THE SIMULATION OF THE SWELLING DYNAMICS OF GELS
BY THE STRESS-DIFFUSION COUPLING MODEL

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The dynamics of gels has been described by the collective diffusion model of gel networks, [1] which well reproduces the swelling phenomena in one axis, such as spherical gels. But the collective diffusion model of gel networks can't reproduce the swelling phenomena in two or three axes. [2] The dynamics of polymer gels should be discussed from the stand point of the dynamics of polymer solutions. Recently, several models, which are based on the two fluids model, have been proposed as dynamics of gels. We have formulated the dynamics and the simulation scheme for large deformation of gels using the stress-diffusion coupling model, in which the continuity of solvent and the coupling between solvent diffusion and network stress are considered. [3]

Here, using the linearized stress-diffusion coupling model of gels, we have analized the free swelling process of long rod/large disk gels and the 1 dim. swelling process of gels clumped between glass plates. (Fig.1) [4] Furthermore, we have developed the gel dynamics simulator named MUFFIN-GelDyna [6] as one of open source simulation softwares belonging to OCTA system (Open Computational Tools for Advanced material technology). [5] GelDyna is the finite-element-method (FEM) simulator and can calculate the large deformation dynamics of gels, accompanying a change of external stimuli, such as, temperature, pressure, and a load of forces, such as gravity, and surface forces. As boundary conditions, permeable surfaces, impermeable surfaces, fixed surfaces or surfaces moving with constant velocity, and load of surface forces, are implemented. Here, using GelDyna, we have simulated the free swelling process of 2D slab gels, 3D long rod gels, and 3D large disk gels, and have reproduced experimentally observed swelling ratios by the stress-diffusion coupling model.

Fig1. Thinkness of gels clumped between glass plates related to time for various width 4.2, 5.0, 9.3, 14.8, 19.3, 29.4, 35.8, 53.1 (mm) 26.0 (mm). These results nicely reproduce the experimental results. [4]

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Abstract

The dynamics of gels has been described by the collective diffusion of polymer networks related to the solvent. The corrective diffusion model of polymer networks described by the Tanaka-Fillmore's equation (TF equation) nicely reproduces the swelling phenomena of a spherical gel. But the TF equation can't reproduce general anisotropic deformations of gels such as the free swelling phenomena of long cylindrical and large disk-like gels. The dynamics of gels should be discussed from the standpoint of the dynamics of polymer solutions. The stress-diffusion coupling model, which are based on the two fluids model, have been proposed as dynamics of polymer solutions and blends, where the continuity of solvent and the mechanical coupling between the solvent diffusion and the polymer stress are considered.

Actually, in general anisotropic deformations of gels such as a deformation under an external stress, the solvent and polymer network of gels can move together by the shear relaxation without pressure gradients. For cylindrical and disk-like gels, the TF equation was extended by taking the shear relaxation and separating the time-scale of the solvent diffusion and that of the shear relaxation of polymer networks. The dynamics of gels should be generally described by the relative motion between the solvent and the polymer of gels with the mechanical coupling between the solvent diffusion and the polymer network stress.

Recently, the anisotropic swelling kinetics of thin-plate gels with rectangular surfaces under mechanical constraint was experimentally investigated. In this system, the top and bottom surfaces of gels were chemically clamped on the glass plates, and the gels could swell and shrink only along the thickness direction between two swollen states by the change of osmotic pressure due to the temperature jumps.

Here, we have formulated the dynamics of gels using the stress-diffusion coupling model, and have theoretically calculated the swelling process of thin-plate gels with rectangular surfaces under mechanical constraint using the linearized stress-diffusion cooupling model of gels based on the two fluids model and the linear elasticity theory.
The Collective Diffusion Model of Gel Networks.  
(Tanaka-Filmore’s Equation, 1979)

**Equation of motion**

\[ \zeta \frac{\partial u_i}{\partial t} = \frac{\partial \sigma_{ij}}{\partial x_j} \]

Simple diffusion of networks in immobile solvent is assumed

\[ \zeta \] : the friction coefficient between the network and the solvent

**Linear elasticity model**

\[ \sigma_{ij} = K \frac{\partial u_k}{\partial x_k} \delta_{ij} + G \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \frac{\partial u_k}{\partial x_k} \delta_{ij} \right) \]

\[ \zeta \frac{\partial u_i}{\partial t} = (K + \frac{G}{3}) \frac{\partial^2 u_k}{\partial x_i \partial x_k} + G \frac{\partial^2 u_i}{\partial x_k \partial x_k} \]

\[ f = \nabla \cdot u \] volume change

\[ \frac{\partial f}{\partial t} = D \Delta f \]

\[ D = (K + \frac{4}{3} G) \frac{1}{\zeta} \]

**Swelling**

Swelling of Spherical Gels has been well explained by TF theory


Photo: Swelling Process of Spherical NIPA T.Tanaka Lab. MIT.
TF Equation can’t describe these problems.

- Patterns and plateau period in deswelling gels. (Matsuo-Tanaka, 1988)
- One-dim. swelling and deswelling under mechanical constraint. (Suzuki-Hara, 2001)

- Swelling of long rod and large disk shaped gels. (Li-Tanaka, 1990)

\[
\begin{align*}
\frac{\partial \sigma_{ij}}{\partial x_j} - \xi \frac{\partial u_i}{\partial t} &= 0 \\
\frac{\partial \sigma_{ij}}{\partial x_j} - \xi \left( \frac{\partial u_i}{\partial t} \right) &= 0
\end{align*}
\]
Stress Diffusion Coupling Model for Gels based on two fluid model

\[ \xi(v_s - v_p) = -(1 - \phi) \nabla p \]  
\[ \xi(v_p - v_s) = -\phi \nabla p + \nabla \cdot \sigma \]  
\[ \nabla \cdot [\phi v_p + (1 - \phi) v_s] = 0 \]

Boundary conditions

- For solvent:
  - Permeable wall (Dirichlet): \( p = p_{\text{out}} \)
  - Deformable boundary (Neumann): \( p_{\text{out}} \)

- For polymer:
  - Impeemable wall (Neumann): \( v_{s,n} = v_{bc,n} \) \( \rightarrow (\nabla p) \cdot n = 0 \)
  - Gel fixed to the boundary (Dirichlet): \( v_p = v_{bc} \)

Force balance:

\[ (\sigma - pI) \cdot n = f_{bc} \]
Linearized Equations

\[ \sigma_{ij} = K \frac{\partial u_k}{\partial x_k} \delta_{ij} + G \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \frac{\partial u_k}{\partial x_k} \delta_{ij} \right) \]  
(4) : linearized stress tensor

\[ (K + \frac{G}{3}) \frac{\partial^2 u_k}{\partial x_i \partial x_k} + G \frac{\partial^2 u_i}{\partial x_k \partial x_k} = \frac{\partial p}{\partial x_i} \]  
(5) : mechanical balance

\[ (1 - \phi)(v_{si} - \dot{u}_i) = -\frac{(1 - \phi)^2}{\xi} \frac{\partial p}{\partial x_i} \]  
(6) : solvent flux

\[ \phi \frac{\partial \dot{u}_i}{\partial x_i} + (1 - \phi) \frac{\partial v_{si}}{\partial x_i} = 0 \]  
(7) : incompressibility (mass balance)

\[ f = \nabla \cdot \mathbf{u} \]  
: volume change

\[ \frac{\partial f}{\partial t} = D \Delta f \quad \nabla \frac{\partial p}{\partial t} = D \nabla (\Delta p) \quad D = \frac{(1 - \phi)^2}{\xi} (K + \frac{4}{3} G) \]  
(8)
Experiment

(A.Suzuki and T.Hara, JCP, V.114 (2001), 5012)

Swelling of thin-plate gels, clamped on glass surfaces

Size of gels
Width $a_0 \times b_0$ (Size of glass surfaces)
Initial thickness $c(t=0) = c_0$, Thickness $c(t)$

Widths of glass surfaces in experiment
$a_0 = 4.2, 5.0, 9.3, 14.8, 19.3, 29.4, 35.8, 58.9$ mm
$b_0 = 26.0$ mm
$c_0 = 0.9$ mm

Initial thicknesses of glass surfaces in experiment
$a_0 = 9.5$ mm
$b_0 = 26.0$ mm
$c_0 = 0.142, 0.402, 0.915, 1.363, 1.774$ mm

FIG. 1. Schematic illustrations of the thin plate NIPA gels synthesized between two slides. Both surfaces are chemically clamped on the glasses. The samples with different thickness and width were prepared.
Experiment
(A.Suzuki and T.Hara, JCP, V.114 (2001), 5012)

by changing the width of glass surfaces
- Swelling is a single exponent relaxation process
- Larger width → Larger relaxation time

relaxation time $\tau$

$$\tau(a_0^{-2} + b_0^{-2}) = 38.33 [\text{min/mm}^2]$$

(swelling)

$$\tau \propto (a_0^{-2} + b_0^{-2})^{-1}$$

by changing the initial thickness of gels
- time evolution of swelling ratio is independent on the initial thickness of gels

Single exponent relaxation process
Swelling analysis by the linearized stress-diffusion coupling model
- Model and Boundary Conditions -

What are solved
\[ p = p(x, y, z, t) \]
\[ u_x = u_x(x, y, z, t) \]
\[ u_y = u_y(x, y, z, t) \]
\[ u_z = u_z(x, y, z, t) \]

\[ \frac{c}{a_0}, \frac{c}{b_0} \ll 1 \]

lowest order

\[ p = p(x, y, t) \]
\[ u_x = u_x(x, y, z, t) \]
\[ u_y = u_y(x, y, z, t) \]
\[ u_z = u_z(z, t) \]

\[ p(x = \pm \frac{a_0}{2}, y, z, t) = p_0 \]
\[ p(x, y = \pm \frac{b_0}{2}, z, t) = p_0 \]

\[ \frac{\partial p}{\partial x}(x = 0, y, z, t) = 0 \]
\[ \frac{\partial p}{\partial y}(x, y = 0, z, t) = 0 \]

clamped on glass surfaces

boundary permeable surfaces

pressure \( p_0 \)

z

x, y

2c(t)

a_0, b_0
Swelling analysis by the linearized stress-diffusion coupling model
- equations of motion -

Mechanical balance on the glass plates (free surfaces)

\[
\int_0^{a_0/2} dx \int_0^{b_0/2} dy (\sigma_{zz} - p) \big|_{z = \pm c} = \int_0^{a_0/2} dx \int_0^{b_0/2} dy [(K - \frac{2}{3} G)(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y}) + (K + \frac{4}{3} G) \frac{\partial u_z}{\partial z} - p] \big|_{z = \pm c} = 0
\] (9)

Mechanical balance between pressure and polymer stress in gels

\[
\begin{aligned}
\frac{\partial p}{\partial x} &= (K + \frac{4}{3} G) \frac{\partial^2 u_x}{\partial x^2} + G \left( \frac{\partial^2 u_x}{\partial z^2} + \frac{\partial^2 u_y}{\partial y^2} \right) + (K + \frac{G}{3}) \frac{\partial^2 u_y}{\partial x \partial y} \\
\frac{\partial p}{\partial y} &= (K + \frac{4}{3} G) \frac{\partial^2 u_y}{\partial y^2} + G \left( \frac{\partial^2 u_y}{\partial z^2} + \frac{\partial^2 u_x}{\partial x^2} \right) + (K + \frac{G}{3}) \frac{\partial^2 u_x}{\partial x \partial y} \\
0 &= (K + \frac{4}{3} G) \frac{\partial^2 u_z}{\partial z^2} + (K + \frac{G}{3}) \left( \frac{\partial^2 u_x}{\partial x \partial z} + \frac{\partial^2 u_y}{\partial y \partial z} \right)
\end{aligned}
\] (10-12)

Equations of motion (by eliminating the velocity of solvent)

\[
\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = (1 - \phi)^2 \zeta \left( \frac{\partial^2 p}{\partial x^2} + \frac{\partial^2 p}{\partial y^2} \right)
\] (13)
Swelling analysis by the linearized stress-diffusion coupling model
- separation of z-dependency -

eq.(12) and clamped boundary conditions on glass surfaces

\[
(K + \frac{4}{3} G)\{\frac{\partial u_z}{\partial z}(z, t) - \frac{\partial u_z}{\partial z}(z = \pm c, t)\} + (K + \frac{G}{3})\{\frac{\partial u_x}{\partial x}(x, y, z, t) + \frac{\partial u_y}{\partial y}(x, y, z, t)\} = 0
\]  

\[A(z, t) = \frac{\partial u_x}{\partial x}(x, y, z, t) + \frac{\partial u_y}{\partial y}(x, y, z, t)\]  

sum is independent on x and y.

eqs.(10,11) leads with eq.(15)

\[
\begin{align*}
\frac{\partial p}{\partial x} &= G\left(\frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2} + \frac{\partial^2 u_x}{\partial z^2}\right) \\
\frac{\partial p}{\partial y} &= G\left(\frac{\partial^2 u_y}{\partial x^2} + \frac{\partial^2 u_y}{\partial y^2} + \frac{\partial^2 u_y}{\partial z^2}\right)
\end{align*}
\]  

(16)

(17)

\[
\begin{align*}
\frac{\partial p}{\partial x} &= -GU_x \\
\frac{\partial p}{\partial y} &= -GU_y
\end{align*}
\]  

(21)

(22)

solve the z-dependency

\[u_x(x, y, z, t) = \{c(t)^2 - z^2\}U_x(x, y, t)\]  

(18)

\[u_y(x, y, z, t) = \{c(t)^2 - z^2\}U_y(x, y, t)\]  

(19)

by the clamped conditions on glass surfaces and the symmetry about z -> -z.
Swelling analysis by the linearized stress-diffusion coupling model
- poisson eq. for pressure -

eq.(15) by separating z-dependency,

\[ a(t) \equiv \frac{\partial U}{\partial x}(x,y,t) + \frac{\partial U}{\partial y}(x,y,t) \]  \hspace{1cm} (23) \hspace{1cm} \left( A(z,t) = \{c(t)^2 - z^2\}a(t) \right) 

(21,22,23)→poisson’eq. for pressure.

\[ \tilde{a}(t) \equiv \frac{\partial^2 p}{\partial x^2} + \frac{\partial^2 p}{\partial y^2} = -Ga(t) \]  \hspace{1cm} (24)

Solve eq.(24) by Fourier transform with B.C.

\[ p(x,y,t) = p_0 - \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} C_{m,n} \tilde{a}(t) \cos\left(\frac{(2m-1)\pi}{a_0} x\right) \cos\left(\frac{(2n-1)\pi}{b_0} y\right) \]  \hspace{1cm} (25)

\[ C_{m,n} = (-1)^{m+n-2} \frac{16}{(2m-1)(2n-1)\pi^2} \left\{ \left(\frac{(2m-1)\pi}{a_0}\right)^2 + \left(\frac{(2n-1)\pi}{b_0}\right)^2 \right\}^{-1} \]

\[ p(x,y,t) = p_0 \left[ 1 - \frac{1}{D\tau} \left\{ \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} C_{m,n} \cos\left(\frac{(2m-1)\pi}{a_0} x\right) \cos\left(\frac{(2n-1)\pi}{b_0} y\right) \right\} \exp\left(-\frac{t}{\tau}\right) \right] \]  \hspace{1cm} (31)
Swelling analysis by the linearized stress-diffusion coupling model - the relaxation time and the swelling ratio -

from eq. of motion (13),

$$\frac{\partial \tilde{u}_z}{\partial z} \bigg|_{z=\pm c} = \frac{(1-\phi)^2}{\zeta} \tilde{a}(t)$$  \hspace{1cm} (26)

from eq.(9),

$$(K + \frac{4}{3}G) \frac{\partial \tilde{u}_z}{\partial z} \bigg|_{z=\pm c} = p_0 - \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{64}{(2m-1)(2n-1)\pi^2} \left\{ \left( \frac{(2m-1)\pi}{a_0} \right)^2 + \left( \frac{(2n-1)\pi}{b_0} \right)^2 \right\}^{-1} \tilde{a}(t)$$  \hspace{1cm} (27)

from eqs.(26,27),

$$\dot{\tilde{a}}(t) = -\tau^{-1} \tilde{a}(t)$$

from eqs.(27,28),

$$\tilde{a}(0) = \frac{p_0}{D\tau}$$  \hspace{1cm} (29)

eqs.(26,28)

$$\frac{c(t)}{c_0} = 1 + p_0(K + \frac{4}{3}G)^{-1}(1 - \exp(-\frac{t}{\tau}))$$  \hspace{1cm} (30)

Single exponent relaxation process
Results
- the relaxation time: $\tau$ -

$\tau^{-1} \equiv D \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{64}{(2m-1)(2n-1)\pi^2} \left( \frac{(2m-1)\pi}{a_0} \right)^2 \left( \frac{(2n-1)\pi}{b_0} \right)^2 \left( a_0^{-2} + b_0^{-2} \right)^{-1}$

$D = 0.026[\text{mm}^2/\text{min}]$

Reproduce linearity
Results
- swelling process and width of gels -

\[
\frac{c(t)}{c_0} = 1 + p_0 (K + 4G)^{-1} (1 - \exp(-\frac{t}{\tau}))
\]

Single exponent relaxation process
Results
- swelling process and initial thickness of gels -

\[
\frac{c(t)}{c_0} = 1 + p_0(K + \frac{4}{3}G)^{-1}(1 - \exp(-\frac{t}{\tau}))
\]

Swelling process is independent on the initial thickness
Results
- pressure and width of gels -

\[ a_0[\text{mm}] \quad b_0=26.0[\text{mm}] \quad p/p_0=1.0(\text{red}),0.0(\text{white}) \]

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Summary

- Theoretical analysis of the anisotropic swelling process of gels by the linearized stress-diffusion coupling model.
- We have nicely reproduced the experimental results.
  → Availability of the stress-diffusion coupling model for the general anisotropic dynamics of gels

Next:
- By applying the MUFFIN/GelDyn simulator to this system, validate the simulator in comparison with the theoretical results.
- Theoretical analysis of long rod and large disk gels.
  (relation of stress-diffusion coupling and Li-Tanaka’s theory?)
- Applications:
  electrolyte gels (artificial muscles, DDS), coating and gelation.
Acknowledgement

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References

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