Dynamics of Volume Transition of Gels

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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]. In the early works, the volume transition was interpreted in analogy with the gas-liquid transition of simple fluids. However, recent studies indicate that such analogy is incorrect[2]. This is demonstrated by two experimental observations[3].

(i) Hysteresis: 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.

(ii) Anomalous dynamics: in the swelling process there is an incubation period during which the whole gel is swollen only slightly, followed by the process of large volume change.

In this work, we shall demonstrate that these phenomena are caused by elastic effect. We solve the complete equation[4] for the swelling dynamics and show that the above phenomena are indeed the results of the elastic effect.

2. Model and basic equation

We investigate the dynamics of the following process. A spherical gel was first in the equilibrium state at a certain temperature (initial temperature). At time $t = 0$, the temperature of the gel is changed to another value (final temperature) and the gel starts to swell (or shrink) until it reaches the final equilibrium state.

To simplify the analysis, we assume that the spherical symmetry is always maintained throughout the process. 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. 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,

$$w_t(R,t) = \frac{r(R,t)}{R}, \qquad w_l(R,t) = \frac{\partial r(R,t)}{\partial R} \tag{1}$$

and the free energy of the gel is written as $a(w_t, w_l)$.

The equation of motion of the gel becomes

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

where $\sigma_t = \frac{1}{2}\partial a/\partial w_t$ and $\sigma_l = \partial a/\partial w_l$ and ζ is the friction constant. For given $a(w_t, w_l)$, this equation is a non-linear partial differential equation for $r(R,t)$, and can describe the dynamics in which there is a large deformation of the network. To solve the equation, boundary conditions are needed. 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. At these boundaries, we assumed the following. (i) at the surface of the gel, the swelling equilibrium is maintained. and (ii) at the interface between the swollen and the collapsed phase, the two phases are in local equilibrium and then Maxwell rule is maintained. As to the free energy we use the standard Flory free energy in which the temperature T is represented by a dimensionless parameter χ that is proportional to $1/T$.

3. Results

The following points are shown by our analysis.

(i) Figure 1 shows the time evolution of the gel radius $L(t)$ when χ is changed from $\chi_{ini} = 4.45$ to various values shown in the figure. Notice that the swelling behavior for $\chi_{fin} = 2.762$ is quite different from those or other values of χ_{fin}. For $\chi_{fin} = 2.762$, $L(t)$ 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. We found that the threshold value of χ, χ_{ts}, is given by the following condition first given by Sekimoto[2].

$$\sigma_l(w, w_{new}; \chi_{ts}) = \sigma_l(w, w; \chi_{ts}) = \frac{a(w, w_{new}; \chi_{ts}) - a(w, w; \chi_{ts})}{w_{new} - w}. \tag{3}$$

This value is different from the threshold value χ_{tc} at which the swollen phase transforms to the collapsed phase. This indicates that the temperature at which the

collapsed phase transforms to the swollen phase is different from the temperature at which the swollen phase transforms to the collapsed phase, i.e. there is a hysteresis.
(ii) Figure 1 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 pseudo steady value for a certain period of time. After sometime, the gel starts to swell again with considerable speed. We found that the incubation period corresponds to the time at which the gel surface crosses the region of the coexistence. If χ_{fin} is small, there is no incubation time. Thus the existence of the incubation period depends on the value of the final temperature (see Figure 2). In the collapsing process, the incubation period exists always regardless of the value of the final temperature.
(iii) The relaxation time is defined as the time at which the gel radius becomes the arithmetic average of the initial and the final value. We found that the relaxation time diverges in proportional to the reciprocal of the difference between the final temperature and the transition temperature. This divergence of the relaxation time is essentially the same phenomenon as that in the one dimensional gel[6]. The incubation period diverges in proportional to the logarithm of the difference between the final temperature and transition temperature.

These results can be explained by the mutual location of the contour of the free boundary and the coexistence boundary, the point of the metastable state and the stable state. The above results, (i), (ii) and (iii) are in agreement with experiments.

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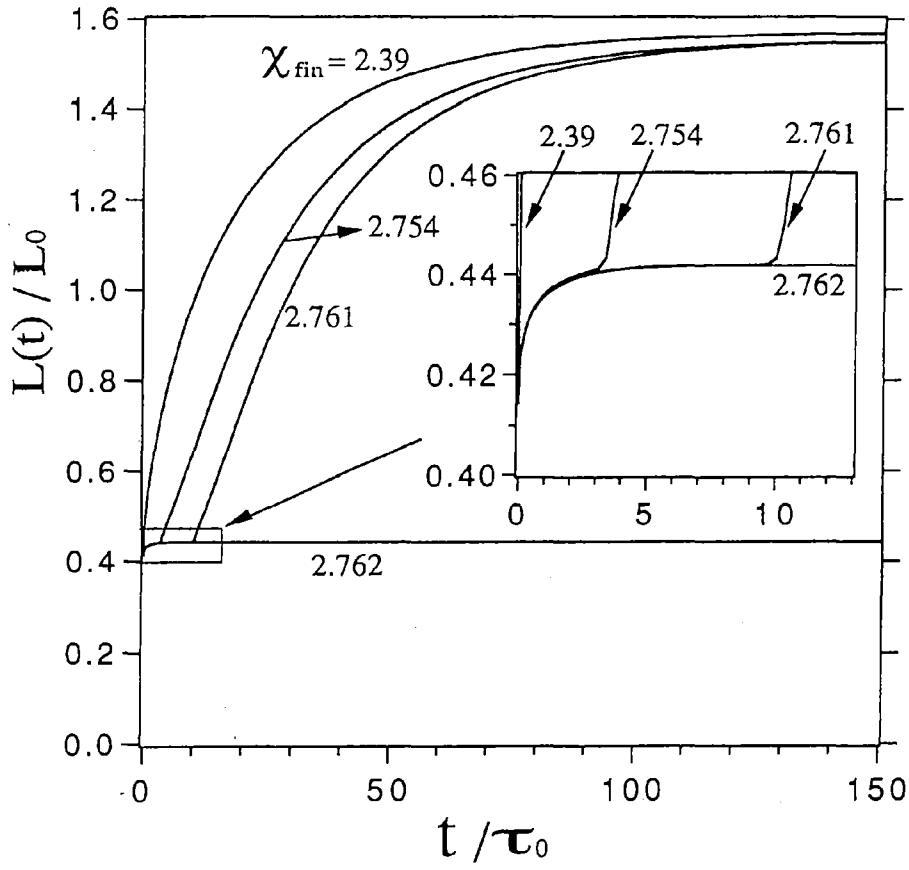

Figure 1: An example of the time evolution of the radius of a spherical gel when the interaction χ parameter is suddenly changed.

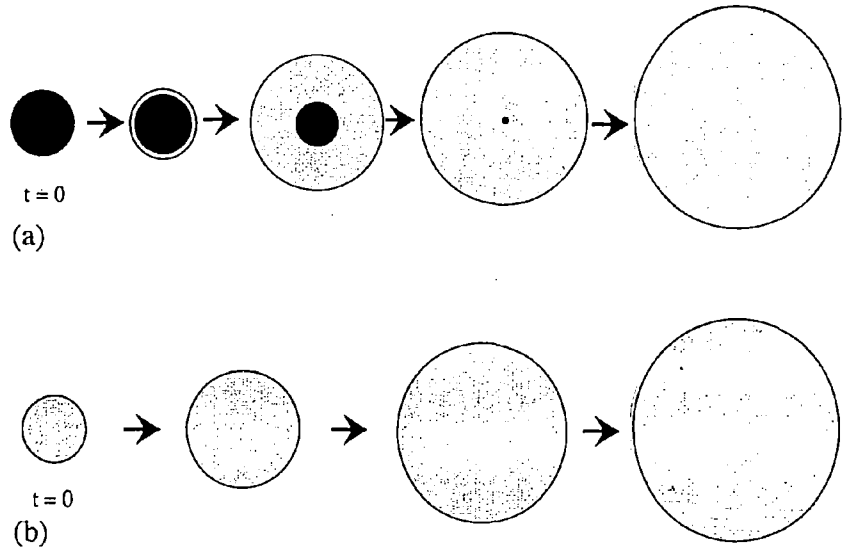

Figure 2: Schematic representation of the swelling behavior of a spherical gel undergoing volume transition, with incubation period (a) and without incubation period (b).