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A new model for the thermally induced volume phase transition of gels

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A theoretical model that considers hydrophobic interaction is proposed for the thermally induced discontinuous shrinkage of hydrogels. In this model, the free energy of a hydrogel is divided into four parts: the elastic free energy of networks formulated according to the theory which takes the limit of elongation into account, the free energy arising from osmotic pressure of dissociated counterions in the gel, the free energy of interactions except for the hydrophobic interaction represented by a virial-type volume interaction equation, and the free energy of the hydrophobic interaction. By the former three terms, the thermally induced swelling of gels and the effects of aspect ratio of segment are expressed. The incorporation of the fourth hydrophobic interaction term makes it possible to explain the thermally induced shrinkage of gels, and suggests the possibility of an explanation of "convexo"-type volume phase transition by means of the hydrophobic interaction.

I. INTRODUCTION

Recently, much attention has been paid to the volume phase transition of hydrogels¹ for its engineering and scientific importance. Discontinuous volume change can be induced by continuous variation of surrounding conditions such as solvent composition,²⁻⁴ salt concentration,⁵ pH,⁶ electric field,⁷ and temperature.^{1,3} Theoretical investigations into the volume phase transition in terms of Flory's mean field theory⁸ have been performed by Tanaka and co-workers.^{1,3,4,9} They succeeded in arriving at a qualitative explanation of the effects of surrounding conditions, except for that of temperature.

Quite recently, Hirotsu¹⁰ suggested that the thermally induced volume phase transition of *N*-isopropylacrylamide gels, typical of thermoshinking gels, might be attributed to the thermal destruction of hydrogen bonds between water molecules and hydrophilic groups such as -CO- and -NH- in the *N*-isopropylacrylamide monomers comprising the gel. However, water molecules also interact strongly with non-polar hydrophobic solutes through the formation of a hydrophobic hydration structure,¹¹ resulting in a hydrophobic interaction. Therefore, this hydrophobic interaction and hydrophilic hydration both need to be considered for the transition phenomena of hydrogels to be understood. The importance of hydrophobic interaction has been pointed out in our previous paper¹² through a calorimetric analysis of hydrogels.

In this paper, we propose a new model which considers hydrophobic interaction to clarify the effects of temperature on volume phase transition.

II. DESCRIPTION OF THE MODEL

The free energy of a gel is ordinarily decomposed into three terms^{1,3,4}: the free energy of mixing between polymer network and solvent G^{mix} , the elastic free energy due to the

deformation of the gel G^{elas} , and the free energy arising from osmotic pressure with dissociated counterions retained by the Donnan effect in the gel G^{osmo} . We follow this procedure and add one more term representing the hydrophobic interaction.

In the present model, we consider only hydrogels prepared in the presence of a large amount of diluent. The following three assumptions are made.

(1) Interactions of monomer units that are far apart in a polymer chain of a gel can be represented as a sum of two-body and three-body interactions.¹³ Such interactions involve monomer-solvent and solvent-solvent interactions but not the hydrophobic interaction.

(2) Hydrophobic interaction gives rise to physical crosslinking points in the chains which comprise the gel.¹⁴ The formation of these crosslinking points divides a chain into connected short chains of equal length. The number of the physical crosslinking points N_b and the number of the short chains N_{sc} produced from the formation of crosslinking points can be connected with the following equation:

$$N_{sc} = 2N_b + 1. \quad (1)$$

(3) Solvent molecules and monomers composing the gel system have the same molar volume.

Under these assumptions, we derive equations for each term of the free energy.

A. Elastic free energy (G^{elas})

The formation of physical crosslinking points increases the number of elastically active chains, leading to an increase in the elastic free energy. Although Tanaka *et al.* employed Flory's equation for the elastic energy, it is known¹⁵ that the equation does not fit all the experimental data regarding elastomers, especially around their maximum expansions. Usually hydrogels contain a large amount of water and are in states of large great expansion. Therefore the present work employs an elasticity equation which takes the limit of elon-

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gation into account.¹⁵ By extending the equation, we can obtain Eq. (2), whose derivation is given in the Appendix:

$$\Delta G^{\text{elas}} = \frac{3}{2} kT \left[n \ln \frac{(1 + \alpha\lambda)^{1 + \alpha\lambda} (1 - \alpha\lambda)^{1 - \alpha\lambda}}{(1 + \lambda)^{1 + \lambda} (1 - \lambda)^{1 - \lambda}} - N_{\text{sc}} \ln \alpha \right], \quad (2)$$

where λ is the initial state index defined as

$$\lambda = R_g/n, \quad (3)$$

$$R_g = (\text{expansion factor of standard state}) R_{g\theta}. \quad (4)$$

In the above equations, k is the Boltzmann constant, T is the absolute temperature, α is the expansion factor, n is the number of segments in a polymer chain, l is the length of a polymer segment, and $R_{g\theta}$ the mean-square end-to-end distance of the polymer chain in its random-walk configuration given by

$$R_{g\theta} = n^{1/2} l. \quad (5)$$

B. Free energy of mixing (G^{mix})

According to assumption (1) the following virial-type expression, which was presented by Lifshitz,¹³ is used for the free energy of mixing:

$$\frac{\Delta G^{\text{mix}}}{kT} = B(\phi - \phi_0) + C(\phi^2 - \phi_0^2), \quad (6)$$

where B and C are the effective second and third virial coefficients, ϕ is the monomer unit concentration in a gel, and ϕ_0 is the value of ϕ in the standard state. The monomer unit concentration is related to the expansion factor as follows:

$$\phi = \phi_0/\alpha^3. \quad (7)$$

For the temperature dependence of virial coefficients, we assume the following formula by analogy with real gas systems:

$$B = B_0(T_r - 1), \quad (8)$$

$$C = C_0(T_r - 1) + C_1, \quad (9)$$

$$T_r = T/T_\theta, \quad (10)$$

where B_0 , C_0 , and C_1 are system-dependent constants, and T_θ is the θ temperature.

C. Free energy due to osmotic pressure (G^{osmo})

Ionizable groups incorporated in the chain dissociate into fixed charges and counterions whose existence causes osmotic swelling pressure and gives rise to the swelling of the gel. We assume the following equation for the counterions based on the van't Hoff equation

$$\frac{\Delta G^{\text{osmo}}}{kT} = -fm \ln(N_s + m), \quad (11)$$

where f is the number of dissociated counterions per polymer chain, m is the total number of the monomer units in the polymer chain, and N_s is the number of solvent molecules contained in the total space occupied by the polymer chain. According to assumption (3), N_s and m can be related to ϕ as follows:

$$\phi = m/(N_s + m). \quad (12)$$

D. Free energy of hydrophobic interaction (G^{hi})

Nem ethy and Sheraga¹⁶ quantitatively investigated the temperature dependence of the hydrophobic interaction between molecules in water and presented the following free energy equation for the temperature range of 0–70 °C:

$$\Delta G^{\text{hydrophobic}} = C_a + C_b T + C_c T^2, \quad (13)$$

where C_a , C_b , and C_c are system-dependent parameters. Equation (13) expresses the molar free energy change for the hydrophobic interaction of molecules. Therefore, the free energy change per polymer chain is given as follows:

$$\Delta G^{\text{hi}} = (C_a + C_b T + C_c T^2) p N_b / N_A, \quad (14)$$

where N_A is the Avogadro number and p is the aspect ratio of the polymer segment. In the present model, p is equivalent to the number of monomer units per segment because of the relations of

$$p = l/v_0^{1/3} \quad \text{and} \quad l = p v_0^{1/3},$$

where v_0 is the volume of monomers and solvent molecules.

III. NUMERICAL CALCULATION OF THE FREE ENERGY EQUATION

From the above equations, the following equation is obtained for the total free energy of the gel:

$$\begin{aligned} \frac{\Delta G}{kT} = & \frac{3}{2} \left[n \ln \frac{(1 + \alpha\lambda)^{1 + \alpha\lambda} (1 - \alpha\lambda)^{1 - \alpha\lambda}}{(1 + \lambda)^{1 + \lambda} (1 - \lambda)^{1 - \lambda}} - N_{\text{sc}} \ln \alpha \right] \\ & + B_0 \phi_0 (T_r - 1) (1/\alpha^3 - 1) \\ & + [C_0 (T_r - 1) + C_1] \phi_0^2 (1/\alpha^6 - 1) \\ & - fm \ln(N_s + m) + (C_a + C_b + C_c) N_b p / N_A kT. \end{aligned} \quad (15)$$

Equation (15) contains two independent variables: the number of the physical crosslinking points N_b , and the expansion factor of the chain α . For the equilibrium swelling of a gel, the osmotic pressure difference between the inside and outside of the gel should be zero. The above condition is equivalent to the minimization of the free energy of the gel by varying the number of solvent molecules N_s , which is represented by a function of N_b and α . Therefore, using a two-dimensional minimization method with respect to the two parameters, we first calculated the energetically local minimum points on the free energy surface for a given temperature, and then determined the transition temperature at which one of these multiple free energy minimum points will disappear.

The calculations were carried out for various values of the parameters, the aspect ratio of segments p and the number ratio of ionizable groups in the chain f . The other parameters were estimated for *N*-isopropylacrylamide hydrogel. All parameters used are tabulated in Table I. The value of v_0 was determined by taking the intermediate value between water and *N*-isopropylacrylamide.¹⁷ The parameters C_a , C_b , and C_c for the hydrophobic interaction were determined from the values of isobutyl substitutes of amino acid, determined by Nem ethy and Sheraga,¹⁶ to represent all interactions including the effect of the main backbone of the chain.

TABLE I. Calculation parameters.

Molar volume of monomer	70	cm ³ /mol
θ temperature	273.15	K
Virial coefficient	B_0 0.891	...
	C_0 -0.568	...
	C_1 0.669	...
Nemethy coefficients	C_a 5460.0	cal/mol
	C_b -35.4	cal/mol/K
	C_c 0.0495	cal/mol/K/K

Since there are no data for the θ temperature and the virial coefficients of this system, we assumed T_θ to be 273.15 K, and estimated the virial coefficients of the gel system from those of gas systems in the vicinity of boil temperature using a corresponding state principle.¹⁸ The virial coefficients used are of about the same order as that of water/alcohol systems.¹⁹

In the calculations, the standard state is chosen to be the state where the polymer chain has the random-walk configuration, and the ratio of the volume of the gel V to the standard state V_0 is determined through Eq. (A8) in the Appendix.

IV. RESULTS AND DISCUSSION

To confirm the applicability of the present model to systems in which the hydrophobic interaction is absent, we first carried out calculations for such a system, and then compared the calculated results with those of Tanaka *et al.*⁹ In these calculations, we applied the Maxwell construction to the osmotic pressure of the gel and determined the equilibrium swelling points. Calculated results were plotted against the reduced temperature at various f values as in Fig. 1(a). Dotted lines in the figure represent the equilibrium state. The calculated results indicate that the gel swells at a higher temperature, and that an increase in f enhances the magnitude of the volume change and lowers the transition temperature. This behavior of the gel is in agreement with that reported by Tanaka *et al.*⁹

The effect of aspect ratio on the transition has been suggested qualitatively by Tanaka and his co-workers⁶ through dimensional analysis. According to their hypotheses a large aspect ratio lowers the reduced temperature and enhances the magnitude of the transition. Figure 1(b) shows results with $p = 3$ and does not take the hydrophobic interaction into account. As shown in the figure, the validity of the suggestion of Tanaka *et al.* is also confirmed by the present model.

Then we performed calculations that did take account of the hydrophobic interaction term. The calculated results are presented in Figs. 2(a) to 2(c). In these figures, the solid lines show the swelling ratio of the gel, dashed-dotted lines represent the calculated result without the hydrophobic interaction and the dashed lines represent thermally induced volume phase transitions. At the same time, the loci of the system are shown by arrows.

Figure 2(a) shows the result for a nonionized ($f = 0$) gel. As seen in the figure, there is a temperature range in

which the gel has two swelling ratios. Thus in this range, two free energy minimum points coexist at each temperature. Schematic diagrams of the curved surface of the free energy calculated at each temperature are presented in Fig. 3. In this figure, T_2 and T_4 correspond to the temperature indicated by the lower and upper dashed lines in Fig. 2(a), respectively. As seen in Fig. 3, there is only one minimum in the state in which there is a large degree of swelling (small N_b and large α) at T_1 . As the reduced temperature increases, another minimum point appears in the shrinking state (large N_b and small α) at T_2 . A further increase in temperature extinguishes the free energy minimum on the side that undergoes the greater degree of swelling (T_4). At the higher temperature (T_5), there is only one free energy minimum point in the shrinking state. Accordingly, shrinking volume phase transition occurs at the upper transition temperature (T_4) during the heating process and, inversely, transition from the shrunken state to the swollen state occurs at the lower transition temperature (T_2) during the cooling process. Though a large hysteresis between transition temperatures exists, this result coincides qualitatively with the experimental results presented by Hirokawa and Tanaka for *N*-isopropyl acrylamide gels.³

On the other hand, Figs. 2(b) and 2(c) demonstrate the effect of ionizable groups on the shape of hydrophobic volume phase transition. In these calculations, f was set at 0.02 in Fig. 2(b) and 0.03 in Fig. 2(c). The other parameters are the same as those presented in Fig. 2(a). As can be seen in Figs. 2(b) and 2(c), owing to the incorporated ionizable groups in the chains, "convexo"-type swelling, which was reported by Katayama *et al.* for a gel obtained from the copolymerization of acrylamide and trimethyl(*N*-acryloyl-3-aminopropyl) ammonium iodide,²⁰ appears in the middle of the reduced temperature range 0–1.5. In these cases, the volume phase transition depends largely on the temperature and its direction, heating or cooling.

Comparison of Figs. 2(b) and 2(c) indicates that an increase in f raises the upper transition temperature, and widens the "convexo" swelling region as well as the magnitude of phase transition. The rise in the upper transition temperature is similar to that seen in *N*-isopropylacrylamide gels with sodium acrylate,²¹ and the widening effect in the "convexo" is consistent with the ordinary swelling mechanism proposed by Tanaka *et al.*^{1,3,4} On the other hand, the lower transition temperature is not affected by f .

In the calculations described above, the strength of the hydrophobic interaction was kept constant. Now we consider the effect of changing the hydrophobic interaction to one quarter of the former calculations. Figure 4 shows the calculated result for $f = 0.03$. The effect of the strength of the hydrophobic interaction is obvious when the figure is compared with Fig. 2(c). The weakening of the hydrophobic interaction raises the upper transition temperature, enhances the magnitude of volume change and lowers the lower transition temperature.

V. CONCLUSION

We have presented a new model for the thermally induced volume phase transition of hydrogels by considering

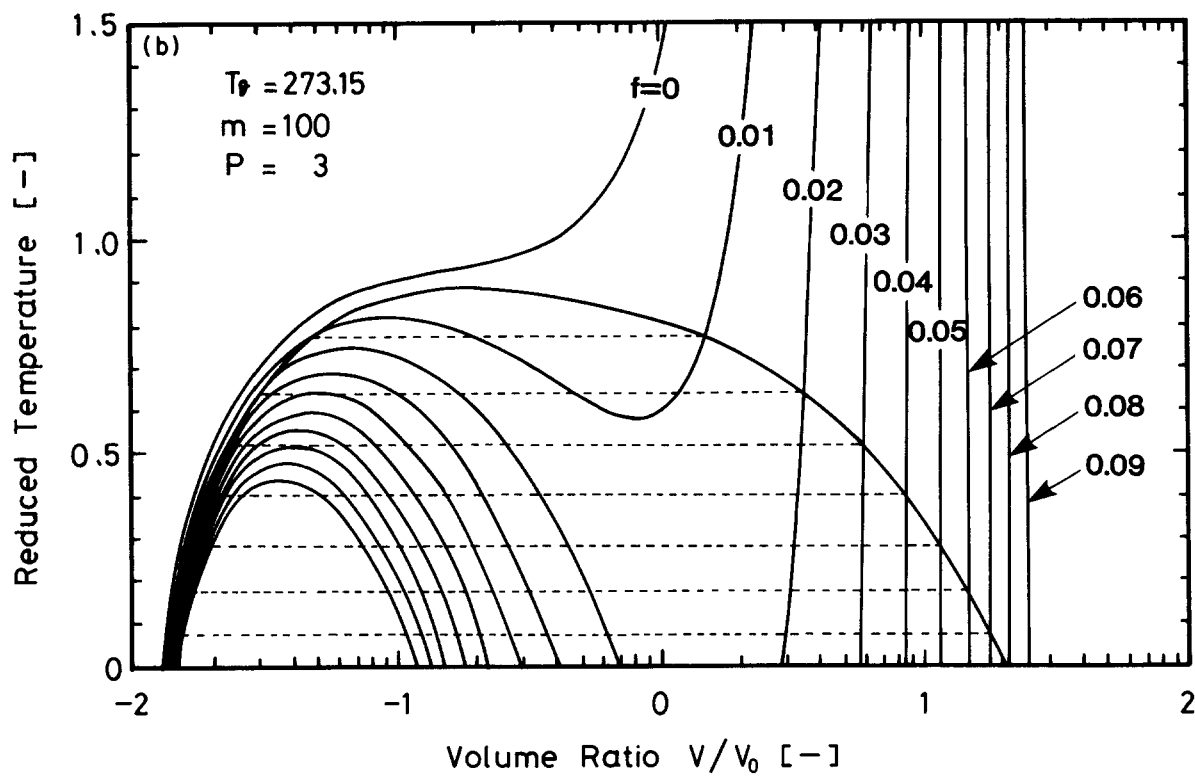
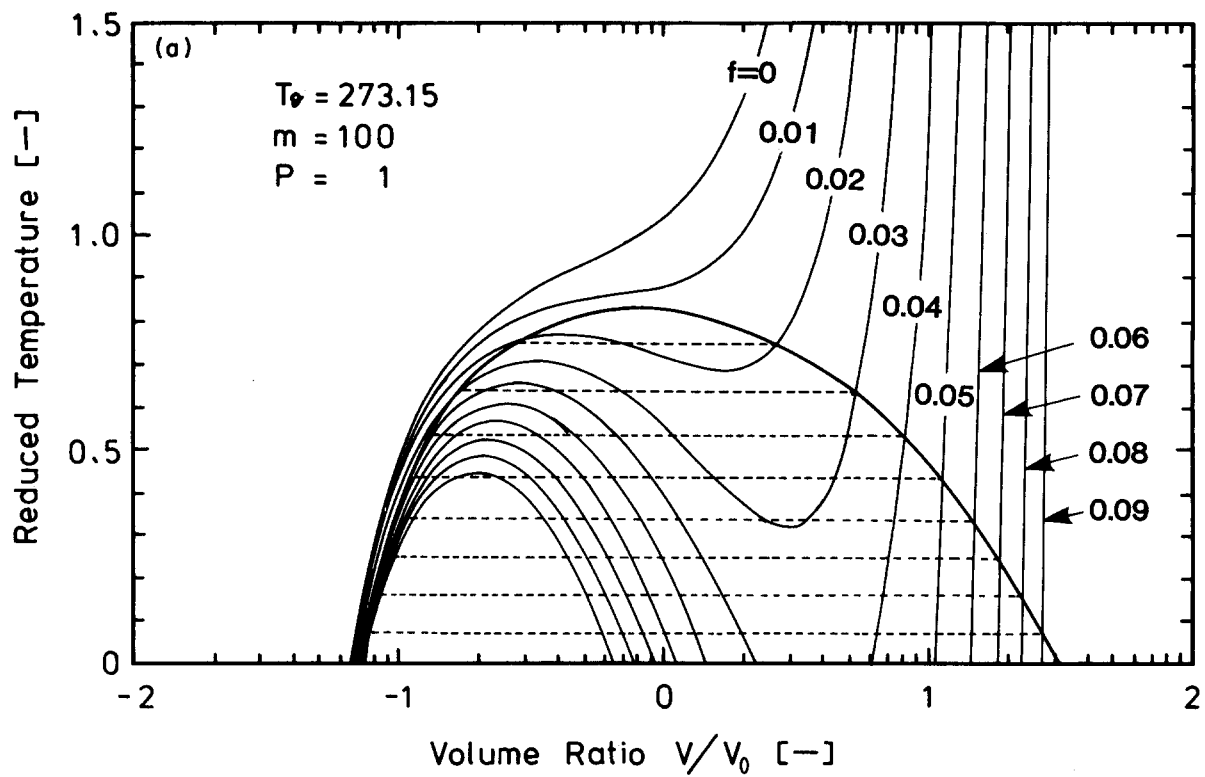


FIG. 1. Equilibrium swelling curves calculated from Eq. (15) for various values of f without the hydrophobic interaction term. (a) $p = 1$, (b) $p = 3$.

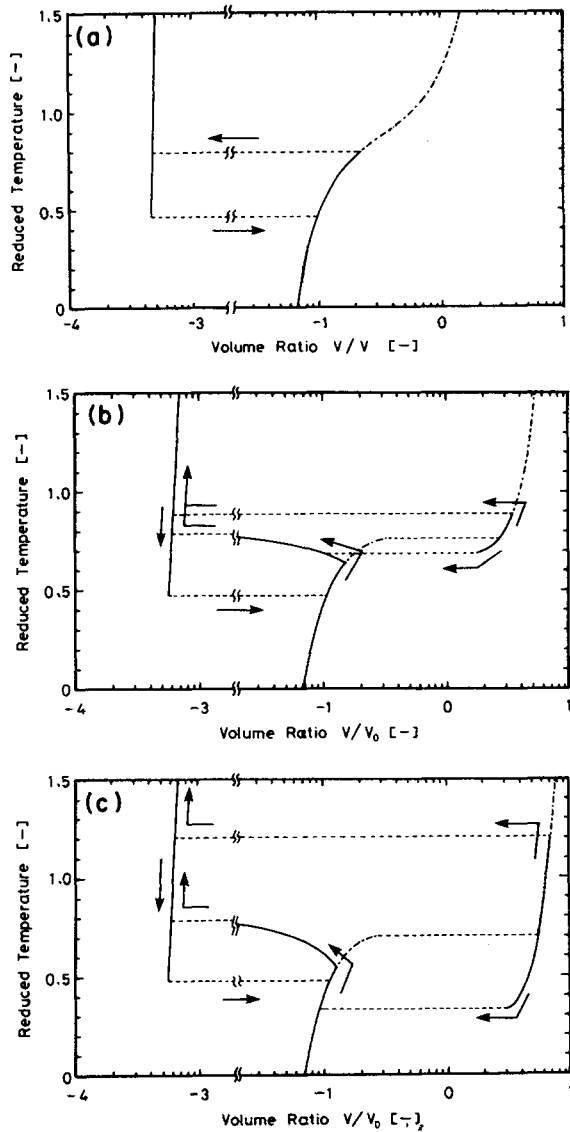


FIG. 2. Temperature dependence of the volume of a hydrogel when the hydrophobic interaction term is considered. (a) $f=0$, (b) $f=0.02$, (c) $f=0.03$.

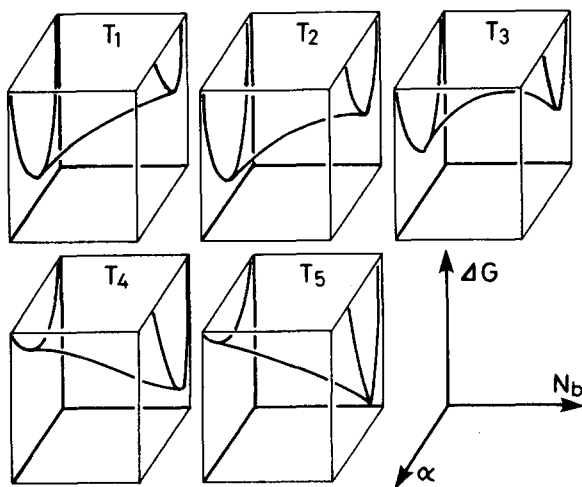


FIG. 3. Schematic diagrams of the temperature dependence of the shape of the free energy surface of Fig. 2(a). In the figure, T_2 is the lower transition temperature and T_4 is the upper transition temperature. The relationship between temperatures is given as follows: $T_1 < T_2 < T_3 < T_4 < T_5$.

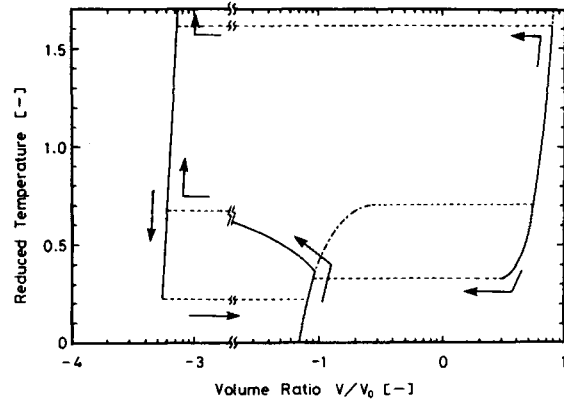


FIG. 4. Effect of the strength of hydrophobic interaction on the volume phase transition of a hydrogel. The strength is reduced to one quarter of the former calculations.

the hydrophobic quasi-crosslinking point formation in the polymer network of gels, and performed relevant numerical calculations. The new model is able to represent various types of volume phase transition including the “convexo” type. Through the calculations the importance of the hydrophobic interaction in aqueous systems is underlined.

APPENDIX: ELASTIC FREE ENERGY CHANGE OF NETWORKS

By extending the elastic equation¹⁵ which takes the limit of elongation into account for the isotropic deformation of a polymer chain in a solution, the following equation can be derived:

$$\Delta G^{elas} = \frac{3}{2} kTn \ln \frac{(1 + \alpha\lambda)^{1 + \alpha\lambda} (1 - \alpha\lambda)^{1 - \alpha\lambda}}{(1 + \lambda)^{1 + \lambda} (1 - \lambda)^{1 - \lambda}} \quad (A1)$$

We have assumed that the effect of the crosslinking points can be described by the following function:

$$S = (\text{const})k \ln \alpha \quad (A2)$$

Accordingly, the free energy of a single chain both of whose ends are fixed to the crosslinking points has the following form:

$$\Delta G^{elas} = \frac{3}{2} kT \left[n \ln \frac{(1 + \alpha\lambda)^{1 + \alpha\lambda} (1 - \alpha\lambda)^{1 - \alpha\lambda}}{(1 + \lambda)^{1 + \lambda} (1 - \lambda)^{1 - \lambda}} - \ln \alpha \right] \quad (A3)$$

Hydrophobic interaction can be expected to lead to polymer chain association in the gel, associated segments of which act as physical crosslinking points. For simplicity, the original chain is assumed to be divided by the association into short chains of equal length. The advantage of utilizing the elastic equation is that it reflects the effect of the elongation limit of the chain. Assuming that the partition of the crosslinking points could be replaced by that of short chains produced from the formation of crosslinking points, the free energy of the polymer chain with crosslinking points has the form

$$\Delta G^{\text{elas}} = \frac{3kT}{2} N_{\text{sc}} \left[\frac{n}{N_{\text{sc}}} \ln \frac{(1 + \alpha' \lambda')^{1 + \alpha' \lambda'} (1 - \alpha' \lambda')^{1 - \alpha' \lambda'}}{(1 + \lambda')^{1 + \lambda'} (1 - \lambda')^{1 - \lambda'}} - \ln \alpha' \right]. \quad (\text{A4})$$

Here, α' and λ' are the expansion factor and the initial state index of the short chains, respectively. The expansion factor of the original chain changes with the formation of crosslinking points. The relationship between the original chain and the short chain is given by

$$\alpha = \alpha' N_{\text{sc}}^{-1/2}. \quad (\text{A5})$$

At the same time, the initial state index of the original chain is related to that of the short chains as follows:

$$\lambda' = \lambda N_{\text{sc}}^{1/2}. \quad (\text{A6})$$

Thus the form of the elastic free energy is given from Eq. (A4) as follows:

$$\Delta G^{\text{elas}} = \frac{3}{2} kT \left[n \ln \frac{(1 + \alpha \lambda)^{1 + \alpha \lambda} (1 - \alpha \lambda)^{1 - \alpha \lambda}}{(1 + \lambda)^{1 + \lambda} (1 - \lambda)^{1 - \lambda}} - N_{\text{sc}} \ln \alpha \right]. \quad (\text{A7})$$

In Eq. (A7), α and λ are the value of the short chains.

In the calculations, we first give the number of crosslinking points N_b and calculate the α and λ , then search for the α that gives the free energy minimum through Eq. (15), and evaluate the expansion factor of the polymer chain that contains the hydrophobic pseudo crosslinking points through Eq. (A5). The ratio of the volume of the gel with

quasicrosslinking points V to the original gel V_0 is given by volume ratio $V/V_0 = \alpha^3$. (A8)

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