

The simulation of large deformation of Gels by Stress-Diffusion Coupled Model

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We have formulated the dynamics and the simulation scheme for large deformation of gels using the Stress-Diffusion Coupled Model. Using this model, we have simulated the shrinking process of 2D slab thermo-responsive gels undergoing spinodal decomposition, in comparison with the collective diffusion model of the gel network. We reproduced the "plateau period" due to the surface skin formation and the pattern formations in the inner region of gels by the Stress-Diffusion Coupled Model.

Key words: shrinking patterns, plateau period, the stress-diffusion coupled model, gels

1. INTRODUCTION

The dynamics of the volume-phase transition process of gels has been described by the collective diffusion model of the gel network,[1] which well reproduces the swelling process. But, it was found experimentally that the shrinking process is strongly decelerated and stopped transiently in a "plateau period" due to the formation of surface skin. In the end of the "plateau period", various patterns appear and the gels restart to shrink.[2,3] These phenomena haven't been reproduced theoretically. Recently, the Stress-Diffusion Coupled Model of gels has been constructed.[4,5] In which, the continuity of solvent and the coupling between solvent diffusion and network stress are considered. Here, we formulate the dynamics and the simulation scheme for large deformation of gels using the Stress-Diffusion Coupled Model. Using this model we simulate the shrinking process of 2D slab gels undergoing spinodal decomposition by finite element method with delaunay triangulation in comparison with the collective diffusion model of the gel network.

2. MODEL

We use the Ginzburg-Landau free energy F and stress tensor Π_{ij} including an elastic energy term:

$$F = \frac{k_B T}{v_1 f} \int dx [f(\phi) + \frac{1}{2} v_0 \frac{\phi}{\phi_0} (tr \underline{W} + 2 \ln \frac{\phi}{\phi_0})] \quad (1)$$

$$\Pi_{ij} = [\phi \frac{\partial f}{\partial \phi} - f(\phi)] \delta_{ij} - v_0 \frac{\phi}{\phi_0} (W_{ij} - \delta_{ij}) \quad (2)$$

Here, W_{ij} is the finger strain tensor, defined

$$W_{ij} = dx_i / dx_{ok} \cdot dx_j / dx_{ok} \cdot \vec{x}_0$$

denote the cartesian coordinates in the relaxed state, V_0 the crosslink number

density in the relaxed state,

ϕ the network volume fraction,

ϕ_0 the network volume fraction in the relaxed

state and v_1 a volume of one monomer.

Volume fraction

of the polymer network is related to the finger

strain tensor, $\phi = \phi_0 (\det \underline{W})^{-1/2}$.

As following, we describe the dynamics of gels by the Stress-Diffusion Coupled Model,[4] derived from the two fluids model.

The solvent velocity related to the polymer-network velocity in gels is proportional to the gradient

of the solvent pressure $p(\vec{x}, t)$ from the Darcy's law:

$$\vec{v}_s - \vec{v}_p = -\gamma^{-1} \vec{\nabla} p. \quad (3)$$

Here, $\vec{v}_s(\vec{x}, t)$ is the solvent velocity,

$\vec{v}_p(\vec{x}, t)$ the polymer-network velocity, $\gamma(\phi)$

a polymer-solvent friction

constant. The volume fraction dependency of

a polymer-solvent friction constant

is $\gamma(\phi) \approx 6\pi\eta_s \xi_b^{-2} \propto \phi^{2\nu/(3\nu-1)}$ from the blob

model. Here, η_s denotes the viscosity of solvent

and ξ_b the blob size, and the exponent ν

equals to 1/2 for Θ -solvent, 3/5 for good

solvent.

The pressure of the solvent is decided

by the balance with the stress of polymer network:

$$\nabla_i p = -\nabla_j \Pi_{ij}. \quad (4)$$

The conservation law and the incompressibility condition are

$$\frac{\partial \phi}{\partial t} = -\vec{\nabla} \cdot (\phi \vec{v}_p), \quad (5)$$

$$\vec{\nabla} \cdot (\phi \vec{v}_p + (1-\phi) \vec{v}_s) = 0. \quad (6)$$

These closed equations describe the Stress-Diffusion Coupled Model.

We reduce these equations and formulate the simulation scheme for deformation of gels, as following. The time-evolution of volume fraction ϕ of the polymer network is calculated by the following continuity equation:

$$\frac{\partial \phi}{\partial t} = \nabla_i L(\phi) \nabla_j \Pi_{ji} \quad (7)$$

where $L(\phi) \approx \phi / \gamma$ is the isotropic Onsager coefficient.

The deformation of the network at each time is determined by the elastic force balance while keeping a local volume fraction of gel in the moment, since the elastic force balance are satisfied instantaneously,

on the other hand the diffusion process is so slow.

This procedure for the elastic force balance is realized

by minimizing the following elastic free energy

F' with the constraint term:

$$F'(\vec{x}) = F(\vec{x}) + \int d^d x \alpha \{ \phi'(\vec{x}) - \phi(\vec{x}_0, t) \}^2 \quad (8)$$

Here, ϕ' denotes the virtual volume fraction of the polymer network for the elastic force balance calculation process. The second term of the right hand side of F' is the constraint term for keeping a local volume fraction $\phi(\vec{x}_0, t)$ of gel, when the coefficient α is large.

3. SIMULATION AND RESULTS

We have used the following function:

$$f(\phi) = -\frac{3}{2}(\phi - \frac{1}{2}) - \frac{9}{2}(\phi - \frac{1}{2})^2 + \frac{81}{4}(\phi - \frac{1}{2})^4 \quad (9)$$

for the Ginzburg-Landau mixing free energy, and carried out

simulations for various crosslink number densities in the spinodal region ($v_0 = 0.05, 0.1, 0.5, 1.0$) and

in the bulk unstable region ($v_0 = 1.5, 2.0$), as seen from Fig.1. In all simulation performed here, the initial volume fraction is $\phi_0 = 0.5$ and the volume fraction dependency of a polymer-solvent friction constant is $\gamma(\phi) \propto \phi^2$ for Θ -solvent.

The unit of length and time is the width of one cycle L_0 and $\tau_0 = \gamma L_0^2 v_1 / k_B T$.

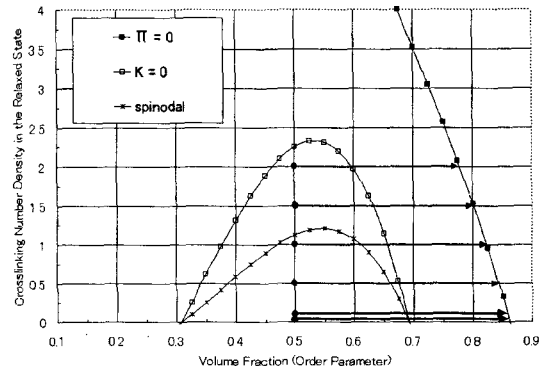


Fig.1. Phase diagram and the linear analysis of instability. We simulate in bulk unstable region ($v_0 = 1.5, 2.0$) and spinodal region ($v_0 = 0.05, 0.1, 0.5, 1.0$).

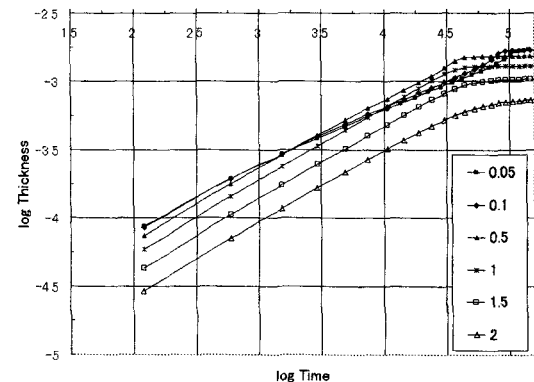
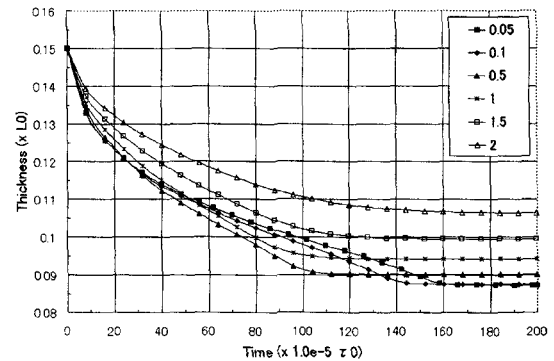


Fig.2 Thickness of gels as a function of time for various crosslink number densities in the collective diffusion model of gel network.

(a) The profile of the time dependency of thickness doesn't show "plateau period". (upper figure)
 (b) The logarithmic scale show the slope of the time dependency of thickness equals to 0.5, the characteristic diffusion exponent. (lower figure)

As seen from Fig.2, in the collective diffusion model of the network, the slope of the time dependency of the thickness equals to 0.5, which is the characteristic diffusion exponent (Fig.2(b)). In the spinodal region in the collective diffusion of gel network the bamboo-like shrinking patterns appear due to phase separations into swollen and shrunken states, as seen in Fig.3, but there is no "plateau period" and "surface skin" formation. (Fig.2(a))

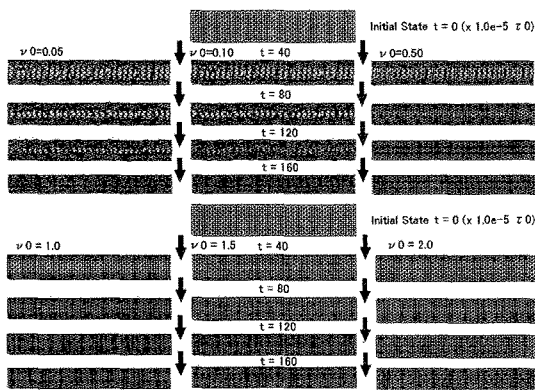


Fig.3 The shrinking patterns in the collective diffusion model of gel network. In the spinodal region the "bamboo-like" shrinking patterns appear due to phase separations into swollen and shrunken states.

As seen from Fig.4, when the gels are soft in the spinodal region in the stress-diffusion coupled model ($V_0 = 0.05, 0.1$), the "plateau period" appears (Fig.4(a)) and the slope of the time dependency of the thickness is larger than 0.5, the characteristic diffusion exponent, both in the early and in the late stage except the "plateau period" (Fig.4(b)) and, as seen in Fig.5, high volume fraction regions ("surface skin") at the surface appears in the early stage of the shrinking process and then the "plateau period" starts. During the "plateau period", the instability grows and the "bubble-like" inner patterns due to the phase separation appear. After finishing the formation of inner patterns of gels, the gels restart to shrink.

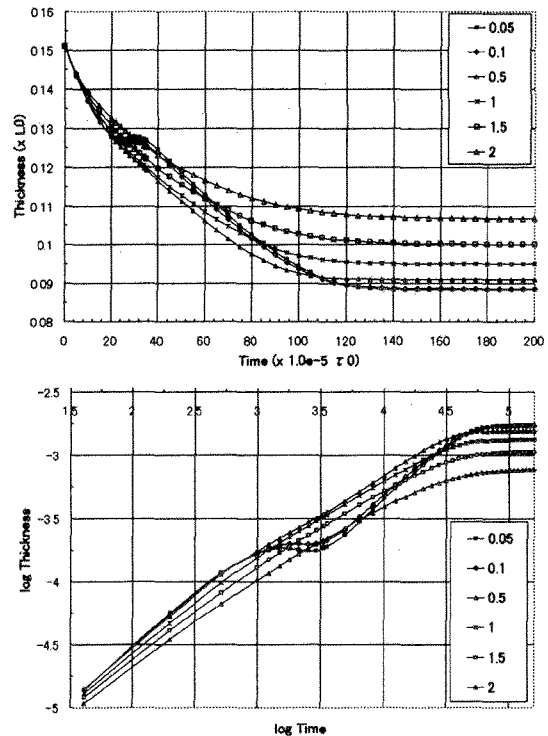


Fig.4 Thickness of gels as a function of time for various crosslink number densities in the stress-diffusion coupled model. (a) The profiles of the time dependency of thickness, some of which show the "plateau period" (between about $t=20$ and 40) in the soft cases of the spinodal region ($V_0 = 0.05, 0.1$). (upper figure) (b) The logarithmic scale show the slope of the time dependency of thickness is larger than 0.5, the characteristic diffusion exponent, in the cases which exhibit the "plateau period". (lower figure)

As seen from Fig.4(a), when the gels are hard in the spinodal region ($V_0 = 0.5, 1.0$), there is no "plateau period", but we can see the phase separation during the shot time, which disappears in the late stage of the shrinking process, as seen in Fig.5. Therefore, the relation of the spinodal region to the "plateau period" may be depends on the size of gels.

When the gels are out of the spinodal region ($V_0 = 1.5, 2.0$), the profiles of the shrinking process are the same as the cases in the collective diffusion model of gel network, as seen in Fig.4(a). In this region, the shrinking processes show the liner phenomena and the gels shrink uniformly, as seen in Fig.5. Therefore, the "plateau period" is related to the non-liner phenomena such as phase separations.

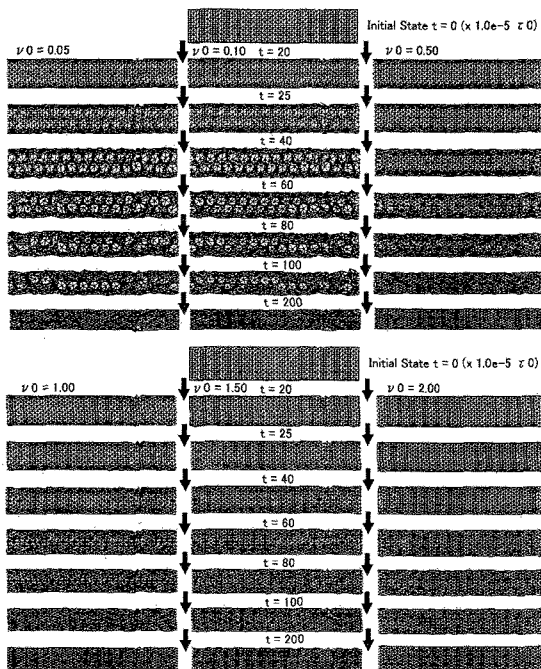


Fig.5 The shrinking patterns in the stress-diffusion coupled model. In the soft cases in the spinodal region ($V_0 = 0.05, 0.1$), the “plateau period” appears during $t=20$ – 40. During the “plateau period”, the instability grows and the “bubble-like” inner patterns due to the phase separation appear. After finishing the formation of inner patterns of gels, the gels restart to shrink. Out of the spinodal region ($V_0 = 1.5, 2.0$), the shrinking processes show the linear phenomena and the gels shrink uniformly, that is the same as the cases in the collective diffusion model of gel network.

4. DISCUSSION AND CONCLUSION

We have reproduced the “plateau period” in the shrinking process of the thermo-responsive gels. During the “plateau period”, the instability grows and the “bubble-like” inner patterns due to the phase separation appear. After finishing the formation of inner patterns of gels, the gels restart to shrink. Those results nicely reproduce the phenomena which were experimentally observed.

But even in the spinodal region, when the gels are hard, there is no “plateau period”, whereas we can see the phase separation during the shot time. We must confirm the reason of the condition of “plateau period” formation, which is maybe related to the condition of the phase separation, the size effect of gels and the velocity of the solvent diffusion at the surface region of gels in the early stage of the shrinking process.

In the linear shrinking process, in which

gels shrink uniformly, the results of the collective diffusion model of gel network and the stress-diffusion coupled model equal. That means that the stress-diffusion coupled model, which can describe the actual solvent diffusion of gels, can reproduce the non-linear shrinking phenomena, which related to the constraint phenomena of the solvent diffusion.

We conclude that the stress-diffusion coupled model of gels is nicely expanded model of the collective diffusion model of gel network, and lots of non-linear phenomena in the volume-phase transition process of gels will can be reproduced by the progress of the stress-diffusion coupled model of gels.

5. ACKNOWLEDGEMENT

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