here are best described in the framework of a wetting theory[7] or a random-field theory. While a binary mixture in a porous medium differs from a random-field Ising magnet in that the order parameter is conserved, metastability will surely survive in a random-field model with a conserved order parameter.

The sodium borosilicate glass was prepared by Kadokura,[8] who determined the pore size from measurements of specific pore volume and surface area. The glass was in the form of rods 2 mm in diameter and 1 cm in length. Samples were prepared by sealing the fluid mixture and a rod into 1-cm spectrophotometer cells. The rod fitted snugly into a cylindrical hole in a Teflon block, which was used to position in it the cell. A sector of the block was cut away, thereby allowing the surrounding mixture to come into contact with 20% of the rod's surface area. A small hole in the block at right angles to the rod allowed light scattered at 90° to be directed to a photomultiplier. The cells were placed in a large well-thermostatted water bath whose temperature was monitored with a quartz thermometer. Two samples were prepared: In one the rod was surrounded by the lower (fluorocarbon-rich) phase when two bulk liquid phases were present in the cell; in the other the rod was in the upper phase.

At each end of the rod the unscattered beam I_f traversed a thin layer of the bulk mixture. Strong opalescence in these two layers of fluid produced a sharp dip in I_f as the critical temperature T_c of the bulk mixture was crossed on cooling. We recorded S, the scattered intensity at 90°, and I_f. Only qualitative information about the turbidity could be determined because the beam emerging from the rod in the forward direction was not well defined.

The phenomena that are observed when the rod and the surrounding fluid are cooled from a temperature above T_c into the two-phase region are typified by Fig. 1 (curve A), which shows S as a function of T. In this run, in which the rod was in the lower portion of the
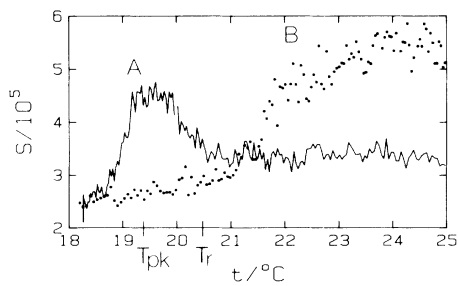

FIG. 1. Intensity (in arbitrary units) of light scattered at 90° from the glass rod as a function of the temperature. Curve A, Cooling at -22 mK min^{-1}; curve B, heating at 37 mK min^{-1}.

fluid, $dT/dt = -22$ mK min^{-1}. The cell had been kept at the initial temperature, 29.5 °C, for 10 h; the sample had then been thoroughly shaken and then allowed to stand for an additional 3 h prior to cooling, so that the rod was initially surrounded by a single homogeneous phase. These times should be compared with the time required for the surrounding mixture to come into compositional equilibrium with the mixture in the glass pores. This time is strongly temperature dependent near the critical point, but several degrees from T_c, it is estimated to be of the order of an hour for our 2-mm-diam rod.

When T_c was crossed, the mixture surrounding the rod separated into two sharply defined phases in only a few minutes, whereas the duration of a run was many hours. From this point on in the experiment the rod was surrounded by the lower bulk phase. The scattering from the rod was unaffected by the bulk transition but started to increase at a temperature T_r, which lies about 1 K below T_c, and reached a maximum at T_{pk}, which is 2.2 K below T_c. At T_r the bulk fluid scattering was very small. Note that the origin of the ordinate in Fig. 1 is not zero—a background scattering exists that is presumably from the glass itself. Although the pore size is much smaller than the wavelength of the laser light ($\lambda = 633$ nm), the empty glass scatters light significantly, giving the rod a bluish cast. The noise in the scattering is an optical coherence effect produced by small motions of the rod and is of no physical interest. The vertical markers in Fig. 1 identify the two characteristic temperatures T_c and T_{pk}.

If the fluid in the rod behaved like that in the bulk, one would observe critical fluctuations, which relax diffusively. Using photon-correlation spectroscopy, we searched for such fluctuations between T_c and T_{pk}, but none were found down to correlation times as short as a few tenths of a microsecond. In this respect the scattering behaves like that from binary mixtures suffused through polyacrylamide and agarose gels.[9]

The initial rise in S on cooling always occurs about 1 K below T_c, independent of the cooling rate. On the other hand, the magnitude of the maximum in S and the temperature at which it occurs are very sensitive to dT/dt. For example, if dT/dt is changed from -22 to -44 mK min^{-1}, $T_c - T_{pk}$ increases from 2.2 to 2.8 K and there is a fivefold increase in the peak height. If dT/dt is decreased to -5 mK min^{-1} the peak disappears. In the opposite limit of a rapid and deep quench below T_c there is an immediate increase in both the turbidity and scattering, with a relaxation time of the order of hours.[10]

To probe the behavior of the peak further, a measurement was performed in which the temperature scan was halted at T_{pk} and S and I_f were measured as functions of time. The scattering decreases in a time of the order of 20 min, while I_f decreases slightly with the same characteristic time. Thus the phenomenon of the peak in S is entirely a transient one. The only way by which we can explain the simultaneous decrease in both S and I_f is to assume that (growing) domains are scattering increasingly in the forward direction during this 20-min interval.

It might be argued that the peak in S is associated with the bulk critical point that has been displaced in temperature simply because the temperature of the rod lags behind that of the surrounding fluid. Separate experiments in which the laser beam passed only through the fluid established, however, that the phase separation occurs at the same temperature even when dT/dt is greatly increased. Convection presumably establishes a uniform temperature throughout the bulk in a very short time and the characteristic time for thermal diffusion through the rod is likewise short, of the order of 1 min.

An explanation that is more consistent with the experiments is that the intensity maximum is associated with a first-order phase transition in the fluid in the pores.[11] The increase in the scattering begins when the phase boundary is crossed and represents the appearance of domains of phase-separating fluid that have grown to a size of the order of the reciprocal of the scattering amplitude, $k^{-1} = 50$ nm. Support for this picture is provided by experiments in which successive rapid quenches were made with the rod in the lower phase. In the first quench (left-hand trace in Fig. 2) the system was rapidly cooled to 20.5 °C, which is just above T_r, and no significant enhancement was observed in S. Further quenches below T_{pk}, however, produce a transient peak in S and the size of the peak increases with the quench depth. This behavior is analogous to temperature jumps below the critical temperature in bulk binary mixtures,[12] each jump producing a shower of small droplets of a new phase, which then grow.

Because of the sample geometry, we were unable to measure the scattering at angles other than 90°. Thus we are unable to determine directly whether the decrease in the peak with time is caused by the growth of droplets to sizes greater than the average pore size (which would lead to a shift in the scattering maximum to smaller angle) or by a decrease in the droplet density.
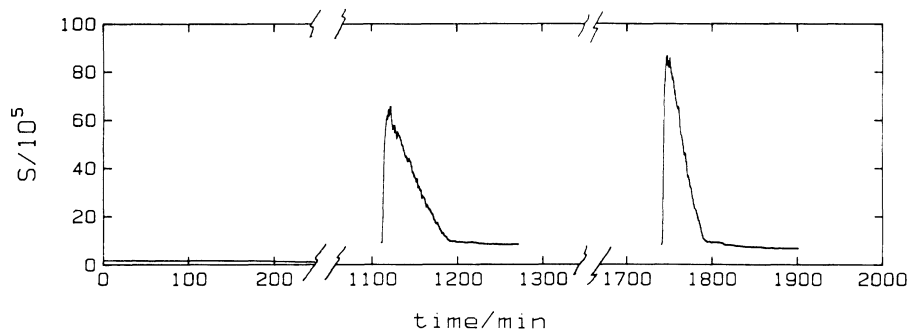
FIG. 2.   Intensity (in arbitrary units) of light scattered at 90° as a function of the time during successive temperature quenches. AT $t = 0$ the system was rapidly quenched from $T = T_c + 1.7$ K to $T = T_c - 1$ K, which lies above T_{pk}. The first steep rise in scattering accompanied a further rapid cooling to $T = T_c - 3$ K and the second peak is associated with a further quench to $T = T_c - 5.2$ K. T_{pk} and T_r are indicated on the abscissa.

Experiments in which the rod is cooled in the vapor phase strongly suggest that the latter hypothesis is correct. With the rod immersed in the fluid above T_c, the cell was vigorously shaken and then allowed to stand for several hours. The cell was then inverted, which left the rod in the vapor phase, and then cooled under the same conditions that produced a peak before. Here again S begins to rise at T_r but now it saturates rather than falling. The time at which the scattering relaxes in this case was determined by successive rapid quench measurements, which produce sharp increases in the scattering that decay with a characteristic time of approximately 3 h, about an order of magnitude longer than observed for quenches with the rod immersed in the fluid phases. The rate of growth of droplets within the rod should be little affected by the surrounding medium; the marked slowing down is therefore consistent with a decrease in the droplet density by diffusion to the surrounding bulk material.

Further evidence for the absence of droplet growth beyond the pore size is found in the measurements of I_f. The turbidity falls as S decreases—the scattering has therefore diminished and has not simply been displaced to smaller angle. Examination of the rod with a 20× microscope has also failed to reveal droplets.

While the behavior on cooling is the same when the rod is in either the upper or lower phase, the phenomena observed on heating are different. As shown in Fig. 1 (curve B), when the rod is heated at a moderate rate in the lower phase from several degrees below T_c to many degrees above, the scattering increases monotonically. (The surrounding fluid is not stirred during the heating and so its composition remains essentially constant.) If the rod is then held at the high temperature, the excess scattering takes tens of hours to relax. (Because of the large difference in density, there is little mixing of the two bulk phases on this time scale.) In contrast, when the rod is heated in the upper phase, the scattering remains unchanged.

The behavior during a heating run from 3.5 K below

T_c to 9.8 K above is shown in Fig. 1. The rod had remained in the lower phase at the initial temperature for 5 d and the heating rate was 37 mK min^{-1}. Note that S starts to level off at about T_c but nevertheless continues to rise. (If the same experiment is carried out in the absence of the rod, i.e., in the bulk mixture surrounding the rod, S remains essentially constant because without stirring the phase-separated mixture does not return to a single homogeneous phase in an interval shorter than several weeks.) If the rod is now kept at the highest temperature, S ultimately decreases to the background value with a relaxation time of about 15 h. This is 2 orders of magnitude longer than the composition diffusion time through a distance equal to the rod diameter.

The increase in S on heating is not observed when the rod is in the upper phase or the vapor phase. We do not have a clear understanding of this phenomenon, but the asymmetry in behavior suggests that wetting must play a role.[7] We have established that the upper (hydrocarbon-rich) phase wets glass and quartz; hence when the rod is in the lower phase, domains of the upper phase may remain in the pores at equilibrium. The upper phase also wets glass in preference to the vapor so that a wetting layer must also be present at the start of heating runs in the vapor phase. In experiments in which the rod is equilibrated with the lower phase at low temperature and the cell is then inverted to bring it into the vapor phase, no enhancement in the scattering is seen.

Several features of the phenomena that we have observed are consistent with a random-field model.[13] The phase separation is displaced to lower temperatures, the temporal concentration fluctuations are quenched, and there is a long-lived metastable state at temperatures above T_c. On the other hand, the random-field model would seem applicable only if ξ in the mixture is large compared with the pore size, and this condition is satisfied in the present experiments only at temperatures very close to T_c. A lowering of the critical temperature could be associated with capillary condensation,[14] but that effect would not explain the lack of fluctuations or

the extreme slowing down.

A question left unanswered by this experiment is whether the transition observed here would be second order (as in a random-field Ising magnet) if mixture in the porous medium were of critical composition and if the quench were sufficiently shallow. The metastability observed on cooling, and even on heating, has blocked our pursuit of this issue. Perhaps specific-heat or latent-heat measurements would be illuminating here.

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Note added.— After this work was completed and this Letter was submitted, we received a preprint by S. B. Dierker and P. Wiltzius in which related measurements were reported on the binary mixture 2,6-lutidine and water contained in Vycor of 3 nm pore diameter.

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[10]An effort to observe such critical scattering in Vycor, which has a pore size of 5 nm, yielded a null result for this mixture and also for a critical mixture of 2,6-lutidine and water. Presumably the composition fluctuations were suppressed at suboptical scales in the smaller pores, even though the liquids are readily absorbed into the glass.

[11]It is conceivable that the critical composition of the fluid in the pores is not the same as that in the bulk; the formation of a wetting layer may also shift the composition within the pores away from the bulk composition. Thus, we are unable to say anything about the order of the transition at the critical composition.

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