

<sup>2</sup>L. Onsager, Remarks, published in *Nuovo Cimento*, Suppl. No. 2, 6, (1949); R. P. Feynmann, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland, Amsterdam, 1955), Vol. 1.

<sup>3</sup>G. A. Williams and R. E. Packard, *Phys. Rev. Lett.* 33, 280 (1974); also G. A. Williams, Ph.D. thesis, University of California, Berkeley, 1974 (unpublished).

<sup>4</sup>M. J. V. Gordon, G. A. Williams, and R. E. Packard, *J. Phys. (Paris)*, Colloq. 39, C6-172 (1978).

<sup>5</sup>L. J. Campbell and R. M. Ziff, Los Alamos Scientific Laboratory Report No. LA 7384-MS, 1978 (unpublished); G. B. Hess, *Phys. Rev.* 161, 189 (1967).

<sup>6</sup>The influence of the container walls on pattern size is completely negligible for almost all experimentally accessible situations. See, for example, L. J. Campbell and R. Ziff, *Phys. Rev. B* (to be published).

<sup>7</sup>H. Lamb, *Hydrodynamics* (Dover, New York, 1945), Sect. 157.

## Spinodal Line and Critical Point of an Acrylamide Gel

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We present direct evidence for the existence of the critical point in an acrylamide gel, the gel consisting of a covalently cross-linked polymer network immersed in an acetone-water mixture. We determined the spinodal line for the gel from the measurements of the scattered light intensity. The spinodal line has a maximum at  $T = (10 \pm 1)^\circ\text{C}$  and a network volume concentration of  $(18 \pm 3)\%$ . This corresponds to the critical point.

In 1977, Tanaka, Ishiwata, and Ishimoto reported measurements of the temperature dependence of the intensity and the correlation time of laser light scattered by the concentration fluctuations in an acrylamide gel.<sup>1,2</sup> As the temperature of the gel was lowered, both the intensity and the correlation time of the scattered light increased by a factor of more than 200 and both appeared to diverge at a certain temperature. Based on Flory's formula for the osmotic pressure of a cross-linked gel, they concluded that the temperature of the divergence corresponded to the metastable spinodal temperature, and that the gel would have no critical point. Recently, Tanaka<sup>3</sup> and Fillmore and Tanaka<sup>4</sup> reported the swelling equilibria of a gel which was immersed in acetone-water mixtures. They observed a reversible collapse of the gel network upon changing the acetone concentration or temperature of the system. It was demonstrated that these phenomena could be understood in terms of a mean-field theory based on an extension of Flory's theory. With this theory, Tanaka predicted the existence of the critical point in the gel associated with a phase separation of the covalently cross-linked polymer network and solvent.

In this Letter, we present direct evidence for the existence of the critical point in an acrylamide gel, the gel consisting of a covalently cross-linked polymer network immersed in an acetone-water mixture. Using measurements of the scattered-light intensity, we determined the spinodal temperature at which the network concentrations diverge for various network concentrations of the gel. The network concentrations were varied by adjusting the degree of swelling of the gel. The highly swollen gel corresponds to a low concentration of the network, and the shrunken gel corresponds to a high network concentration. We observed a maximum temperature in the spinodal line which corresponds to the critical point. We also determined the equilibrium concentration of the gel when it is immersed in a large volume of an acetone-water mixture at different temperatures. The combination of both the spinodal line and the swelling equilibrium line gives us the entire phase diagram of the gel. These data are analyzed by the mean-field theory presented previously.<sup>3</sup>

Acrylamide gels were prepared by dissolving 5 g acrylamide, 0.133 g *N,N'*-methylene-bisacrylamide, 40 mg ammonium persulfate, and 400  $\mu\text{l}$

tetramethylethylene-diamine in 100 ml water. This solution was then poured into glass tubes. It took approximately 30 min for gelation at room temperature. The gels were left in the tubes for twelve days. They were then removed, cut into 1-cm-long pieces, and dried at 30°C. Each dried gel was then put into an acetone-water mixture having a composition ratio of 44:56 by volume. After a certain amount of the mixture had soaked into the network, the gel was taken out of the mixture and put into an ampoule. The ampoule was immediately sealed to prevent any loss of the solvent. In this way gels of different concentrations were prepared. The network concentration of each gel was determined by measuring the weights of the dry and the swollen gel.

For each sample, the scattered light intensity at a 90° angle was determined as a function of temperature. Figure 1 shows the inverse of the intensity of light scattered from an 8% (by volume) gel ( $1/I$ ) as a function of the inverse absolute temperature ( $1/T$ ). It has been shown that, in the mean-field approximation,  $1/I$  vs  $1/T$  is linear and this relation was proven experimentally.<sup>1,5</sup> We fit the experimental points with a straight line and obtained the spinodal temperature from the intercept of the straight line with the  $1/T$  axis which corresponds to infinite scattered light intensity. The deviation of the data points from the straight line as the spinodal temperature is approached probably results from

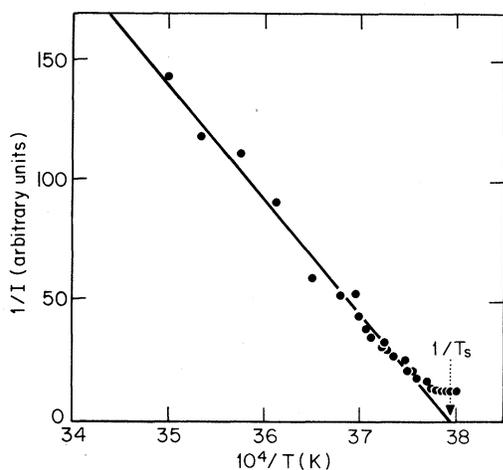


FIG. 1. The temperature dependence of the inverse intensity of light scattered from an 8% acrylamide gel having a 44% acetone-water mixture as the gel fluid.  $T_s$  denotes the spinodal temperature at which the concentration fluctuations of the network diverge.

multiple scattering of the light. The spinodal temperature is plotted as a function of gel concentration in Fig. 2(a) (open circles).

We also determined the equilibrium concentration of the gel which was immersed in a large volume of the acetone-water mixture at various temperatures. The volume concentrations were determined by weighing the dry and then swollen gel (the specific density of the network was 1.8). They are plotted in Fig. 2(a) (solid circles).

Let us now calculate theoretically the spinodal

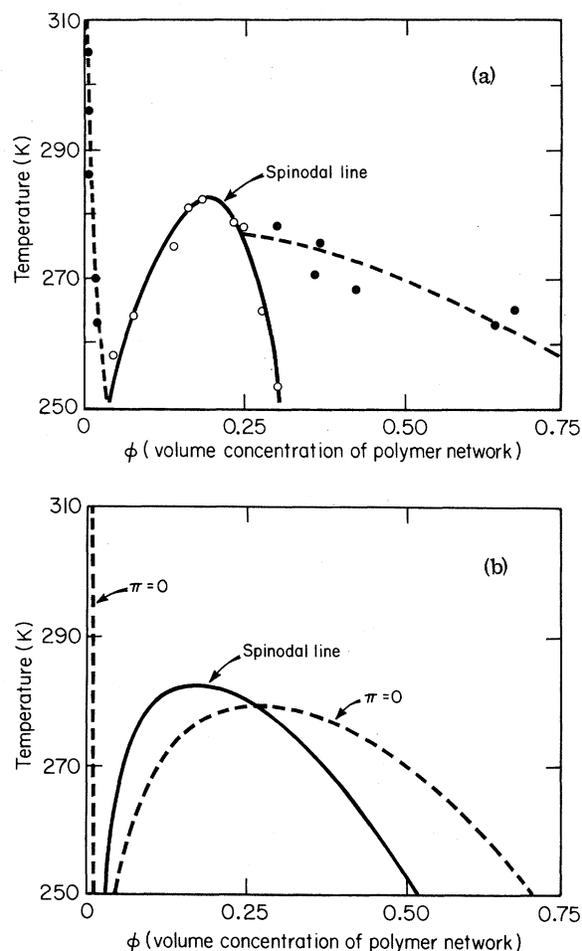


FIG. 2. (a) The spinodal line (open circles) determined by light-scattering measurements. The solid circles denote the equilibrium concentrations of the acrylamide gel with is immersed in a 44% acetone-water mixture at different temperatures. (b) The spinodal line (solid curve) and the zero-osmotic-pressure line (dotted curve) calculated from Eqs. (2) and (3) in the text. The latter represents the equilibrium concentration of a gel which is immersed in a large amount of fluid. The parameters used are shown in the text.

line and the equilibrium concentration for a gel immersed in fluid. The latter is given by the condition of zero osmotic pressure since the osmotic pressure of a fluid is zero. The mean-field expression of the osmotic pressure is given by<sup>2,6</sup>

$$\pi = -N_A k T \left\{ \ln(1 - \varphi) + \varphi + \frac{\Delta H - T \Delta S}{2kT} \varphi^2 + \frac{v_0}{Nv} \left[ \left( \frac{\varphi}{\varphi_0} \right)^{1/3} - \frac{\varphi}{2\varphi_0} \right] \right\}, \quad (1)$$

where  $N_A$  is Avogadro's number,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\varphi$  is the network concentration,  $\Delta H$  and  $\Delta S$  are the differences in the enthalpy and entropy of a polymer segment when it is in contact with other segments from when it is in contact with solvent molecules,  $v_0$  is the specific volume of the solvent molecule,  $v$  is that of a polymer segment,  $N$  is the number of segments in one polymer chain whose both ends terminate at the neighboring crosslinks, and  $\varphi_0$  is the network concentration at which the polymer chain has a random-walk configuration. The zero-osmotic-pressure line is thus given by

$$\frac{\Delta H}{kT} = \frac{\Delta S}{k} - 2 \left\{ \ln(1 - \varphi) + \varphi + \frac{v_0}{Nv} \left[ \left( \frac{\varphi}{\varphi_0} \right)^{1/3} - \frac{\varphi}{2\varphi_0} \right] \right\} \frac{1}{\varphi^2}. \quad (2)$$

The spinodal line is given by the condition of infinite compressibility of the network that is,  $\partial \pi / \partial \varphi = 0$ . Thus the spinodal line is expressed as

$$\frac{\Delta H}{\Delta T} = \frac{\Delta S}{k} + \left\{ \frac{1}{1 - \varphi} - \frac{v_0}{Nv\varphi\varphi_0} \left[ \frac{1}{3} \left( \frac{\varphi}{\varphi_0} \right)^{-2/3} - \frac{1}{2} \right] \right\}. \quad (3)$$

The  $\pi = 0$  curve and the spinodal curve calculated from Eqs. (2) and (3) are plotted in Fig. 2(b). The parameters used are  $\Delta S = 5.5 \times 10^{-16}$  erg/deg,  $\Delta H = 2.1 \times 10^{-13}$  erg,  $\varphi_0 = 0.0045$ ,  $v_0/Nv = 0.0026$ .

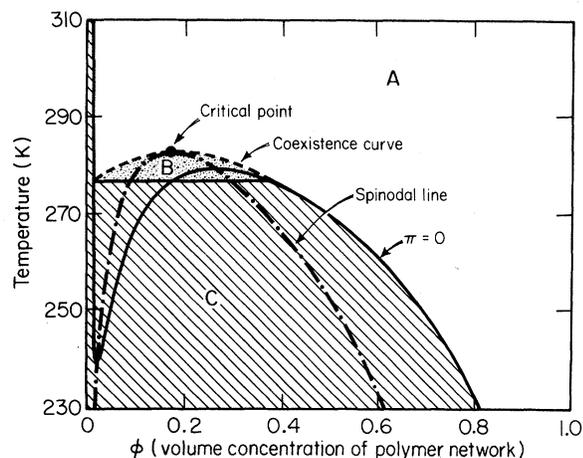


FIG. 3. The phase diagram of a gel (from Ref. 3). If a gel state is represented by a point in region A, the gel is stable; in region B, the gel separates into two gel phases having concentrations represented by two equal-temperature points on the coexistence curve; and in region C, in which the osmotic pressure is negative, the gel shrinks, separating from its fluid, until it reaches the zero-osmotic-pressure line.

We have a qualitative agreement between the theory and the experimental results.

Figure 3 shows the phase diagram of the gel calculated with use of the equation of state, Eq. (1). The way of construction of the phase diagram has been shown in Ref. 3 in detail. If a gel state is represented by a point in region A, the gel is stable; in region B, the gel separates into two gel phases having concentrations represented by two equal-temperature points on the coexistence curve; in region C, in which the osmotic pressure is negative, the gel shrinks, separating from its fluid, until it reaches the zero-osmotic-pressure line.

Now that the existence of the critical point has been demonstrated, it would be very important to study in detail the critical behavior of the gel in its vicinity.

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<sup>1</sup>T. Tanaka, S. Ishiwata, and C. Ishimoto, *Phys. Rev. Lett.* **38**, 771 (1977).

<sup>2</sup>T. Tanaka, *Phys. Rev. A* **17**, 763 (1978).

<sup>3</sup>T. Tanaka, *Phys. Rev. Lett.* **40**, 820 (1978).

<sup>4</sup>D. J. Fillmore and T. Tanaka, to be published.

<sup>5</sup>Reference 1 shows that  $1/I$  is proportional to  $K + 4/3\mu$ , where  $K$  is the bulk modulus and  $\mu$  is the shear modulus of the network. Since  $\mu \ll K$  in the entire temperature range, except very close to the spinodal temperature, we can neglect the contribution of the shear modulus in analyzing the data.

<sup>6</sup>P. J. Flory, *Principles of Polymer Chemistry* (Cornell Univ. Press, Ithaca, N. Y., 1953), p. 576.