Critical Behavior of Density Fluctuations in Gels[*]

Toyoichi Tanaka, Shin'ichi Ishiwata,[†] and Coe Ishimoto[‡]
Department of Physics and Department of Biology,[‡] Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139
(Received 7 December 1976)

The temperature dependence of the intensity and of the correlation time of laser light scattered by the network density fluctuations in polyacrylamide gels is reported. The density fluctuations show critical behavior at −17°C. This behavior is quantitatively explained as a phase transition of a binary mixture of the covalently cross-linked polymer network and the fluid medium.

In this Letter, we report measurements of the temperature dependence of the intensity and the correlation time of laser light scattered by the polymer network density fluctuations in polyacrylamide gels. Both the intensity and the correlation time of the scattered light increase by a factor more than 200 as temperature decreases and appear to diverge at a certain temperature. This behavior has not previously been theoretically predicted or observed in gels. We give a quantitative interpretation of our measurements using a theory analogous to the mean-field theory of phase separation in binary fluid mixtures; and we show that light scattering experiments may provide information fundamentally important to understanding of the physics of gels.

Tanaka, Hocker, and Benedek[1] and de Gennes[2] presented a theory which describes the density fluctuations in a gel polymer network and showed that the longitudinal elastic modulus of the network can be determined from the intensity of light scattered from the fluctuations. They also showed that the ratio of the elastic modulus and the frictional coefficient of the network in the fluid medium can be determined from the correlation time of the scattered light.[1,2] The theory has been confirmed experimentally by Tanaka, Hocker, and Benedek,[1] Ware,[3] and Munch *et al.*[4] According to the theory, we take as a model for a gel an infinite cross-linked polymer network immersed in a fluid medium. The normal modes of the density fluctuations in the gel network can be described as overdamped phonons with wave vectors, $\vec{q}$.[1] The phonons in the network are overdamped because of the large frictional drag by the fluid medium proportional to the velocity of the network relative to the fluid medium. The incident light in the gel is scattered by such overdamped phonons and the correlation function of the scattered-light field is expressed in the following way[1]:

$$\langle E(\vec{q},t)E(\vec{q},0)\rangle = C(\varphi\,\partial n^2/\partial\varphi)^2\frac{kT}{(K+\frac{4}{3}\mu)}\exp[-(K+\tfrac{4}{3}\mu)q^2t/f]. \tag{1}$$

Here E is the amplitude of the scattered-light field, $\vec{q}$ is the scattering vector, n is the refractive index of the whole gel, φ is the volume concentration of the polymer network, k is the Boltzmann constant, T is the absolute temperature, K and μ are the bulk and shear moduli of the network in the fluid medium, and C is a constant depending only on the optical geometry. The frictional coefficient, f, multiplied by the velocity of the network relative to the fluid medium gives the frictional force per unit volume of the network. The combination, $K+\frac{4}{3}\mu$, corresponds to the longitudinal modulus of the network. In our experiments the network concentration, φ, was 0.025, and we make the approximation, $\varphi(\partial n^2/\partial\varphi) \sim n^2-n_f^{\,2}$, where n_f is the refractive index of the fluid medium. We measured n and n_f independently using an Abbe refractometer and found that $n^2-n_f^{\,2}$ had the value 0.0065 ± 0.0003 and was constant throughout the temperature region of our experiments; n_f was measured on the supernatant which was left above the gel upon gelation and was in equilibrium with the fluid in the network. Then Eq. (1) shows that the intensity of the scattered light, $I=\langle E^2(\vec{q})\rangle$, is proportional to $kT/(K+\frac{4}{3}\mu)$. Also the reciprocal correlation time, or the decay rate, is given by $\Gamma=(K+\frac{4}{3}\mu)q^2/f$ as shown in Eq. (1).

The bulk modulus, K, is φ times the derivative of the osmotic pressure, π, of the gel with respect to φ. Using the formula for the osmotic pressure of a swollen network,[5] we obtain

$$K = \varphi\,\partial\pi/\partial\varphi$$

$$= \varphi\frac{\partial}{\partial\varphi}\left\{-\frac{kT}{v_0}\left[\frac{\nu_e v_0}{V}(\varphi^{1/3}-\tfrac{1}{2}\varphi)+\ln(1-\varphi)+\varphi+\left(\frac{B}{kT}+A\right)\varphi^2\right]\right\}, \tag{2}$$

$$= kT\left[\frac{\nu_e}{V}\left(\frac{\varphi}{2}-\frac{\varphi^{1/3}}{3}\right)+\left(\frac{1}{1-\varphi}-\frac{2A}{k}\right)\frac{\varphi^2}{v_0}\right]-\frac{2B}{v_0}\varphi^2, \tag{3}$$

where v_0 is the partial molar volume of the solvent, A is the entropy gain, and B is the enthalpy gain upon mixing one segment of a polymer constituting the network into the solvent, ν_e is the number of constituent polymers in a unit volume before mixing, and V is the dry volume of the gel network of a unit volume. The entropy A and enthalpy B may include contributions of van der Waals forces, hydrophobic interactions, and hydrogen bonds. The first term in Eq. (3) is the bulk modulus arising from the rubber elasticity of the expanded network. The second term is the contribution of the entropy of mixing of the network and the fluid; and the third term is the enthalpy of mixing. These latter two terms correspond to the derivative of the second virial term of the osmotic pressure of a solution which uses the mean-field approximation. The first virial term, proportional to $-\nu kT$ (where ν is the number of solute molecules) and dominant in a solution, is not present since it is negligible in a gel because ν is unity.[5,6] In place of this term, however, there is the term due to the rubber elasticity of the expanded network.

The shear modulus, μ, of a gel can be calculated using the theory of rubber elasticity[5]:

$$\mu = (\nu_e kT/2V)(\varphi+\tfrac{1}{2}\varphi^{5/3}). \tag{4}$$

There is no contribution of a free energy of mixing to μ since there is no volume change in the network upon shear deformation. From Eqs. (3) and (4), we see that it is possible to write the longitudinal modulus as

$$K+\tfrac{4}{3}\mu = a(T-T_s), \tag{5}$$

where

$$a \equiv k\left[\frac{\nu_e}{V}(\tfrac{7}{6}\varphi-\tfrac{1}{3}\varphi^{1/3}+\tfrac{1}{3}\varphi^{5/3})+\left(\frac{1}{1-\varphi}-\frac{2A}{k}\right)\frac{\varphi^2}{v_0}\right], \tag{6}$$

and

$$T_s \equiv 2B\varphi^2/(av_0). \tag{7}$$

Equation (5) shows that the longitudinal modulus vanishes at $T = T_s$.

The intensity and the decay rate of the correlation function of laser light (He-Ne, 15-mW incident power) scattered at 90° from a 2.5% polyacrylamide gel [acrylamide:*bis*-acrylamide:water = 37.5:1:1500 (weight/weight at mixing)] are shown as a function of temperature in Fig. 1. The experimental apparatus and procedures are essentially the same as those reported in Ref. 1. Both the intensity and the correlation time increase as the temperature decreases, and they appear to diverge at approximately −17°C. This behavior is completely reversible in the temperature range shown. The possibility that its origin is the formation of ice can be excluded for the following reasons: (1) The freezing temperature of the gel was below −17°C. (2) In either the gel or the separated fluid medium, formation of local domains of ice would increase the intensity of scattered light and decrease the refractive index, since the refractive index of ice (1.309) is much less than the refractive index of water (1.335 at 0°C). It was already stated that $n^2 - n_f^2$ is constant with respect to changes in temperature. The fact that it is constant indicates that if ice is not formed in the separated fluid medium, neither

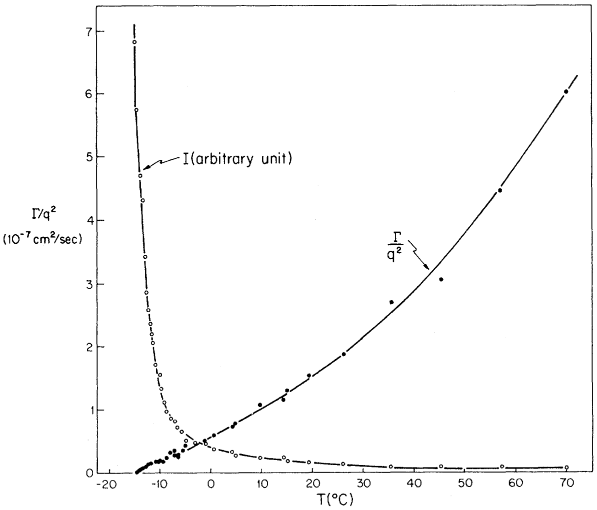

FIG. 1. Intensity, I, and the reciprocal correlation time (decay rate), $\Gamma = (K+\frac{4}{3}\mu)q^2/f$, of laser light scattered by a 2.5% polyacrylamide gel. Γ is divided by the square of the scattering vector, $|\vec{q}|^2$.

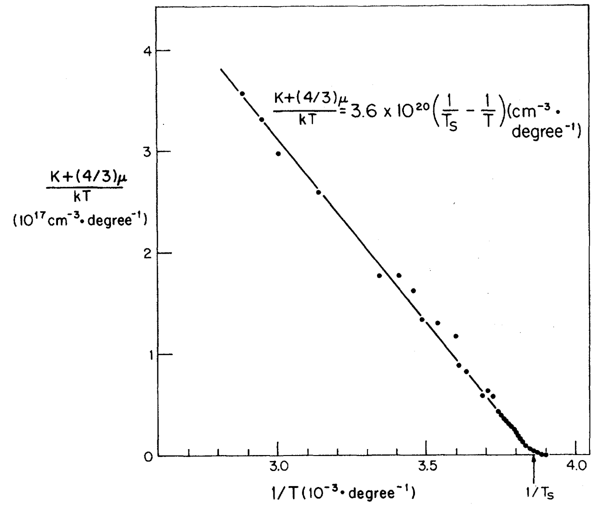

FIG. 2. Inverse of the laser-light intensity scattered by a 2.5% polyacrylamide gel as a function of reciprocal absolute temperature.

is it formed in the gel. In order to detect any formation of ice in the separated fluid medium, the intensity of light scattered by the separated fluid medium was measured and found to be constant in the temperature range −17°C to 80°C. Therefore, ice is not formed in the gel in this temperature range. The critical behavior of the gel is thus due to a divergent increase of concentration fluctuations of the polymer network and not due to the formation of local domains of ice.

In Fig. 2 the inverse of the measured intensity, $1/I$, is plotted against $1/T$. Over a wide temperature range, $1/I$ varies in proportion to $(T-T_s)/T = T_s(1/T_s - 1/T)$ as predicted in Eqs. (1) and (5).

We also calculated the frictional coefficient, f, from the correlation time and the values of $K + \frac{4}{3}\mu$ obtained from the measurements of scattered light intensity discussed above. The data are shown in Fig. 3. Since f does not increase as temperature decreases near T_s, the slowing down of the network density fluctuations is attributable to the diminishing longitudinal modulus of the network. The fricitional coefficient represents the hydrodynamic drag experienced by the network as it moves through the fluid and is proportional to the viscosity of the fluid, η, and also depends on the hydrodynamic structure of the network; η was measured on the gel supernatant mentioned above and found to be nearly equal to the viscosity of water. The behavior of f/η shows that as the temperature decreases, the effective "pore size" becomes larger and appears to diverge as T approaches T_s (Fig. 3). If f becomes very

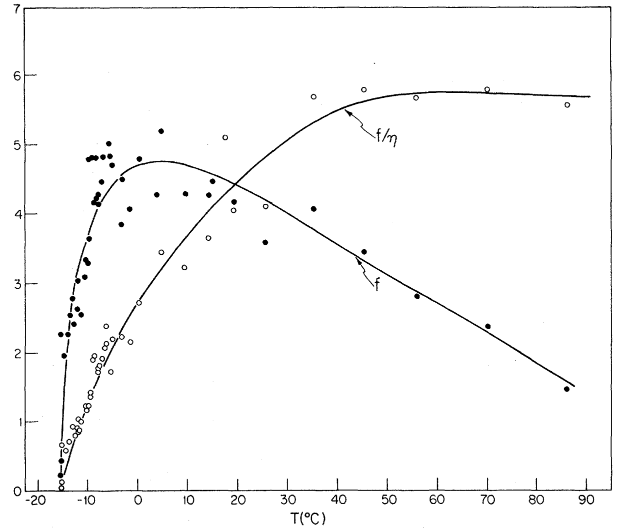

FIG. 3. The friction coefficient, f, of a 2.5% polyacrylamide gel obtained from the intensity and the correlation time of scattered laser light. The ratio of f to the viscosity of the gel fluid, η, is also plotted as a function of temperature. f is given in units of 10^{10} dyn sec/cm^4; and f/η is given in units of 10^{12} dyn sec/cm^4 poise.

small and only the network were held, the fluid would flow out of the network because of gravity. The rate of such flow, however, is estimated to be 100 Å/sec at the lowest measured value of f (10^9 dyn sec/cm^4). In our experiments the samples were contained in cuvettes and there was no problem of drainage of the fluid.

The agreement between our intensity measurements and the prediction of Eqs. (1) and (5) indicates that the divergence and the slowing down of the network density fluctuations in the gel may be considered as a phase separation of a binary mixture of the network and the fluid medium. Equations for the osmotic bulk modulus of a solution and that of a gel network are similar except for the importance of the term proportional to $-\nu kT$ for a solution, and for the additional rubber-elasticity term, $(-\nu_e/V)kT(\frac{1}{2}\varphi^{1/3} - \frac{1}{2}\varphi)$, for a gel. The shear modulus contributes to the longitudinal modulus in a gel, whereas it does not in a solution. In both cases, the divergence of the fluctuations is a result of the equalization of the moduli due to the mixing enthalpy and the mixing entropy to the longitudinal modulus. As the temperature approaches T_s, the spatial correlation among the segments of the network polymers increases and the movements of the segments become correlated and slow down. The presence of the different terms in the osmotic pressure gives rise to different features of a gel and a solution. In the gel, phase separation occurs where π, given within the curly bracket of Eq. (2), vanishes.[5] Simple evaluation of Eqs. (2), (6), and (7) shows that this always happens at a higher temperature than where the bulk modulus or the longitudinal modulus goes to zero.[7] Thus there is no true critical point in a gel and our temperature T_s corresponds to a metastable spinodal temperature.[8] Figure 2 shows a slight, but systematic, deviation near T_s of the intensity of scattered light from the prediction of Eq. (5). This could be caused by spinodal decomposition and is the subject of further investigations. It was possible for us to study metastable states because the equilibration time is very long. The time required by the gel to attain a new equilibrium is given as the relaxation time in Eq. (1): $\tau = f/[(K+\frac{4}{3}\mu)q^2]$. As an example, if a 2.5% polyacrylamide gel of thickness 1 cm is compressed by applying pressure on the network alone, then $q \sim 2\pi/(1\ \text{cm})$ and for $(K+\frac{4}{3}\mu)/f \sim 10^{-7}$ cm^2/sec, τ is approximately 70 hours. Near T_s, τ becomes much longer. Since in laser-light scattering $q \sim 10^5$ cm^2/sec and $\tau \sim 1$ msec, fluctuations with these large wave vectors can be observed even in a metastable state.

In closing, we wish to point out an additional advantage of light scattering to study the properties of gels. Conventional macroscopic measurements of gel elasticity are in fact made under constant-volume conditions because of the long time required for the fluid medium to enter or leave the network on a macroscopic scale. These measurements determine only the shear modulus, μ, (which results entirely from the rubber elasticity) and do not show the singularity observed in light scattering. We conclude that light scattering is an ideal tool to study the physical properties of gel, including both potential physiological problems (such as a possible relationship between contraction of a vitreous gel and retinal detachment) and problems of fundamental physical significance (such as the relation of gelation to the percolation problems).[9]

We thank I. Ohmine, J. D. Litster, and G. B. Benedek for helpful discussions.

---

[*] Work supported by National Institute of Health, National Eye Institute, and Massachusetts Institute of Technology Health Sciences Fund.

[†] Muscular Dystrophy Association Fellow.

[1] T. Tanaka, L. O. Hocker, and G. B. Benedek, J. Chem. Phys. 59, 5151 (1973).

[2] See the discussions on the theory of P. G. de Gennes in J. P. Munch *et al.*, J. Polymer Sci. 14, 1097 (1976), and J. Phys. (Paris) 35, 239 (1974).

[3] B. Ware, private communication.

[4] See Munch *et al.*, Ref. 2.

[5] P. J. Flory, *Principles of Polymer Chemistry* (Cornell Univ. Press, Ithaca, New York, 1953).

[6] B. Chu and F. J. Schoenes, Phys. Rev. Lett. 21, 6 (1968); R. Kubo, *Statistical Mechanics* (North-Holland, Amsterdam, 1971).

[7] Discussion on gel dynamics in connections with the phase diagram for a gel will be reported elsewhere.

[8] Spinodal lines are usually defined as $K=0$. In the case of a gel, longitudinal density fluctuations diverge at $K+\frac{4}{3}\mu=0$, and this may be used as a definition of the spinodal lines.

[9] P. G. de Gennes, J. Phys. (Paris) 37, L-1 (1976).