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Light scattering from a binary-liquid entanglement gel

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Light-scattering experiments have been carried out on an entanglement gel with a binary-liquid mixture as solvent. The onset temperature for critical opalescence has a composition dependence which is similar to the coexistence curve of the free-liquid mixture. This system resembles previously reported work on the cross-linked gel polyacrylamide in two ways: (1) As temperature is lowered toward the critical temperature of the free-liquid mixture, the binary-fluid gel exhibits a strong and increasing light scattering over a broad temperature region of several kelvins, and (2) no appreciable temporal fluctuations are observed throughout this temperature region. Two added features are observed in the present, entanglement-gel measurements: (a) Gel samples with solvent composition both near and off the critical composition of the free-liquid mixture exhibit similar light-scattering behavior, and (b) a Lorentzian-squared fit to the light-scattering angular distributions yields a characteristic wave number which does not change with temperature and an amplitude which shows a very strong dependence on the temperature.

I. INTRODUCTION

A recent paper reported unusual light-scattering properties for swollen gels whose solvent is a binary-liquid mixture with a nearby critical point.[1] As the temperature of such a binary-liquid gel was lowered toward the free-liquid coexistence curve, no sharp transition was observed but rather the light-scattering intensity increased gradually (over a range of several K) until the gel became opaque. Throughout this region of strong and temperature-varying scattering intensity, the temporally fluctuating signal was extremely weak, representing only about 1% of the total intensity.

Many possible explanations could easily be ruled out on the basis of the available evidence. The polymer network is clearly not acting like a full participant in a ternary mixture; there is abundant literature[2] on ternary systems of polymer + binary liquid and all show sharp phase transitions even though the coexistence curves can become quite contorted. The broadened temperature region of light scattering and the lack of an observable deswelling of the gel with temperature support the argument that the polymer network more closely approximates a field imposed on the liquids. If one regards the polymer-liquid interaction as a wetting problem with negligible relaxation of the polymer matrix and a dominant contribution from a difference in surface free energy of wetting the polymer with one liquid phase or the other, then it is attractive to regard the random spacing of polymer strands as imposing a random (chemical potential) field on the binary liquid. Brochard and de Gennes[3] and de Gennes[4] have discussed this approach in a mean-field picture, and de Gennes[4] and Andelman and Joanny[5] have extended the discussion to include questions of metastability. Lipowsky and Fisher have also applied random-field theory to the wetting problem.[6]

In this paper we present the results of a study of an entanglement gel whose light-scattering properties are as close to ideal as those of the cross-linked gel polyacrylamide on which most of the earlier work was based. It is useful to compare results for such gels both because of differences in the mechanism and reversibility of their polymer networks and also because their pore sizes are probably quite different (random-field predictions should apply only at temperatures where the liquid-mixture correlation length is longer than the correlation length of the polymer network). We find the behavior of the entanglement gel, gellan gum, to be qualitatively similar to that of polyacrylamide but sufficiently different in quantitative detail to place interesting limits on the applicability of a random-field model to the entanglement gel. In particular, we find that the light-scattering structure factors for gellan gum are essentially identical in wave-number dependence on and off the critical composition. In addition, the characteristic lengths in gellan gum's frozen state (strongly suppressed temporal fluctuations) do not change with temperature as they did for polyacrylamide. The choice of gels and details of sample preparation are discussed in Sec. II below. Measurements of cloud-point "coexistence" curves and relaxation time scales are presented in Sec. III, followed by a discussion of light-scattering angular distributions in Sec. IV. Section V contains a discussion of possible explanations of the phenomena.

II. SAMPLE CHOICE AND PREPARATION

In the original work, agarose was reported to have a cloud-point curve which very closely follows the free-binary-liquid coexistence curve.[1] Since agarose is an entanglement gel it would have been desirable to measure its light-scattering properties along with those of a cross-linked gel. Unfortunately agarose is of grayish color, a strong light scatterer even when its solvent is pure water. This scattering property of the polymer network tended to obscure scattering from the phase-separating liquid, particularly since the polymer scattering (even with a pure water solvent) showed strong temporal fluctuations over a broad band of time scales. Because of this difficulty all light-scattering angular distributions in the earlier work were for polyacrylamide, which is extremely clear when its solvent is either pure water or a binary mixture in its one-phase region. Gellan gum is a very clear entanglement gel whose non-light-scattering properties are closely akin to those of agarose.[7] We have made gellan gum samples of 0.6 wt. % polymer. After the samples gelled in pure water, water and isobutyric acid (IBA) were added to give the global composition indicated below. Despite several attempts to add the IBA before gelation occurred, we have not succeeded in making these gels other than by adding the IBA diffusively after gelation. It is not known whether or not IBA is a good solvent for this polymer. On the other hand, the completed water gels only deswell modestly when the IBA is added (about 35% for gellan gum and 15% for agarose), and then the swelling does not change observably (as much as 10%) with temperature over the temperature range of this study, at least on a time scale of several weeks. Figure 1 shows swelling curves for gellan gum and agarose as a function of IBA concentration. In each case relative swelling was measured by observing changes in volume and the absolute values shown in Fig. 1 were established from the ratio of the total mass of the initial water gel to the mass of the polymer in that gel. Deswelling is a stronger function of IBA concentration for polyacrylamide, as can be seen in Fig. 2, but again there is no observable temperature dependence to the swelling of these gels once they deswell to accommodate the IBA concentration. The samples were cylinders of height 30 mm and diameter 10 mm. As will be discussed below, these became uniform (through the height of the column) in the temperature dependence of their light scattering within several months.

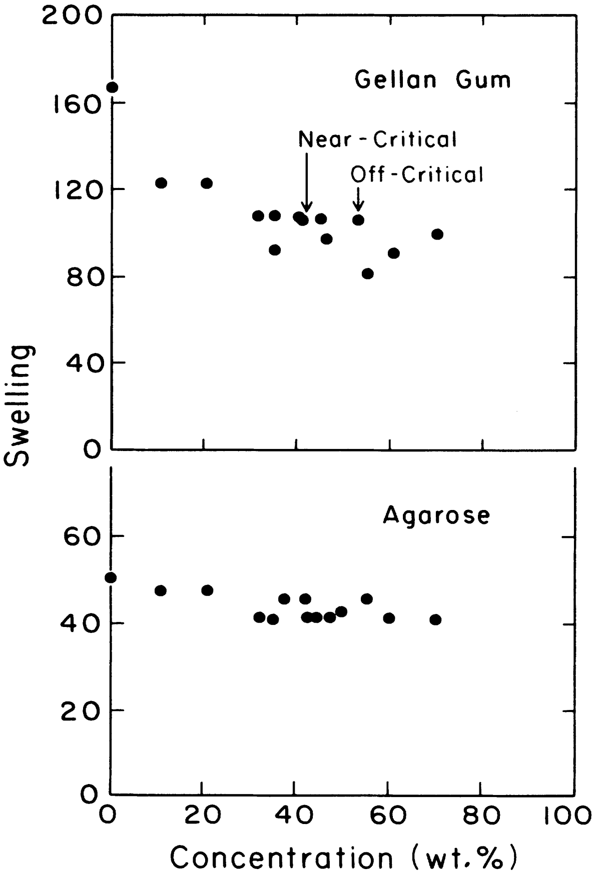

FIG. 1. Swelling curves for (top) gellan gum and (bottom) agarose gels as a function of IBA concentration in the solvent mixture. Arrows indicate the compositions of the samples used in the light-scattering measurements discussed in the text.

Unfortunately, little is known about length scales within the polymer matrices of these gels. Random-field theory (RFT) applies only to systems where the correlation length of the liquid mixture is long compared with the correlation length of the field. According to gel electrophoresis measurements on proteins,[7] the 7% polyacrylamide of Ref. 1 should have a pore size of ~30 Å, well below the liquid correlation length within ~ ±3 K of the critical point. Thus if one associates pore size, the size of the largest molecule which can enter the network, with the matrix correlation length, there is a substantial temperature range within which the polyacrylamide might be expected to impose a random field. No equivalent pore size is available for gellan gum, but rough estimates of pore size from the molecular weight of viruses known to enter other polysaccharide gels of similar polymer concentration give a length scale ~500–1000 Å. If the correlation length of this polymer network is really as large as 500 Å, the range of temperatures around T_c within which random-field results might apply is only ±0.1 K. On the

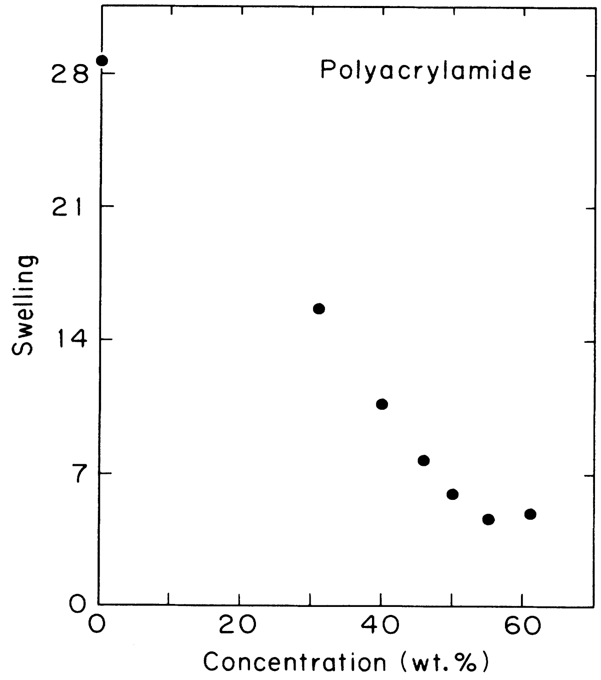

FIG. 2. Swelling curve for polyacrylamide gels as a function of IBA concentration in the solvent mixture.

other hand, the random polymer matrix should probably be expected to have length scales considerably smaller than the largest virus which will embed itself in the gels.

III. CLOUD-POINT CURVES

There appears to be no true coexistence curve for this system but rather a steady increase of light scattering as temperature is reduced. In place of a coexistence curve, we measure a cloud point curve, the variation with solvent composition of the temperature at which an arbitrary turbidity is reached. If the choice of turbidity is varied, the "cloud-point" curve shifts up or down several kelvins in temperature but does not change shape dramatically unless one sets the cloud point at the extremely weak scattering intensities discussed below for scattering at 28° C. The cloud-point curve for gellan gum with IBW (a solvent which is a mixture of water and IBA) is shown in Fig. 3. (The dashed curve in Fig. 3 is the coexistence curve of the free-liquid mixture.[8]) The cloud points were measured 15 times in as many weeks (beginning six weeks after the samples were fabricated) and the data shown in the figure represent the average of the last three measurements, by which time it is believed that the fluid within the gel had fully equilibrated with the supernatant liquid. The standard deviations of the measurements are for all concentrations smaller than the symbols used in Fig. 3. The restriction to the last three measurements is rather conservative since the cloud-point curve changed only slightly during the last 9 of the 15 weeks. The agarose cloud-point curve [Fig. 1(a) of Ref. 1] was also remeasured 12 times and the average of the last three measurements is shown in Fig. 4 with standard deviations indicated when they are larger than the symbol sizes. A polyacrylamide curve is shown in Fig. 5. As was reported in Ref. 1, the exact temperature for the onset of cloudiness in a polyacrylamide sample fluctuates week-to-week over ~2K in an apparently random manner (with other light-scattering properties very reproducible once all temperatures in a given series of measurements are referred to the series' onset temperature). No such fluctuations of onset temperature are seen for either gellan gum or agarose samples. The uncontrolled fluctuations of the several polyacrylamide samples in a cloud-point measurement result in week-to-week shifts in the detailed shape of the curve for this system, but the observation is always similar to that shown in Fig. 5 where the curve closely follows the shape of the binary-liquid coexistence curve from the water-rich side through the critical region and then turns toward higher temperature at a composition slightly but significantly higher

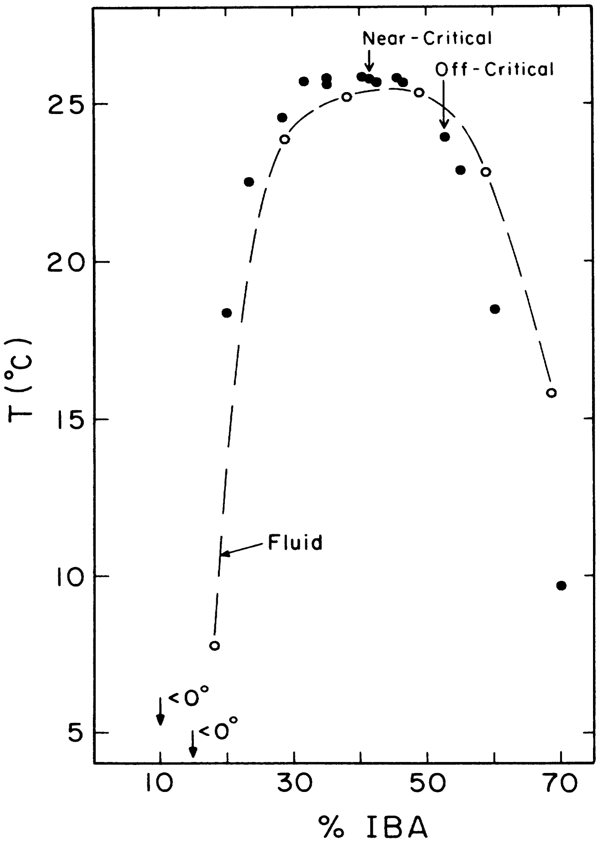

FIG. 3. Cloud-point data for the entanglement gel, gellan gum + IBW. The pure binary-liquid coexistence curve is shown as a dashed curve. Arrows indicate the concentration of the two samples used for the light-scattering measurements discussed in the text.

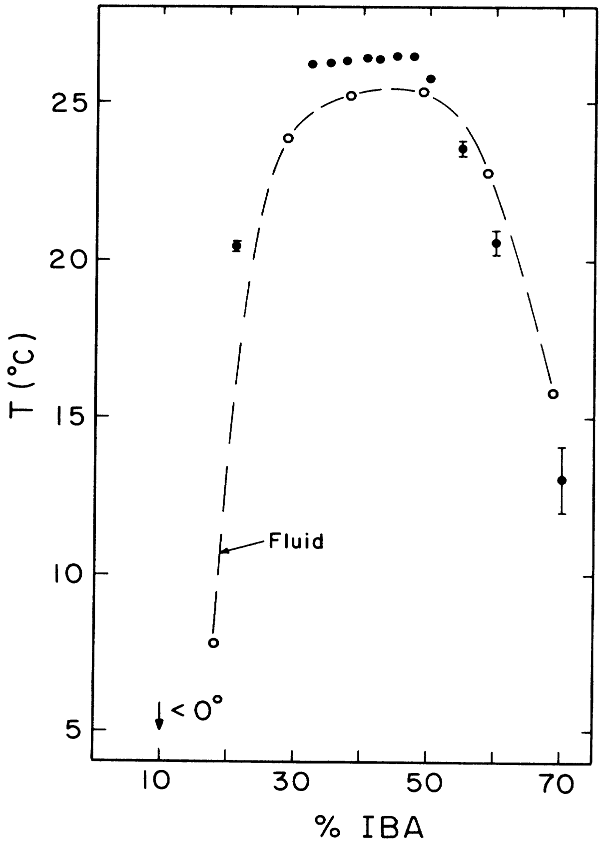

FIG. 4. Cloud-point data for the entanglement gel, agarose + IBW. The pure binary-liquid coexistence curve is shown as a dashed curve.

($\sim 55\%$ IBA compared with the critical value of 40–45%) than the critical value. All the angular distribution data of Ref. 1 were measured for samples of 43% IBA—i.e., near critical composition. At present, one can only speculate on the reason the polyacrylamide curve departs from the liquid coexistence curve at high IBA concentrations; one very plausible possibility is that the θ temperature (known to be $-17\,^{\circ}\mathrm{C}$ for a pure water solvent[9]) is increasing with composition and finally is close enough to be able to distort the curve at $\geq 55\%$ IBA.

As was discussed in Ref. 1, binary-liquid gels will show history-dependent behavior if their temperature is cycled back and forth through their cloudy regions with time scales on the order of a day. However, reproducible results are easily attained if the sample is "annealed" for at least three days at high temperatures (at least 3 K above the onset of weak cloudiness) before each cycle of measurement. All the data presented herein have been obtained with this annealing procedure. In all cases the scattering intensities reported herein are set up "immediately" when the temperature is changed (i.e., on the time scale for thermal diffusion to bring the entire sample to temperature equilibrium); if the temperature is then held constant, the scattering intensity relaxes with a very long characteristic time (≥ 200 h for samples of a few millimeters diameter) which is always consistent with the time expected for composition diffusion to exchange material with the supernatant liquid. Thus, the scattering measured within a few minutes or hours after a temperature quench probes a rather stable state wherein the gel is constrained not to exchange material with the external reservoir; whether this "rather stable state" is a true constrained equilibrium or a very long-lived metastable state is at present unknown. We have cooled the samples at many rates up to a maximum of ~ 200 mK/min, and none of the results reported herein is dependent on the cooling rate.

Cloud-point curves for both agarose and gellan gum show a pronounced flattening at the top. If these curves were used to extract a value for the critical exponent β, the free-liquid value of $\frac{1}{3}$ might not apply to the top of either curve. Unfortunately, the uncertainties in our data prevent our assigning a meaningful upper limit to the renormalized β. In principle the critical composition is also renormalized by the imposition of a field, but only a very small shift ($\sim 5\%$) is seen in the center of our cloud-point curves from the free-liquid critical composition.

IV. LIGHT-SCATTERING MEASUREMENTS

As was the case with the binary-liquid–polyacrylamide system, temporal fluctuations are largely frozen out in the IBW–gellan-gum system; i.e., in the cloudy region the fluctuating part of the light-scattering intensity is only a few percent of the total intensity. For this reason the discussion will concentrate on measurements of the structure factor. Figure 6 shows IBA–gellan-gum light-scattering angular distributions for an off-critical, 53% IBA, sample at several temperatures. Figure 7 shows angular distributions for a near-critical sample (i.e., a sample whose composition, 41% IBA, is near that of the top of the cloud-point curve). In each case the very weak scattering measured 5–10 K above the free-liquid critical temperature is taken to be a background and is subtracted from the measured intensities at each temperature. For each sample the small-angle scattering increases first as temperature is lowered toward the cloud point, but as temperature is further reduced the angular distribution flattens out into a Lorentzian or Lorentzian-squared shape (our data slightly

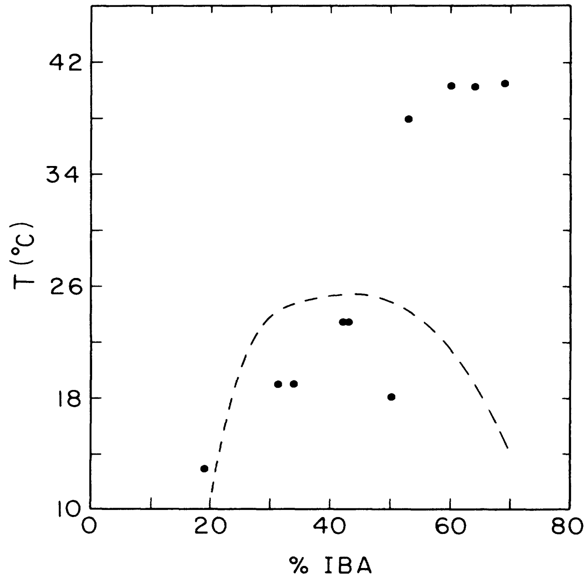

FIG. 5. Cloud-point data for the cross-linked gel, polyacrylamide + IBW. The pure binary-liquid coexistence curve is shown as a dashed curve. Temperatures have been shifted to agree with the normalization of Ref. 1.

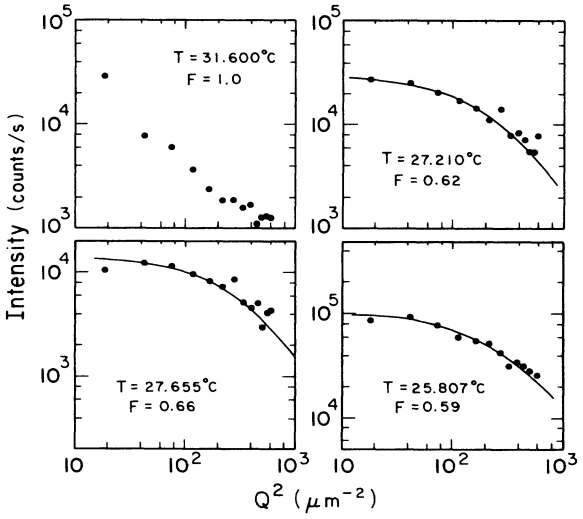

FIG. 6. Light-scattering intensity, in arbitrary units, of an off-critical sample, 53% IBA, of gellan gum + IBW as a function of scattering angle for various temperatures. The cloud point from Fig. 3 for this sample is 23.95 °C. F is the fraction of the incident light intensity transmitted through the sample.

favor a Lorentzian-squared shape but we cannot completely rule out the Lorentzian shape experimentally) whose characteristic wave number, 2×10^5 cm^{-1}, corresponds to an angle $\simeq100°$. We have analyzed these angular distributions as having Lorentzian-squared shapes partly because the data favor this shape and partly because the lack of temporal fluctuations inclines one to expect a Lorentzian-squared shape. The characteristic wave numbers would all shift by a constant factor $\sqrt{2}$ if we assumed a Lorentzian, but all the qualitative features discussed below would be retained. Figures 8 and 9 show the characteristic wave numbers κ as a function of temperature for the off-critical and near-critical samples, respectively, where κ is extracted by fitting the observed angular distribution to the form

$$I(q)=\frac{B}{(q^2+\kappa^2)^2}\ .$$

Two important features appear in Figs. 8 and 9. First, there is no temperature variation to κ. Second, both samples show measurably strong scattering setting in at the same temperature ($\sim$28 °C) with the same angular distribution shape. Figure 10 shows $I(0)$ versus T for the two samples. Since $I(0)=B\kappa^{-4}$ and κ is approximately independent of temperature, Fig. 10 is equivalent to a plot of B versus T. Each sample exhibits scattering which increases rapidly as T decreases, with the near-critical sample doubling intensity in roughly 0.5 K and the off-critical sample in $\sim$0.7 K. The data for the critical sample can be fit with a power law whose exponent varies drastically with the assumed value of T_c; the minimum exponent is $\sim$3.2 for $T_c=25.3$ °C and the exponent increases as T_c is lowered. This is distinctly different from the cross-linked case. The polyacrylamide samples showed a constant value of B, in accordance with the random-field model to be discussed below. This dramatic difference in the behavior of B occurs despite the strong similarity of the two gels' intensity variations with temperature because $I(0)=B\kappa^{-4}$ grows so rapidly if κ shrinks with decreasing temperature.[10]

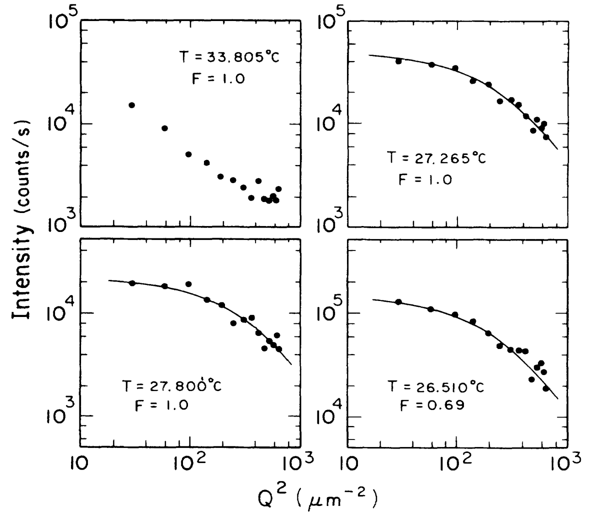

FIG. 7. Light-scattering intensity, in arbitrary units, of a near-critical sample, 41% IBA, of gellan gum + IBW as a function of scattering angle for various temperatures. The cloud point from Fig. 3 for this sample is 25.77 °C. F is the fraction of the incident light intensity transmitted through the sample.

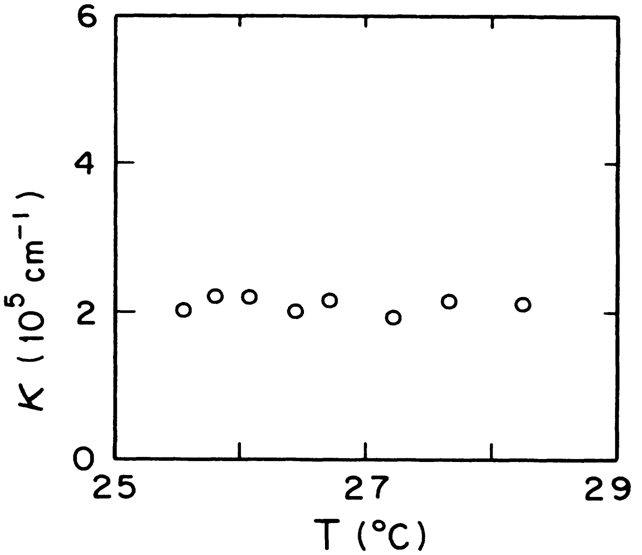

FIG. 8. κ, as extracted from a Lorentzian-squared fit of $I(q)$, vs temperature for the off-critical sample. The cloud point from Fig. 3 for this sample is 23.95 °C.

The Lorentzian-squared analysis can proceed to lower temperature for the off-critical sample because of its slower intensity increase and because its cloud point is lower but where both samples can be measured with manageably small multiple scattering, the two samples behave in a very similar manner.

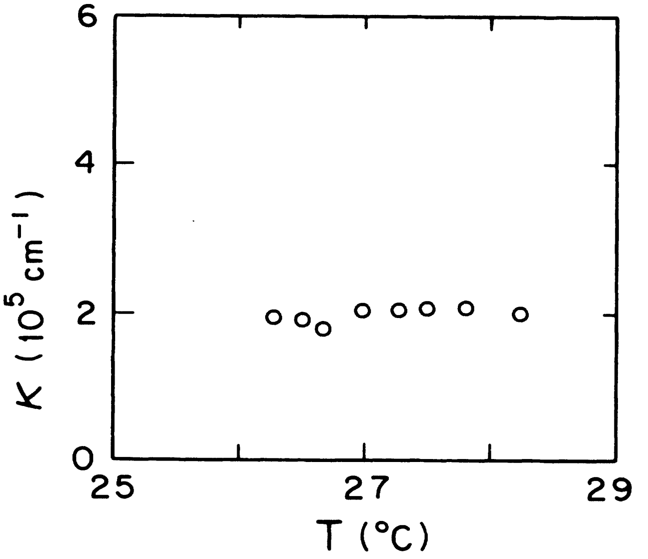

FIG. 9. κ, as extracted from a Lorentzian-squared fit of $I(q)$, vs temperature for the near-critical sample. The cloud point from Fig. 3 for this sample is 25.77 °C.

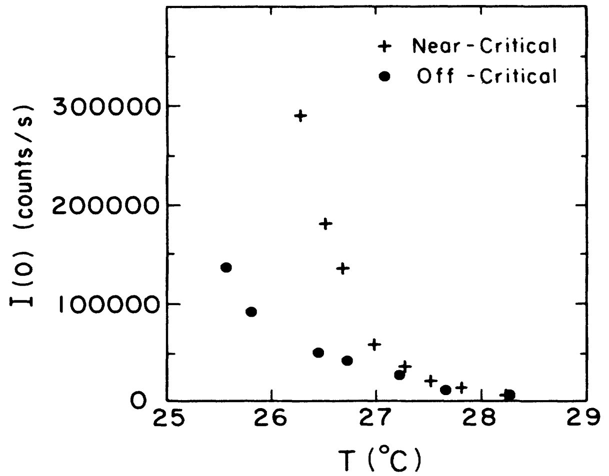

FIG. 10. $I(0)=B\kappa^{-4}$, in arbitrary units, extrapolated from light-scattering angular distribution measurements as a function of temperature for (+) the near-critical sample, 41% IBA, and (●) the off-critical sample, 53% IBA. The cloud points from Fig. 3 for these samples are 25.77 and 23.95 °C, respectively.

V. DISCUSSION AND CONCLUSIONS

The temperature independence of κ noted above is distinctly different from the behavior of the IBW–polyacrylamide system whose κ versus T values are shown in Fig. 11, and whose B is constant. A very attractive explanation of the data in Fig. 11 is to invoke a random-field model for the polymer-liquid interaction; following de Gennes[4] we expect κ to follow the relation

$$\kappa^2=\pm\xi^{-2}+(\kappa^2 l^4)^{-1}\ , \tag{1}$$

where the plus sign is used for $T>T_c$, the minus sign for $T<T_c$, and where ξ is the free-liquid correlation length

$$\xi=\xi_0\epsilon^{-\nu} \tag{2}$$

and

$$\epsilon=(T-T_c)/T_c\ , \tag{3}$$

with T_c arbitrarily shifted to account for renormalization of the coexistence curve by an average polymer-liquid interaction. l represents the strength of the random field

$$l=aN^{1/2}/\Delta\ , \tag{4}$$

where Δ is the difference of the polymer's interactions with each of the two liquids, a is the monomer size, and N is the number of monomers between cross links. The solid curve shown in Fig. 11 is a fit to the data in which l and T_c were varied to give $T_c=24.34$ °C (for the free liquid $T_c=26.12$ °C) and $l=119$ Å while ξ_0 was fixed at 2 Å (appropriate to IBW in the two-phase region). Since a is of the order 10 Å, $l\sim 120$ Å implies that $N^{1/2}/\Delta$ is of order 10. The isobutyric-acid–polyacrylamide interaction is not known so it is difficult to estimate Δ, but $N^{1/2}/\Delta\sim 10$ seems reasonable for this strongly cross-linked gel with a not-too-great difference in the monomer interaction with the two liquids. Thus the fit shown in Fig. 11 is encouraging for the random-field approach to the cross-linked gel polyacrylamide despite the rather distorted coexistence curve shown in Fig. 5. Furthermore, $l\sim 120$ Å is quite consistent with the freezing out of temporal fluctuations. In general, one expects the light-scattering intensity to be of the form

$$I(q,t)=\frac{Ae^{-\Gamma t}}{q^2+\kappa^2}+\frac{B}{(q^2+\kappa^2)^2}\ . \tag{5}$$

The ratio A/B should be $\sim 1/l^2\sim 10^{12}$ cm^{-2} so the second, nonfluctuating term should dominate as it does when $\kappa\sim 10^5$ cm^{-1}.

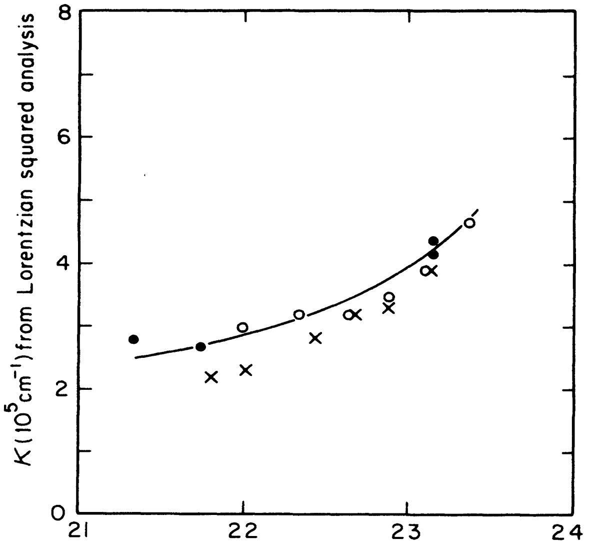

FIG. 11. κ, as extracted from a Lorentzian-squared fit of $I(q)$, vs temperature for a polyacrylamide + IBA sample. Temperatures have been shifted to agree with the normalization discussed in Ref. 1. Different symbols indicate results from different passes through the temperature range.

If one now turns to the results of Figs. 8 and 9 for the entanglement gel, gellan gum, it is immediately apparent that the situation is qualitatively different from that of polyacrylamide. The constancy of κ with T can be accommodated in Eq. (1) only if T_c is shifted high above 28 °C; the observed light scattering is so weak in the region above 28 °C that this possibility can immediately be rejected. A more plausible alternative is to argue that the systems are frozen into long-lived metastable states[4,5,11,12] at relatively high temperatures (i.e., well above T_c) and so cannot show the equilibrium freezing behavior of Eq. (1). In this case $\kappa\gg 1/l$ so l must be considerably larger than for the polyacrylamide system, a reasonable possibility because, as noted above, $N^{1/2}$ could be much larger in the entanglement gel and, since both polymers are very water soluble, Δ may be similar for both cases. Such a large value of l would again be consistent with the suppression of temporal fluctuations. However, the metastability alternative has two complicating features: (i) The time to relax toward equilibrium is quite long. The cloudiness which appears immediately when the system is quenched relaxes on a time scale $\sim 10^6$ sec. This time scale is of the order of the diffusion time for exchange between the gel and the supernatant liquid and thus should be regarded as a lower limit for the metastable time scale of the random-field system. We know of no estimates for the metastable time scale for a liquid-polymer system; estimates of metastable time scales for random-field magnets are reported to be $\sim 10^3$ sec while experiments observe much longer times,[13] and (ii) the cross-linked gel follows Eq. (1) in a very reasonable way into and probably through the critical region (although it too shows relaxation times $\sim 10^6$ sec).

A second and possibly more severe difficulty for treating IBW–gellan gum as a random-field system is the similarity of light scattering for the off-critical and near-critical samples. Both samples freeze into the same angular distribution shape at the same temperature. Fisher[12] predicts a strong flattening of the coexistence curve and Ogielski[14] calculates a reduction in the critical exponent from $\frac{1}{3}$ to 0.05 (as discussed above, we do observe some flattening of this curve but cannot place useful limits on β). This is possibly a strong enough effect to place the onset of freezing at close to the same temperature for both samples, but between the compositions of the two samples the much stronger variation with temperature of the cloud-point curve would then be difficult to explain.

Finally, current random-field models with Gaussian distributions require B to be a constant. While refinements of the model[15] might be expected to introduce some temperature dependence to B, the rapid change observed in the present experiment is probably too strong a variation to be accommodated.

Since the system freezes into a long-lived state of characteristic length $2\pi/\kappa = 3000$ Å at a temperature well above the free-liquid critical point, it is tempting to assume that the solvent correlation length is very short compared to 3000 Å and that the large length scale is imposed on the liquid system by long-range spatial correlations in the polymer network (i.e., departures from randomness in the imposed field). If these assumptions are correct, two possibilities arise depending on whether or not the polymer network is random on length scales less than 3000 Å. In the first case, the gel pore size does not represent the smallest length scale in the polymer network but only the largest commonly occurring cavity in which biological molecules could become embedded. In this case the system would still be a random-field system, but one which required some correction for long-range polymer correlations. We are not aware of any work which assesses the effects of correlations on a random-field system. Ogielski's calculations[14] predict that for a random-field system $I(0)$ should vary as $\epsilon^{\tilde{\gamma}}$ where $\tilde{\gamma}$ is between 3 and 5; our measurement is consistent with such a large exponent, although there is an obvious problem with the frozen value of κ. In the second case, 3000 Å is at or near the smallest length scale in the polymer network. If this is so, each polymer strand acts like a constant applied field in its neighborhood and should influence the local solvent composition, which might allow sufficient contrast in index of refraction to explain the Lorentzian-squared light scattering at any one temperature far above T_c. On the other hand, it is quite difficult to explain the observed temperature dependence of the light scattering in this way. The extremely weak scattering above 30 °C and the strong $\tilde{\gamma} > 3$ increase below 28 °C are not easily reconciled with the free-liquid behavior (free liquid $\gamma \sim 1.2$). If this problem can be overcome, the light-scattering contrast deep in the one-phase region would be an adsorption phenomenon, closely analogous to the much better studied wetting in the two-phase region. The abundant critical wetting literature[6,16] has concentrated on the behavior of liquid mixtures near a plane wall; this system may well provide a case where approximately half the solvent is near a "wall." Levinson *et al.*[17] have discussed the wetting of a single strand.

In summary, these considerations leave us in the following quandary: All the binary-liquid gels we have studied show a broadened region of strong and changing light scattering near the free-liquid coexistence curve. None of these gels deswells observably as temperature is changed through the region of the coexistence curve, and this approximate rigidity of the polymer matrix in the presence of the liquid's attempt to phase separate strongly favors treating the polymer-liquid interaction as an imposed field. Light scattering from the cross-linked gel fits in well with the random-field picture despite some difficulty with long metastable time scales, but that from the entanglement gel does not. While it is not easy to explain this discrepancy and further work is clearly warranted, one possible explanation involves nonrandom structures at long range in the polymer matrix. Such correlations are poorly understood for all gels, but there is more evidence for micrometer-sized structures in entanglement gels than there is for cross-linked gels. Another possibility might involve improving on the mean-field approximation in the random-field formulations.

ACKNOWLEDGMENTS

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