# Theory of one-dimensional swelling dynamics of polymer gels under mechanical constraint

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Recently, the swelling kinetics of thin-plate gels with rectangular surfaces under mechanical constraint was experimentally investigated [A. Suzuki and T. Hara, J. Chem. Phys. **114**, 5012 (2001)]. 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 when the osmotic pressure of the solvent is changed. Here, we analyze this process using the linearized stress-diffusion coupling model of gels based on the two fluids model. The result is somewhat unusual in that the time evolution of the thickness is described by a single exponential even though the swelling is governed by the diffusion of solvent. This result and that the characteristic relaxation time depends on the lengths of the rectangular surfaces and not on the thickness of gels agree well with the experiment.

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## I. INTRODUCTION

A gel placed in solution absorbs (or desorbs) the solutions and swells (or shrinks) when the temperature or the solution composition is changed. The dynamics of this process was first analyzed by Tanaka and Fillmore (TF). They considered the swelling of a spherical gel and proposed the following equation (TF equation) to describe the kinetics of swelling [2]:

$$\zeta \dot{\mathbf{u}}(\mathbf{r},t) = \nabla \cdot \boldsymbol{\sigma}(\mathbf{r},t), \tag{1}$$

where $\mathbf{u}(\mathbf{r},t)$ is the displacement of a point $\mathbf{r}$ of the polymer network at time $t$, $\boldsymbol{\sigma}$ is the stress tensor of the polymer network, and $\zeta$ the friction constant associated with the motion of the polymer relative to the solvent. This equation explained the characteristic feature of the swelling phenomena of a spherical gel [3]; the relaxation time $\tau$ is of the order of $d^2/D$, where $d$ is the diameter of the gel and $D$ is the collective diffusion constant.

Recently, Suzuki and Hara reported the experimental results which cannot be interpreted by the TF equation [1]. They studied the swelling kinetics of thin-plate gels shown in Fig. 1, where the top and bottom surfaces were chemically clamped on the glass plates, and the gels could swell and shrink only along the thickness direction between the glass plates. Experimental results show that the time evolution of the thickness is well described by a single exponential and that the characteristic relaxation time $\tau$ depends on the lengths of the rectangular surfaces and not on the thickness of gels: $\tau \simeq D^{-1}(a_0^{-2}+b_0^{-2})^{-1}$, where $a_0$ and $b_0$ are the lengths of rectangular surfaces.

The experiment of Suzuki and Hara cannot be described by the TF equation as we shall show in later sections. In fact, it has been realized that the TF equation cannot reproduce general anisotropic deformations of gels such as the free swelling phenomena of long cylindrical and large disklike gels [6]. As an alternative, the stress-diffusion coupling model, which are based on the two fluids model, has been proposed. In this model, the coupling between the solvent diffusion and the polymer stress are considered [4,5].

Here, we formulate the dynamics of gels using the stress-diffusion coupling model, and calculate the swelling process of thin-plate gels with rectangular surfaces under mechanical constraint. The result shows an unusual feature of the stress-diffusion coupling model.

## II. The stress-diffusion coupling model

We first explain the stress-diffusion coupling model. Let $\mathbf{u}(\mathbf{r},t)$ be the displacement of the point located at $\mathbf{r}$ in the reference state and $\dot{\mathbf{u}}(\mathbf{r},t)$ be its time derivative [$\dot{\mathbf{u}}(\mathbf{r},t) = \partial \mathbf{u}(\mathbf{r},t)/\partial t$]. Let $\mathbf{v}_s(\mathbf{r},t)$ be the velocity of the solvent. The equations of motion which determine $\mathbf{u}(\mathbf{r},t)$ and $\mathbf{v}_s(\mathbf{r},t)$ are as follows [4]:

$$\zeta(\mathbf{v}_s - \dot{\mathbf{u}}) = -(1-\phi)\nabla p, \tag{2}$$

$$\nabla \cdot (\boldsymbol{\sigma} - p\mathbf{I}) = 0, \tag{3}$$

$$\nabla \cdot [\phi \dot{\mathbf{u}} + (1-\phi)\mathbf{v}_s] = 0. \tag{4}$$

Here, $\zeta$ is the friction constant associated with the motion of the polymer relative to the solvent, $\phi$ is the volume fraction of polymer, $p$ is the pressure, and $\mathbf{I}$ is the unit tensor defined
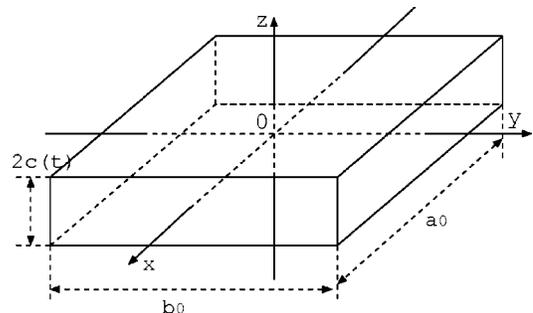


FIG. 1. Model of the thin-plate gel.

by $I_{ij} = \delta_{ij}$. The first equation represents Darcy's law for the permeation of solvent through the gel network. The second equation stands for the force balance, where $\boldsymbol{\sigma}$ is the stress of the gel network. The third equation stands for the incompressibility condition.

The stress $\boldsymbol{\sigma}$ is given by the constitutive equation for the gel network. Here, we use the linearized form for the stress tensor:

$$\sigma_{ij} = K\sum_k \frac{\partial u_k}{\partial x_k}\delta_{ij} + G\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3}\sum_k \frac{\partial u_k}{\partial x_k}\delta_{ij}\right), \quad (5)$$

where $K$ is the bulk modulus and $G$ is the shear modulus of gels. Equations (3) and (5) give

$$\sum_k \left[\left(K + \frac{G}{3}\right)\frac{\partial^2 u_k}{\partial x_i \partial x_k} + G\frac{\partial^2 u_i}{\partial x_k \partial x_k}\right] = \frac{\partial p}{\partial x_i}. \quad (6)$$

From Eq. (2), the solvent flux relative to the polymer network is described as

$$v_{si} - \dot{u}_i = -\frac{(1-\phi)}{\zeta}\frac{\partial p}{\partial x_i}. \quad (7)$$

The volume fraction $\phi$ can be regarded as constant in the linear analysis. Hence, the incompressibility condition, Eq. (4), is described as

$$\sum_i \left[\phi\frac{\partial \dot{u}_i}{\partial x_i} + (1-\phi)\frac{\partial v_{si}}{\partial x_i}\right] = 0. \quad (8)$$

Equations (6)–(8) are the closed set which determine $\mathbf{u}(\mathbf{r},t)$, $\mathbf{v}_s(\mathbf{r},t)$ and $p(\mathbf{r},t)$.

To solve the set of equations, we need boundary conditions. There are two kinds of boundary conditions, each describing the mechanical condition and the condition of solvent permeation.

(i) Mechanical condition. If the mechanical force $\mathbf{f}_{bc}$ acting on the boundary is known, the mechanical balance equation has to be imposed:

$$(\boldsymbol{\sigma} - p\mathbf{I})\cdot\mathbf{n} = \mathbf{f}_{bc} \text{ for a deformable boundary.} \quad (9)$$

On the other hand, if the velocity of the gel network at the boundary $\mathbf{v}_{bc}$ is known, the equation to be imposed is

$$\dot{\mathbf{u}} = \mathbf{v}_{bc} \text{ for gels fixed to a boundary.} \quad (10)$$

(ii) Solvent permeation at the boundary. If the solvent can permeate freely at the boundary, the pressure $p$ must be continuous at the boundary.

$$p = p_{out} \text{ for a permeable wall,} \quad (11)$$

where $p_{out}$ is the osmotic pressure outside the gel.

On the other hand, if the solvent cannot permeate through the boundary, the normal velocity $(\mathbf{v}_s - \dot{\mathbf{u}})\cdot\mathbf{n}$ ($\mathbf{n}$ being the unit vector normal to the boundary) must be zero. Using Eq. (7), this condition can be written as

$$(\boldsymbol{\nabla}p)\cdot\mathbf{n} = 0 \text{ for an impermeable wall.} \quad (12)$$

## III. THEORETICAL ANALYSIS OF THE SWELLING OF A THIN-PLATE-LIKE GEL

We consider a thin-plate-like gel shown in Fig. 1. The top and bottom surfaces of the gel are chemically clamped on the glass plates, and the gel can swell and shrink only along the one-dimensional thickness direction. We take the origin of the coordinates at the center of the thin-plate gel. Let $a_0$, $b_0$, and $2c_0$ be the initial length of the edge of the gel. We assume that the thickness of the gel is much smaller than the side length of the gel. We consider the situation that the osmotic pressure $p_{out}$ of the external solutions is changed from 0 to $p_0$. Our objective is to find out the time dependence of the thickness $2c(t)$ of the gel.

Now, since the gel is fixed at the glass plate, we can assume that the displacement vector $(u_x, u_y, u_z)$ is of the same order of the thickness of the gel $c(t): u_x, u_y, u_z \sim c(t)$. Therefore, the terms of $\partial_x u_i$ and $\partial_y u_i$ are much smaller than those of $\partial_z u_i$. In such a case, Eq. (6) can be approximated as

$$\frac{\partial p}{\partial x} = \left(K + \frac{4}{3}G\right)\frac{\partial^2 u_x}{\partial x^2} + G\left(\frac{\partial^2 u_x}{\partial y^2} + \frac{\partial^2 u_x}{\partial z^2}\right)$$
$$+ \left(K + \frac{G}{3}\right)\left(\frac{\partial^2 u_y}{\partial x \partial y} + \frac{\partial^2 u_z}{\partial x \partial z}\right) \cong G\frac{\partial^2 u_x}{\partial z^2}, \quad (13)$$

$$\frac{\partial p}{\partial y} = \left(K + \frac{4}{3}G\right)\frac{\partial^2 u_y}{\partial y^2} + G\left(\frac{\partial^2 u_y}{\partial x^2} + \frac{\partial^2 u_y}{\partial z^2}\right)$$
$$+ \left(K + \frac{G}{3}\right)\left(\frac{\partial^2 u_x}{\partial x \partial y} + \frac{\partial^2 u_z}{\partial z \partial y}\right) \cong G\frac{\partial^2 u_y}{\partial z^2}, \quad (14)$$

$$0 = \left(K + \frac{4}{3}G\right)\frac{\partial^2 u_z}{\partial z^2} + G\left(\frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2}\right)$$
$$+ \left(K + \frac{G}{3}\right)\left(\frac{\partial^2 u_x}{\partial x \partial z} + \frac{\partial^2 u_y}{\partial y \partial z}\right) \cong \left(K + \frac{4}{3}G\right)\frac{\partial^2 u_z}{\partial z^2}. \quad (15)$$

Here, we have assumed that the pressure $p(x,y,z,t)$ is independent of $z$, since the equilibration time of the pressure in $z$ direction is of the order of $c_0^2/D$ and is negligibly small compared with the characteristic time of the swelling (which is $a_0^2/D$).

By eliminating the velocity of solvent from Eqs. (7) and (8), we have

$$\frac{\partial \dot{u}_x}{\partial x} + \frac{\partial \dot{u}_y}{\partial y} + \frac{\partial \dot{u}_z}{\partial z} = \frac{(1-\phi)^2}{\zeta}\left(\frac{\partial^2 p}{\partial x^2} + \frac{\partial^2 p}{\partial y^2} + \frac{\partial^2 p}{\partial z^2}\right). \quad (16)$$

Since $|\partial\dot{u}_x/\partial x|$ and $|\partial\dot{u}_y/\partial y|$ are much smaller than $|\partial\dot{u}_z/\partial z|$, and $p$ is independent of $z$, Eq. (16) can be approximated by

$$\frac{\partial \dot{u}_z}{\partial z} = \frac{(1-\phi)^2}{\zeta}\left(\frac{\partial^2 p}{\partial x^2} + \frac{\partial^2 p}{\partial y^2}\right). \quad (17)$$

The boundary conditions are described as

$$\begin{cases} p(x = \pm a_0/2, y, t) = p_0 \\ p(x, y = \pm b_0/2, t) = p_0 \end{cases} \text{ for the boundary at the side,}$$

$$(18)$$

$$\begin{cases} u_x(x, y, z = \pm c, t) = 0 \\ u_y(x, y, z = \pm c, t) = 0 \end{cases} \text{ for the top and bottom boundary.}$$

$$(19)$$

Furthermore, since there is no external force acting on the glass plate, the total force acting on the glass plate must be zero. This condition is written as

$$\int_{-a_0/2}^{a_0/2} dx \int_{-b_0/2}^{b_0/2} dy (\sigma_{zz} - p)_{z=\pm c} = 0. \qquad (20)$$

From Eq. (15), we have

$$u_z = A(t)z, \qquad (21)$$

where $A(t)$ is independent of $x$ and $y$ since the thickness of the gel is uniform. Since $|\partial u_x/\partial x|$ and $|\partial u_y/\partial y|$ are much smaller than $|\partial u_z/\partial z|$, $\sigma_{zz}$ is given by

$$\sigma_{zz} = \left(K + \frac{4}{3}G\right)A(t), \qquad (22)$$

and Eq. (20) is written as

$$\left(K + \frac{4}{3}G\right)A(t) = \frac{1}{a_0 b_0}\int_{-a_0/2}^{a_0/2} dx \int_{-b_0/2}^{b_0/2} dy\, p(x,y,t). \quad (23)$$

Equations (17) and (21) lead the following Poisson equation for the pressure $p(x,y,t)$:

$$\frac{\partial^2 p}{\partial x^2} + \frac{\partial^2 p}{\partial y^2} = a(t), \qquad (24)$$

where

$$a(t) \equiv \frac{\zeta}{(1-\phi)^2}\dot{A}(t). \qquad (25)$$

This Poisson equation can be solved by the Fourier transformation under the boundary condition of Eq.(18):

$$p(x,y,t) = p_0 - \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} C_{m,n}\cos\left(\frac{(2m-1)\pi}{a_0}x\right)$$
$$\times \cos\left(\frac{(2n-1)\pi}{b_0}y\right)a(t), \qquad (26)$$

where

$$C_{m,n} = (-1)^{m+n}\frac{16}{(2m-1)(2n-1)\pi^2}\left\{\left(\frac{(2m-1)\pi}{a_0}\right)^2 + \left(\frac{(2n-1)\pi}{b_0}\right)^2\right\}^{-1}. \qquad (27)$$

Equation (23) gives

$$\left(K + \frac{4}{3}G\right)A(t) = p_0 - a(t)\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\frac{64}{\{(2m-1)(2n-1)\pi^2\}^2}$$
$$\times \left\{\left(\frac{(2m-1)\pi}{a_0}\right)^2 + \left(\frac{(2n-1)\pi}{b_0}\right)^2\right\}^{-1}. \qquad (28)$$

Equations (25) and (28) give the following relation:

$$\tau\dot{A}(t) = p_0\left(K + \frac{4}{3}G\right)^{-1} - A(t), \qquad (29)$$

where $\tau$ is the relaxation time defined by

$$\tau \equiv D^{-1}\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\frac{64}{\{(2m-1)(2n-1)\pi^2\}^2}\left\{\left(\frac{(2m-1)\pi}{a_0}\right)^2 + \left(\frac{(2n-1)\pi}{b_0}\right)^2\right\}^{-1}. \qquad (30)$$

Here, $D$ is the collective diffusion constant of gels defined by $D \equiv (1-\phi)^2(K+4G/3)/\zeta$. From Eq. (29), we can solve $A(t)$ as follows:

$$A(t) = p_0\left(K + \frac{4}{3}G\right)^{-1}\left\{1 - \exp\left(-\frac{t}{\tau}\right)\right\}. \qquad (31)$$

Here, we used the initial condition $A(0)=0$. Therefore, Eq. (21) leads

$$u_z(z,t) = p_0\left(K + \frac{4}{3}G\right)^{-1}\left\{1 - \exp\left(-\frac{t}{\tau}\right)\right\}z. \qquad (32)$$

The time evolution of the thickness of gels $c(t)$ is obtained as follows:

$$\frac{c(t)}{c_0} = 1 + p_0\left(K + \frac{4}{3}G\right)^{-1}\left\{1 - \exp\left(-\frac{t}{\tau}\right)\right\}. \qquad (33)$$

These results show that the time evolution of the thickness of gels is described by a single exponential and the characteristic relaxation time depends on the lengths of the rectangular surfaces and not on the thickness of gels.

From Eqs.(26), (27), and (31), the time evolution of pressure in gels are solved as follows:

$$p(x,y,t) = p_0\left[1 - \frac{1}{D\tau}\left\{\sum_{m=1}^{\infty}\sum_{n=1}^{\infty} C_{m,n}\cos\left(\frac{(2m-1)\pi}{a_0}x\right)\right.\right.$$
$$\left.\left.\times \cos\left(\frac{(2n-1)\pi}{b_0}y\right)\right\}\exp\left(-\frac{t}{\tau}\right)\right]. \qquad (34)$$

From Eqs. (13) and (14), the displacements $u_x$ and $u_y$ are described as follows:

$$u_x(x,y,z,t) = \frac{1}{2G}\frac{\partial p}{\partial x}(x,y,t)(c_0^2 - z^2), \qquad (35)$$
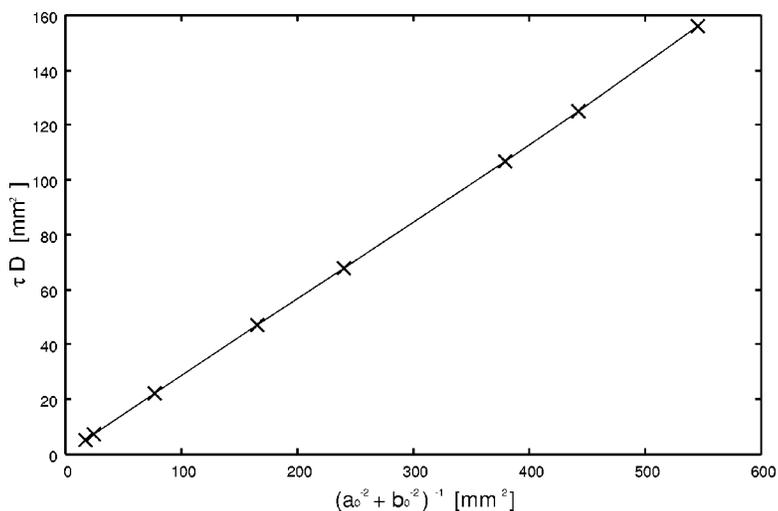
FIG. 2. The relaxation time $\tau$ is plotted against $(a_0^{-2}+b_0^{-2})^{-1}$ by varying $a_0$ for fixed $b_0$ =26.0 mm.

$$u_y(x,y,z,t) = \frac{1}{2G}\frac{\partial p}{\partial y}(x,y,t)(c_0^2 - z^2). \qquad (36)$$

Here, we use the boundary conditions described by Eq. (19).

## IV. COMPARISON WITH EXPERIMENTS

We now compare the result of the present analysis with the experiment of Suzuki and Hara.

Equation (33) shows that the time evolution of the thickness of gels is described by a single exponential. This agrees well with the experimental results [Fig. 2(a) of Suzuki and Hara [1]]. By comparing the theoretical results with the experimental results, we can see that the swelling ratio in the equilibrium state is related to the ratio of the elasticity and the change of osmotic pressure of gels, $p_0(K+\frac{4}{3}G)^{-1}$. From the experimental results of the swelling process, $p_0(K+\frac{4}{3}G)^{-1}$ can be calculated to be about 1.5.

Figure 2 shows the size dependence of the relaxation time. We plotted $\tau D$ against $(a_0^{-2}+b_0^{-2})^{-1}$, as it was done by Suzuki and Hara. The relaxation time $\tau$ is nicely in proportion to the values of $(a_0^{-2}+b_0^{-2})^{-1}$ in agreement with the experimental results [Fig. 3(b) of Suzuki and Hara [1]]. By comparing the theoretical results with the experimental ones, we can see that the collective diffusion constant $D$ in the

experiment is calculated to be about 0.026 mm$^2$/min.

The time evolution of pressure of gels are calculated by Eq. (34) and shown in Fig. 3.

The profiles of the time evolution of the pressure are invariant during the swelling process, and this is one of the special properties of the diffusion in a single exponential swelling process.

## V. DISCUSSION

In this paper, we have ignored the fast process whose time scale is shorter than $t_f \simeq c_0^2/D$. The swelling process involving this fast process is schematically shown in Fig. 4. In the short time scale of $t_f \sim c_0^2/D$, the gel swells at the side boundary. The volume change $\Delta V$ is about $\Delta V \simeq \sqrt{Dt_f}c_0 2\pi a_0 \simeq c_0^2 a_0$. Hence, the change of the thickness is $\Delta V/a_0^2 \simeq c_0^2/a_0$, which can be neglected for a thin gel. In the time scale of $t \sim a_0^2/D$, the solvent can diffuse from the side boundary into the center of the gel, and the change of the thickness of the gel is observed in this time scale.

We have shown that the change of the gel thickness is described by a single exponential function. This comes from the fact that the gel is constrained by rigid glass plates. If the gel is constrained by flexible impermeable membranes
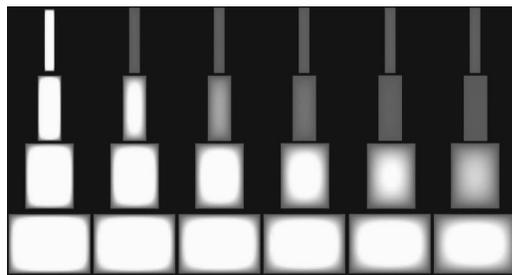


FIG. 3. The time evolution of the pressure $p$ in gels ($p$ =0:white→$p_0$:gray) for various widths of the glass plates with $a_0$=4.2,9.3,19.3,35.8 mm (from upper figures to lower ones) and fixed $b_0$=26.0 mm, at times $t$=0,3200,6400,9600,128000, 16000 min (from left figures to right ones).
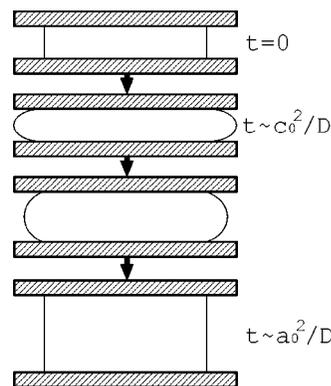


FIG. 4. The schematics of the swelling process of the gel constrained by rigid glass plates related to the time scale.
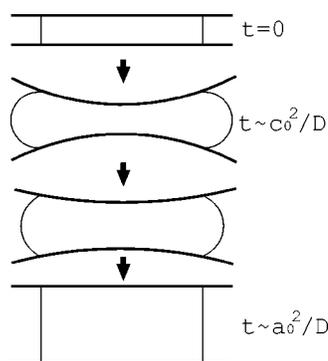
FIG. 5. The schematics of the swelling process of the gel constrained by flexible impermeable membranes related to the time scale.

shown in Fig. 5, the swelling behavior will be quite different. For this case, the $z$ component of displacement vector $u_z$ depends on $x$ and $y$ coordinate, and we should solve the pressure $p=p(x,y,t)$ and the displacement vector $\mathbf{u} =[u_x(x,y,z,t),u_y(x,y,z,t),u_z(x,y,z,t)]$.

From Eq. (15), we have

$$u_z = A(x,y,t)z. \tag{37}$$

Thus $\sigma_{zz}$ is given by

$$\sigma_{zz} = \left(K + \frac{4}{3}G\right)A(x,y,t). \tag{38}$$

Since there is no external force acting on the flexible membrane, $\sigma_{zz}-p$ must be zero:

$$\sigma_{zz} - p(x,y,t) = 0. \tag{39}$$

From Eqs. (37)–(39), we have the relation

$$u_z = \left(K + \frac{4}{3}G\right)^{-1} p(x,y,t)z. \tag{40}$$

From Eqs. (17) and (40), we can show that the pressure $p(x,y,t)$ satisfies the following diffusion equation:

$$\frac{\partial p}{\partial t} = D\left(\frac{\partial^2 p}{\partial x^2} + \frac{\partial^2 p}{\partial y^2}\right). \tag{41}$$

This diffusion equation can be solved under the condition of Eq. (18) with the initial condition $p(x,y,t=0)=0$:

$$p(x,y,t) = p_0\left[1 - \sum_{m=1}^{\infty}\sum_{n=1}^{\infty}(-1)^{m+n}\frac{16}{(2m-1)(2n-1)\pi^2}\right.$$
$$\times \cos\left(\frac{(2m-1)\pi}{a_0}x\right)\cos\left(\frac{(2n-1)\pi}{b_0}y\right)$$
$$\left.\times\exp\left(-\frac{t}{\tau_{m,n}}\right)\right], \tag{42}$$

where $\tau_{m,n}$ is the multimode relaxation time:

$$\tau_{m,n} \equiv D^{-1}\left\{\left(\frac{(2m-1)\pi}{a_0}\right)^2 + \left(\frac{(2n-1)\pi}{b_0}\right)^2\right\}^{-1}. \tag{43}$$

From Eq. (40), the thickness of the gel is given by

$$\frac{c(x,y,t)}{c_0} = 1 + \left(K + \frac{4}{3}G\right)^{-1} p(x,y,t). \tag{44}$$

Therefore, when the gel is constrained by flexible impermeable membranes, the thickness of the gel is not uniform and the process involves many relaxation times. This is in sharp contrast to the gel constrained by rigid impermeable plates.

## VI. SUMMARY

In this paper, we have calculated the swelling process of thin-plate gels with rectangular surfaces under mechanical constraint using the linearized stress-diffusion coupling model of gels based on the two-fluid model. We have shown that the theory reproduces several characteristic features of experimental results, such that the time evolution of the thickness is described by a single exponential and that the characteristic relaxation time depends on the lengths of the rectangular surfaces and not on the thickness of gels.

These results show that the stress-diffusion coupling model of gels, which considers the relative motion between the solvent and the polymer of gels together with the mechanical coupling between the solvent diffusion and the polymer network stress, correctly describes the dynamics of the general anisotropic deformation of gels.

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