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Hysteresis and Incubation in the Dynamics of Volume Transition of Spherical Gels

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ABSTRACT: The dynamics of volume transition of a spherical gel is studied theoretically. The time evolution of the radius and the strain of the gel are calculated numerically. It is shown that (i) the threshold temperature at which the swelling starts to take place is different from the temperature at which the collapsing starts (i.e., there is a hysteresis), (ii) in the swelling process there is an incubation period during which the whole gel is swollen only slightly, followed by the main process in which a large volume change is caused by the motion of the interface between the swollen state and the collapsed state, and (iii) the incubation time becomes longer as the final temperature approaches the threshold temperature. These results are in agreement with experimental observations.

1. Introduction

Certain kinds of polymer gels immersed in a solvent exhibit a discontinuous change of equilibrium volume when external conditions such as temperature or solvent composition are changed continuously. This change is known to be a first-order phase transition and is called the volume transition.[1,2] The ratio of the volume change can be as large as hundreds. The phase with the smaller volume is called the collapsed phase, and that with the larger volume the swollen phase.

In the earlier works[3,4] the volume transition was interpreted in analogy with the gas−liquid transition of simple fluids. However, recent studies indicate that such analogy is incorrect.

Experimentally, Hirokawa and Tanaka[5] reported that the threshold temperature at which the collapsed phase of the gel transforms to the swollen phase is different from the temperature at which the swollen phase transforms to the collapsed phase: there is a hysteresis. The temperature difference was only 0.2 °C for nonionic gels, but can be as large as 10 °C for ionic gels.[6] This strange phenomenon, however, was not taken seriously since the experiment also showed that the transition temperature depends on gel samples.[6]

A theoretical argument for the importance of the hysteresis was given by Sekimoto.[7] He showed that the hysteresis is an intrinsic property of the volume transition of gels. His argument is as follows. Consider a gel immersed in an abundant solvent. Let $A(V,T)$ be the free energy of the whole system (i.e., the gel plus the surrounding solvent) when the gel volume is V and the temperature is T. The equilibrium volume of the gel is determined by the condition that $A(V,T)$ be minimum with respect to V, i.e.

$$\frac{\partial A}{\partial V} = 0 \tag{1}$$

Figure 1a shows a schematic representation of the temperature dependence of $A(V,T)$ obtained by mean field theory.[3,4] The classical theory argues that if $A(V,T)$ has double minima, the state with lower free energy must be chosen, and therefore the volume transition takes place at a temperature at which the free energy of the two minima become equal to each other (i.e., the temperature T_M in Figure 1a). This argument is entirely analogous to the gas−liquid phase transition: if $F(V,T)$ is the Helmholtz free energy of a fluid system, the equilibrium volume of the system under pressure P is determined by the condition that

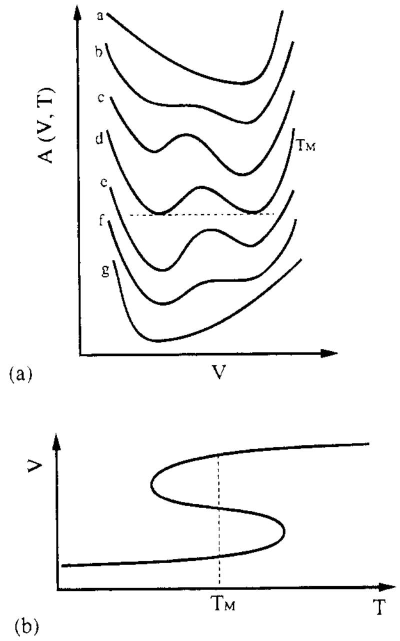

Figure 1. (a) Schematic diagram of the free energy of a gel undergoing volume transition. $A(V,T)$ is the free energy of the state that the gel is homogeneous and has a volume V at temperature T. T_M denotes the Maxwell temperature at which the free energies of the two local minima are equal to each other. (b) The volume V at which $\partial A/\partial V$ is zero is plotted against the temperature.

$$A(V,T) = F(V,T) + PV \tag{2}$$

be minimum with respect to V. The gas−liquid transition takes place at the temperature at which the two local minima of $A(V,T)$ become equal to each other. We call such a temperature the Maxwell temperature T_M, as it is decided by the Maxwell construction.

In the case of gels, however, the above argument has a pitfall. Consider what happens in the intermediate state of the transition where the two phases coexist with each other (see Figure 2). In the gas−liquid transition,

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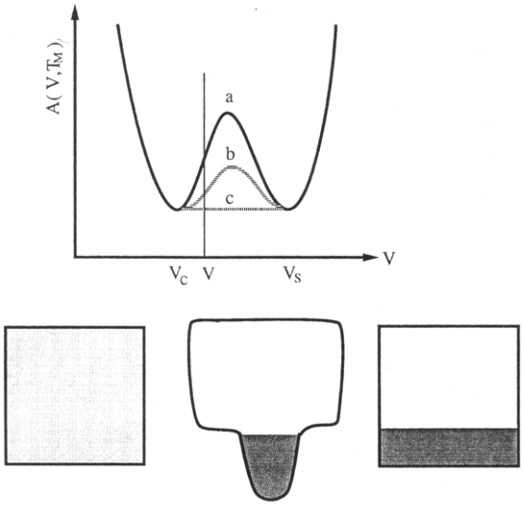

(a) (b) (c)

Figure 2. Free energy of a gel or fluid at the Maxwell temperature. Curve a denotes the free energy subject to the constraint that the density of the whole system is homogeneous. Curves b and c denote the minimum value of the free energy allowing phase separation. Curve c corresponds to the gas–liquid transition. Since the gas and liquid phases can coexist with no cost of free energy, curve c is horizontal between V_c and V_s. Curve b corresponds to gels. When the swollen phase coexist with the collapsed phase, both phases must be deformed from the equilibrium state. Consequently, the free energy curve of gels is above the horizontal line.

the two phases coexist as shown in Figure 2c. In this case, the cost of the free energy for the two phases to coexist is the interfacial energy, which is proportional to $V^{2/3}$ and can be negligible compared with the bulk energy. In gels, on the other hand, for the swollen phase and the collapsed phase to coexist, both phases must be deformed as shown in Figure 2b. In this case, the coexistence cost is the elastic energy of deformation and is proportional to the volume of the gel. Therefore the phase transition cannot take place at the Maxwell temperature T_M where the free energy of the two phases are equal to each other: the temperature has to be higher (or lower) than T_M in order to overcome the coexistence cost. The temperature difference is independent of the gel volume but can depend on the shape of the gel.

Sekimoto[7] discussed the condition for the volume transition of a spherical gel to take place and successfully explained the hysteresis effect observed by Matsuo et al.[6] for NIPA gel.

Although Sekimoto's argument is convincing, several questions remain.

(i) Sekimoto discussed the condition for the formation of the new phase but did not discuss whether the new phase grows or not. As the new phase grows, there is a larger elastic deformation, which may stop the growth of the new phase in a certain configuration. Indeed Kuroki and Sekimoto[8] showed that certain coexistence configurationa can be arrested.

(ii) Sekimoto did not discuss the dynamics of the volume transition. Experimentally, Matsuo and Tanaka[6] reported that the swelling and deswelling dynamics are quite anomalous. For example, when a collapsed phase turns into swollen phase, there is a certain incubation period during which the volume of the gel does not change appreciably. The main swelling takes place afterward.

In this paper, we shall answer these questions by solving the complete equation for the swelling dynamics.[9] In an earlier work[10] we discussed the dynamics of the volume transition in the one-dimensional case where the gel is confined in a narrow tube and can swell only in the longitudinal direction. In this situation, however, the phenomenon of hysteresis and the incubation do not appear and the above questions were not addressed.

In this paper, we consider the swelling and deswelling dynamics of a spherical gel. To simplify the analysis, we assume that spherical symmetry is always maintained throughout the process. This assumption, though useful to simplify the problem, excludes certain interesting phenomena such as wrinkling and bubbling,[11] which are known to take place during the course of large volume changes. These phenomena are related to elastic instabilities and may be suppressed in certain situations if the temperature is changed moderately. Despite the simplification in the model, we shall show that the swelling kinetics of the volume transition is rather complex.

2. Basic Equations

2.1. The Problem. We consider the following situation. A spherical gel is immersed in a solvent. Initially, the gel is in equilibrium in a stress-free state and has a volume V_{ini}. At time $t = 0$, the temperature is changed suddenly; then the gel will swell or deswell to have the final equilibrium volume V_{fin}. We shall discuss how the radius and the strain of the gel will change in time.

To describe the state of the gel, we choose a reference state and label each point of the gel by its radial distance R from the center in the reference state. Let L_0 be the length of the gel in the reference state; then $0 \le R \le L_0$. The state of the gel at a certain time t is represented by a function $r(R,t)$, which is the radial distance of the point R at time t.

For a spherically symmetric gel, the deformation of each gel element is uniaxial and can be characterized by the two principal strains,

$$w_{\mathrm{t}}(R,t) = \frac{r(R,t)}{R}, \qquad w_{\mathrm{l}}(R,t) = \frac{\partial r(R,t)}{\partial R} \tag{3}$$

We call them the transversal strain and the longitudinal strain, respectively. The deformation state of each gel element can be represented by a point in the two-dimensional plane $(w_{\mathrm{t}}, w_{\mathrm{l}})$. It will be shown later that such representation is useful to understand the strange dynamics in the volume transition. We shall call such a plane the deformation phase space.

2.2. The Free Energy. The free energy of the spherical gel is written as

$$A = \int_0^{L_0} a(w_{\mathrm{t}}, w_{\mathrm{l}}) 4\pi R^2 \, \mathrm{d}R \tag{4}$$

where $a(w_{\mathrm{t}}, w_{\mathrm{l}})$ is the free energy per unit volume of the reference state. In eq 4 the interfacial energy is neglected because it is much smaller than the elastic energy. In general, $a(w_{\mathrm{t}}, w_{\mathrm{l}})$ is a sum of two parts, the free energy of mixing and the free energy of elastic deformation. In our problem, we use, for simplicity, the Flory–Huggins type free energy[12] for ionic gels in a salt-free condition

$$a(w_{\mathrm{t}}, w_{\mathrm{l}})/k_{\mathrm{B}}T = v_1^{-1}(\phi_0/\phi)[(1-\phi)\ln(1-\phi) + \chi(T)\phi(1-\phi)] + (\nu_0/2)[2w_{\mathrm{t}}^2 + w_{\mathrm{l}}^2 - (1+2f)\ln(\phi_0/\phi)] \tag{5}$$

where ϕ and ϕ_0 are the volume fractions of polymer in the current and the reference states, respectively, v_1 is the specific volume of solvent, ν_0 is the number of chains per unit volume of gel in the reference state, f is the number of ionic groups per subchain, and $\chi(T)$ is the temperature-dependence interaction parameter. In this paper, we shall regard $\chi(T)$ as the only parameter that depends on temperature and consider the change of χ, rather than the temperature itself. The volume fraction ϕ is expressed by w_t and w_l as

$$\phi = \phi_0 / w_t^2 w_l \qquad (6)$$

We define σ_t and σ_l as the partial derivative of a with respect to w_t and w_l:

$$\sigma_t(w_t,w_l) \equiv \frac{1}{2}\frac{\partial a(w_t,w_l)}{\partial w_t}, \qquad \sigma_l(w_t,w_l) \equiv \frac{\partial a(w_t,w_l)}{\partial w_l} \qquad (7)$$

They correspond to the force acting on the unit area in the reference state. The factor $^1/_2$ in the first equation accounts for the fact that the deformation is uniaxial with degenerate principal strains w_l, w_t, and w_t.

2.3. Kinetic Equation. To derive the time evolution equations for *r(R,t)*, we use the variational principle.[9,13] According to it, the time derivative of *r(R,t)*

$$\dot{r} \equiv \frac{\partial r(R,t)}{\partial t} \qquad (8)$$

is determined by the condition that the Rayleighan

$$Y = \frac{1}{2}W + \dot{A} \qquad (9)$$

be minimized with respect to $\dot{r}$. In eq 9 W denotes the energy dissipation per unit time, and $\dot{A}$ denotes the time derivative of the free energy A.

The energy dissipation W is written as

$$W = \int_0^{L_0} \tilde{\zeta}(w_t,w_l)[\dot{r}(R,t) - v_s(R,t)]^2 4\pi R^2 \, \mathrm{d}R \qquad (10)$$

where $v_s(R,t)$ is the solvent velocity at point R and $\tilde{\zeta}(w_t,w_l)$ is the friction constant. For a spherical gel, the bulk velocity is zero, whence

$$\phi\dot{r} + (1 - \phi)v_s = 0 \qquad (11)$$

Therefore eq 10 is rewritten as

$$W = \int_0^{L_0} \zeta(w_t,w_l)\dot{r}^2 4\pi R^2 \, \mathrm{d}R \qquad (12)$$

where $\zeta(w_t,w_l) = \tilde{\zeta}(w_t,w_l)/(1 - \phi)^2$.

On the other hand, $\dot{A}$ is obtained from eq 4 as

$$\dot{A} = \int_0^{L_0}\left(\frac{\partial a}{\partial w_t}\frac{\partial w_t(R,t)}{\partial t} + \frac{\partial a}{\partial w_l}\frac{\partial w_l(R,t)}{\partial t}\right)4\pi R^2 \, \mathrm{d}R$$

$$= \int_0^{L_0}\left(2\sigma_t(w_t,w_l)\frac{\dot{r}}{R} + \sigma_l(w_t,w_l)\frac{\partial \dot{r}}{\partial R}\right)4\pi R^2 \, \mathrm{d}R \qquad (13)$$

Substituting eqs 12 and 13 into eq 9, we have

$$Y = \int_0^{L_0}\left(\frac{1}{2}\zeta\dot{r}^2 + 2\frac{\dot{r}}{R}(\sigma_t - \sigma_l) - \dot{r}\frac{\partial \sigma_l}{\partial R}\right)4\pi R^2 \, \mathrm{d}R + [4\pi R^2 \sigma_l \dot{r}]_0^{L_0} \qquad (14)$$

Then the condition $\delta Y / \delta \dot{r} = 0$ gives

$$\zeta\frac{\partial r}{\partial t} = \frac{\partial \sigma_l(w_t,w_l)}{\partial R} + 2\,\frac{\sigma_l(w_t,w_l) - \sigma_t(w_t,w_l)}{R} \qquad (15)$$

This equation has the same form as the classical equation for a small volume change,[14] but it should be noted that eq 15 is valid even if the volume change is very large. The same equation can be derived from a different formulation.[15]

2.4. Boundary and Initial Conditions. In order to solve eq 15, we need boundary and initial conditions. There are two boundaries; one is the outer boundary between the gel and the solvent, and the other is the inner boundary between the swollen phase and the collapsed phase. The latter boundary appears when the two phases coexist. Both boundary conditions are obtained from the local equilibrium assumption.

At the surface of the gel, the swelling equilibrium is maintained. Therefore,

$$\sigma_l(w_t,w_l) = 0 \qquad \text{at } R = L_0 \qquad (16)$$

Equation 16 determines w_l ($=\partial r/\partial R$) for given w_t ($=r/R$). Notice that the value of $\partial r/\partial R$ at the outer boundary changes with time since w_t changes with time.

At the interface between the collapsed phase and the swollen phase, w_t, must be continuous, but w_l can be discontinuous. Let (w_t,w_{Ms}), (w_t,w_{Mc}) be the strain of the gel at the interface. The condition that the two phases are in local equilibrium gives (see refs 18 and 19).

$$\left.\frac{\partial a(w_t,w_l)}{\partial w_l}\right|_{w_l=w_{Ms}} = \left.\frac{\partial a(w_t,w_l)}{\partial w_l}\right|_{w_l=w_{Mc}} = \frac{a(w_t,w_{Ms}) - a(w_t,w_{Mc})}{w_{Ms} - w_{Mc}} \qquad (17)$$

This equation determines w_{Mc}, w_{Ms} as a function of w_t.

Finally, the initial condition is

$$w_t(R,0) = w_l(R,0) = w_{ini} \qquad (18)$$

where w_{ini} is the swelling ratio in the equilibrium state as $\chi = \chi_{ini}$. For given $\sigma_t(w_t,w_t)$, $\sigma_l(w_t,w_l)$, and $\zeta(w_t,w_l)$, the above set of equations (eqs 15–18) determine *r(R,t)*.

2.5. Scaling Relation. There is a scaling relation which holds generally for any functional form of $a(w_t,w_l)$ and $\zeta(w_t,w_l)$.[10] One can prove easily that if *r(R,t)* is a solution for the set of equations 15–18, then $\alpha r(\alpha R,\alpha^2 t)$ is a solution for the gel with length αL_0. This means that if the size of the specimen is increased by a factor α, then the time needed for the swellings to take place will increase by the factor α^2. Such a scaling property has been confirmed experimentally.[6,20]

2.6. Numercial Calculation. We solved the above set of nonlinear equations numerically. The detail of the numerical procedure is described in the Appendix.

In the calculation shown below, we use the Flory–Huggins type free energy (eq 5), fixing the parameters ϕ_0, v_1, ν_0, and f as $\phi_0 = 0.07$, $v_1 = 3 \times 10^{-29}$ m^3, $\nu_0 = 1.2 \times 10^{27}$ m^{-3}, and $f = 2.0$. This corresponds to *N*-isopropylacrylamide (NIPA)/sodium acrylate gel in pure water. The same set of parameters is used by Sekimoto.[7] We shall consider the variation of χ only.

The friction constant $\zeta(w_t,w_l)$ is assumed to be constant independent of w_t and w_l. This assumption is perhaps unrealistic since ζ will increase drastically in the collapsed state where ϕ is close to 1. However, we

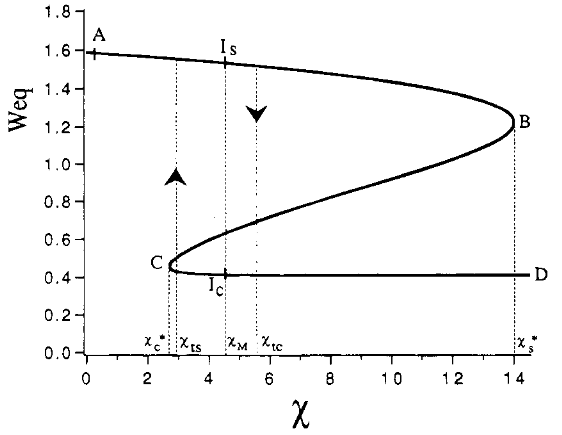

Figure 3. Equilibrium swelling ratio for the present model of the free energy. AB and CD denote the collapsed branch and the swollen branch, respectively. χ_c* and χ_s* corresponds to the end of the branches. At χ_M, the free energy of the swollen branch becomes equal to that of the collapsed branch. χ_{ts} and χ_{tc} indicate the transition χ parameter determined by Sekimoto.

chose this assumption deliberately since we wanted to study the effect of the free energy on the dynamics. The results for other form of $\zeta(w_t,w_l)$ will be reported elsewhere.

The calculation was performed for dimensionless quantities. The unit of length is L_0 and the unit of time is

$$\tau_0 = \frac{\zeta L_0^{\,2}}{k_B T v_1} \tag{19}$$

3. Equilibrium Properties

Before showing the dynamical process, we first discuss the equilibrium properties.

The equilibrium swelling ratio w is determined by $\partial a(w,w)/\partial w = 0$. From eq 5, it follows

$$\chi = \frac{w^3}{\phi_0^{\,2}}\left[-\ln\left(1 - \frac{\phi_0}{w^3}\right)w^3 - v_1\nu_0 w^2 + \frac{v_1\nu_0(1+2f)}{2} - \phi_0\right] \tag{20}$$

This is plotted in Figure 3. It is seen that in a certain range of χ, i.e., $\chi_c^* \le \chi \le \chi_s^*$, eq 20 has three solutions of w: w_1, w_2, and w_3 ($w_1 < w_2 < w_3$). The solutions w_1 and w_3 correspond to the metastable state, and w_2 the unstable state. We call the contour of the point (χ,w_3) the swollen branch, and the contour (χ,w_1) the collapsed branch.

The χ_M in Figure 3 represents the χ at which the free energy of the swollen phase and that of collapsed phase become equal to each other, i.e., $a(w_1,w_1,\chi_M) = a(w_3,w_3,\chi_M)$. This equation corresponds to the Maxwell temperature.

The χ_{ts} (and χ_{tc}) in Figure 3 are the threshold χ parameters at which the collapsed to swollen (and swollen to collapsed) phase transition starts to take place. They are determined by Sekimoto[7] as follows.

When a collapsed phase turns into a swollen phase, a thin layer of swollen phase must appear on the surface of the gel. Since the layer is thin, the swollen phase is significantly deformed from the isotropic state, while the collapsed phase remains in the isotropic state. Since w_t must be continuous at the interface, the deformation of the collapsed phase and that of the swollen phase are written as (w,w) and (w,w_{new}), respectively. The condition that the swollen phase is in equilibrium with the collapsed phase is (see eq 17)

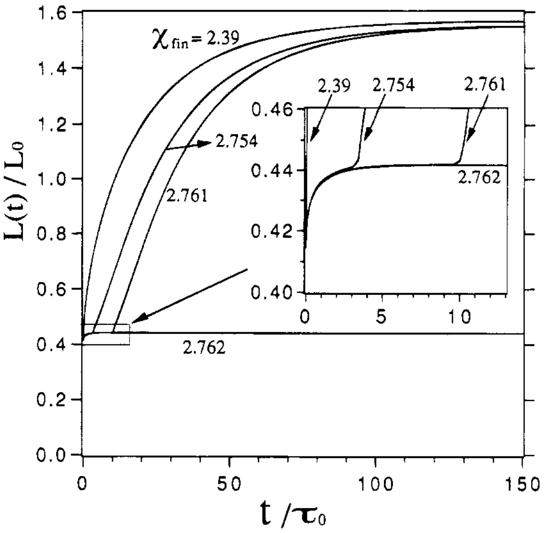

Figure 4. Time evolution of the radius of a gel when χ is suddenly changed from $\chi_{\text{ini}} = 4.45$ to various values of χ_{fin} indicated in the figure. The gel was initially in the collapsed state and in equilibrium at $\chi_{\text{ini}} = 4.45$.

$$\sigma_l(w,w_{\text{new}};\chi) = \sigma_l(w,w;\chi) = \frac{a(w,w_{\text{new}};\chi) - a(w,w;\chi)}{w_{\text{new}} - w} \tag{21}$$

On the other hand, the condition that the swollen phase is in equilibrium with the pure solvent gives

$$\sigma_l(w,w_{\text{new}};\chi) = 0 \tag{22}$$

Equations 21 and 22 give

$$\sigma_l(w,w;\chi_{ts}) = 0, \qquad \sigma_l(w,w_{\text{new}};\chi_{ts}) = 0, \qquad a(w,w_{\text{new}};\chi_{ts}) = a(w,w;\chi_{ts}) \tag{23}$$

This set of equations determines w, w_{new}, and χ_{ts}. The same set of equations give the other threshold χ parameter χ_{tc}, where $w_{\text{new}} < w$.

For the present model of free energy, the numerical values of these χ parameters are

$$\chi_c^* = 2.701, \qquad \chi_{ts} = 2.7613, \qquad \chi_M = 4.45, \qquad \chi_{tc} = 5.532, \qquad \chi_s^* = 14.02 \tag{24}$$

4. Swelling Dynamics

4.1. Characteristic Behavior in Swelling. First we fix the initial state at the point I_c in Figure 3 and study how the gel swells when χ is varied from χ_{ini} to a smaller value χ_{fin}. We fix χ_{ini} at 4.45 but the following description will perhaps hold for any initial state provided it is on the collapsed branch.

Figure 4 shows the time evolution of the gel radius $L(t)$ when χ is changed from $\chi_{\text{ini}} = 4.45$ to various values shown in the figure. Notice that the swelling behavior for $\chi_{\text{fin}} = 2.762$ is quite different from those or other values of χ_{fin}. For $\chi_{\text{fin}} = 2.762$, $L(t)$ increases only slightly ($L(\infty)/L(0) = 1.08$), while $L(t)$ increases dramatically for other χ_{fin}.

This demonstrates that there is a certain threshold χ parameter below which a large volume change can take place. In the following we shall show that this threshold value is given by χ_{ts}; i.e., if χ_{fin} is larger than χ_{ts}, the

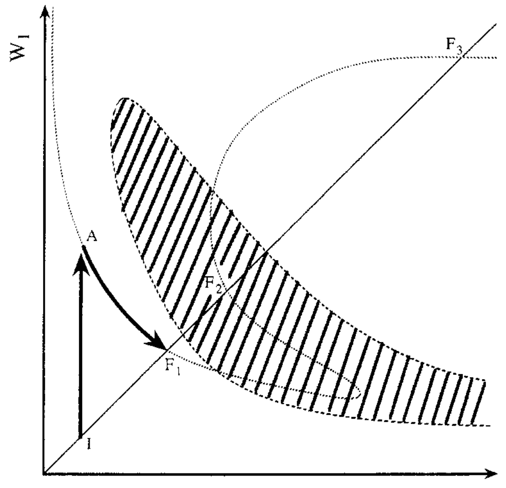

Figure 5. Schematic diagram of the deformation phase space for $\chi_{\text{fin}} = 2.762$. The dotted line indicates the contour of the free boundary, and the hatched region indicates the coexistence region. The thin solid line is the isotropic line ($w_l = w_t$). The points F_1, F_2, and F_3 correspond to the three solutions w_1, w_2, and w_3 in Figure 3. The thick solid line indicates the trajectory of the surface element of the gel when χ is changed from χ_{ini} to χ_{fin}.

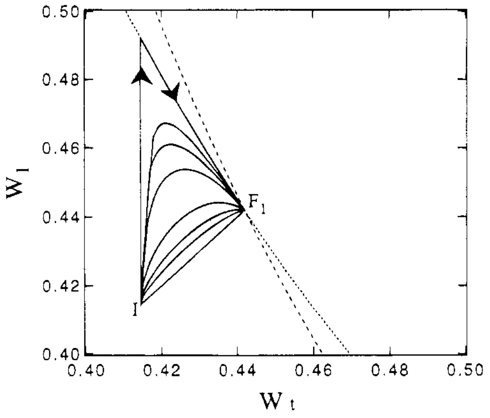

Figure 6. Calculated trajectories of various gel elements for the change of $\chi_{\text{ini}} = 4.45$ and $\chi_{\text{fin}} = 2.762$. Each solid line corresponds to the gel elements at $R/L_0 = 1.0, 0.98, 0.96, 0.875, 0.75, 0.5, 0.04$, and 0.0 from top to bottom.

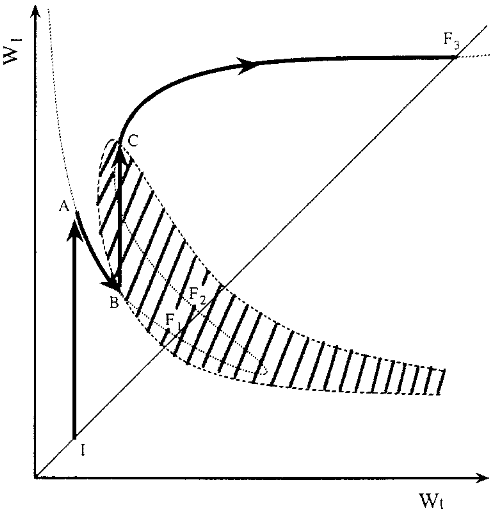

Figure 7. Schematic diagram of the deformation phase space for $\chi_{\text{fin}} = 2.761$. The meaning of the lines is the same as in Figure 5.

swelling is small, while if χ_{fin} is smaller than χ_{ts}, the swelling is large.

To understand the origin for the threshold behavior, we studied the motion of each gel element in the deformation phase space. They are schematically illustrated in Figures 5 and 7. We found that two curves in this space are important. One is the contour of the free boundary, i.e., the set of points satisfying $\sigma_l(w_t,w_l) = 0$. The surface element must be on this curve. The other is the contour of the coexistence boundary, i.e., the points (w_t,w_{Mc}) and (w_t,w_{Ms}) which satisfy eq 17. If a gel element is located inside the coexistence region surrounded by this curve, it will phase separate into the swollen state (w_t,w_{Ms}) and the collapsed state (w_t,w_{Mc}).

Figure 5 is a schematic diagram of the deformation phase space for χ_{fin} larger than χ_{ts}. Here the contour of the free boundary is indicated by the dashed line and the contour of the coexistence boundary is indicate by the dotted line. The three points F_1, F_2, and F_3 are the intersections between the free boundary line, $\sigma_l(w_t,w_l) = 0$, and the isotropic line, $w_l = w_t$. They correspond to the three solutions w_1, w_2, and w_3 in Figure 3. The points F_1 and F_3 are the local minima of the free energy surface while the point F_2 is the local maximum. The point I in Figure 5 represents the initial step $(w_{\text{ini}},w_{\text{ini}})$.

Using the diagram of Figure 5, we can explain the characteristic swelling behavior for $\chi_{\text{fin}} > \chi_{\text{ts}}$. When χ is changed from χ_{ini} to χ_{fin}, the surface element must move to a point on the free boundary contour. Since $w_t = r/R$ cannot change discontinuously in time, while $w_l = \partial r/\partial R$ can, the surface element jumps vertically to the point A. As time goes on, the surface element gradually moves from the point A to the local minimum F_1 along the free boundary contour. Other inner elements follow similar trajectories. The actual trajectories obtained by numerical calculations are shown in Figure 6. Since none of the points cross the coexistence boundary, the swelling is not associated with a phase transition.

Now when χ_{fin} is smaller than χ_{ts} the contours become as they are shown in Figure 7. In this case, the swelling behavior is entirely different. When χ is changed to χ_{fin}, the surface element jumps from the point I to the point A and then gradually moves along the contour of the free boundary toward the point F_1, which is the local minimum of the free energy. However, as it moves toward F_1, it crosses the coexistence boundary. When this happens, a swollen-phase appears on the surface of the gel. Consequently, the surface element jumps to the point C. Since the new phase is highly deformed, the surface element moves further from the point C to the final equilibrium point F_3 in order to relax the energy of deformation. Accompanying this motion, other gel elements move along similar trajectories. The actual trajectories obtained by numerical calculation are shown in Figure 8.

Comparing Figure 5 with Figure 7, we can now see why the swelling is small for $\chi_{\text{fin}} = 2.762$ but large for $\chi_{\text{fin}} = 2.761$. In the former case, the trajectory of the boundary element does not cross the coexistence boundary, while the trajectory crosses the coexistence bundary in the latter case. The transition between the two cases occurs when the three lines, i.e., the free boundary line, the coexistence boundary line, and the isotropic line, meet at the same point. This condition precisely corresponds to Sekimoto's condition (eq 23). We thus confirm that Sekimoto's condition actually gives the threshold χ value for the transition to take place.

4.2. Small Swelling without Phase Transition. The time evolution of $w_l(R,t)$ for $\chi_{\text{fin}} = 2.762$ is shown

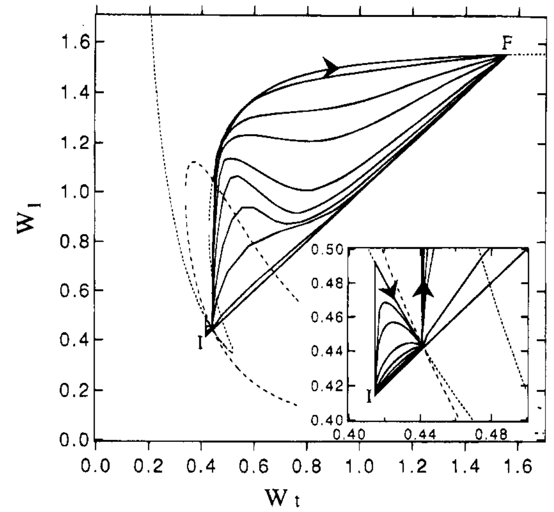

Figure 8. Calculated trajectories of various elements for the change of $\chi_{ini} = 4.45$ and $\chi_{fin} = 2.761$. Each solid line corresponds to the gel elements at $R/L_0 = 1.0, 0.98, 0.96, 0.875, 0.75, 0.5, 0.04$, and 0.0 from top to bottom.

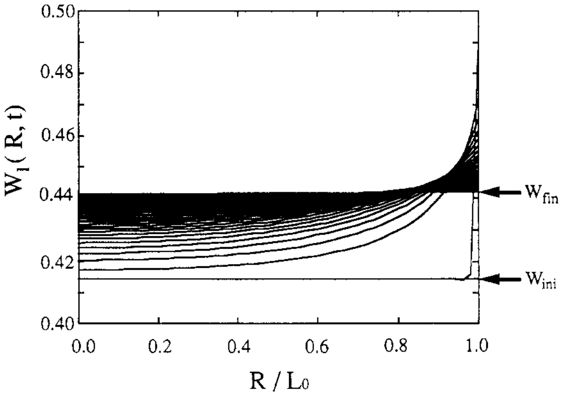

Figure 9. Time evolution of $w_l(R,t)$ when χ is changed from $\chi_{ini} = 4.45$ to $\chi_{fin} = 2.762$. Each line indicates the profile of $w_l(R,t)$ plotted at every $0.12\tau_0$.

in Figure 9. In this case, since $w_{fin} - w_{ini}$ is small, the swelling dynamics can be described by a linear equation. For a small deviation from the equilibrium, the free energy $a(w_t,w_l)$ can be expanded around (w_{fin},w_{fin}) as follows.

$$a(w_t,w_l) = \frac{2}{3}G(w_t - w_l)^2 + \frac{1}{2}K(2w_t + w_l - 3w_{fin})^2 \tag{25}$$

where G and K are shear and bulk modulus respectively. They are given by

$$\left.\frac{\partial^2 a}{\partial w_l^2}\right|_{w_t=w_{fin}} = \frac{4}{3}G + K$$

$$\left.\frac{\partial^2 a}{\partial w_t^2}\right|_{w_t=w_{fin}} = \frac{4}{3}G + 4K \tag{26}$$

Equations 15 and 25 give a linear equation for $u(R,t) = r(R,t) - w_{fin}R$

$$\zeta\frac{\partial u}{\partial t} = \left(K + \frac{4}{3}G\right)\left[\frac{\partial^2 u}{\partial R^2} + \frac{2}{R}\frac{\partial u}{\partial R} - \frac{2u}{R^2}\right] \tag{27}$$

The equation has been solved by several authors.[14,16,17] The characteristic time of swelling is given by

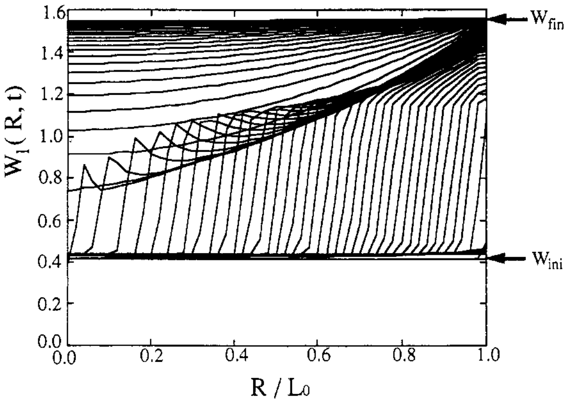

Figure 10. Time evolution of $w_l(R,t)$ when χ is changed from $x_{ini} = 4.45$ to $\chi_{fin} = 2.761$. Each line indicates the profile of $w_l(R,t)$ plotted at every $2.4\tau_0$.

$$\tau \simeq \frac{\zeta L_0^2}{K + {}^4/_3 G} \tag{28}$$

Figure 9 indicates that $w_l(R,t)$ near the gel surface shows a maximum as a function of time: w_l near the surface first increases and then decreases to the final value w_{fin} while w_l in the inner region monotonically increases to w_{fin}. The maximum arises from the negative slope of the free boundary line at point F_1 (i.e., $\mathrm{d}w_l/\mathrm{d}w_t < 0$) and can be reproduced by the linear swelling equation.

4.3. Large Swelling with Phase Transition.

Figure 4 indicates that the swelling behavior is anomalous for $\chi_{fin} = 2.761$ and 2.754. When χ is changed to χ_{fin}, the gel radius $L(t)$ increases slightly and stays at a certain pseudosteady value for a certain period of time. After sometime, say t_1, the gel starts to swell again with considerable speed. We shall call the initial period between 0 and t_1 the incubation period. From the explanation given for Figure 7, it is clear that the incubation period corresponds to the period that the surface element moves from point A to point B in Figure 7. The large swelling starts when the surface element crosses the coexistence boundary, i.e., when the swollen phase appears on the surface.

The time evolution of $w_l(R,t)$ for $\chi_{fin} = 2.761$ is shown in Figure 10. Figures 8 and 10 show that the swelling process can be divided into three stages (see Figure 11a).

(i) Incubation period: During the incubation period, the gel is in the collapsed branch. The surface element moves along the free boundary line until it crosses the coexistence line at time t_1. The swelling kinetics of this period is described by the linear swelling equation 27, where K and G should be evaluated by eq 26 at the pseudoequilibrium point F_1.

(ii) Coexistence period: At $t = t_1$, a thin layer of the swollen phase appears on the surface of the gel, and there is a sharp interface between the swollen phase and the collapsed phase. In principle, the interface should be represented by a vertical line across which w_l is discontinuous. In Figure 10, however, the interface is denoted by a region where $\mathrm{d}w_l/\mathrm{d}R$ is large. This is due to a rather crude numerical scheme employed in the present study. One can develop a numerical scheme which precisely determines the position of the interface, but we did not attempt it here.

As time goes on, the swollen phase grows and the interface moves toward the center. At time t_2, the interface reaches the center and disappears. The coexistence period is the time between t_1 and t_2.

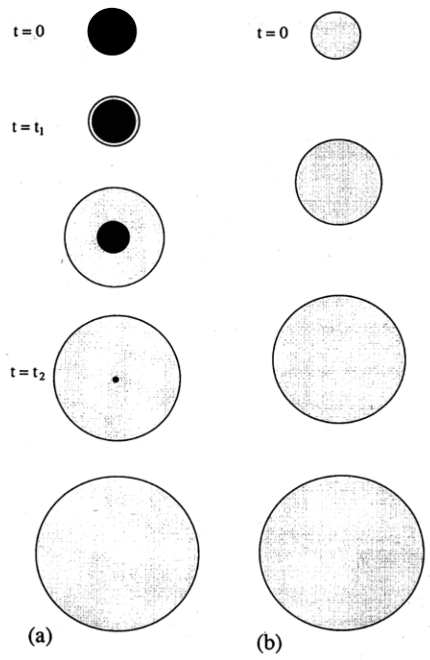

Figure 11. Schematic diagram of the swelling behavior with phase coexistence (a) and without phase coexistence (b).

(iii) The period of one-phase swelling: At time t_2, the collapsed phase disappears, but the gel is not yet in the equilibrium state and continues to swell. Since there is no sharp interface, the process can be approximately described by the linear equation (eq 27), where the elastic constant K and G must be evaluated at the final equilibrium point F_3.

Figure 12 shows the time evolution of the volume change of each gel element plotted in real space. Notice that the volume change taking place in the coexistence period is not very large; a large volume change takes place in the period of the one-phasing swelling.

4.4. Relaxation and Incubation Time. In order to quantify the swelling speed, we studied two characteristic times, the incubation time τ_{incu}, and the swelling time, τ_{swell}. Here, τ_{incu} is the time at which the new phase appears on the gel surface, i.e., $\tau_{incu} = t_1$, and τ_{swell} is the time at which the gel radius $L(t)$ becomes equal to the arithmetic average of the initial and final values, i.e., $L(\tau_{swell}) = (L(\infty) + L(0))/2$. Figure 13 shows τ_{incu} and τ_{swell} as a function of χ_{fin}. It is seen that (i) both τ_{incu} and τ_{swell} diverge as χ_{fin} approaches χ_{ts} and that (ii) the incubation time is visible only when χ_{fin} becomes close enough to χ_{ts}.

The divergence of τ_{incu} can be explained as follows. The incubation time is given by the time at which the surface element reaches point B in Figure 7, i.e., $w_l(L_0, \tau_{incu}) = w_{lB}$. During the incubation period the time evolution of $w_l(L_0,t)$ can be approximately written as

$$w_l(L_0,t) - w_1 \propto \exp\left(-\frac{t}{\tau}\right) \tag{29}$$

where τ is the longest relaxation time obtained from the linear diffusion equation. Thus $\tau_{incu} \simeq \tau \ln|w_{lB} - w_1|^{-1}$. Now when χ_{fin} is close to χ_{ts}, w_{lB} and w_1 are close to each other, and we can assume $|\chi_{fin} - \chi_{ts}| \propto |w_{lB} - w_1|$. Therefore the incubation time diverges as

$$\tau_{incu} \propto \ln|\chi_{fin} - \chi_{ts}|^{-1} \tag{30}$$

The divergence of χ_{swell} has the same origin as that for the one-dimensional case since the swelling is essentially one-dimensional in the initial stage. Therefore the divergence of χ_{swell} is described by

$$\chi_{swell} \propto \frac{1}{|\chi_{fin} - \chi_{ts}|} \tag{31}$$

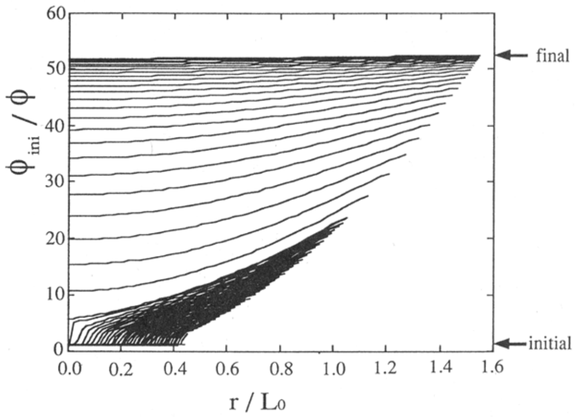

Figure 12. Time evolution of the specific volume of each gel element; $w_t^2 w_l/w_{ini}^3 = \phi_{ini}/\phi$ is plotted against the distance from the center in the real space. The time interval between the consecutive curves is $0.12\tau_0$.

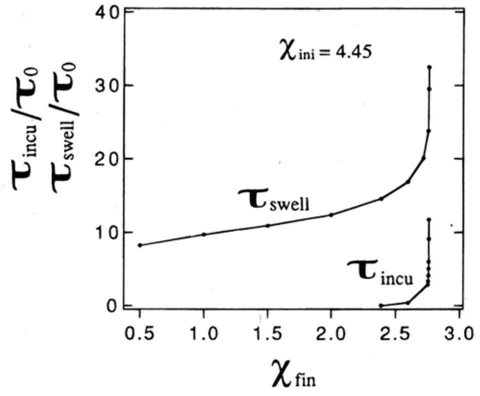

Figure 13. The swelling time and the incubation time are plotted against χ_{fin}, where χ_{ini} is fixed at 4.45.

4.5. Large Swelling without Volume Transition. It must be mentioned that the discontinuous interface between the swollen phase and the collapsed phase does not always appear for $\chi_{fin} < \chi_{tc}$. If χ_{fin} becomes very small (much smaller than χ_c^{*}), the collapsed phase cannot be stable, and the swelling can take place without having the interface. The case of $\chi_{fin} = 2.39$ shown in Figure 4 is an example of such a case. In this case, there is no incubation period. The trajectories of gel elements are shown in Figure 14. The time evolution of w_l and the schematic of swelling behavior are shown in Figures 15 and 11b, respectively. Here there is no discontinuity in w_l.

5. Collapsing Dynamics

5.1. Characteristic Behavior in Collapsing. We studied the collapsing dynamics for the following situation. We fix the initial state at the point I_s in Figure 3 and change χ to a larger value χ_{fin}. Figure 16 indicates the time evolution of the gel radius. Again, the gel shrinks only slightly for $\chi_{fin} = 5.53$ but shrinks considerably for $\chi_{fin} = 5.54$ and 5.55. This is because the threshold χ parameter for collapsing, $\chi_{tc} = 5.532$, is between 5.53 and 5.54. The schematic trajectories of the surface element in the deformation phase space are shown in Figures 17 and 19. For $\chi_{fin} < \chi_{tc}$ (Figure 17), the local minimum F_3 toward which the surface element

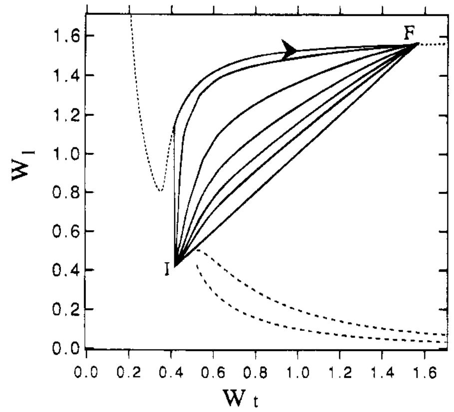

Figure 14. Trajectories of various elements for the change of $\chi_{ini} = 4.45$ and $\chi_{fin} = 2.39$. Each solid line corresponds to the gel elements at $R/L_0 = 1.0$, 0.96, 0.875, 0.75, 0.625, 0.5, and 0.0 from top to bottom.

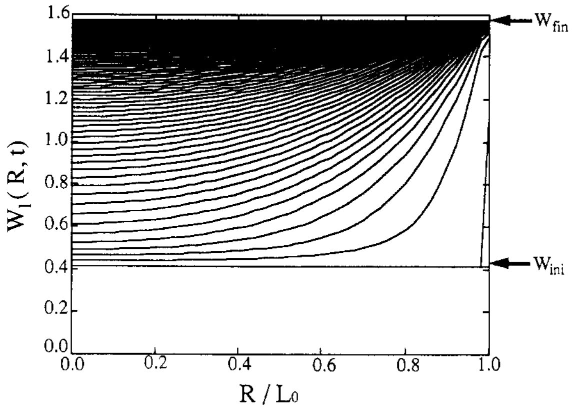

Figure 15. Time evolution of $w_l(R,t)$ when χ is changed from $\chi_{ini} = 4.45$ to $\chi_{fin} = 2.39$. Each line indicates the profile of $w_l(R,t)$ plotted at every $1.2\tau_0$.

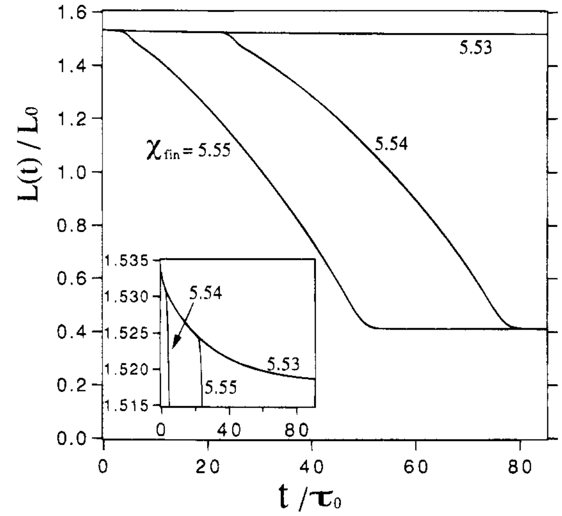

Figure 16. Time evolution of the radius of a gel when χ is suddenly changed from $\chi_{ini} = 4.45$ to various values χ_{fin} indicated in the figure. The gel was initially in the swollen state at $\chi_{ini} = 4.45$.

approaches is outside the coexistence region. Therefore the surface element moves as I → A → F_3. On the other hand, for $\chi_{fin} > \chi_{tc}$ (Figure 19), the local minimum F_3 is inside the coexistence region. Consequently, the surface element moves as I → A → B → C → F_1. The actual trajectories obtained by numerical calculations are shown in Figures 18 and 20.

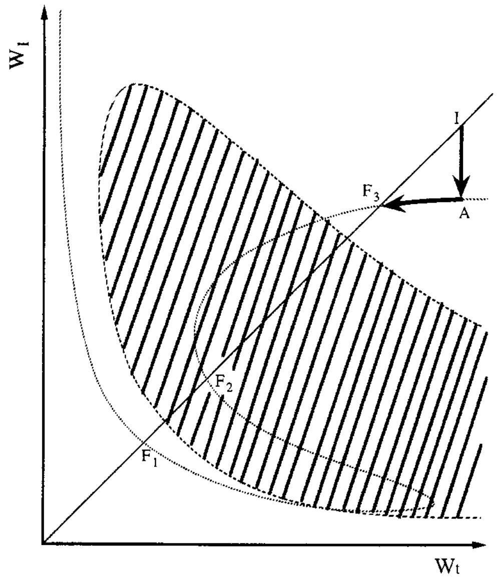

Figure 17. Schematic diagram of the deformation phase space for $\chi_{fin} = 5.53$. See Figure 5 for the meaning of the curves.

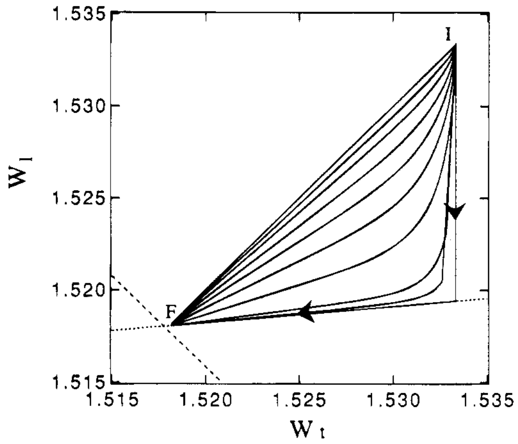

Figure 18. Calculated trajectories of various elements for the change of $\chi_{ini} = 4.45$ and $\chi_{fin} = 5.53$.

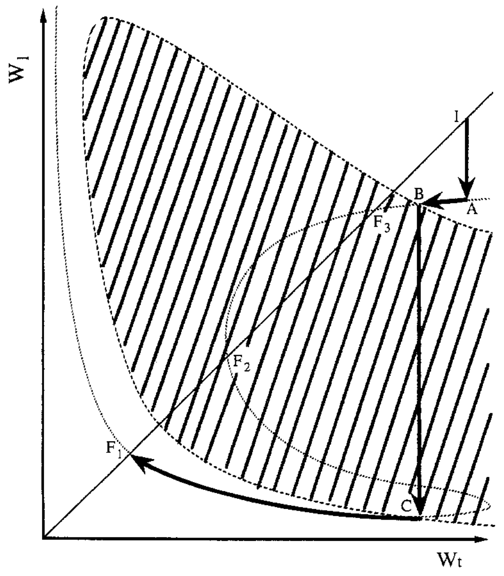

Figure 19. Schematic diagram of the deformation phase space for $\chi_{fin} = 5.54$. See Figure 5 for the meaning of the curves.

5.2. Small Collapsing without Phase Transition. Figure 21 shows the time evolution of $w_l(R,t)$ for $\chi_{fin} = 5.53$, which is below χ_{tc}. Since the change in r is small, the process can be described by the linear equation (eq 27). In this case, w_l decreases monotonically since the

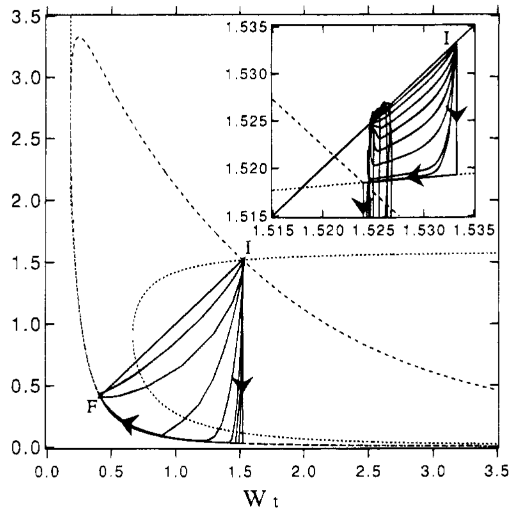

Figure 20. Calculated trajectories of various elements for the change of $\chi_{ini} = 4.45$ and $\chi_{fin} = 5.53$.

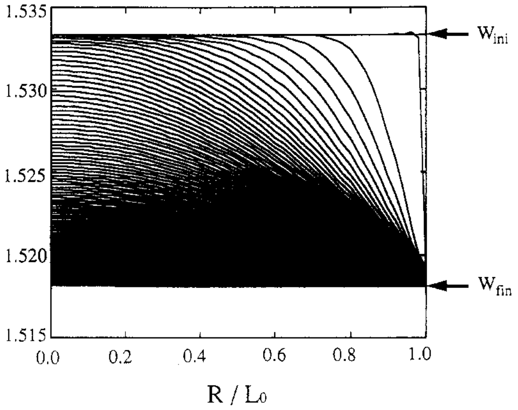

Figure 21. Time evolution of $w_l(R,t)$ when χ is changed from $\chi_{ini} = 4.45$ to $\chi_{fin} = 5.53$. Each line indicates the profile of $w_l(R,t)$ plotted at every $0.12\tau_0$.

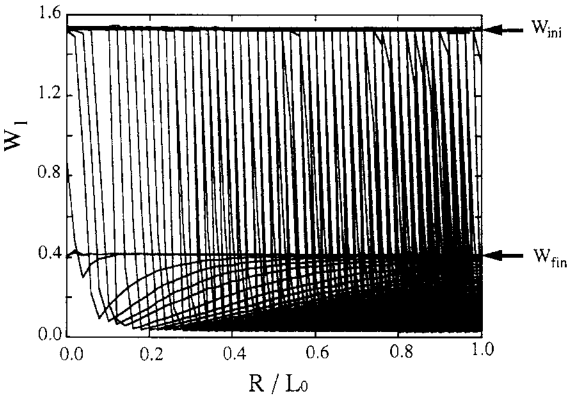

Figure 22. Time evolution of $w_l(R,t)$ when χ is changed from $\chi_{ini} = 4.45$ to $\chi_{fin} = 5.54$. Each line indicates the profile of $w_l(R,t)$ plotted at every $0.12\tau_0$.

slope dw_l/dw_t along the free boundary line is now positive.

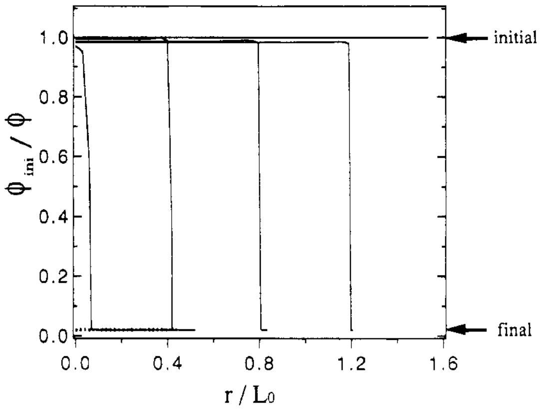

Figure 23. Time evolution of the specific volume of each gel element; $w_t^2 w_l/w_{ini}^3 = \phi_{ini}/\phi$ is plotted against the distance from the center in the real space. The time interval between the consecutive curves is $0.12\tau_0$. The dotted line indicates the specific volume of each element in the final equilibrium state.

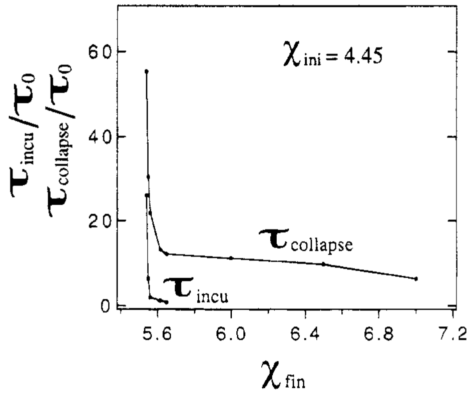

Figure 24. The collapsing time and the incubation time are plotted against χ_{fin}, where χ_{ini} is fixed at 4.45.

5.3. Large Collapsing with Phase Transition. Figure 22 shows the time evolutions of $w_l(R,t)$ for $\chi_{fin} = 5.54$, which is above χ_{tc}. The characteristic feature of the collapsing is the same as that of swelling: there are also three stages, the incubation, coexistence, and one-phase collapsing. In the case of swelling, the major volume change takes place in the one-phase swelling stage. On the other hand, in the case of collapsing, the major volume change is caused during the coexistence period. Figure 23 shows the change of the specific volume in real space.

5.4. Relaxation and Incubation Time for Collapsing. As in the case of swelling, we define two characteristic times, τ_{incu} and $\tau_{collapse}$, for the collapsing process. Figure 24 shows how τ_{incu} and $\tau_{collapse}$ depend on χ_{fin}. It is seen that both τ_{incu} and $\tau_{collapse}$ diverge as χ_{fin} approaches χ_{tc}. The divergence may be described by $\ln(\chi_c - \chi_{tc})^{-1}$.

6. Summary

We have studied the swelling and collapsing dynamics of spherically symmetric gels. By solving the nonlinear diffusion equation, we have confirmed that there is a hysteresis and that the transition temperature is given by Sekimoto's condition. We have found that when the swelling or collapsing is associated with a phase transition, there is an incubation period before the main volume change takes place. The incubation period is needed for the appearance of a new phase on the gel surface. The incubation period increases sharply as the temperature approaches the threshold temperature. These results are in agreement with experiments.[6]

Acknowledgment. We thank Prof. K. Sekimoto for his stimulating and helpful discussions.

Appendix

To find a numerical scheme, it is convenient to use the variational principle. We divide the radius L_0 of the gel in the reference state into N segments and replace the continuous function $r(T,t)$ by a piecewise linear function

$$r(R,t) = r_i(t) + \frac{r_{i+1}(t) - r_i(t)}{\Delta R}(R - R_i) \qquad \text{for } R_i \le R \le R_{i+1} \quad (32)$$

where $R_i = iL_0/N$, $\Delta R = R_{i+1} - R_i = L_0/N$, and $r_i(t)$ is the parameter to be determined numerically. Substituting eq 32 into eq 12, we have

$$W = \sum_{i=0}^{N-1} \int_{R_i}^{R_{i+1}} \zeta \dot{r}(R,t)^2 \mathrm{r}\pi R^2 \, \mathrm{d}R = 4\pi\Delta R \sum_{i=0}^{N-1} \zeta \Bigg[\left(\frac{1}{3}R_i^{\ 2} + \frac{1}{2}\Delta R R_i + \frac{1}{5}(\Delta R)^2\right)\dot{r}_{i+1}^{\ 2} + \left(\frac{1}{3}R_i^{\ 2} + \frac{1}{3}\Delta R R_i + \frac{1}{10}(\Delta R)^2\right)\dot{r}_i \dot{r}_{i+1} + \left(\frac{1}{3}R_i^{\ 2} + \frac{1}{6}\Delta R R_i + \frac{1}{30}(\Delta R)^2\right)\dot{r}_i^{\ 2}\Bigg] \quad (33)$$

Similarly

$$\dot{A} = 4\pi \sum_{i=0}^{N-1} \{\sigma_t(w_{ti}, w_{li})\Delta R R_i \dot{r}_i + \sigma_l(w_{ti}, w_{li}) R_i^{\ 2}(\dot{r}_{i+1} - \dot{r}_i)\} \quad (34)$$

where $w_{ti} = r_i R_i$ and $\omega_{li} = (r_{i+1} - r_{i-1})/2\Delta R$. The $\dot{r}_i$ are now determined by the condition $\partial(W/2 + \dot{A})/\partial \dot{r}_i = 0$. This gives

$$\frac{1}{2}\frac{\zeta}{R_i^{\ 2}}\Bigg[\left(\frac{1}{3}R_{i+1}^{\ 2} + \frac{1}{3}\Delta R R_{i-1} + \frac{1}{10}(\Delta R)^2\right)\dot{r}_{i-1} + \left(\frac{2}{3}(R_{i-1}^{\ 2} + R_i^{\ 2}) + \left(R_{i-1} + \frac{1}{3}R_i\right)\Delta R + \frac{7}{15}(\Delta R)^2\right)\dot{r}_i + \left(\frac{1}{3}R_i^{\ 2} + \frac{1}{3}\Delta R R_i + \frac{1}{10}(\Delta R)^2\right)\dot{r}_{i+1}\Bigg] = (\sigma_l(w_{ti+1}, w_{li+1}) - \sigma_l(w_{ti-1}, w_{li-1}))/2\Delta R + 2(\sigma_l(w_{ti}, w_{li}) - \sigma_t(w_{ti}, w_{li}))/R_i \qquad (i = 1, 2, ..., N - 1) \quad (35)$$

$$\frac{1}{2}\frac{\zeta}{R_N^{\ 2}}\Bigg[\left(\frac{1}{3}R_{N-1}^{\ 2} + \frac{1}{3}\Delta R R_{N-1} + \frac{1}{10}(\Delta R)^2\right)\dot{r}_{N-1} + \left(\frac{2}{3}(R_{N-1}^{\ 2} + R_N^{\ 2}) + \left(R_{N-1} + \frac{1}{3}R_N\right)\Delta R + \frac{7}{15}(\Delta R)^2\right)\dot{r}_N\Bigg] = (\sigma_l(w_{tN}, w_{lN}) - \sigma_l(w_{tN-1}, w_{lN-1}))/\Delta R + 2(\sigma_l(w_{tN}, w_{lN}) - \sigma_t(w_{tN}, w_{lN}))/R_N \qquad (i = N) \quad (36)$$

where $r_0 = 0$ and w_{lN} is the solution of eq 16 for $w_t = w_{tN}$.

Special consideration is needed for the coexistence region. In ref 10, we showed that the boundary condition at the inner interface is automatically accounted for by using the modified free energy obtained by the Maxwell construction. Let (w_t, w_{Mc}) and (w_t, w_{Ms}) be the solution of eq 17. We assume that in the region $w_{Mc} < w_l < w_{Ms}$, $a(w_t, w_l)$ is given by the following form

$$a_{\mathrm{Maxwell}}(w_t, w_l) + \frac{a(w_t, w_{Ms}) - a(w_t, w_{Mc})}{w_{Ms} - w_{Mc}}(w_l - w_{Mc}) + a(w_t, w_{Mc}) \quad (37)$$

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