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Swelling Kinetics of Polymer Gels

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ABSTRACT: The kinetics of gel swelling is theoretically analyzed by considering coupled motions of both the solvent and the polymer network. This model avoids the two process approach of Li and Tanaka, in which the solvent motion is indirectly considered. Analytical solutions of solvent and network movement are found from the collective diffusion equations for a long cylindrical and a large disk gel. For a cylindrical gel, the speed of solvent motion is proportional to $-r/(2a)$ along the radial direction and z/a along the axial direction, respectively. Here r and z represent radial and axial coordinates, respectively, and a is the radius of the cylinder. The flow diagram of the solvent is obtained. It is also found that the solvent motion can be independently derived from Li−Tanaka's isotropy and continuity conditions without solving the collective diffusion equations. The swelling behavior is obtained at the gel boundary and also in the interior of the gel.

I. Introduction

The kinetics of the gel swelling process has attracted considerable interest in the past decade. Many applications ranging from controlled drug release to gel actuators are directly related to the swelling kinetics.[1−8]

A theory of the swelling of gel networks was first derived from the theory of elasticity by Tanaka, Hocker, and Benedek (THB).[9] Tanaka and Fillmore[10] employed that theory to describe the swelling kinetics of spherical gels, assuming that the shear modulus of the gel is negligible compared with the osmotic bulk modulus. Their model led to a relaxation time proportional to the square of the linear size of the gel and inversely proportional to the collective diffusion constant of the network. Later, Peters and Candau[11,12] extended Tanaka and Fillmore's model to long cylindrical and large disk gels for which the shear modulus cannot be neglected.

These previous theories all assumed that the motion of the solvent could be neglected. This assumption, however, is only true for spherical gels. As first pointed out by Onuki, the motion of the solvent directly contributes to swelling kinetics.[13] Except in the case of spherical gels, the swelling process changes both the bulk and shear energy of the polymer network. The solvent motion helps the system to minimize the total energy. The motion of the solvent depends strongly on the geometry of the gel and governs the friction force and the swelling kinetics.

Recently, Li and Tanaka (L−T) presented a theory[14−16] of gel swelling kinetics for arbitrary shapes. Instead of considering directly the motion of both the network and solvent, they decomposed the swelling process into two imaginary processes. The first process is a pure network diffusion process described by a collective diffusion equation with zero solvent velocity. This process increases the shear energy of the sample. In the second process, the solvent moves together with the network so that the solvent velocity is the same as the network velocity. This process minimizes the total energy. The effect of solvent motion is therefore included in the second process.

Although analytical solutions describing the swelling at the gel boundary have been derived by Li and Tanaka, it is not easy to visualize the solvent motion in their approach. Some earlier work has considered the motion of both the gel network and the solvent,[13,14] and partial progress has been made for long cylindrical gels. This paper presents a theoretical analysis of the kinetics of gel swelling and solvent motion by directly solving the coupled equations of motion for a network and solvent in the case of long cylindrical and large disk gels. It is also found that the solvent motion can be independently derived from L−T's isotropic condition (minimum shear energy) and continuity condition without solving the coupled collective diffusion equations.

II. Theory

A. Review of L−T's Theory. The collective diffusion equation is expressed as

$$f\frac{\partial \boldsymbol{u}}{\partial t} = \nabla\cdot\sigma \tag{1}$$

where f is the friction coefficient between the network and the solvent. $\mathbf{u}(\mathbf{r}, t)$ is the displacement vector of a point $\mathbf{r}$ in the network from its final equilibrium location after the gel reaches equilibrium. σ is the stress tensor and is described by[17]

$$\sigma_{ik} = K\nabla\cdot\boldsymbol{u}\delta_{ik} + 2\mu\left(u_{ik} - \frac{1}{3}\nabla\cdot\boldsymbol{u}\delta_{ik}\right) \tag{2}$$

with $u_{ij} = (\partial u_i/\partial x_j + \partial u_j/\partial x_i)/2$ where K and μ are the bulk and shear modulus, respectively.

The governing equation for minimizing the shear energy in L−T's theory[14] is

$$\delta F_{sh} = 0 \tag{3}$$

where F_{sh} is the shear energy of a gel of arbitrary shape. The equation states that the change of the total shear energy in response to any small change in shape under the constant volume condition should be zero.

For a long cylindrical gel, they obtained the solution

$$u_r(r,t) = \Delta\sum_{n=1}^{\infty} A_n e^{-D_e q_n^2 t} J_1(q_n r) \tag{4}$$

where the coefficients A_n are determined by the initial

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conditions. Δ ($=u_r(a,0)$) is defined as the total change of the radius of the gel. J_1 is the Bessel function of first order. α_n ($=q_n a$) are eigenvalues determined by the boundary condition. D_e is the apparent collective diffusion coefficient, which is related to the kinetic process and determined by

$$\frac{\partial(D_e t)}{\partial t} = \frac{D}{1+\lambda} \tag{5}$$

$$\lambda(r,t) = \frac{r}{2z}\left(\frac{\partial\mu_z}{\partial t}\right)\Big/\left(\frac{\partial\mu_r}{\partial t}\right) \tag{6}$$

where the collective diffusion constant D is defined by $D = (K + 4\mu/3)/f$. At the boundary of $r = a$, they obtained $D_e = 2D/3$, and

$$u_r(a,t) = \Delta\sum_{n=1}^{\infty} B_n e^{-(2/3)Dq_n^2 t} \tag{7}$$

where $B_n = A_n J_1(q_n a)$. For a large disk gel a similar solution is obtained with $D_e = D/3$ at the boundary.

B. Basic equations of This Theory. To include the solvent motion, eq 1 can be revised as follows,

$$\frac{\partial \boldsymbol{u}}{\partial t} = \frac{\partial \boldsymbol{w}}{\partial t} + \frac{1}{f}\nabla\cdot\sigma \tag{8}$$

where $\partial\mathbf{w}/\partial t$ is the velocity of the solvent. Equation 3 remains valid.

The continuity requirement is given by the equation

$$(1-\phi)\nabla\cdot\left(\frac{\partial \boldsymbol{w}}{\partial t}\right) + \phi\nabla\cdot\left(\frac{\partial \boldsymbol{u}}{\partial t}\right) = 0 \tag{9}$$

where ϕ is the fractional volume of the gel network. For small ϕ, eq 9 can be simplified as

$$\nabla\cdot\frac{\partial \boldsymbol{w}}{\partial t} = 0 \tag{10}$$

Equations 3, 8, and 10 form a set of basic equations with the boundary condition $\sigma_{\text{normal}} = 0$ where σ_{normal} is the normal stress on the gel surface. The initial condition is $\sigma_{ik} = \pi_0\delta_{ik}$ where π_0 is the osmotic pressure of the gel.

C. Long Cylindrical Gels. Let us first consider a long cylindrical gel. The displacements of the network and the solvent in such a system can be written as

$$\boldsymbol{u}(\boldsymbol{r},t) = u_r(r,t)\boldsymbol{r}_0 + u_z(z,t)\boldsymbol{z}_0 \tag{11}$$

$$\boldsymbol{w}(\boldsymbol{r},t) = w_r(r,t)\boldsymbol{r}_0 + w_z(z,t)\boldsymbol{z}_0 \tag{12}$$

where $\mathbf{r}_0$ and $\mathbf{z}_0$ are the unit vectors along the radial and axial directions, respectively. In this case, deformation at the ends of the long cylinder gel relative to that at its side is small and neglected. The changes in radial and axial directions are independent of each other. Using eqs 11 and 12, eq 8 can be separated into two equations for the axial and radial directions, respectively.

$$\frac{\partial u_r}{\partial t} = \frac{\partial w_r}{\partial t} + D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u_r}{\partial r}\right) - \frac{1}{r^2}u_r\right] \tag{13}$$

$$\frac{\partial u_z}{\partial t} = \frac{\partial w_z}{\partial t} + D\frac{\partial^2 u_z}{\partial z^2} \tag{14}$$

The boundary condition for the long cylinder can be rewritten as

$$\left.\left[\frac{\partial u_r}{\partial r} + (1-2R)\left(\frac{u_r}{a} + \frac{\partial u_z}{\partial z}\right)\right]\right|_{r=a} = 0 \tag{15}$$

where $R = \mu/(K + 4\mu/3)$ is the ratio of the shear modulus to the longitudinal modulus. The restraint condition given in eq 3 produces the isotropic identity for the long cylinder,[14]

$$\frac{u_z(z,t)}{z} = \frac{u_r(a,t)}{a} \tag{16}$$

Combining eq 16 and the boundary condition of eq 15, we obtain

$$\left.\frac{\partial u_r}{\partial r}\right|_{r=a} + 2(1-2R)\frac{u_r(a,t)}{a} = 0 \tag{17}$$

Substituting eq 16 into eq 14, we obtain

$$\frac{\partial w_z}{\partial t} = \frac{z}{a}\frac{\partial u_r(a,t)}{\partial t} \tag{18}$$

Substituting eq 18 into eq 10 gives the differential equation for $\partial w_r/\partial t$. We have solved this equation with natural boundary condition $\partial w_r/\partial t|_{r=0} = 0$,

$$\frac{\partial w_r}{\partial t} = -\frac{r}{2a}\frac{\partial u_r(a,t)}{\partial t} \tag{19}$$

It is clear from eqs 16, 18, and 19 that the solvent velocity $\partial w_r/\partial t$, $\partial w_z/\partial t$ and the axial displacement of the network u_z are all related to the radial displacement of the network u_r. Let us now derive the analytical solution of u_r. Substituting eq 19 into eq 13,

$$\frac{\partial u_r}{\partial t} + \frac{r}{2a}\frac{\partial u_r(a,t)}{\partial t} - D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u_r}{\partial r}\right) - \frac{1}{r^2}u_r\right] = 0 \tag{20}$$

The solutions of eq 20 are the Bessel functions of the first order. So u_r can be written as

$$u_r(r,t) = \Delta\sum_{n=1}^{\infty} T_n(t)\, J_1(q_n r) \tag{21}$$

Here $u_r(r, t)$ is normalized to $u_r(a,0) = \Delta$. Let us also expand $\partial w_r/\partial t$ in Bessel functions of the first order,

$$\frac{\partial w_r(r,t)}{\partial t} = \Delta\sum_{n=1}^{\infty} F_n(t)\, J_1(q_n r) \tag{22}$$

Substituting eqs 21 and 22 to eq 13 and separating the variables t and r, we have

$$\frac{T_n'(t) - F_n(t)}{DT_n(t)} = -q_n^2 \tag{23}$$

One can solve eq 23 and obtain

$$T_n(t) = \left[A_n + \int_0^t F_n(x)e^{Dq_n^2 x}\,\mathrm{d}x\right]e^{-Dq_n^2 t} \tag{24}$$

where q_n($=\alpha_n/a$) are determined by the boundary condition (eq 15), which can be rewritten as

$$\frac{\alpha_n J_0(\alpha_n)}{J_1(\alpha_n)} - 4R + 1 = 0 \tag{25}$$

Substituting eq 24 to eq 21, we get

$$u_r(r,t) = \Delta \sum_{n=1}^{\infty} \left[A_n + \int_0^t F_n(x) e^{Dq_n^2 x} \, \mathrm{d}x \right] e^{-Dq_n^2 t} J_1(q_n r) \tag{26}$$

The initial condition for the long cylinder turns out to be $u_r(r,0) = r/a$. Using this initial condition in eq 26 gives

$$\sum_{n=1}^{\infty} A_n J_1(q_n r) = \frac{r}{a} \tag{27}$$

Using the orthogonality relations of Bessel functions, the coefficients A_n can be determined,

$$A_n = \frac{2(3 - 4R)}{\alpha_n^2 - (4R - 1)(3 - 4R)} \frac{1}{J_1(\alpha_n)} \tag{28}$$

Substituting eq 27 for r/a in eq 19, then comparing it with eq 22, one can obtain the following,

$$F_n(t) = -\frac{A_n}{2\Delta} \frac{\partial u_r(a,t)}{\partial t} \tag{29}$$

Inserting eq 29 to eq 26,

$$u_r(r,t) = \sum_{n=1}^{\infty} A_n \left[\Delta - \frac{1}{2} \int_0^t \frac{\partial u_r(a,\tau)}{\partial \tau} e^{Dq_n^2 \tau} \, \mathrm{d}\tau \right] e^{-Dq_n^2 t} J_1(q_n r) \tag{30}$$

Let $r = a$ in eq 30,

$$u_r(a,t) = \sum_{n=1}^{\infty} B_n \left[\Delta - \frac{1}{2} \int_0^t \frac{\partial u_r(a,\tau)}{\partial \tau} e^{Dq_n^2 \tau} \, \mathrm{d}\tau \right] e^{-Dq_n^2 t} \tag{31}$$

where $B_n = A_n J_1(\alpha_n)$. From eqs 16, 18, 19, and 30, one can see that motions of both network and solvent have been separately solved along the radial and the axial directions. These solutions are explicitly expressed as a function of $u_r(a,t)$. In the space distribution, the speed of solvent motion is proportional to $-r/2a$ along the radial direction and z/a along the axial direction. The magnitude of the speed decreases to zero gradually with the increase of time.

Several special cases are given below. For $t << \tau_1$ ($1/\tau_1 = Dq_1^2$), $u_r(r,t) = \exp(DQ^2 t/3)\tilde{u}_r$, where $Q^2 = \sum B_i q_i^2$ and $\tilde{u}_r = \Delta \sum A_n \exp(-Dq_n^2 t) J_1(q_n r)$. For $t >> \tau_1$, $u_r(r,t) \propto \exp[-2Dq_1^2 t/(2 + B_1)] J_1(q_1 r)$.

As the bulk modulus K approaches zero, we have

$$u_r(r,t) = \Delta \frac{r}{a} e^{-(2/3)Dq_1^2 t} \tag{32}$$

which is identical to eq 29 in L−T's paper[14] and valid for any t. Previous solutions for two special cases of $t << \tau_1$ and $t >> \tau_1$ consistently reduce to the same form of eq 32 by using the relations $B_1 = 1$, $B_i = 0$, and $A_i = 0$ for $i > 1$ as $K \to 0$.

D. Comparison with L−T's Results. To compare the current results with previous work by L−T, we rewrite eq 13 as

$$\frac{\partial u_r}{\partial t}\left(1 - \frac{\partial w_r/\partial t}{\partial u_r/\partial t}\right) = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u_r}{\partial r}\right) - \frac{1}{r^2}u_r\right] \tag{33}$$

Using eq 16 and eq 19, the λ parameter defined by L−T (eq 6) can be written as

$$\lambda(r,t) = -\left(\frac{\partial w_r}{\partial t}\right) \Big/ \left(\frac{\partial u_r}{\partial t}\right) \tag{34}$$

Combining eq 33 and eq 34, we have

$$\frac{\partial u_r}{\partial t} = \frac{D}{1 + \lambda}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u_r}{\partial r}\right) - \frac{u_r}{r^2}\right] \tag{35}$$

where the apparent diffusion coefficient is reduced by a factor $1/(1 + \lambda) = (\partial u_r/\partial t)/(\partial(u_r - w_r)/\partial t)$. This equation is similar to eq 10 in L−T's paper.[14] Since the motion of the solvent is in the opposite direction of $\partial u_r/\partial t$, the relative speed and displacement of network are, i.e., decreased by a factor $(1 + \lambda)$ over that expected by pure diffusion theory. Compared with the results of pure diffusion theory, the friction force increases and the relaxation process slows down accordingly.

Equation 13 is the Bessel equation with a free term. This free term can be expanded into a Bessel series. Let us write the solution for eq 35 in the form[14] of eq 4. Comparing eqs 4 and 30, we find that D_e is only a function of time t. Substituting $u_r(r,t)$ into eq 35 and comparing the coefficients of Bessel functions of the equation in the approximation that λ is independent of r, we obtain eq 5, which was derived by Li−Tanaka through a two-process approach using the same approximation. At $K = 0$, λ is $^1/_2$ and independent of r, so $D_e = 2D/3$ from eq 5. This is in agreement with eq 32.

The difference of D_e/D between L−T's theory and the present theory is given in the following.

	D_e/D (L−T's)	D_e/D (present)
sphere	1	1
cylinder	2/3	$2/(2 + B_1)$
disk	1/3	$1/(1 + 2B_1)$

where B_1 is related to the ratio of the shear modulus and longitudinal modulus. $B_1 = A_1 J_1(\alpha_1)$ for a long cylindrical gel, and $B_1 = A_1 \sin \alpha_1$ for a large disk gel, which will be discussed in detail in the Appendix. The differences between the L−T results and ours could be revealed by more accurate swelling kinetic measurements using a large cylindrical gel due to its very slow kinetics. It is noted that the values of D_e/D in the present theory can be used not only at the boundary but also in the interior of the gel and are valid for $t >> \tau_1$, which corresponds to a single-exponential relaxation in swelling and shrinking processes. When the bulk modulus approaches zero, $B_1 = 1$; the values of D_e/D obtained from the present theory are the same as ones obtained from L−T's theory.

In Onuki's calculation,[18] he obtained the stress-free boundary condition at $r = a$ as

$$\frac{\alpha_n J_0(\alpha_n)}{J_1(\alpha_n)} = 4R \frac{(e_\perp + e_{||})}{(2e_\perp + e_{||})} \tag{36}$$

The volume change $\nabla \cdot \mathbf{u}$ can be expressed as

$$\nabla\cdot\boldsymbol{u} = \sum_{n=1}^{\infty} A_n \frac{\alpha_n}{a} J_0\left(\frac{\alpha_n r}{a}\right) e^{-\Omega_n t} \tag{37}$$

As K approaches infinity, $J_0(\alpha_n) = 0$. Therefore, $\nabla\cdot\mathbf{u} = 0$ at $r = a$.

From L−T's theory, $\nabla\cdot\mathbf{u}|_{r=a} = -\Delta(t/D)\sum(A_n/\tau_n)\exp(-D_e q_n^2 t)J_1(q_n a)(\partial D_e/\partial r)$, for $K \to \infty$, and $\partial D_e/\partial r = 0$ because D_e is independent of r. Therefore, $\nabla\cdot\mathbf{u} = 0$ for $K \to \infty$ at $r = a$, in agreement with Onuki's result.

From the present theory, we used the same equation (eq 25) as L−T's for the boundary condition to determine eigenvalues α_n. The volume change can be expressed as

$$\nabla\cdot\boldsymbol{u} = \Delta\sum_n T_n(t)\left[J'_1\left(\alpha_n\frac{r}{a}\right)\frac{\alpha_n}{a} + \frac{J_1\left(\alpha_n\frac{r}{a}\right)}{r} + \frac{J_1(\alpha_n)}{a}\right] \tag{38}$$

From the relation between Bessel functions, $J'_1(x) = J_0(x) - J_1(x)/x$, we obtain

$$\nabla\cdot\boldsymbol{u} = \Delta\sum_n \frac{T_n(t)}{a}\left[\alpha_n J_0\left(\alpha_n\frac{r}{a}\right) + J_1(\alpha_n)\right] \tag{39}$$

As $K \to \infty$, $\alpha_n J_0(\alpha_n) = -J_1(\alpha_n)$. Therefore, $\nabla\cdot\mathbf{u} = 0$ for $K \to \infty$ at $r = a$, in agreement with Onuki's result.

E. Velocity Field of Solvent. One of the major results from this generalized gel diffusion model is the motion of the solvent, as expressed by eq 18 and eq 19. Here we demonstrate that the radial and axial components of solvent motion can be derived from the volume conservation and isotropic swelling conditions. Let us first consider the radial component. According to volume conservation, the volume change (δV) during a period of time (δt) for a gel cylinder (with radius r and length $2l$ at time t) is related with the solvent velocity relative to gel network (v) and the side area (S) by the expression $\delta V = \nu S\delta t$ where $\delta V = \pi r^2(2l)(2\delta r/r + \delta l/l)$, $v = \partial w_r/\partial t - \partial u_r/\partial t$, $S = 2\pi r(2l)$, $\delta r = -\delta u_r(r,t)$, and $\delta l = -\delta u_z(l,t)$. Note that we have neglected the end effect. Combining the isotropic swelling condition eq 18, $\delta l/l = -\delta u_r(a,t)/a$ and the equation $\delta V = \nu S\delta t$, we obtain eq 19. The axial component of the solvent motion (eq 18) can be directly obtained through $\nabla\cdot(\partial\mathbf{w}/\partial t) = 0$. Therefore, the solvent motion can be independently derived from L−T's isotropic condition and continuity condition without using the coupled collective diffusion equations.

Let us now discuss the solvent velocity field. Rewrite eqs 18 and 19 as

$$\frac{\partial w_z(z,t)}{\partial t} = \frac{z}{a}f(t) \tag{40}$$

$$\frac{\partial w_r(r,t)}{\partial t} = -\frac{r}{2a}f(t) \tag{41}$$

where $f(t)$ is $\partial u_r(a, t)/\partial t$, which decreases to zero as the time approaches infinity. Figure 1 shows the solvent motion pattern according to eqs 40 and 41. The solvent always moves toward the inside along the radial direction and toward the ends along the axial directions. Due to the solvent motion, the relative velocity between the network and the solvent is $(1 + \lambda)\partial u_r/\partial t$ in the radial direction but zero in the axial direction. In L−T's approach, the zero relative motion in the axial direction is built in based on the two-step process.

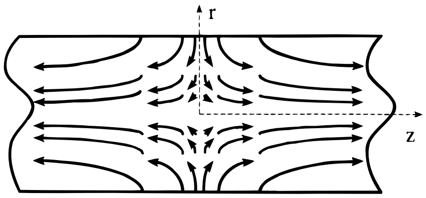

Figure 1. Solvent motion pattern for a long cylindrical gel in its swelling process. The drawing is scaled according to eqs 40 and 41.

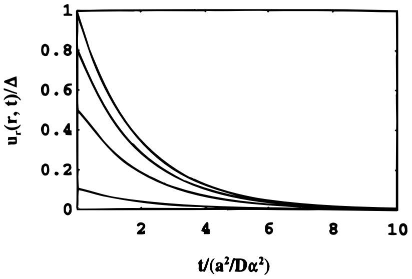

Figure 2. Typical curves for long cylindrical gel swelling. The displacement $u_r(r,t)$ is drawn as a function of time t. The curves are corresponding to $r/a = 0.1, 0.5, 0.8, 1$ from the bottom to the top.

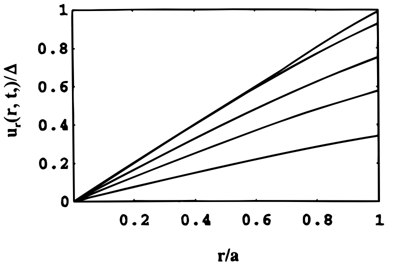

Figure 3. Typical curves for long cylindrical gel swelling. The displacement $u_r(r,t)$ is drawn as a function of radius r. The curves are corresponding to $t/(a^2/D\alpha^2) = 0, 0.1, 0.5, 1, 2$ from the top to the bottom.

The swelling process is controlled by elasticity and friction. The elastic force makes the whole gel network swell until the stress tensor disappears everywhere inside the gel. The friction force dissipates the elastic energy and slows down the swelling process. The collective diffusion coefficient D, which is proportional to the longitudinal elastic modulus $(K + 4\mu/3)$ and inversely proportional to the friction coefficient f, determines the swelling process. Taking the solvent motion into consideration, the apparent collective diffusion coefficient D_e is less than D by a factor of $1/(1 + \lambda)$. Therefore, the whole swelling process is slower in the radial direction than it is expected based on the pure diffusion theory.

A numerical solution of eq 30 has been obtained. Figure 2 shows the normalized swelling displacement u_r/Δ versus normalized time $t/(a^2/D\alpha^2)$. The network motion is coupled with solvent motion, resulting in isotropic gel swelling. Correspondingly, the time dependence of u_r cannot be described by exponential forms. The swelling ratio as a function of radial distance r/a is shown in Figure 3. From the figure, one can see that the swelling behavior is obtained not only at the boundary ($r = a$) but also inside the gel ($r < a$). The previous work has only yielded the solutions at the boundary.[14−16]

A similar derivation on a large disk gel is given in the Appendix. The major results are given below. The

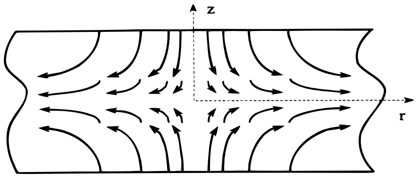

Figure 4. Solvent motion pattern for a large disk gel in its swelling process. The drawing is scaled according to eqs A6 and A7.

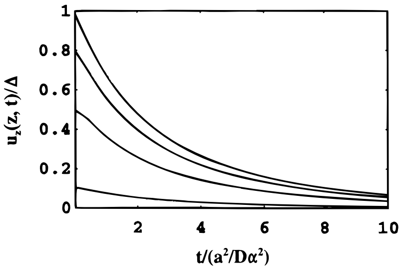

Figure 5. Typical swelling curves for a large disk gel. The displacement $u_z(z,t)$ is drawn as a function of time t. The curves are corresponding to $z/a = 0.1, 0.5, 0.8, 1$ from the bottom to the top.

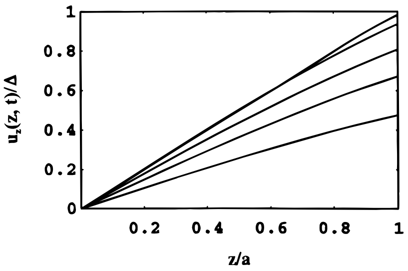

Figure 6. Typical swelling curves for a large disk gel. The $u_z(z,t)$ is drawn as a function of z. The curves are corresponding to $t/(a^2/D\alpha^2) = 0, 0.1, 0.5, 1, 2$ from the top to the bottom.

solvent motion pattern of the large disk gel is shown in Figure 4. The swelling ratio for a large disk gel as function of time t and axial distance z is shown in Figures 5 and 6, respectively.

It is noted that Onuki's theory[18] can lead to similar results about the solvent motion (such as eq 19), although detailed calculations such as the boundary conditions and eigenfunctions employed by us and by Onuki are different. After some approximations, our approach is identical to Onuki's approach. This work has extended our understanding of hydrogel swelling kinetics in the following areas: (a) Our work has modified and extended L−T's theory. (b) We have established that L−T's consideration of isotropic condition and the continuity condition are equivalent to considering the motion of the solvent for long cylindrical and large disk gels. (c) We have obtained detailed flow diagrams of the solvent in the gel network for long cylindrical gels and large disk gels. These diagrams can be experimentally tested.

III. Conclusion

In this work, we have modified and extended Li and Tanaka's calculations by including the motions of both the solvent and the gel network. Using the new swelling equations, we have calculated the solvent velocity field and studied the swelling process of the network for a long cylindrical and a large disk gel. The motion patterns of solvent have been obtained. The results for network kinetics are obtained without using L−T's two processes approach. We have found that the swelling process is slower than expected based on the pure diffusion theory. From analytical solutions of our generalized gel swelling equations, we obtain the gel swelling behavior not only at the surface but also in the interior of gels. The analysis presented here could be used for many applications where nonspherical gels are used.

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Appendix. Swelling Kinetics of Large Disk Gels

A similar analysis can be also applied to a large disk gel. The basic equations are

$$\frac{\partial \boldsymbol{u}}{\partial t} = \frac{\partial \boldsymbol{w}}{\partial t} + D\nabla^2 \boldsymbol{u} \tag{A1}$$

$$\nabla\cdot\frac{\partial \boldsymbol{w}}{\partial t} = 0 \tag{A2}$$

$$\frac{u_r(r,t)}{r} = \frac{u_z(a,t)}{a} \tag{A3}$$

where $u_z(z, t)$ is normalized to $u_z(a,0) = \Delta$ and a is the half thickness of the disk. The boundary condition is

$$\left[\frac{\partial u_z}{\partial z} + (1 - 2R)\left(\frac{u_r}{r} + \frac{\partial u_r}{\partial r}\right)\right]\Bigg|_{z=\pm h} = 0 \tag{A4}$$

And the initial condition is

$$u_z(z,0) = \pm\frac{z}{a}u_z(\pm a,0) \tag{A5}$$

Assuming that solvent movements in r and z directions are independent, we have

$$\frac{\partial w_r(r,t)}{\partial t} = \frac{r}{a}\frac{\partial u_z(a,t)}{\partial t} \tag{A6}$$

$$\frac{\partial w_z(z,t)}{\partial t} = -2\frac{z}{a}\frac{\partial u_z(a,t)}{\partial t} \tag{A7}$$

$$u_r(r,t) = \frac{r}{a}u_z(a,t) \tag{A8}$$

$$u_z(z,t) = \sum_{n=1}^{\infty} A_n\left[\Delta - 2\int_0^t \frac{\partial u_z(a,\tau)}{\partial \tau} e^{Dq_n^2\tau}\,\mathrm{d}\tau\right] e^{-Dq_n^2 t}\sin(q_n z) \tag{A9}$$

Here, $u_z(a,t)$ satisfies

$$u_z(a,t) = \sum_{n=1}^{\infty} A_n\left[\Delta - 2\int_0^t \frac{\partial u_z(a,\tau)}{\partial \tau} e^{Dq_n^2\tau}\,\mathrm{d}\tau\right] e^{-Dq_n^2 t}\sin(\alpha_n) \tag{A10}$$

The eigenvalues α_n are determined by

$$R = \frac{1}{2} + \frac{1}{4}\alpha_n c\cot(\alpha_n) \tag{A11}$$

The coefficients A_n are given by initial condition,

$$A_n = \frac{4}{\alpha_n} \frac{\sin \alpha_n - \alpha_n \cos \alpha_n}{2\alpha_n - s \sin(2\alpha_n)} \tag{A12}$$

References and Notes

(1) Tanaka, T. *Am. Chem. Soc. Symp*. **1992**, *480*, 1.
(2) Li, Y.; Tanaka, T. *Annu. Rev. Mater. Sci.* **1992,** *22*, 243.
(3) Shibayama, M.; Tanaka, T. *Adv. Polym. Sci.* **1993,** *109*, 1.
(4) Hoffman, A. S. *J. Controlled Release* **1987**, *6*, 297.
(5) Peppas, N. A.; Langer, R. *Science* **1994,** *263*, 1715.
(6) Osada, Y.; Okuzaki, H.; Hori, H. *Nature* **1992**, *355*, 242.
(7) Hu, Z.; Zhang, X.; Li, Y. *Science* **1995**, *269*, 525.
(8) Kajiwara, K.; et al. *Polymer Gels*; Plenum Press: New York and London, 1990.
(9) Tanaka, T.; Hocker L.; Benedek, G. *J. Chem. Phys.* **1973**, *59*, 5151.
(10) Tanaka, T.; Fillmore, D. *J. Chem. Phys.* **1979**, *70*, 1214.
(11) Peters, A.; Candau, S. J. *Macromolecules* **1986**, *19*, 1952.
(12) Peters, A.; Candau, S. J. *Macromolecules* **1988**, *21*, 2278.
(13) Onuki**,** A. *Dynamics and Statistics of Patterns*; World Science, 1989.
(14) Li, Y.; Tanaka, T. *J. Chem. Phys.* **1990,** *92*, 1365.
(15) Li, Y.; Tanaka, T. *Springer Proc. Phys., Heidelberg* **1990,** *52*, 44.
(16) Li, Y.; Tanaka, T. *Polymer Gels*; Plenum Press: New York, 1991.
(17) Landau, L. D.; Lifshitz, E. M. *Theory of Elasticity*; Pergamon Press: Oxford, 1986.
(18) Onuki**,** A. *Adv. Polym. Sci.* **1993**, *109*, 97.
(19) Zrinyi, M.; Rosta, J.; Horkay, F. *Macromolecules* **1993**, *26*, 3097.

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