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Dynamic light scattering from binary-liquid gels

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Dynamic light scattering is observed for an entanglement gel, gellan gum, whose solvent is a critical mixture of isobutyric acid and water. We observe a length scale l_x below which the sample shows two correlation times and above which only one (diffusive) correlation time is seen. This length scale grows as a power law as $T \rightarrow T_c$. Several observed features of this system, including critical exponents for dynamic and static light scattering, are inconsistent with available model estimates.

Several recent investigations have suggested the possibility that random-field theory may apply to binary liquids which are trapped inside gels or porous media like Vycor glasses.[1-5] In this approach, the glass or polymer imposes a random chemical potential on the liquid mixture, and, for the theory to be applicable,[1] the pore size of the gel or glass must be smaller than the correlation length of the liquid mixture. Experiments with both gels[2,3] and Vycor[4,5] show unusual effects, some of which fit in with the random-field picture and some of which appear not to fit in. The gels are somewhat more surprising sources of fields than Vycor since the polymer networks might be expected to have too much freedom to relax to be treated as temporally static, and it is only the experimental observation that the gels do not shrink on time scales of months after temperature changes which leads one to treat the networks as imposing an external field rather than acting as a full participant in a ternary mixture. It would be desirable to have modified random-field theories with some provision for partial local annealing of disorder (as must almost certainly occur in a gel) and for weak spatial correlations in the imposed field, but at present the only available theoretical predictions are from models of quenched random disorder so the quantitative comparisons presented below will be restricted to such oversimplified models.

The gel and Vycor systems complement each other in their shortcomings. The Vycor structure is more clearly rigid but should not be truly random in its spatial distribution (since it is a product of spinodal decomposition) and excludes the liquid mixture from a very large fraction of the sample volume (while the gel and magnetic systems involve, respectively, little and no steric blocking). In any case, both the gel and the Vycor provide interesting examples of disordered chemical systems whose relation to each other, to disordered magnetic systems, and to available theories for disordered materials should be explored.

Dierker and Wiltzius (DW) have recently reported[4] observing a systematic trend in dynamic light scattering from 7930 Vycor whose pores (pore size ~30 Å) were filled with a critical mixture of 2,6 lutidine and water, a mixture which has an inverted coexistence curve. As the temperature of the system was raised toward the critical point (which was shifted from 34 to ~60 °C by the applied field), the autocorrelation function gradually crossed over from the single exponential characteristic of a purely diffusive process to a more complicated form which combined two terms, a diffusive exponential and a second term which, they argue, scales with $\ln(t)/\ln(\tau)$ rather than t/τ. Ogielski and Huse[6] have argued that the second term results from activated processes such as those discussed by Villain[7] and Fisher[8] as trapping random-field systems in long-lived metastable states. Huse[9] discusses the dynamics in terms of a length scale l_x below which diffusion is fast and the activated process provides the limiting time. On scales longer than l_x, diffusion is expected to provide the limiting time scale. As temperature approaches T_c, l_x should grow, according to Huse, as

$$l_x \sim \exp(c\xi^{\psi}) \sim \exp(C\epsilon^{-\nu\psi}) \;, \tag{1}$$

where $\epsilon = (T - T_c)/T_c$ and the exponent $\psi \simeq 1.5$. DW did not observe the progress of this length scale with temperature.

In this paper, we report the results of dynamic light scattering measurements on the entanglement gel, gellan gum, whose solvent is a critical mixture of isobutyric acid and water (IBW). IBW has a normal coexistence curve (upper critical point at $T_c = 26.4$ °C). Static light scattering measurements[3] have shown this system to have a region of strong opalescence which sets in at roughly 28 °C and grows stronger as the temperature is reduced to 26 °C, below which point multiple-scattering effects prevented further measurements. Above 30 °C the scattering is very weak and appears to be dominated by scattering from the polymer network. In the region between 28 and 26 °C, the static light scattering exhibits a Lorentzian-squared shape and increases dramatically in intensity. If one extracts a renormalized critical exponent for the susceptibility, the result is $\tilde{\gamma} > 3.2$ with $T_c < 25.3$ °C. During the year since the static measurements[3] were made on this critical IBW-gellan gum sample, the sample has shrunk from a swelling (total gel mass/polymer mass) of 105 to a value of 90 with a concommitant increase in the light scattering from the polymer. However, the scattering at temperatures above 30 °C remains weak and the opalescence reported earlier for the region below 30 °C still dominates the scattering in that temperature range. In this paper, we restrict our discussion to the region below 30 °C.

Our measurements were made by scattering 632.8 nm light from a He-Ne laser from the sample whose temperature fluctuations were controlled to be less than 1 mK. At the higher temperatures (near 30 °C), autocorrelation functions at all scattering angles exhibited only one correlation time, T_1, and could be well reproduced by fitting with the form

$$g_2(t)=\langle n\rangle^2[1+f(A)e^{-2t/T_1}]\ . \qquad (2)$$

A typical example is shown in Fig. 1(a). As the temperature was reduced, the autocorrelations for the larger wave numbers (angles) began to deviate from this form and to need a second characteristic time. As temperature was further reduced, a second correlation time was needed at successively smaller wave numbers until all observed wave numbers showed this feature. Figure 1(a) shows an autocorrelation function of this kind. Where more than one correlation time is needed we have fitted the data with the form

$$g_2(t)=\langle n\rangle^2\{1+f(A)[(1-R)e^{-t/T_1}+Re^{-t/T_2}]^2\}\ . \qquad (3)$$

Using this form, the larger correlation time T_2 is, in general, established with much less certainty than is T_1. The autocorrelations of DW spanned 500 sample intervals, far larger than the 80 intervals shown in Fig. 1. We have measured several 360 interval autocorrelation functions, but even with these extra intervals we do not see features which require a power law for the second process rather than an exponential decay. Our data can be equally well fitted by using a power law with no qualitative change in the results reported below. DW do not show how difficult it would be to fit their data with the form of Eq. (3).

T_1 is presumably diffusive and related to the critical behavior of the free liquid mixture. We find in general that the inverse of T_1 does indeed increase as q^2, allowing the extraction of a diffusion constant. A typical case is shown in Fig. 1(c). We have not observed T_2 to vary with q in any systematic way. It is in most cases roughly constant as q is varied at a given temperature. Thus, it does not appear to arise from a diffusive process and is consistent with the possibility that the second process is activated. A typical example is shown in Fig. 1(d). DW found that their second correlation time varied as q^2. We do not see any reason to expect a q^2 dependence for an activated process such as they believe theirs to be.

We cannot confidently extract critical exponents from our data because we do not know T_c. And we cannot confidently establish T_c from any one feature of our static or dynamic light scattering because essentially all critical exponents can be expected to be renormalized in the presence of a random field,[6-8] or from whatever more sophisticated model of disorder may eventually be found to apply. Since random-field theory is the closest available theory, it is of interest to compare our results with its predictions. If one assumes that random-field theory should apply to gellan gum[10] and that the static light scattering intensities reported in Ref. 3 establish a reasonable upper limit on T_c at 25.3 °C, then we can put limits on some exponents on the basis of the present measurements. Figure 2(a) shows the diffusion constant (extracted from T_1^{-1}) vs $T-T_c$ for $T_c=25.3$ °C. Here there is surprisingly little scatter in the data when one considers how small a fraction of the total light scattering intensity the fluctuating signal repre-

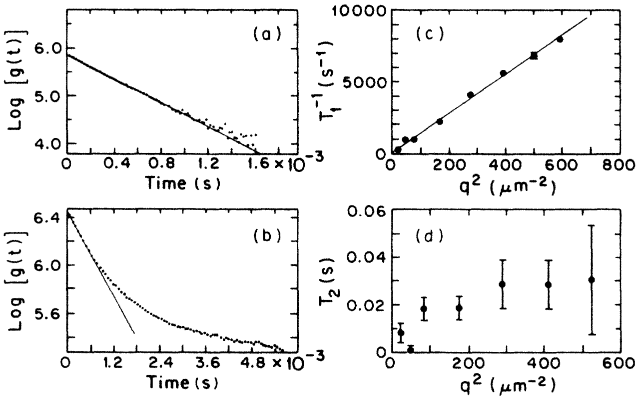

FIG. 1. Autocorrelation functions at 50° angle for (a) $T=30.2$ °C and (b) $T=26.28$ °C; (c) T_1^{-1} vs q^2 at 31.32 °C; (d) T_2 vs q^2 at 26.61 °C.

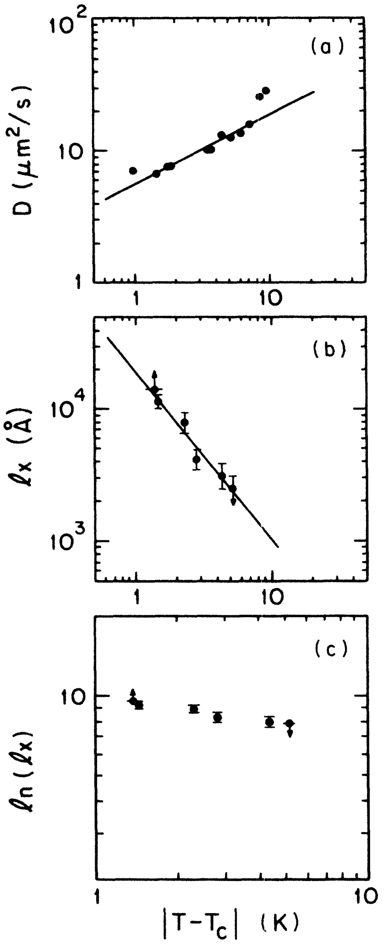

FIG. 2. (a) Diffusion constant D vs $|T-T_c|$. With the normal liquid viscosity this corresponds to length scales ranging from 40 to 120 Å; (b) l_x vs $|T-T_c|$; and (c) $\ln(l_x)$ vs $|T-T_c|$. $T_c=25.3$ °C is used for all data.

sents. The straight line shown in the figure has slope $\tilde{\nu}=0.52$, slightly less than the free-liquid value of 0.63 and even farther from the random-field value of 1.0.

Since the static and dynamic light scattering measure two independent critical exponents ($\tilde{\gamma}$ and $\tilde{\nu}$, respectively), it is interesting that these cannot simultaneously be brought into agreement with either the free-liquid Ising-model exponents or those of the random-field theory for any assumed value of T_c. At $T_c=25.3\,^{\circ}\mathrm{C}$, $\tilde{\gamma}=3$ in rough agreement with random-field calculations and much larger than the Ising-model value of 1.26. Decreasing the assumed value of T_c increases both exponents, driving $\tilde{\gamma}$ to very large values as $\tilde{\nu}$ becomes more reasonable, e.g., if $T_c=20\,^{\circ}\mathrm{C}$, $\tilde{\nu}=1.2$, and $\tilde{\gamma}=13$. As was originally the case for the development of understanding of critical phenomena in simpler systems, we cannot know whether or not these measurements are within the scaling regime.

Figures 2(b) and 2(c) present the most striking single result of this experiment, the dependence on $|T-T_c|$ of $l_x=2\pi/q_x$. q_x has been extracted directly from observing the angle at which the autocorrelation function crosses over from showing one to more than one correlation time. As such, it and its temperature dependence are insensitive to the details of the parametrizations of Eqs. (2) and (3). The uncertainties in our measurements of l_x come strictly from the sizes of the angular steps between our autocorrelation measurements. In Fig. 2(b), we plot l_k vs $|T-T_c|$ for $T_c=25.3\,^{\circ}\mathrm{C}$. This gives $l_x \sim |T-T_c|^{1.3}$. The exponent increases if we lower T_c.

Huse argues[9] that $l_x \sim \exp(c\xi^{\psi}) = \exp(C\epsilon^{-\nu\psi})$. Figure 2(c) presents our data in a form suitable for comparison with Huse's prediction. We find $\psi \sim 0.35$ over a very wide range of assumed values of T_c (i.e., the product $\tilde{\nu}\psi$ varies with T_c in just the same way as does the independently measured $\tilde{\nu}$). This is much smaller than Fisher's calculation[8] which says $\psi=1.5$.

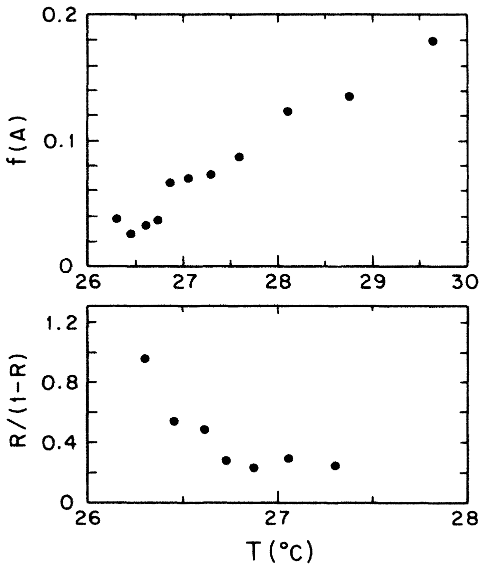

FIG. 3. Top: $f(A)$ from correlation functions taken at 100° angle vs temperature. Bottom: Angle-averaged ratio of R and $(1-R)$ vs temperature.

Figure 3 allows one to assess the relative importance of the various processes involved in light scattering from this gel. In the upper half of the figure, $f(A)$ from Eq. (3) is shown as a function of temperature. In the absence of static background scattering and under the assumption that all fluctuations arise from Gaussian random processes, this should be a purely geometry-dependent quantity[11] which we have measured to be 0.25 for our apparatus by using a pure critical mixture of IBW. The strong dc component of the scattering discussed in Ref. 3 drastically reduces $f(A)$ as the temperature is reduced toward T_c. This scattering appears static even on time scales long in comparison with T_2. We do not understand this static scattering in detail but have discussed it extensively in Ref. 3; it arises from the liquid mixture and can be coupled to the polymer matrix only by the matrix modifying the local fluid composition. One might argue that this scattering signal provides a reference phase which turns our correlation function from homodyne to heterodyne. Whether or not such a change should be made in Eqs. (2) and (3), there would be no important change to any result in this paper, and in particular, T_2 is two orders of magnitude too large and has the wrong q dependence to arise from a transition from one scattering regime to the other. In the lower half of Fig. 3 we show the ratio of the second process amplitude R to the diffusive amplitude $(1-R)$. The importance of the second process clearly increases rapidly as temperature is reduced into the critical region, much as was the case in the DW work.[4]

In summary, we observe dynamic light scattering effects in IBW-gellan gum which are qualitatively similar but crucially different in detail from those seen in Vycor by DW.[4] The appearance and growth in relative importance of a second correlation time is qualitatively the same in both cases. Our most important result, one apparently not seen in the Vycor experiment, is the observation of a systematic shift with temperature of a length scale l_x, below which two processes with distinctly different time scales contribute to the autocorrelation function and above which only the usual diffusive time scale needs to be invoked. This length scale increases with reduced temperature as shown in Figs. 2(b) and 2(c). The second, nondiffusive process is not well understood, nor is the relation of the relatively weak temporally fluctuating signal to the much stronger static scattering discussed in our earlier papers. While some features of random-field theory agree with the data for these systems, there are enough discrepancies to argue a need for a more general model of disorder.

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