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Temperature Hysteresis and Morphology of Volume Phase Transition of Gels

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Temperature hysteresis is theoretically studied for the volume phase transition of chemically cross-linked gels. The condition of the appearance of a "surface skin layer" of new phase is formulated and calculated. The result predicts that the surface skin layer is destabilized near the critical point of the transition due to volume fluctuations. We discuss the relevance of this result to inaccessibility to the Ising critical point [L. Golubović and T. C. Lubensky, Phys. Rev. Lett. **63**, 1082 (1989)].

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Volume phase transition in chemically cross-linked polymer gels (chemical gels, for short) has been studied by many people both experimentally and theoretically [1]. The transition between a swollen phase and a shrunken phase looks apparently like the liquid-gas transition in fluids, where the density field characterizes the transition. The volume phase transition of gels, however, has several distinguished features due to elastic coupling between the density and shear deformation. At the critical point, the second order transition where the bulk osmotic modulus K vanishes does not exhibit Ising critical behavior [2]. This is due to the long-range interaction among the local densities, mediated by the shear deformation [3] caused by local swelling or shrinking. (Experimentally, however, the magnitude of the shear modulus at the critical point seems to be a subtle issue [4, 5].) On the other hand, far from the critical point, the coexistence between the shrunken phase and swollen phase in the bulk gel shows a spongelike domain structure [6], and this structure is quite stable due to the elastic coupling, though rigorously the system is in a metastable state. In this Letter we focus on the effect of this coupling on the transition temperature. Hysteresis is a common feature of first order transitions. The effect of uniaxial loading on the transition temperature was measured and analyzed [7], but the link between this effect and the temperature hysteresis has been overlooked. The width of hysteresis is bounded either by the spinodal instability ($K + \frac{4}{3}\mu = 0$) or by the bulk instability ($K = 0$), μ and K being shear and bulk moduli , respectively. These instabilities correspond to different modes of deformations as long as $\mu \neq 0$ [8]. But these criteria give only upper bounds of hysteresis, as we describe in detail below. To make the following discussion clear, we shall define the time domain of our interest. We recall that, practically, we can never observe the thermally activated nucleation in the bulk of gels near the (rigorous) thermodynamic transition point [8]. Unlike the systems with short-range interaction [9], energy cost in the activation energy is not governed by the interfacial energy, but by the shear deformation energy which accompanies the local change of the density of gel. Because of the absence of characteristic length in the elasticity theory, the scaling argument [6, 8] shows that the activation energy of nucleation in the bulk is proportional to the volume of gel and is therefore macroscopic. Though we consider only the short-time phenomena in the above sense, we also assume that the time domain is large enough that the system is always in osmotic balance with surrounding solvent. The osmotic relaxation occurs through the permeation of solvent [10], whose relaxation time is typically several tens of minutes for spherical or rodlike gels with a diameter ~ 1 mm [11]. We note that for a system in a single-phase state, the osmotic balance implies also isotropic deformation. An important experimental observation is that in the study of the deswelling transition of a spherical gel [11], where the temperature hysteresis was also measured, the transition begins by the appearance of a new phase domain on the surface of the gel ("surface skin layer"). We develop an analysis on how the observed transition temperature is related with the formation of the surface skin layer. Then we extend our argument to the transition which begins from the edges or the vertices of the sample. The present consideration is fairly general for the systems with long-range interaction, and among those systems the gel is one of the most suitable systems to study, because the thermodynamic states of gels can be observed and controlled by many experimental methods, either physically or chemically, and also because the dynamics within gels occurs on moderate time scales (cf., in metal alloys the global change of composition takes practically an infinite time). For the moment we consider only uniaxial deformations with the axis being normal to the gel surface, and describe them by the transversal and the longitudinal (local) elongation ratios, λ_t and λ_l, respectively, measured from an appropriate isotropic and homogeneous reference state [12]. We note that the deformation of a surface skin layer is asymptotically uniaxial in the very proximity of the transition, even though the gel surface has a finite curvature.

In the numerical calculation which we will show later, we employ the Flory model free energy [13]. The free energy per unit mass of monomers, α', is a function of the Flory-Huggins parameter χ and the ion content per

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chain of gel network, f, as well as λ_t and λ_l. Although the qualitative result will be independent of the present choice of model, an important point is that the model includes those variables like χ and f which play the same roles as pressure and temperature, respectively, in the liquid-vapor transition [14]. We apply the interface condition of the gel [15] to the present geometry, in which the new phase with $(\lambda_t, \lambda_l) = (\lambda, \lambda_s)$ coexists with the original isotropic phase with $(\lambda_t, \lambda_l) = (\lambda, \lambda)$. Noting also the osmotic balance with surrounding solvent, the condition becomes

$$\left.\frac{\partial\alpha'}{\partial\lambda_l}\right|_{(f,\chi,\lambda,\lambda)} = \left.\frac{\partial\alpha'}{\partial\lambda_l}\right|_{(f,\chi,\lambda,\lambda_s)} = 0\,, \tag{1}$$

$$\alpha'(f,\chi,\lambda,\lambda) = \alpha'(f,\chi,\lambda,\lambda_s), \tag{2}$$

where the notation $(\cdot)|_{(f,\chi,\lambda,\lambda_s)}$, etc., means to evaluate the function $(\cdot)$ at $(f,\chi,\lambda_t,\lambda_l) = (f,\chi,\lambda,\lambda_s)$, etc. Equations (1) and (2) define in the (f,χ) plane a curve which we shall call the *uniaxial transition curve.* It is schematically shown by a solid curve in Fig. 1(a). In order to make it easier to grasp the topological structure of the curves and of the manifolds which we will introduce below [Figs. 1(a), 1(b), and 1(c)], we exaggerated a portion of smaller values of χ as compared with the result of our numerical calculation (see below and Fig. 2). In Fig. 1(a) we have also shown two other curves: The broken curve shows the spinodal at which the uniaxial osmotic modulus $K + \frac{4}{3}\mu$ vanishes, or equivalently

$$\left.\frac{\partial\alpha'}{\partial\lambda_l}\right|_{(f,\chi,\lambda,\lambda)} = \left.\frac{\partial^2\alpha'}{\partial\lambda_l^2}\right|_{(f,\chi,\lambda,\lambda)} = 0 \tag{3}$$

under osmotic balance. The dotted curve in Fig. 1(a) shows the bulk instability $(K = 0)$, along which $\partial\{\alpha'\,|_{(f,\chi,\lambda,\lambda)}\}/\partial\lambda = \partial^2\{\alpha'\,|_{(f,\chi,\lambda,\lambda)}\}/\partial\lambda^2 = 0$ holds. The two branches of bulk instability meet at the (real) critical point [2], where $\partial^3\{\alpha'\,|_{(f,\chi,\lambda,\lambda)}\}/\partial\lambda^3$ vanishes.

We see from Fig. 1(a) that the (uniaxial) transition temperature on which χ depends shows hysteresis. Using (1) and (2) we can identify on this curve the portion representing the transition from an isotropically swollen phase to a uniaxially shrunken phase $(\lambda > \lambda_s)$ and the portion representing the transition from an isotropically shrunken phase to a uniaxially swollen phase $(\lambda < \lambda_s)$. The uniaxial transition curve and the spinodal touch with each other. This point, where $\partial^3\alpha'/\partial\lambda_l^3\,|_{(f,\chi,\lambda,\lambda)}$ vanishes, can be identified with the inaccessible, or "hidden," Ising critical point of the gel [2] (see also [3]); we can check it by evaluating the Ising-like part of the effective Hamiltonian of [2] using the tree approximation. The inaccessibility of the Ising critical point is generally due to the presence of a certain unstable fluctuation mode as clarified in [3]. On the other hand, we see in Fig. 1(a) that the uniaxial transition curve touches with the two branches of the bulk instability curve. This observation,

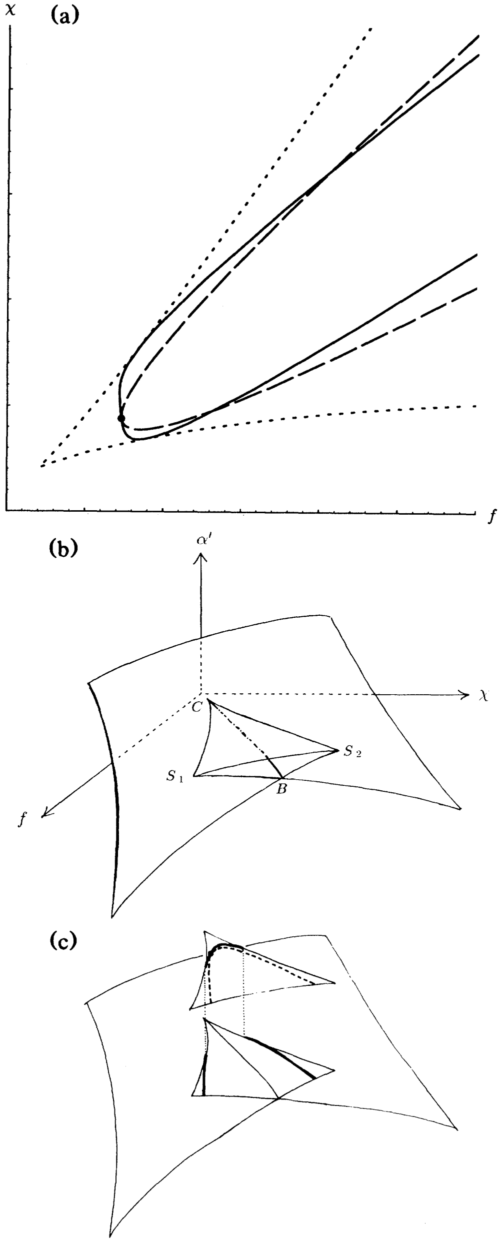

FIG. 1. (a) In the plane of the Flory-Huggins parameter χ and the ionic content incorporated into the network, f, we show what we call the uniaxial transition curve (the solid curve) on which a uniaxially deformed phase coexists spatially with an isotropic phase under osmotic equilibrium. The dashed curve shows the spinodal on which an isotropic phase in osmotic equilibrium becomes unstable against uniaxial deformation. The "hidden" Ising critical point is marked by the thick dot. (b) A "swallow-tail" shaped manifold in the space of (f,χ,α'), representing the isotropic states in osmotic equilibrium, where α' is the free energy per unit mass of monomers of gel. (c) The uniaxial transition curve (thick solid curve) and the spinodal curve (thick dashed curve) are drawn on the same manifold as in (b). The part S_1CS_2 which corresponds to unstable states has been lifted out for easier viewing.

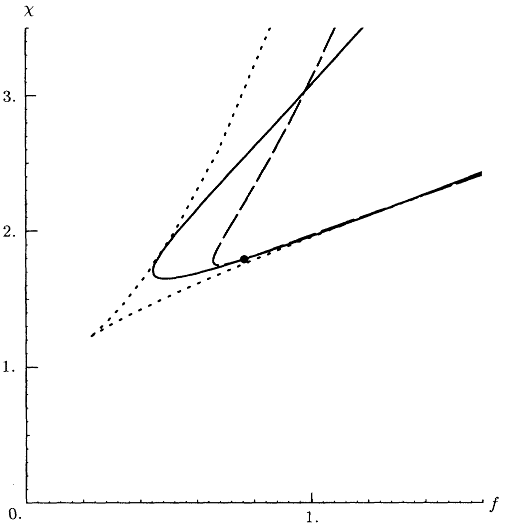

FIG. 2. The result of model calculation of transition curves and instability curves. The assignments of the curves are the same as in Fig. 1(a). The hidden Ising critical point is at $(f,\chi) = (0.77, 1.79)$ (the thick dot).

as well as the fact that people observed the surface skin layer [11], leads us to anticipate a crossover of the uniaxial transition through the bulk instability from an unstable manifold including the hidden Ising critical point to a metastable manifold.

We could verify this by studying in the (f,χ,α') space the manifold representing the isotropic states of the gel under osmotic equilibrium, i.e., $\partial\{\alpha' |_{(f,\chi,\lambda,\lambda)}\}/\partial\lambda = 0$; see Fig. 1(b). First we briefly explain this "swallow-tail" shaped manifold. In the region of (f,χ), where α' has three values, the highest α' value corresponds to the unstable state with $K < 0$ and the remaining two are metastable ones with $K > 0$. (As discussed before, the distinction between metastable and stable is immaterial in the time domain of our consideration.) The boundaries of the unstable manifold, CS_1 and CS_2, correspond to the bulk instability ($K = 0$). The intersection CB in Fig. 1(b) is the so-called "triphasic-equilibrium" [12], the equilibrium in a rigorous thermodynamic sense among two isotropic phases and the surrounding solvent. In our time domain, however, such coexistence can be observed only in a long rodlike gel [16].

From (1) we note that both the uniaxial transition curve and the spinodal curve in Fig. 1(a) can be drawn *on* the manifold of Fig. 1(b) [17]. They are shown in Fig. 1(c). There, for ease of viewing, the unstable submanifold S_1CS_2 is lifted above the rest of the manifold. We see that the whole spinodal curve is on the unstable manifold, implying that spinodal instability is never attained in our time domain of consideration. On the other hand, the uniaxial transition curve lies partly on the unstable manifold with $K < 0$ and partly on the metastable manifolds with $K > 0$. The vertical thin dotted lines in Fig. 1(c) show the location at which this curve "crosses over" from the metastable manifold to the unstable one through $K = 0$.

A numerical calculation was done using the Flory model free energy, $\alpha'/k_BT = v_1^{-1}(\phi_0/\phi)\ [(1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)] + \frac{1}{2}\nu_0[2\lambda_t^2 + \lambda_l^2 - (1+2f)\ln(\phi_0/\phi)]$, where the volume fraction of monomers, ϕ, is given by $\phi_0/(\lambda_t^2\lambda_l)$, with ϕ_0 being the volume fraction of the reference state [12]. v_1 is the specific volume of solvent, and ν_0 is the number of chains per unit volume of gel in the reference state. We have chosen the same parameter values as those having been used to fit the experimental phase diagram of N-isopropylacrylamide (NIPA)/sodium-acrylate gel in pure water [11, 18]: $\phi_0 = 0.07$, $v_1 = 3 \times 10^{-26}\ell$, and $\nu_0 = 1.2 \times 10^{24}\ell^{-1}$. The result is shown in the (f,χ) plane (Fig. 2). Though the portion of smaller χ values is rather crowded, the topological structure of the curves is the same as that in Fig. 1(a).

We can draw the following predictions from the analysis above. If the ionic content, f, is not far above the critical point value, the transition begins without forming the surface layer of a new phase, since on the metastable manifold in Fig. 1(b) the state points of a given f do not meet with the uniaxial transition curve. On the other hand, for strongly charged polyelectrolyte gel, or for large enough values of f, the state points of a given f reach the uniaxial transition curve below the stability limits CS_1 or CS_2, and therefore the transition takes place through the formation of a surface layer of new phase, as it was observed in [11].

We note that our analysis on the morphology of transition is not an exhaustive one in the following two aspects: the possibility of a surface layer which is nonuniform along the lateral direction of the surface and the possibility of a transition that begins at nonplanar surfaces. Concerning the first point, we studied the stability of these new phases against the spatial undulation of the free surface of the gel (buckling instability) [8, 15, 19] , though the details are not shown here. The result was that, for our chosen parameter values, the shrunken surface layer that appears from the swollen phase is always stable against buckling along the uniaxial transition curve, while the swollen surface layer appearing on the isotropically shrunken phase is always unstable against buckling, as experimentally observed [20]. It implies that, in Fig. 2, the lower part of the transition curve should be modified toward the larger χ values. Near the critical point, experiments [21] suggest the formation of oblate dropletlike or needlelike domain on the surface of the gel. The linear stability analysis does not predict such domains [8] and, therefore, nonlinear analysis like the one given above should be done in the future. Also a systematic experimental study of the surface morphology of gels near and/or off the critical point is strongly encouraged.

On the other hand, about the possibility of transition from nonplanar surfaces, we can generalize qualitatively the analysis presented above to the cases where the new domain is formed on the edges or the vertices of a sample of gel. (As noted earlier, finite curvature of the sample surface has no effect on the transition condition.) Let us assume that a sample of gel has the edges with dihedral angle Θ ($< \pi$) or the vertices with solid angle Ω ($< 2\pi$). The transition conditions of such geometries can be formally written. They are in a different form from Eqs. (1) and (2), including Θ or Ω as dimensionless parameters. Since displacements in a sample are less constrained near these edges or vertices, we expect that the transition of such a sample begins at these singularities rather than at a smooth surface of the sample. In this case the transition temperature should depend on the geometrical parameters Θ (or Ω). We may expect that these functions of Θ or Ω are the monotonic functions which interpolate between the uniaxial transition temperature and the triphasic-equilibrium temperature mentioned before. For example, the deswelling transition of a cubic sample of gel will be observed at a temperature which is between that of the spherical sample and that of the tetrahedral sample.

This apparently incredible prediction seems, however, to explain successfully the following experimental observation. In the experiment of a thin rodlike gel [16], a slight change of temperature causes the growth of a stable phase domain along the rod axis, i.e., from the ends toward the center of the rod, but no growth was observed in the radial direction, i.e., from the surface towards the axis of the rod. Suppose that a rodlike sample of NIPA/sodium acrylate gel is first swollen in water until it reaches equilibrium. If, then, the temperature is raised to above a certain threshold value, the shrinking transition first begins at the circular edges of the ends of the rod. (NIPA is a thermoshrinking gel.) Once the transition takes place, these domains grow towards the cylinder axis of the rod until they form almost isotropic domains near the ends of the rod. Since the (rigorous) thermodynamic transition temperature must be lower than the threshold temperature mentioned just before, these isotropic domains on the ends grow and gradually replace the isotropic swollen domain in the middle of the rod. However, on the side surface of the swollen domain, the formation of a surface layer of shrunken phase is still suppressed, as experimentally observed [16], so long as the temperature is kept below the uniaxial transition temperature.

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[1] For a review, see Phase Transition in Gels, edited by K. Dušek (Springer, Berlin, to be published).
[2] L. Golubović and T. C. Lubensky, Phys. Rev. Lett. **63**, 1082 (1989).
[3] A. I. Larkin and S. A. Pikin, Zh. Eksp. Teor. Fiz. **56**, 1664 (1969) [Sov. Phys. JETP **29**, 891 (1969)].
[4] Y. Li and T. Tanaka, J. Chem. Phys. **90**, 5161 (1989).
[5] M. Rubinstein, A. Ajdari, L. Leibler, and J. Bastide, Makromol. Chem. Macromol. Symp. **62**, 61 (1992).
[6] K. Sekimoto, N. Suematsu, and K. Kawasaki, Phys. Rev. B **39**, 4912 (1989).
[7] S. Hirotsu and A. Onuki, J. Phys. Soc. Jpn. **58**, 1508 (1989).
[8] A. Onuki, Phys. Rev. A **38**, 2192 (1988).
[9] For a review, see J. D. Gunton, M. San Miguel, and P. S. Sahni, *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. 8, p. 267.
[10] T. Tanaka, L. O. Hocker, and G. B. Benedek, J. Chem. Phys. **59**, 5151 (1973).
[11] E. S. Matsuo and T. Tanaka, J. Chem. Phys. **89**, 1695 (1988).
[12] B. Erman and P. J. Flory, Macromolecules **19**, 2342 (1986).
[13] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University, Ithaca, NY, 1953), pp. 595–602.
[14] K. Sekimoto, KEK proceedings 92-10, 6 (1992) (in Japanese).
[15] K. Sekimoto and K. Kawasaki, Physica (Amsterdam) **154A**, 384 (1989).
[16] S. Hirotsu, J. Chem. Phys. **88**, 427 (1988).
[17] We can easily show that the definition of osmotic equilibrium, $\partial\{\alpha'|_{(f,\chi,\lambda,\lambda)}\}/\partial\lambda = 0$ is equivalent to the previous definition $\{\partial\alpha'/\partial\lambda_l\}|_{(f,\chi,\lambda,\lambda)} = 0$ in Eq. (1).
[18] S. Hirotsu, Y. Hirokawa, and T. Tanaka, J. Chem. Phys. **87**, 1392 (1987).
[19] K. Sekimoto and K. Kawasaki, J. Phys. Soc. Jpn. **56**, 2997 (1987).
[20] T. Tanaka, S.-T. Sun, Y. Hirokawa, S. Katayama, J. Kucera, Y. Hirose, and T. Amiya, Nature (London) **325**, 796 (1987).
[21] S. Hirotsu and A. Kaneki, in *Dynamics of Ordering Processes in Condensed Matter*, edited by S. Komura and H. Furukawa (Plenum, New York, 1987), p. 481.