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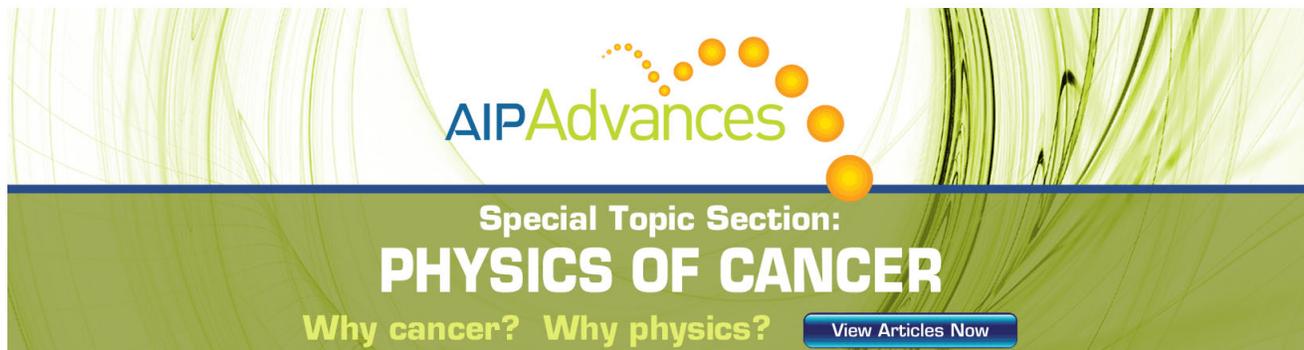
Effects of strongly selective additives on volume phase transition in gels

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We investigate volume phase transition in gels immersed in mixture solvents, on the basis of a three-component Flory-Rehner theory. When the selectivity of the minority solvent component to the polymer network is strong, the gel tends to shrink with an increasing concentration of the additive, regardless of whether it is good or poor. This behavior originates from the difference of the additive concentration between inside and outside the gel. We also found the gap of the gel volume at the transition point can be controlled by adding the strongly selective solutes. By dissolving a strongly poor additive, for instance, the discontinuous volume phase transition can be extinguished. Furthermore, we observed that another volume phase transition occurs far from the original transition point. These behaviors can be well explained by a simplified theory neglecting the nonlinearity of the additive concentration. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4732857]

I. INTRODUCTION

Swelling behavior of a polymer network was first investigated by Flory and Rehner.[1] On the basis of this work, discontinuous volume phase transition (VPT) of gels was predicted theoretically.[2] Hence, the VPT has received much attention from both scientific and industrial viewpoints.[3–5] In various types of gels, addition of solutes into the solvent often plays very important roles in their volume change.[3–6] For example, the VPT was first realized in a polyacrylamide (PAA) gel immersed in a mixture of water and acetone.[3] In this experiment, the solvent quality, or χ parameter, is controlled by changing the volume fraction of the acetone. It is also well known that addition of salts dramatically affects the behaviors of ionic gels.[7–9] Furthermore, a nonioninc hydrated gel such as poly(*N*-isopropylacrylamide) gel (NIPA) changes its volume discontinuously. In the hydrated gels, the VPT is attributed to temperature-dependence of hydrogen bondings of the polymer network.[6,10] It has been reported that its VPT is affected by adding salts[11–14] and other additives.[15–21] Although some microscopic theories are devoted to explain the VPT,[21–24] there remain unresolved problems. For instance, the transition point is lowered by dissolving salts,[12–14] whereas it is raised with surfactants.[16] The difference between these additive effects remains unclear. Interestingly, is was reported that the discontinuous transition of the NIPA gel disappears when NaI is dissolved.[14] We consider that a macroscopic description will also help us to understand these unresolved phenomena.

It is often assumed that the composition of a mixture solvent is same in and out of a gel. This assumption is referred to as single liquid approximation (SLA). The SLA is experimentally confirmed in a NIPA gel in a dimethyl sulfoxide-water mixture, for instance.[25] However, the compositions of mixture solvents are not necessarily homogeneous.[25–27] There, the difference of the composition between the interior and exterior of the gel would lead to a dramatic effect on its volume change. Some extended Flory-Huggins models dealing with a polymer network and two species of solvent molecules were developed to investigate the volume change of a polymer network in a mixture solvent.[26–30] In these theories, the volume change is characterized by the compositions of the three components and three χ parameters. They were studied systematically for fixed sets of the χ parameters. Usually, the χ parameters in polymer systems depend on environment parameters such as temperature. Since it is quite complicated to incorporate the temperature-dependences of the χ parameters, the swelling behavior in mixture solvents has not been fully understood.

Recently, the effects of solutes with strong selective solvation on phase behaviors of a water-oil mixture was investigated.[31–33] By dissolving a very small amount of strongly hydrophobic solute into the water-oil mixture, the oil-rich phase containing the solute is precipitated even in the one-phase region. This finding implies that such solutes would affect the VPT in gels.

The aim of this study is to clarify the effect of the additives on the VPT in gels, based on a simple theoretical argument. In particular, we focus on the cases, in which one of the solvent components has strong selectivity to the polymer network. So far, the VPT is realized in hydrophilic gels (polyelectrolyte and hydrated ones). Our model is based on a simple Flory-Huggins theory, so that it is also applicable to hydrophobic polymer networks. Then, we hope our model will help one to find VPT in other new types of gels.

II. MODEL FREE ENERGY

Swelling behaviors of gels are well described by the Flory-Rehner theory.[1] The free energy F consists of a mixing part F_{mix} and an elastic part F_{el} as

$$F = F_{\text{mix}} + F_{\text{el}}. \tag{1}$$

For a gel immersed in a mixture solvent, the mixing free energy F_{mix} is given by[26–28,30,32]

$$F_{\text{mix}} = k_{\text{B}} T v_0^{-1} [V_{\text{g}} f(\phi_{1\text{g}}, \phi_{2\text{g}}, \phi_3) + V_{\text{s}} f(\phi_{1\text{s}}, \phi_{2\text{s}}, 0)], \tag{2}$$

where k_B is the Boltzmann constant and T is the temperature. V_g and V_s are the volumes of the interior and exterior of the gel, respectively. In this model, we assume that the volumes of each monomeric unit of the polymer network and the solvent molecules are equal to a characteristic volume v_0 for simplicity. $f(\phi_1, \phi_2, \phi_3)$ is the Flory-Huggins type mixing free energy of the ternary system as[34]

$$f(\phi_1, \phi_2, \phi_3) = \phi_1 \ln \phi_1 + \phi_2 \ln \phi_2 + \sum_{i<j} \chi_{ij} \phi_i \phi_j. \quad (3)$$

Here, ϕ_1 and ϕ_2 are the volume fractions of the first and second components of the mixture solvent, respectively. In Eq. (2), ϕ_{ig} and ϕ_{is} stand for the volume fraction of the ith component ($i = 1, 2$) in and out of the gel. ϕ_3 is the volume fraction of the polymer network. Since all the polymer chains are chemically connected forming a single network, the polymers are not dissolved outside the gel, that is, $\phi_{3s} = 0$. In Eq. (3), the first two terms stem from the translational entropy of the solvent molecules. Here, the translational entropy of the network is neglected. The last term is the interaction energy among the solvent molecules and the monomeric units of the network. χ_{ij} is the interaction parameter between the ith and jth components.

We employ Flory's rubber elasticity as[35]

$$F_{el} = \frac{1}{2} k_B T \nu V_{g0} \left\{ \sum_{k=x,y,z} \gamma_k^2 - 3 - 2B \ln(\gamma_x \gamma_y \gamma_z) \right\}, \quad (4)$$

where V_{g0} is the volume of the gel in a reference state, ν is the density of cross linking points in the reference state, and γ_k is the elongation ratio in the k-axis ($k = x, y, z$). B is a nonlinear elastic coefficient. In polyelectrolyte gels, the translational entropy of the counter-ions is renormalized into B as $B + b$, where b is the number of the dissociable monomeric unit per effective chain. In this study, however, we do not consider the electric charges explicitly. In the case of isotropic swelling, the elongation ratio is coupled with the volume fraction of the polymer network as

$$\gamma_k = \left(\frac{V_g}{V_{g0}} \right)^{1/3} = \left(\frac{\phi_{30}}{\phi_3} \right)^{1/3}, \quad (5)$$

where ϕ_{30} is the volume fraction of the network in the reference state. Therefore, the elastic energy Eq. (4) is rewritten by a function of ϕ_3 as,

$$F_{el} = \frac{1}{2} k_B T \nu V_{g0} \left\{ 3 \left(\frac{\phi_{30}}{\phi_3} \right)^{2/3} - 2B \ln \left(\frac{\phi_{30}}{\phi_3} \right) \right\}. \quad (6)$$

We impose the incompressible conditions for both in and out of the gel,

$$\phi_{1g} + \phi_{2g} + \phi_3 = 1, \quad (7)$$

$$\phi_{1s} + \phi_{2s} = 1. \quad (8)$$

Here, we define a grand potential as

$$\Omega = F_{mix} + F_{el} - \mu_2(V_g \phi_{2g} + V_s \phi_{2s}) + \kappa(V_g + V_s), \quad (9)$$

where μ_2 and κ are Lagrange multipliers to conserve the amount of the second component and the total volume. The

equilibrium state is characterized by minimizing Ω,

$$\frac{\partial \Omega}{\partial \phi_{2g}} = \frac{\partial \Omega}{\partial \phi_{2s}} = 0. \quad (10)$$

$$\frac{\partial \Omega}{\partial V_g} = \frac{\partial \Omega}{\partial V_s} = 0, \quad (11)$$

Then, we obtained the equilibrium conditions

$$\tilde{\mu}(\phi_{2g}, \phi_3) = \tilde{\mu}(\phi_{2s}, 0) \left(= \frac{v_0 \mu_2}{k_B T} \right), \quad (12)$$

$$\frac{k_B T}{v_0} (\tilde{\Pi}_0 + \tilde{\Pi}_{ad} + \tilde{\Pi}_{el}) = 0, \quad (13)$$

where $\tilde{\mu}$ is the reduced chemical potential given by

$$\tilde{\mu}(\phi_2, \phi_3) = \ln \frac{\phi_2}{1 - \phi_2 - \phi_3} + \chi_{12}(1 - 2\phi_2 - \phi_3) + (\chi_{23} - \chi_{31})\phi_3. \quad (14)$$

Equations (12) and (13) represent the balances of the chemical potential for the second component and the osmotic pressure, respectively.

$\tilde{\Pi}_0$ is a part of the osmotic pressure for the gel without the second solvent component. It stems from the mixing free energy and given by

$$\tilde{\Pi}_0 = -\phi_3 - \chi_{31}\phi_3^2 - \ln(1 - \phi_3). \quad (15)$$

$\tilde{\Pi}_{el}$ is the contribution of the elasticity as

$$\tilde{\Pi}_{el} = -\nu v_0 \left\{ \left(\frac{\phi_3}{\phi_{30}} \right)^{1/3} - B \left(\frac{\phi_3}{\phi_{30}} \right) \right\}. \quad (16)$$

If the solvent does not contain the additive $\phi_2 = 0$, the balance of the osmotic pressure is expressed by $\tilde{\Pi}_0 + \tilde{\Pi}_{el} = 0$.

$\tilde{\Pi}_{ad}$ is the contribution of the second component and is given by

$$\tilde{\Pi}_{ad} = -\ln \left(1 - \frac{\phi_{2g}}{1 - \phi_3} \right) + \ln(1 - \phi_{2s}) - \chi_{12}(\phi_{2g}^2 - \phi_{2s}^2) + G\phi_{2g}\phi_3, \quad (17)$$

where $G = \chi_{23} - \chi_{31} - \chi_{12}$ is a parameter describing the affinity of the second component to the polymer network. $\tilde{\Pi}_0$ and $\tilde{\Pi}_{ad}$ come from the mixing free energy F_{mix}. If $G < 0$ and $|G| \gg 1$, the additive tends to be adsorbed selectively to the polymer network. If $G \gg 1$, on the other hand, the additive would be expelled from the gel.

In this study, we assume that the binary solvent is completely mixed outside the gel. We note that the volume of the equilibrated gel does not change if we add more mixture solvent whose composition is equal to the equilibrated outer solvent. Hence, we take a limit of $V_s/V_g \to \infty$ with fixing ϕ_{2s}, so that ϕ_{2s} is uniquely determined for a fixed μ_2. Hereafter, we use ϕ_{2s} as a control parameter.
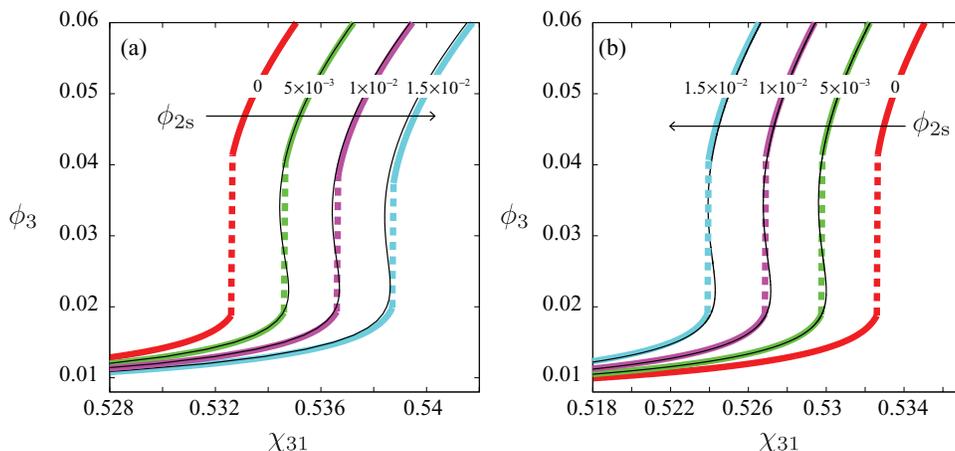
FIG. 1. The swelling curves of a gel immersed in a mixture solvent. We set $\phi_{30} = 1.0 \times 10^{-2}$, $\nu v_0 = 1.0 \times 10^{-5}$, $B = 1.15$, and $\chi_{12} = 0.0$. In the absence of additives, the gel undergoes volume phase transition with increasing χ_{31}. We dissolve solutes of $\chi_{23} = -1.0$ (pro-gel) in (a) and $\chi_{23} = 1.0$ (anti-gel) in (b). The black solid lines are calculated from Eq. (21).

III. RESULTS AND DISCUSSIONS

A. The first volume phase transition

We numerically study the effects of additives on volume changes of gels. First, we focus on the cases, in which the gel can undergo VPT without additives. We set $\phi_{30} = 1.0 \times 10^{-2}$, $\nu v_0 = 1.0 \times 10^{-5}$ and $B = 1.15$. The effective chain polymerization is $N = \phi_{30}/\nu v_0 \gg 1$ and $\phi_{30} \sim N^{-1/2}$.[26]

We vary χ_{31} continuously to induce the volume change with fixing the other parameters. We obtain the swelling curves of the gel by solving Eqs. (12) and (13) numerically. Figure 1 shows the swelling curves for several values of ϕ_{2s}. In the absence of additives, the VPT occurs at $\chi_{31} = \chi_{31t}^{(0)}$ (≈ 0.5327). In Fig. 1(a), we dissolve the additive of $\chi_{12} = 0.0$ and $\chi_{23} = -1.0$, which has affinity to the polymer network (pro-gel). As its concentration ϕ_{2s} is increased, the transition point shifts to higher χ_{31}. In Fig. 1(b), the additive of $\chi_{12} = 0.0$ and $\chi_{23} = 1.0$ is dissolved into the solvent. This additive dislikes the polymer network (anti-gel). It is shown that the transition point shifts to lower χ_{31} with an increasing ϕ_{2s}. For the cases as in Fig. 1, the SLA can explain the effects

of the solute on the volume changes qualitatively. In the SLA, the volume fractions of the solvent components inside the gel are assumed to be $\phi_{1g} = (1 - \phi_3)(1 - \phi_{2s})$ and $\phi_{2g} = (1 - \phi_3)\phi_{2s}$. Then, the interaction parameter between the polymer network and the mixture solvent is approximated as

$$\tilde{\chi}_{31} = \chi_{31}(1 - \phi_{2s}) + \chi_{23}\phi_{2s} - \chi_{12}\phi_{2s}(1 - \phi_{2s})$$
$$= \chi_{31} + G\phi_{2s} + \mathcal{O}(\phi_{2s}^2). \tag{18}$$

This means that the interaction parameter changes effectively with ϕ_{2s} depending on G. For the plotted range in Fig. 1(a) ($\chi_{31} \in [0.528, 0.542]$), G remains negative, so that the solvent becomes more good, swelling the gel with an increasing ϕ_{2s}. As shown in Fig. 1(b), on the other hand, the solvent changes to more poor and the gel shrinks with ϕ_{2s} for the solute of positive G.

In Fig. 1, the absolute value of the resulting G is rather small ($|G| \lesssim 2$). Next, we study the effects of solutes of strong selectivity $|G| \gg 1$. Figures 2(a) and 2(b) show the swelling curves in the mixture solvents of $\chi_{23} = -10.0$ and $\chi_{23} = 10.0$, respectively. The other parameters
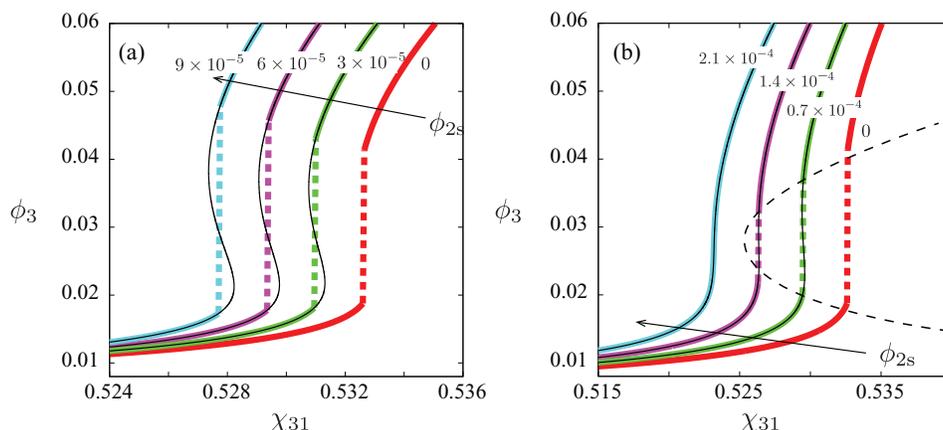
FIG. 2. The swelling curves of a gel immersed in a mixture solvent. We set $\phi_{30} = 1.0 \times 10^{-2}$, $\nu v_0 = 1.0 \times 10^{-5}$, $B = 1.15$, and $\chi_{12} = 0.0$. We dissolve solutes of $\chi_{23} = -10.0$ (pro-gel) in (a) and $\chi_{23} = 10.0$ (anti-gel) in (b). The black solid lines are calculated from Eq. (21). The additives have strong selectivities to the polymer network.
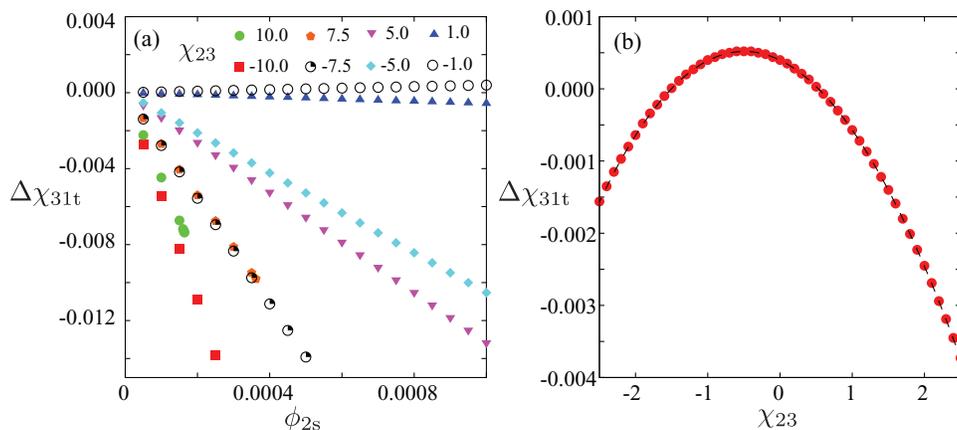
FIG. 3. (a) The shifts of the transition point from $\chi_{31t}^{(0)}$ are shown for several values of χ_{23}. The shift is numerically obtained with the same parameters as in Figs. 1 and 2. For $\chi_{23} = 7.5$ and 10.0, the transition points are terminated since the discontinuous volume changes disappear. (b) The dependence of $\Delta\chi_{31t}$ on χ_{23} is plotted for $\phi_{2s} = 0.001$. The broken curve represents $g(\phi_{3c}, \bar{G})$ [Eq. (26)] with $\phi_{3c} = 0.0267$ and $\chi_{31t}^{(0)} = 0.5327$.

are the same as those in Fig. 1. In the both cases, the transition points are shifted to lower χ_{31}, regardless of whether the solute is good or poor. This behavior is in contrast to the volume changes in Fig. 1 and indicates the SLA does not work well when the additives have the strong selectivity to the polymer network.

Figure 3(a) shows the dependences of the transition shift $\Delta\chi_{31t}$ on the additive concentration ϕ_{2s}, where $\Delta\chi_{31t} = \chi_{31t} - \chi_{31t}^{(0)}$ and $\chi_{31t}^{(0)}$ is the transition point without additives. An increase of $\Delta\chi_{31t}$ is observed for $\chi_{23} \approx -1.0$, whereas $\Delta\chi_{31t}$ is lowered with an increasing ϕ_{2s} for the other additives. In the plotted range of ϕ_{2s}, $\Delta\chi_{31t}$ has linear dependence on ϕ_{2s}. The transition shifts for $\phi_{2s} = 0.001$ are plotted with respect to χ_{23} in Fig. 3(b). It indicates a non-monotonic behavior of the transition point.

The difference of the additive effects between $\chi_{23} = -1.0$ and $\chi_{23} = -10.0$ is notable, since the both additives have tendencies to be adsorbed onto the polymer network. When $|\chi_{23}|$ is small, the difference between ϕ_{2g} and ϕ_{2s} is rather small. As explained by Eq. (18), the addition of the solute with negative χ_{23} makes the mixture solvent more good to the polymer. Thus, the gel is simply swollen with an increasing ϕ_{2s}. If χ_{23} (or G) is negatively large enough, on the other hand, the concentration of the solute inside the gel becomes much larger than that outside gel, i.e., $\phi_{2g} \gg \phi_{2s}$ [see Eq. (19)]. By shrinking its volume, the polymer network tends to increase the contact points to the additive molecules. This nonlinear effect would give rise to the difference between $\chi_{23} = -1.0$ and $\chi_{23} = -10.0$.

Figure 2 also shows that the gap of the volume transition depends on the additive concentration when the additive has strong selectivity. As ϕ_{2s} is increased, the volume gap is increased for $\chi_{23} = -10.0$ [see Fig. 2(a)], while it is decreased for $\chi_{23} = 10.0$ [Fig. 2(b)]. For $\chi_{23} = 10.0$, in particular, the gap disappears eventually at a certain concentration $\phi_{2s} = \phi_{2st}$, above which the gel does not undergo the VPT [see below]. Figure 4 plots the gap of the volume fraction $\Delta\phi_{3t} (= \phi_{3t+} - \phi_{3t-})$ at the transition point, where ϕ_{3t+} and ϕ_{3t-} are the volume fractions just below and above the tran-

sition point. For a large positive value of χ_{23}, $\Delta\phi_{3t}$ decreases toward zero with an increasing ϕ_{2s}.

It is known that the elasticity parameter B influences the nature of the VPT.[3] Figure 5 shows the swelling curves of a gel of $B = 1.10$ with varying χ_{31}. In the absence of additive, the volume of this gel changes continuously. By dissolving the pro-gel additive of $\chi_{23} = -10.0$, the swelling curve becomes non-monotonic with respect to χ_{31}, so that the gel undergoes the VPT. Figures 2(b) and 5 indicate that we can arbitrarily induce or erase the VPT by adding solutes with the strong selectivities.

We assume that only a subtle amount of the additive is dissolved in the outer solvent, i.e., $\phi_{2s} \ll 1$. From Eq. (12), the volume fraction of the additive inside the gel is expressed by

$$\phi_{2g} = (1 - \phi_3)e^{-G\phi_3}\phi_{2s} + \mathcal{O}(\phi_{2s}^2). \tag{19}$$
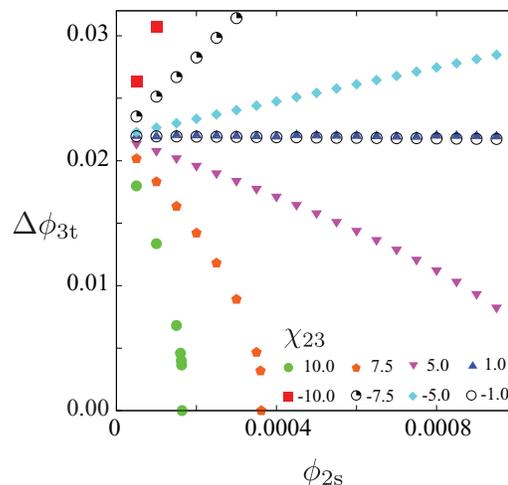
FIG. 4. The gap of the volume fraction ϕ_3 at the transition is plotted with ϕ_{2s}. We set $\phi_{30} = 1.0 \times 10^{-2}$, $vv_0 = 1.0 \times 10^{-5}$, $B = 1.15$, and $\chi_{12} = 0.0$ as in Figs. 1 and 2.
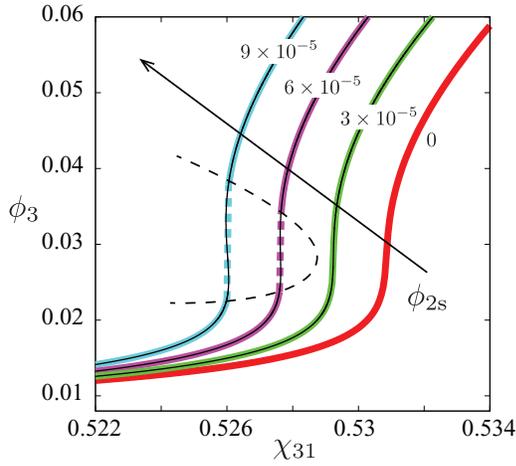
FIG. 5. The swelling curves of a gel immersed in a mixture solvent. We set $\phi_{30} = 1.0 \times 10^{-2}$, $vv_0 = 1.0 \times 10^{-5}$, $B = 1.10$, and $\chi_{12} = 0.0$. We dissolve the pro-gel solute of $\chi_{23} = -10.0$. The black solid lines are calculated from Eq. (21). When $\phi_{2s} = 0$, the gel changes its volume continuously without VPT.

Substituting Eq. (19) into Eq. (17), we obtain

$$
\tilde{\Pi}_{ad} = \ln(1 - \phi_{2s}) - \ln(1 - \phi_{2s}e^{-G\phi_3})
$$
$$
+ G\phi_3(1 - \phi_3)e^{-G\phi_3}\phi_{2s} + \mathcal{O}(\phi_{2g}^2)
$$
$$
= [e^{-G\phi_3}\{1 + G\phi_3(1 - \phi_3)\} - 1]\phi_{2s} + \mathcal{O}(\phi_{2g}^2). \quad (20)
$$

Then, the swelling curve is approximately given from Eqs. (15), (16), and (20) by

$$
\chi_{31} \cong -\phi_3^{-2}\ln(1 - \phi_3) - \alpha\phi_3^{-5/3} + (\beta - 1)\phi_3^{-1}
$$
$$
+ [e^{-G\phi_3}\{1 + G\phi_3(1 - \phi_3)\} - 1]\phi_3^{-2}\phi_{2s}, \quad (21)
$$

where $\alpha = vv_0/\phi_{30}^{1/3}$ and $\beta = vv_0B/\phi_{30}$. Since the right hand side of Eq. (21) includes χ_{31} via G, we cannot obtain an analytical solution of χ_{31}. Then, we replace G to $\bar{G} = \chi_{23} - \chi_{31t}^{(0)} - \chi_{21}$ and regard $\bar{G}$ as a fixed parameter. The approximated curves of Eq. (21) are drawn in Figs. 1, 2, and 5. They are well in agreement with the numerical solutions.

Regarding β as a variable, a tri-critical point of the VPT is given by

$$
\left.\frac{\partial\chi_{31}}{\partial\phi_3}\right|_{\phi_{3c},\beta_c} = 0, \quad \left.\frac{\partial^2\chi_{31}}{\partial\phi_3^2}\right|_{\phi_{3c},\beta_c} = 0. \quad (22)
$$

Here, α is treated to be fixed. By solving Eq. (22), we obtain ϕ_{3c} and β_c, which give the swelling curve passing through the tri-critical point. In the vicinity of the tri-critical point, the swelling curve is approximated by

$$
\chi_{31} \approx \chi_{31t} - \frac{\beta - \beta_c}{\phi_{3c}^2}(\phi_3 - \phi_{3c}) + \frac{u}{6}(\phi_3 - \phi_{3c})^3, \quad (23)
$$

where u is a positive constant. If $\beta < \beta_c$, the curve of χ_{31} changes monotonically with ϕ_3, such that the gel volume changes continuously with changing χ_{31}. On the other hand, inflection points appears when $\beta > \beta_c$. If so, the gel becomes mechanically unstable, so that it exhibits the discontinuous volume changes as $\Delta\phi_{3t} = 2\sqrt{(\beta - \beta_c)/u}/\phi_{3c}$ at $\chi_{31} = \chi_{31t}$.[3]

The part of the osmotic pressure $\tilde{\Pi}_{ad}$ shifts the tri-critical point in Eq. (23) as

$$
\chi_{31t} = \chi_{31t}^{(0)} + g(\phi_{3c}, \bar{G})\phi_{2s}, \quad (24)
$$

$$
\beta_c = \beta_c^{(0)} + h(\phi_{3c}, \bar{G})\phi_{3c}^2\phi_{2s}. \quad (25)
$$

Here, $\beta_c^{(0)}$ gives the tri-critical point in the case of $\phi_{2s} = 0$. From Eq. (21), the prefactors g and h are given by

$$
g(\phi_3, G) = \phi_3^{-2}[e^{-G\phi_3}\{1 + G\phi_3(1 - \phi_3)\} - 1], \quad (26)
$$

$$
h(\phi_3, G) = \phi_3^{-3}[2 - e^{-G\phi_3}\{G^2\phi_3^2(1 - \phi_3) + 2G\phi_3 + 2\}]. \quad (27)
$$

g and h change their signs depending on ϕ_3 and G. Their dependences are shown in Fig. 6. If $g(\phi_3, G)$ is positive, the transition point shifts to higher χ_{31} with an increasing ϕ_{2s} and *vice versa*. Eq. (26) for $\phi_{2s} = 0.001$ is drawn in the broken curve in Fig. 3(b). Here, we set $\phi_{3c} = 0.0267$ and $\chi_{31t} = 0.5327$. This approximated curve is in agreement with the numerical
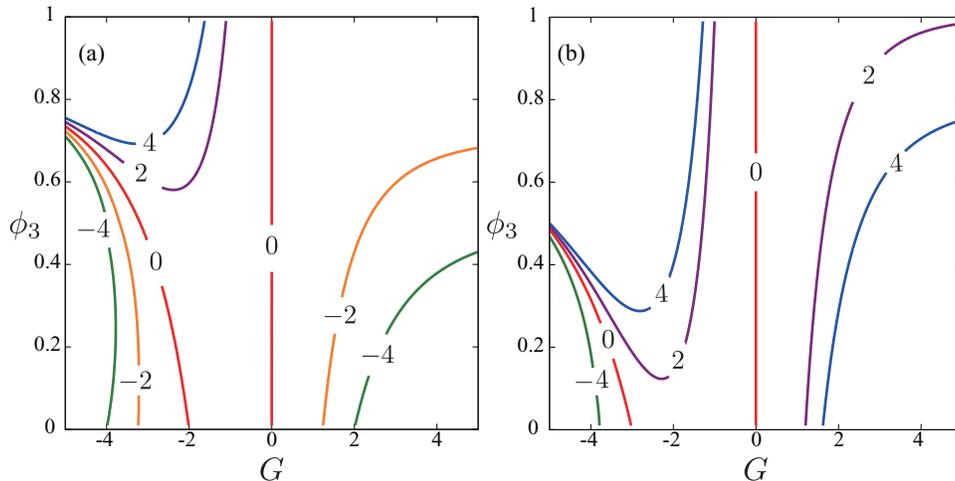
FIG. 6. The contours of the functions g [Eq. (26)] and h [Eq. (27)] are drawn in G-ϕ_3 planes (a) and (b), respectively. The transition point is increased linearly with ϕ_{2s} in the region of for positive g. In the region of negative h, the volume gap of the transition point is increased.
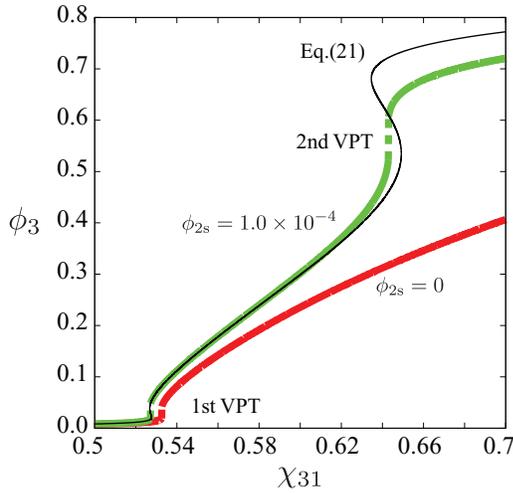
FIG. 7. The swelling curves of a gel immersed in a mixture solvent in a wider range of χ_{31}. We set $\phi_{30} = 1.0 \times 10^{-2}$, $\nu v_0 = 1.0 \times 10^{-5}$, $B = 1.15$, and $\chi_{12} = 0.0$. We dissolve the strongly good solute of $\chi_{23} = -10.0$ and $\phi_{2s} = 1.0 \times 10^{-4}$. The black solid lines are calculated by Eq. (21). The second volume phase transition is induced.

FIG. 8. The theoretical curves of $\partial \chi_{31}^{(0)}/\partial \phi_3$ and $-h(\phi_3, G)\phi_{2s}$ are shown. When $\partial \chi_{31}^{(0)}/\partial \phi_3 < -h(\phi_3, G)\phi_{2s}$, the gel becomes mechanically unstable, showing the second volume phase transition.

solution. When $\phi_{3c} \ll 1$, $g \approx -G(G+2)/2$ and it changes its sign at $G = 0$ and $G = -2$. A large negative h enhances the discontinuity of the volume change as observed in Fig. 2(b). If $\phi_{3c} \ll 1$, h is expressed as $h \approx G^2(G+3)/3$ and it changes its sign at $G = -3$. Thus, we can possibly induce the VPT even in a gel, which originally shows a continuous volume change, by adding solute of $-G \gg 3$. The gap of the VPT disappears as $\Delta\phi_{3t} \propto \sqrt{\phi_{2st} - \phi_{2s}}$, where $\phi_{2st} = \{\beta - \beta_c^{(0)}\}h^{-1}\phi_{3c}^{-2}$. This disappearing behavior is observed in Fig. 4.

In this paper, only the numerical solutions for $\chi_{12} = 0.0$ are presented. However, we confirmed that the essentially same features are observed for any set of χ_{12} and χ_{31} if the resultant G is the same.

B. The second volume phase transition

In Fig. 7, we plot the swelling curves in a wider range of χ_{31}. We set $\phi_{30} = 1.0 \times 10^{-2}$, $\nu v_0 = 1.0 \times 10^{-5}$, $B = 1.15$, $\chi_{12} = 0.0$, and $\chi_{23} = -10.0$. It is indicated that another discontinuous volume phase transition can occur at χ_{31} larger than χ_{31t} corresponding to the first transition. We confirmed that this second phase transition is observed even if $\nu = 0$ (or, $\alpha = \beta = 0$), while the first one disappears. This fact indicates that this second instability is independent of the network elasticity and has a physical mechanism different from those for well-studied volume phase transitions.[3]

Scott reported that various types of phase diagrams are realized for ternary mixtures (polymer solutions in binary mixtures).[34] They can have several critical points, below which three phases coexist. Analogous to the ternary mixtures, we consider that the second volume transition observed in Fig. 7 is attributed to the bulk instability of the mixing free energy. Since there are some differences between ternary mixtures and gels in mixture solvents, the Scott's argument cannot be simply applied to the gel systems. The most important differences are that a gel has the elasticity and never exhibits a one-phase homogeneous state.
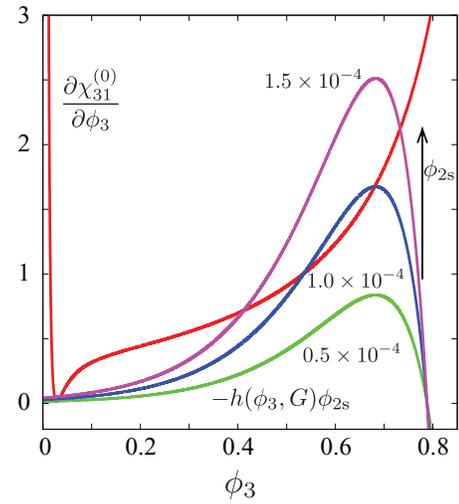
We have not obtained a simple explanation on the second transition, since nonlinearities, which are hard to treat analytically, would play important roles in the bulk instability. In Fig. 7, we also draw the swelling curve obtained by Eq. (21), which neglects the nonlinearity of ϕ_{2s}. The approximated curve also exhibits the second transition, although it does not coincide quantitatively with the numerical solutions for large ϕ_3. However, this fact implies that the nonlinearity of ϕ_2 has a minor contribution to the essential mechanism of the second transition.

As discussed above, the gel becomes mechanically unstable when $\partial \chi_{31}/\partial \phi_3 < 0$. In Fig. 8, we plot $\partial \chi_{31}^{(0)}/\partial \phi_3$ and $-h(\phi_3, G)\phi_{2s}$, where $\chi_{31}^{(0)}(\phi_3)$ is the swelling curve of the gel in the solvent of the first component. In the range satisfying $\partial \chi_{31}^{(0)}/\partial \phi_3 < -h(\phi_3, G)\phi_{2s}$, the gel would exhibit a discontinuous volume change. It is indicated that strong nonlinearity of $h(\phi_3, G)$ with respect to ϕ_3 is a possible origin of the second transition.

IV. SUMMARY AND REMARKS

We studied the volume phase transition of gels immersed in binary mixtures, based on the three-component Flory-Rehner model. Assuming that the volume fraction of the second solvent component is small, we reformulated the Flory-Rehner model into a simple model with a new parameter $G(= \chi_{23} - \chi_{31} - \chi_{12})$. From numerical solutions and the simplified theory, we found the following behaviors of the volume phase transition of the gel.

(i)   When the selectivity of the second component to the polymer network is small, the composition of the mixture solvent in the gel is close to that out of the gel. Here, the single liquid approximation works well. The renormalized interaction parameter between the solvent and the network depends linearly on the composition of the binary mixture. Thus, we can swell the gel by

dissolving the additive good to the network, whereas, the gel is shrunken when the poor additive is dissolved.

On the other hand, the difference of the composition becomes large when the additive selectivity is strong. Owing to the nonlinearity of the composition difference, the gel tends to be shrunken as the additive concentration is increased, regardless of whether it is good or poor. From the simplified theory, the dependence of the transition point on the additive concentration is found to be proportional to $\partial \chi_{31t}/\partial \phi_{2s} \approx g(\phi_{3c}, \bar{G})$, which is approximated as $g \approx -\bar{G}(\bar{G}+2)/2$ for a hyper swollen gel.

(ii) By dissolving the strongly poor additive, we can extinguish the discontinuous volume phase transition. Furthermore, we can induce the volume phase transition in the gel, which does not exhibit the discontinuous gap in the absence of the additive, by dissolving the strongly good additive. In the vicinity of the (first) tri-critical point, this behavior is well described by the simplified theory as shown in Fig. 6(b).

(iii) Far from the transition point, we found that another volume phase transition can occur. This second instability is observed even if the elasticity is negligible. The transition is caused by the mixing instability. Our theory indicates that the nonlinearity of ϕ_3, which is well described by Eq. (27), does have a major contribution to the transition.

Here, we make some remarks about our results.

(1) If only van der Waals interaction is taken into account, the interaction parameters should be positive, *i.e.*, $\chi_{ij} \geq 0$. However, a variety of molecular forces, such as ion-dipole interaction, hydrogen bonding and hydrophobic interaction, would also influence the volume phase transition of the gel. When studying their contributions explicitly, we have to consider the microscopic degrees of the freedom in a more specific manner.[21, 23, 24] In this work, we assume that the macroscopic χ parameter can have a large negative value, by renormalizing these microscopic degrees into them. In a future work, we would like to investigate the connections of such microscopic interactions and our phenomenological theory. Effects of the selective salts[31] on polyelectrolyte gels are also interesting.

(2) Effects of additives on thermo-sensitive NIPA and PAA gels have been intensively studied.[11–21] However, there remain some problems which are difficult to explain by conventional theories. Although our model is very simple, it can predict counterintuitive behaviors. It would be helpful to elucidate some of unresolved problems.

For instance, Ishidao *et al.* studied the volume transition of NIPA gels in aqueous solutions.[25] They observed that the concentration of 1-propanol inside the gel is larger than that outside the gel. This indicates that this additive has more good affinity to the polymer network than water, so that one can imagine that addition of the 1-propanol makes the mixture solvent more good. However, the NIPA gel is shrunken by dissolving a small amount of this additive. In this paper, we show considering the nonlinearities of G and ϕ_3 enables us to understand such a counterintuitive behavior. Here, we note that the mixing of two solvents decreases the effective interaction parameter in usual cosolvents with $\chi_{12} > 0$ [see Eq. (18)].

Furthermore, Annaka *et al.* reported that the volume change of NIPA becomes continuous by dissolving NaI.[14] Ordinary theories cannot describe any additive-induced disappearance of discontinuous transition. As commented in Ref. 14, the disappearance of the VPT is considered to be attributed to the interaction between the salt and the polymer network. We consider that resultant inhomogeneities of the ion concentrations also play a key role in this continuous volume change, as discussed in this paper. Since our model considers only one species of solute and neglects the electrostatic interactions, however, it cannot explain this experimental result quantitatively.

Since only a few experiments have reported the difference of the additive concentrations between in and out of the gels,[25, 36] however, we cannot verify the quantitative validity of our model yet. Further experimental studies are highly desired.

(3) So far, thermo-sensitivities of gel volumes have been found only in hydrophilic gels such as polyelectrolytes and NIPA. In them, the electrostatic interactions (including hydrogen bondings) would play important roles more and less. Our model is based on the Flory-Huggins free energy, so that it can be applied ubiquitously to many types of polymer networks including hydrophobic (lipophilic) ones. We hope our model will help one to find volume phase transitions in gels other than polyelectrolytes, NIPA, PAA, and their derivatives.

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[1]P. J. Flory and J. Rehner, J. Chem. Phys. **11**, 512 (1943); **11**, 521 (1943).
[2]K. Dušek and D. Patterson, J. Polym. Sci., Part A-2. **6**, 1209 (1968).
[3]T. Tanaka, Phys. Rev. Lett. **40**, 820 (1978).
[4]T. Tanaka, D. Fillmore, S.-T. Sun, I. Nishio, G. Swislow, and A. Shah, Phys. Rev. Lett. **45**, 1636 (1980).
[5]T. Tanaka, Sci. Am. **244**, 124 (1981).
[6]Y. Hirokawa and T. Tanaka, J. Chem. Phys. **81**, 6379 (1984).
[7]I. Ohmine and T. Tanaka, J. Chem. Phys. **77**, 5725 (1982).
[8]J. Rička and T. Tanaka, Macromolecules **17**, 2916 (1984).
[9]A. Fernández-Nieves, A. Fernández-Barbero, and F. J. de las Nieves, J. Chem. Phys. **115**, 7644 (2001).
[10]T. Amiya, Y. Hirokawa, Y. Hirose, Y. Li, and T. Tanaka, J. Chem. Phys. **86**, 2375 (1987).
[11]S. Hirotsu, Y. Hirokawa, and T. Tanaka, J. Chem. Phys. **87**, 1392 (1987).
[12]T. G. Park and A. S. Hoffman, Macromolecules **26**, 5045 (1993).
[13]H. Inomata, S. Goto, K. Otake, and S. Saito, Langmuir **8**, 687 (1992).
[14]M. Annaka, K. Motokawa, S. Sasaki, T. Nakahira, H. Kawasaki, H. Maeda, Y. Amo, and Y. Tominaga, J. Chem. Phys. **113**, 5980 (2000).

[15] S. Hirotsu, J. Phys. Soc. Jpn. **56**, 233 (1987).

[16] E. Kokufuta, Y.-Q. Zhang, T. Tanaka, and A. Mamada, Macromolecules **26**, 1053 (1993).

[17] H. Kawasaki, S. Sasaki, H. Maeda, S. Mihara, M. Tokita, and T. Komai, J. Phys. Chem. **100**, 16282 (1996).

[18] S. Sasaki, H. Kawasaki, and H. Maeda, Macromolecules **30**, 1847 (1997).

[19] D. Dhara and P. R. Chatterji, Langmuir **15**, 930 (1999).

[20] S. Koga, S. Sasaki, and H. Maeda, J. Phys. Chem. B **105**, 4105 (2001).

[21] F. Tanaka, T. Koga, and F. M. Winnik, Phys. Rev. Lett. **101**, 028302 (2008).

[22] S. Sasaki and H. Maeda, Phys. Rev. E **54**, 2761 (1996).

[23] H. Kojima and F. Tanaka, Macromolecules **43**, 5103 (2010).

[24] H. Kojima and F. Tanaka, Soft Matter **8**, 3010 (2012).

[25] T. Ishidao, Y. Hishimoto, Y. Iwai, and Y. Araki, Colloid Polym. Sci. **272**, 1313 (1994).

[26] V. V. Vasilevskaya, V. A. Ryabina, S. G. Starodubtsev, and A. R. Khokhlov, Polym. Sci. U.S.S.R. **31**, 784 (1989).

[27] T. Iwatsubo, K. Ogasawara, A. Yamasaki, T. Masuoka, and K. Mizoguchi, Macromolecules **28**, 6579 (1995).

[28] W. R. Krigbaum and D. K. Carpenter, J. Polym. Sci. **14**, 241 (1954).

[29] G. M. Bristow, Trans. Faraday Soc. **55**, 1246 (1959).

[30] O. Okeowa and J. R. Dorgan, Macromolecules **39**, 8193 (2006).

[31] R. Okamoto and A. Onuki, Phys. Rev. E **82**, 051501 (2010).

[32] A. Onuki and R. Okamoto, Curr. Opin. Colloid Interface Sci. **16**, 525 (2011).

[33] A. Onuki, R. Okamoto, and T. Araki, Bull. Chem. Soc. Jpn. **84**, 569 (2011).

[34] R. L. Scott, J. Chem. Phys. **17**, 268 (1949).

[35] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University, Ithaca, New York, 1953).

[36] T. Iwatsubo and T. Shinbo, J. Macromol. Sci., Phys. **B40**, 1017 (2001).