

## Critical Behavior in Gels Saturated with Binary Liquid Mixtures

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Polyacrylamide, agarose, and silica gels have been prepared with solvents which are near-critical binary liquid mixtures. Near the critical temperature of the free liquid mixtures, the binary-liquid gel exhibits a broad region wherein light-scattering intensity is large and varies monotonically with temperature. Some features of this scattering suggest that the gel matrix acts like a random field. Only very weak temporal fluctuations are observed throughout this broad transition region.

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A variety of novel effects might be expected in a gel whose solvent is a critical binary liquid mixture, principally because the gel pore size is small enough to affect strongly the hydrodynamics of phase separation and because the polymer strands should interact differently with the constituents of the liquid mixture. At a minimum the presence of the porous medium should slow down the gravitationally induced late stages of spinodal decomposition.<sup>1</sup> Considerably more dramatic effects would be expected if, as is normally assumed, the gel polymer altered the local chemical potential and thus took an active role in the phase separation process.<sup>2</sup> In this paper we report observations on critical behavior and (frustrated) phase separation in the imprisoned solvents of binary-liquid gels.

The gels exhibit a complex of temperature-, concentration-, and time-dependent phenomena which are dramatically different from the behavior of the free liquid mixture and which are not easily understood without treating the gel as an active, but not too strongly interacting participant in the process. Our principal findings are as follows: (a) very strong light scattering begins immediately after quenching the gel into the two-phase region of the corresponding fluid mixture; (b) this scattering does not cease for hundreds of hours; (c) the onset temperature for critical opalescence has a concentration dependence which is similar to the coexistence curve of the free liquid mixture; (d) the region of equilibrium opalescence is broadened over several kelvin; (e) diffusively relaxing composition fluctuations are almost completely suppressed; and (f) for part of the temperature range, the angular distribution of light scattering departs measurably from the pure Lorentzian seen in free liquid mixtures. Some of the observed features resemble

those of a random-field system.<sup>3,4</sup>

We have made binary-liquid gels with both reversibly and permanently crosslinked gel matrices, viz. agarose (AR), 1 wt%, and polyacrylamide (PAA), 7 wt%. The well-studied mixtures isobutyric acid plus water (IBW)<sup>5</sup> and 2,6-lutidine plus water (LW)<sup>6</sup> were used as solvents. Qualitatively similar results also were obtained with silica gel and mixtures of polypropylene glycol plus water. The gels were prepared either by diffusing the organic liquid into a preexisting water gel from a supernatant liquid-mixture layer or by adding the organic component before gelation of the water gel was complete. The latter method worked only with AR at lutidine or IB concentrations below the critical concentration. In PAA/LW, considerable shrinkage was observed at and above the critical lutidine concentration. This large shrinkage was not seen in the AR systems. In PAA/IBW the shrinkage was much smaller at low IB concentrations, less than 10% by volume at the critical concentration (60% water). Typical cylindrical samples had 7 mm radius and 30 mm height. The samples reached equilibrium in about two weeks; i.e., after two weeks their shrinkage was complete, their light scattering was independent of position in the gel, and measurements made with two-week-old samples could be reproduced six months later.

Figure 1 shows the temperatures and concentrations at which certain (subjectively determined) degrees of opalescence appeared in AR/LW and AR/IBW (1, barely visible; 2, strong; 3, opaque). The curves are very close to the simultaneously determined coexistence curves of the fluid mixtures, leaving no doubt that the opalescence indeed is caused by the solvent. There is a slight shift to higher concentrations in both cases. The concen-

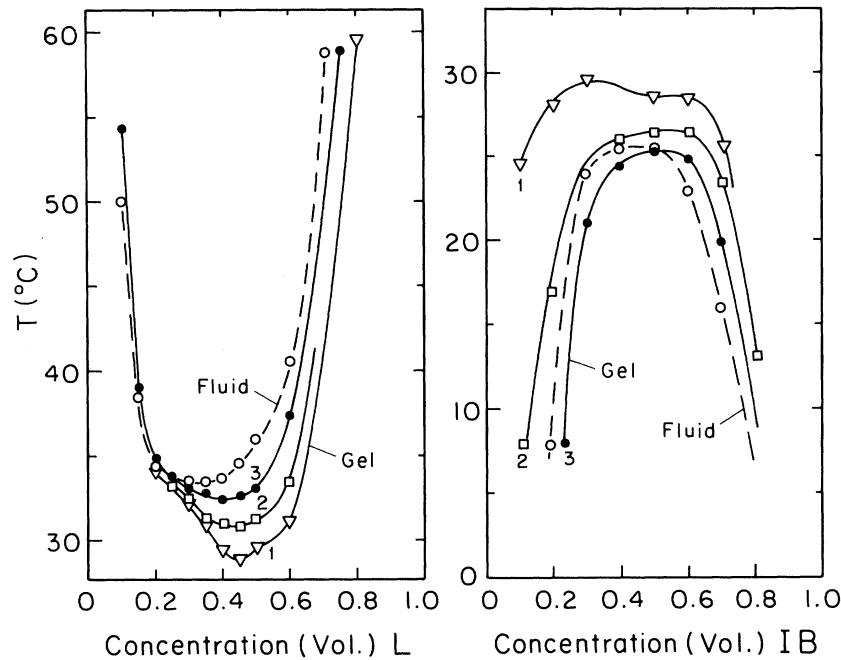


FIG. 1. "Coexistence" curves for AR/LW (left) and AR/IBW (right) and of the respective fluid mixtures.

trations in Fig. 1 are averages for the supernatant fluid plus gel for samples prepared by the first method. Samples prepared by the second method yielded almost the same results, indicating that the distribution of concentration between fluid and gel phases, at least in AR/LW, is close to equal. The temperatures at which the samples reach a certain degree of opalescence were found to fluctuate erratically by about 2 K from week to week. However, the light-scattering information presented below is quite reproducible once the measurements are referred to the onset temperature measured the same day.

With 6328-Å laser illumination, two striking temporal features of light scattering were observed. First, at small angles we observed no twinkling of the sort normally<sup>7</sup> seen in critically opalescent systems. In fact, no short-time correlation could be found in the scattering spectrum of AR gels, indicating that the underlying strong fluctuations must be heavily frustrated and (quasi) static. Near-critical PAA/IBW gels did show two short correlation times of  $10^{-4}$  and  $10^{-3}$  sec which are close to that reported by Tanaka, Hocker, and Benedek<sup>8</sup> for PAA/water gel, and to that exhibited by the free critical IBW mixture,<sup>5</sup> respectively. However, the amplitudes of these contributions are extremely small compared to that of the corresponding static scattering.

The second peculiar light-scattering feature is a

characteristic fluctuation time of the order of 1 h. With the detector limited to one or two coherence areas, the peak-to-valley ratio for these strong, slow intensity variations exceeds 10. We found the same type of fluctuations to be present in pure water/PAA gels, where the scattering is extremely weak, and in the considerably enhanced scattering from a water/PAA gel doped with 0.4- $\mu$ m polystyrene beads. It thus appears that these are fluctuations of the gel matrix, with the liquid mixture merely serving to amplify the scattering intensity. This effect thus may be useful for the study of gel matrix dynamics since the ability to amplify the signal by changing temperature eliminates the possibility that the fluctuations are merely due to scattering from dust.

The temperature dependence of the scattering intensity (averaged over many coherence areas) is shown in Fig. 2 for a near-critical PAA/IBW sample. In making these measurements we have attributed all scattering intensity at 40°C to uninteresting background processes and have subtracted this background from all intensities measured at lower temperatures; the correction is small except at the smallest angles of Figs. 2 and 3. At small angles (top curve of Fig. 2) a gradual increase over a large range of temperature decrease (32° to 22°C) is seen. At large angles (lower curves) the scattered intensity begins to increase at much lower temperatures, say 24°C, but rises very fast upon further

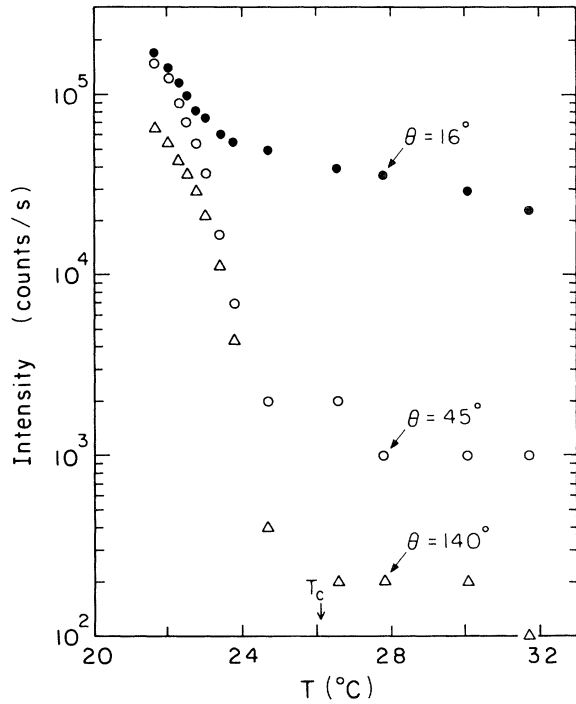


FIG. 2. Light-scattering intensity as a function of temperature for three different angles; PAA/IBW. The arrow at 26.1°C indicates the critical temperature of the free liquid mixture.

cooling. Below 21.5°C the scattering continues to increase, eventually saturating at ~18°C, but multiple scattering is so clearly a problem that we have not presented the measurements. This spreading of the region of strong critical scattering over ~5 K is very different from the behavior of the free liquids whose indices of refraction are closely enough matched to confine the strong critical scattering within a few tens of millikelvin on either side of  $T_c = 26.1^\circ\text{C}$ .

The gel scattering characteristics result in a dramatic change of the angular distribution at various temperatures as can be seen in Fig. 3. The parameter TF associated with each curve is a measure of turbidity (and hence the degree of multiple scattering) at the different temperatures; it denotes the fraction of incident light transmitted by the 14-mm-thick sample. Above 24°C, the experimental data show a power-law dependence of scattered intensity  $\mathcal{I}$  versus wave number, with the data well fitted with  $\mathcal{I}$  proportional to  $q^{-2.5}$ . Below 24°C the plots are bell shaped and can be fitted equally well with linear or squared Lorentzian functions. The limited available range of  $q$  values prevents us from distinguishing between these two interesting possibilities, although there is a slight preference for

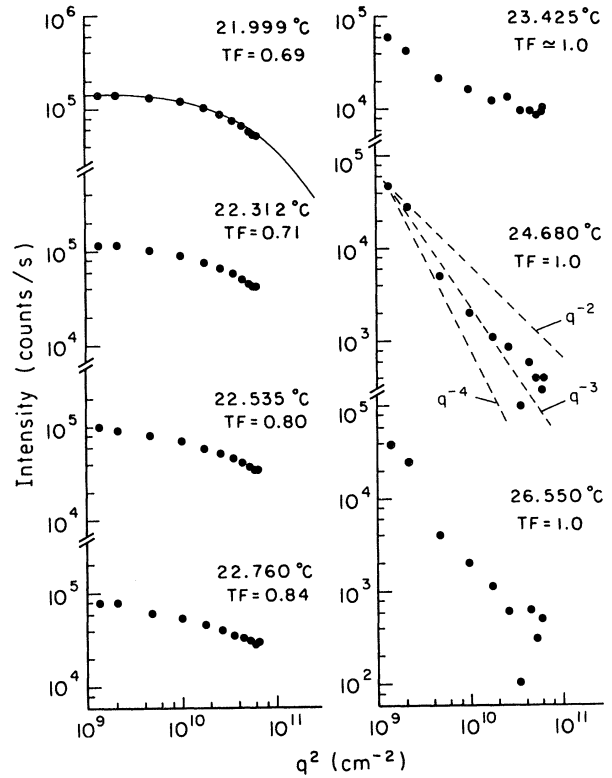


FIG. 3. Light-scattering intensity as a function of scattering angle for various temperatures; PAA/IBW.

Lorentzian-squared function in some of the fits. As seen from Fig. 3, the half-width of the Lorentzian functions is of the order of  $10^5 \text{ cm}^{-1}$ .

While we presently have no complete explanation for the phenomena described above, we can usefully comment on some theoretical approaches. Since the light-scattering intensity is a function of temperature but not of time (at least over several days), it seems clear that the gel matrix prevents phase-separated regions from growing to length scales large compared to the wavelength of visible light. We discuss four possible roles which the gel-solvent interaction might play, only the last of which (that of a random field) is consistent with our findings and with existing models for gel structure: (a) The gel could merely offer passive steric blocking to droplet growth. However, this would leave unexplained the observed broadening of the transition. (b) The gel might be a fully participating component in a mixture, which should properly be viewed as a ternary system. However, were all three of these components to be in full equilibrium with each other, broadening of the transition would be unexpected.<sup>9</sup> (c) The gel matrix might act on

the binary mixture like an external field with nonzero average over macroscopic lengths. Such a field would tend to broaden the transition by taking the system away from the critical point<sup>7</sup> (although this asymmetric system would eventually reach its coexistence curve on lowering  $T$  and experience a first-order transition). If, however, this average field (or chemical potential) were so large as to give the broadening we observe, it should also dramatically reduce the scattering intensity in the one-phase region. In this case strong scattering should only appear when the system abruptly experiences the first-order phase transition. In contrast, the very strong scattering we observe changes steadily with temperature as the transition is approached, suggesting that the system will pass rather close to its critical point. (d) The gel imposes a random field whose average value is zero. This random field should broaden the transition,<sup>3,4</sup> reduce the amplitude of the temporal fluctuations, and if strong enough, destroy the transition.<sup>10</sup> (We are assuming that the lower critical dimension is two rather than three.) Our detailed observations in PAA/IBW are consistent with all of these effects.

In summary, when a binary liquid mixture is imprisoned in a gel matrix, the liquid's phase transition is dramatically broadened in temperature, and the average scattering intensity remains large, despite a strong suppression of temporal fluctuations. Qualitatively these effects are consistent with a random-field behavior. Further, the strong scattering due to the attempted phase separation provides an amplification of slow effects from gel-

matrix processes, and this may eventually allow otherwise inaccessible gel phenomena to be studied.

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