

Collapse of Gels and the Critical Endpoint

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Collapse of polyacrylamide gels is observed upon changing temperature or fluid composition. It is explained in terms of mean-field theory based on the extension of Flory's formula for free energy of gels. Theory predicts, and I have observed, existence of a critical endpoint in the phase equilibria.

In this Letter, I report observation of the collapse of the polymer network in polyacrylamide gels. Collapse occurs upon lowering the temperature or upon increasing the acetone concentration of the acetone-water gel fluid mixture. It can be explained in terms of mean-field theory based on the extension of Flory's formula for the free energy of gels. There are essential differences between phase separation of gels and that of binary fluid mixtures due to the covalent crosslinks in the gel polymer network. Theory predicts, and I have observed in polyacrylamide gels, the existence of a critical endpoint when the segment length of the polymer is a certain value.

A gel consists of a crosslinked polymer network immersed in a fluid medium. Covalently crosslinked polyacrylamide in acetone-water mixtures of various compositions was used in the experiments. The gels were prepared as follows: 5 g acrylamide, 0.133 g bisacrylamide, 40 mg ammonium persulfate, and 160 μ l tetramethylethylenediamine (TEMED) were dissolved in water and made up to 100 ml. The solution is poured into glass tubes with diameter 5 mm. It appears to take approximately 1 h for gelation at room temperature. For each tube, a 1-cm segment from the middle of the tube was used. These gels were immersed in acetone-water mixtures. Fluid composition between the inside and outside of a gel is equalized by diffusion in a few hours. Equilibrium, however, is reached only after the gel adjusts its volume, which requires several days at room temperature. The swelling ratio, ϕ^*/ϕ , of the volume fraction occupied by the network in the gel before (ϕ^*) and after (ϕ) the volume change was determined by measuring the volumes of the gel before (V^*) and after (V) the volume change since $\phi^*/\phi = V/V^*$. In our experiments, ϕ^* was 0.05. Figure 1 shows the dependence of the swelling ratio on the acetone concentration in the fluid medium. Solid circles are data for gels left in the gelation tubes for approximately 30 days before the gel fluid was ex-

changed with the acetone-water mixture. Open circles are data for gels left in the tubes for approximately 3 days. The role of this curing time will be discussed later. In gel I there is a discrete transition at an acetone concentration of 41%, whereas in gel II there is a nearly continuous transition at an acetone concentration of 39%. Similar observations were made when the acetone concentration was fixed and the temperature was varied. Figure 2 shows the dependence of the swelling ratio on temperature. The acetone concentration was 42% for gel I and 40% for gel II. We observed again a discrete transition in gel I and a nearly continuous transition in gel II.

In order to understand these phenomena, let us examine theoretically the osmotic pressure, π , of a gel. I use Flory's formula¹ with proper mod-

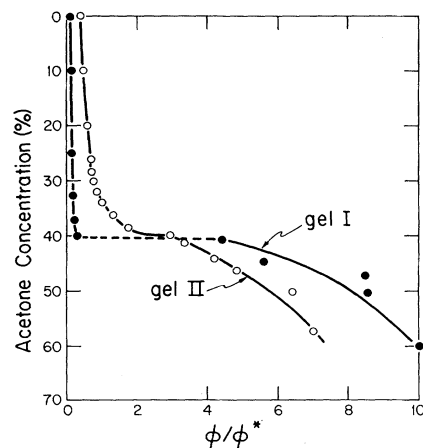


FIG. 1. The swelling ratio of a polyacrylamide gel as a function of the acetone concentration in the acetone-water gel fluid mixtures at 23°C. ϕ^* and ϕ are the volume fraction of the gel before and after the volume change, respectively. Solid circles are data for gel I left in gelation tubes for 30 days before the gel fluid was exchanged with the acetone-water mixture. Open circles are for gel II left in gelation tubes for 3 days.

ifications:

$$\pi = -RT \left\{ \ln(1 - \varphi) + \varphi + \frac{\Theta}{2T} \varphi^2 + \nu_0 \left[\left(\frac{\varphi}{\varphi_0} \right)^{1/3} - \frac{\varphi}{2\varphi_0} \right] \right\}. \tag{1}$$

Since $\varphi \ll 1$ in our experiments, I expand the first term to obtain

$$\pi \approx RT \varphi_0^3 \left[\frac{1}{2\varphi_0} \left(1 - \frac{\Theta}{T} \right) \rho^2 + \frac{\rho^3}{3} + S \left(\frac{\rho}{2} - \rho^{1/3} \right) \right] \text{ (with } \rho \equiv \varphi/\varphi_0, S \equiv \nu_0/\varphi_0^3 \text{ for } \varphi \ll 1), \tag{2}$$

where R is the gas constant, T is the absolute temperature, Θ is the theta temperature¹ and φ_0 is the volume fraction of the uncrosslinked single polymer chain in the absence of interaction among segments in the chain; $\nu_0 = n_0 v_0$ where n_0 is the number of crosslinks per volume of the gel with the volume fraction $\varphi = \varphi_0$, and v_0 is the effective volume of each crosslink unit. The first two terms in Eq. (1) represent the entropy and the third term the enthalpy of mixing of the polymer network and the fluid. The last term represents the excess rubber elasticity of the network due to volume changes of the gel.¹ It is important that the elastic term is generally not a function simply of φ as was given by Flory,¹ but of φ/φ_0 . He assumed that the dry gel satisfies the condition of no polymer interactions¹ ($\varphi_0 = 1$). As we shall see later, however, φ_0 must be much smaller than unity for a gel to undergo collapse. No collapse is possible for a gel with $\varphi_0 \sim 1$.

Equation (2) shows that the shapes of the isotherms (π vs φ) depend on the parameters, φ_0 , ν_0 , and S . The parameter S determines the rela-

tive contribution of the rubber elasticity and the mixing free energy to the osmotic pressure. As we shall see later, the numerical value of S plays an essential role in determining the size of the collapse of a gel. A microscopic interpretation of the parameter S can be seen by the following simple argument. Let the single polymer chain consist of N free-jointed segments of radius a and length b . Then, the rms end-to-end distance of the single polymer is $R \sim N^{1/2}b$. Since R is also the rms distance between neighboring crosslinks,

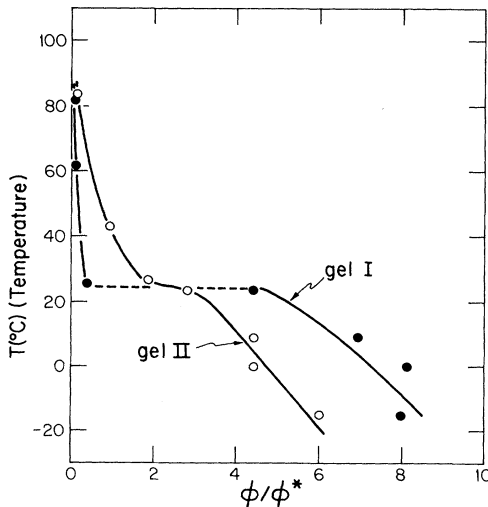


FIG. 2. The temperature dependence of the swelling ratio of the polyacrylamide gels. Solid circles are data for gel I immersed in the acetone-water mixture (42% acetone concentration). Open circles are data for gel II immersed in 40% acetone-water mixture.

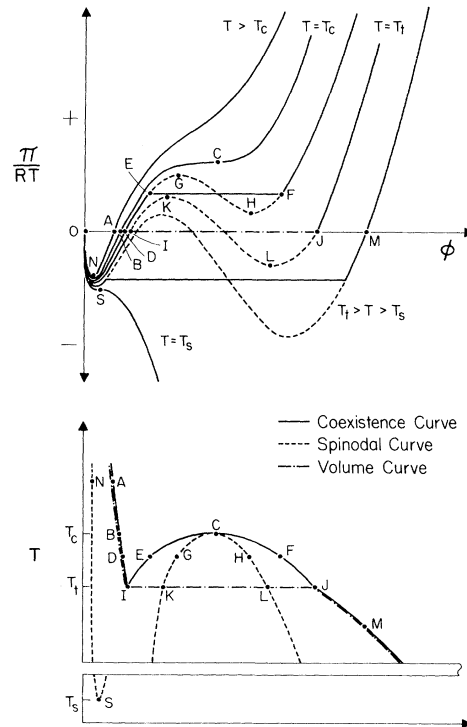


FIG. 3. (a) The osmotic pressure of a gel as a function of the volume fraction of the network at various temperature. The values, $S = 600$, $\varphi_0 = 0.01$, and $\Theta = 400^\circ\text{K}$ were used. T_c denotes the critical temperature (310°K), T_t is the temperature at which collapse occurs (303°K), and T_s is the minimum in the spinodal curve (210°K). (b) The coexistence curve (solid line), the spinodal curve (dotted line), and the volume curve (broken line).

we see that $\nu_0 \sim ba^2/R^3$, and $\varphi_0 \sim Nba^2/R^3$. From these relations, $S \sim (b/a)^4$. Figure 3(a) shows the isotherms at various temperatures calculated for $S = 600$ ($b/a \sim 5$), $\varphi_0 = 0.01$ and $\Theta = 400^\circ\text{K}$. From these isotherms one can obtain the relation between φ and T at phase boundaries. Two conditions are required for stable phases. First, the osmotic pressure must be positive or zero. If it is negative, the gel separates into two phases for which $\pi = 0$. These correspond to pure fluid and a gel with the volume fraction for which $\pi = 0$. These conditions provide the points in the descending curve of Fig. 3(a), for example, *A*, *B*, *D*, and *I*. Second, even if $\pi \geq 0$, along each isotherm the gel must satisfy the condition of thermodynamic stability. When the isotherm contains van der Waals loops the stability conditions are obtained by using the Maxwell construction.² As is well known from this construction, values of φ along the horizontal Maxwell line are of unstable states.² The endpoints of the Maxwell line [e.g., points *E* and *F* in Fig. 3(a)] represents volume fractions along the coexistence curve. The values of volume fractions between these points and the maximum and the minimum of the van der Waals loops are of metastable states. The maximum and the minimum of the loops fix the volume fractions along the spinodal curve, within which no metastability is allowed.² On the spinodal curve the amplitude and relaxation time of concentration fluctuations diverge, as has recently been observed in polyacrylamide gels using photon correlation spectroscopy.^{3,4} Using these considerations it is possible to construct the coexistence curve and spinodal curve shown in Fig. 3(b).

The volume curve, which represents the equilibrium volumes for different temperatures, can be also derived from these isotherms. It is defined by the condition, $\pi = 0$, which assures the equilibrium between the gel and the surrounding fluid. π is zero at the intersect of each isotherm with the φ axis [e.g., *A* for $T > T_c$ and *B* for $T = T_c$ in Fig. 3(a)]. The volume curve obtained in this way is shown in Fig. 3(b), and shows a discrete transition at a temperature T_i at which the Maxwell line in the isotherm touches the φ axis.

All the elements required for a complete phase diagram for a gel is contained in Fig. 3(b). At any temperature and the volume fraction in the region between the coexistence curve and the volume curve the gel will separate into two different gels having volume fractions determined by the intersects of the $T = \text{const.}$ line with the coexistence curve. For values of φ and T beneath the

volume curve, the gel will also separate into those phases determined by the intersects of the $T = \text{const.}$ line with the volume curve and the T axis (pure fluid).

I believe that the experimentally observed collapse of gel I obtained by lowering the temperature shown in Fig. 2 corresponds precisely to the volume curve represented in Fig. 3(b). Also, I believe that the experimentally observed collapse of the gel upon increasing the acetone concentration (gel I in Fig. 1) corresponds to the volume curve, with the understanding that the temperature dependence of the osmotic pressure [Eq. (2)] enters as Θ/T . In the experiments of changing acetone concentration Θ changes, whereas in the temperature experiments T changes. The other parameters in Eqs. (1) and (2), that is, ν_0 and φ_0 , characterize the network structure and are independent of acetone concentration. Change in acetone concentration only changes Θ (100°C change in T corresponds to 50% change in acetone concentration). In fact, in order to observe the collapse at room temperature, Θ must be $\sim 130^\circ\text{C}$. Normally, for pure water Θ is $\sim 30^\circ\text{C}$ and, therefore, acetone-water mixture was used to raise Θ .

Having interpreted the collapses of gel I, let us now consider the volume curves of gel II. Careful examinations of Eq. (2) show that the critical points exist only for $S \geq S_e \equiv (3/5)(40/9)^4$. As the value of S decreases and approaches S_e the size of the collapse (e.g., $\varphi_J - \varphi_I$) decreases and becomes zero at $S = S_e$ (Fig. 4). Below S_e the volume curve is no longer discrete and there is no critical point. The critical point terminates at $\varphi = \varphi_e \equiv \frac{40}{9}^{3/2} \varphi_0$ and $T = T_e \equiv \Theta / (1 - \frac{34}{15} \varphi_e)$, which

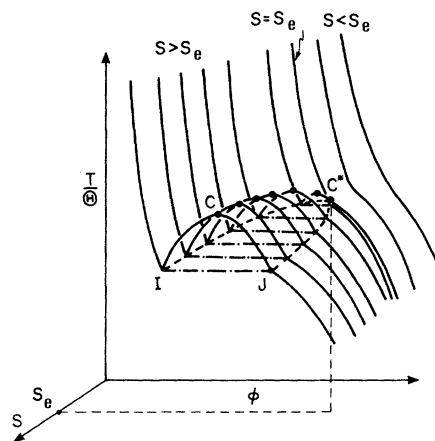


FIG. 4. The dependence of equation of state on the parameter S . At $S = S_e$ the critical point disappears (point c^*). This corresponds to the critical endpoint.

may be called the critical endpoint.⁵⁻⁷ I believe that I have observed the critical endpoint in the volume curves of gel II: at 39% acetone concentration in Fig. 1 and at 25°C in Fig. 2. I now examine why S can be expected to be different for gel I and gel II. Both were prepared using water as gel fluid in precisely the same way. The gel network began to form in both samples within 10 min after the solution was made. However, the time required for the formation of all the possible crosslinks is quite long, because uncrosslinked branches move more slowly and the likelihood of finding another uncrosslinked end is small. Thus, the number of uncrosslinked branches and hence b/a or the value of S changes slowly in time. The value of S is fixed in time by the washing away of the catalyst TEMED during the exchange of the gel fluid with acetone-water mixture. This latter takes only a few hours. In gel I the exchange took place 30 days after preparation, whereas in gel II it occurred only 3 days after preparation. It is reasonable that gel I and gel II have markedly different values of S . In fact, I estimate that $S \sim 1000$ for gel I and $S \sim 55$ for gel II. The success of the present conceptual framework for the understanding of the collapse of gels makes it desirable to conduct further investigation of the quantitative dependence of S on curing time and catalyst concentration. It is also of great interest to study the critical behaviors of gels near the critical endpoint.

It should be noted that there are theoretical predictions of the collapse of a single polymer in a solution.⁸⁻¹¹ Mazur and McIntyre¹² reported a decrease in the radius of gyration of polystyrene chain in cyclohexane using scattered light intensity measurements. There are possible applications of the present study to physiological phe-

nomena such as vitreous collapse in retinal detachment.¹³

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