

## Gel Dynamics

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Continuum mechanical model is proposed for dynamical processes in gels that involve coupling between the elastic deformation and solvent permeation. Basic equations are derived by two methods, by a physical argument, and by a variational principle. The model is then applied to discuss the swelling of gels, in which solvent permeation causes deformation, and the squeezing of gels, in which mechanical force induce solvent permeation. The model is also applied to the dynamics of the volume transition of gels. It is shown that the elasticity of gels creates various unusual features in the phase transition dynamics.

KEYWORDS: swelling, squeezing, variational principle, volume transition, elastic effect

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### 1. Introduction

Gel is an elastic material swollen with a fluid.<sup>1,2)</sup> An example of a gel is an edible jelly. When a solution of gelatin is kept in a refrigerator, the solution loses its fluidity and becomes a gel. The gel is a soft elastic material; it can be easily deformed by hand, but it recovers its original shape when the hand is released. The gel contains a large amount of water, which can permeate through the gel. The permeation of water can be controlled by a mechanical force: the liquid in a soft jelly can be squeezed out by applying some weight to the top of the jelly.

Most gels are made of polymers. By creating bridges between polymers (either by a chemical reaction or by forming physical junctions), the fluid state of the polymer solution is transformed to an elastic state, i.e., a gel [see Fig. 1(a)]. An example of this type of gel is the small beads used in diapers. When placed in water, the beads absorb a volume of water up to thousands times larger than their own volume.

Gels can also be made from colloidal solutions. By changing the condition of the solvent (such as the PH or salt concentration), the colloidal particles aggregate to form a three-dimensional network as shown in Fig. 1(b). Examples of this type of gel are yogurt and bean curd.

This state of matter (elastic materials containing fluids) are ubiquitous in our everyday life: they are found in foods, cosmetics, and medicines. Gels are also important in industry: in printing and coating, one needs to preserve the shape of a material while the solvent is evaporating. Many processes in the fabrication of electronic devices rely on this state of matter. Gels are also important in agricultural, biological, and environmental applications. The fact that our bodies are made of gels indicates their importance.

The purpose of this article is to discuss the non-equilibrium phenomena that take place in gels. The problems we are addressing are illustrated in Fig. 2.

- (1) Swelling and drying; [Fig. 2(a)]: a dry gel placed in a water absorbs water and swells. Conversely, the gel shrinks as the water evaporates from the surface. This process is not just a process of volume change: During the process, stress field is created within the gel, which causes the deformation of the gel, and in some cases, creates cracks within the gel.

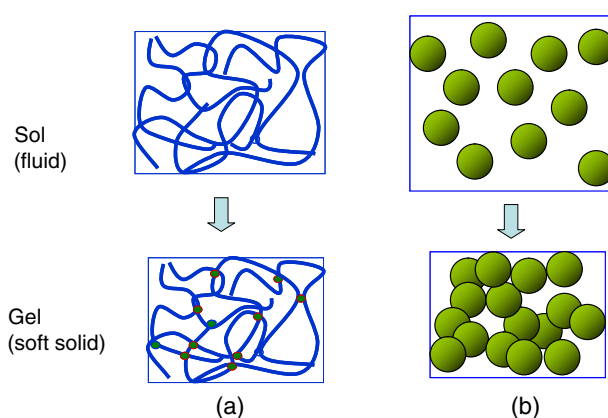


Fig. 1. (Color online) Process of forming gels. (a) Gelation of polymer solutions and (b) gelation of colloidal solutions.

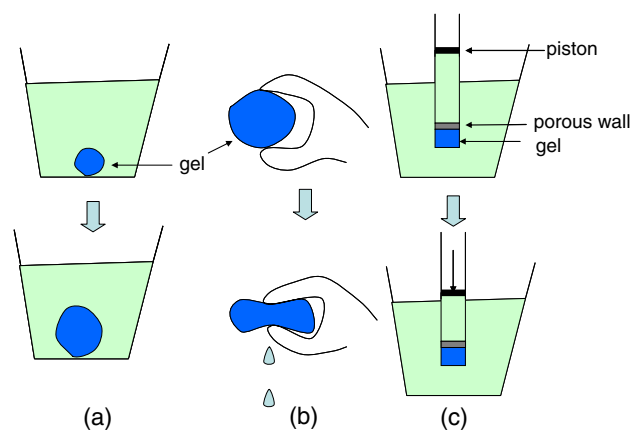


Fig. 2. (Color online) (a) Swelling of a gel, (b) squeezing a gel, and (c) pumping water into a gel.

- (2) Squeezing; [Fig. 2(b)]: When a gel is squeezed, the stress squeeze out the solvent from the gel.
- (3) Forced permeation; [Fig. 2(c)]: When a solvent on one side of the gel is pressed by a piston, it will permeate through the gel.

These phenomena are seen in our everyday life, and have been used in many industrial processes for a long time. However, the theoretical aspects of the phenomena seem to

have been ignored or have attracted little attention compared with their applications. Accordingly, theories for the above phenomena have not been worked out. Early works on gel dynamics focused on the analysis of dynamic light scattering and the swelling of gels.<sup>3,4)</sup> Tanaka and Filmore<sup>4)</sup> proposed an equation describing the swelling of gels, but it turned out that this equation is only valid for spherical gels. This has been corrected by Tanaka and coworkers,<sup>1,5)</sup> but equations describing the general gel dynamics have not been derived.

The purpose of this article is to provide a general framework by which one can discuss the swelling and squeezing of gels using the same basic equations. The framework can be constructed in the same way as the two-fluid model for solutions. In fact, from the viewpoint of continuum mechanics, a gel can be regarded as a homogeneous mixture of a fluid (solvent) and a solid (a network made of polymers or colloidal particles). We call this model the fluid–solid model.

The idea of the fluid–solid model is not new. Continuum mechanical models for mixtures of solids and fluids have been studied in geophysics in which the flow of underground water is coupled with the elastic deformation of the ground. The mechanics dealing with such phenomena is called poromechanics (the mechanics of porous materials).<sup>6–8)</sup> Although the gel dynamics discussed here has some common features with poromechanics, there are differences.

Firstly, a gel is a very soft material. It can be easily deformed and can change its volume enormously: the volume of a fully swollen gel can be thousands times larger than the dry gel. Therefore, the model must be able to describe large deformations and large volume changes.

Secondly, the bulk modulus of a gel is much larger than the shear modulus, and therefore gel can be regarded as an incompressible material. Hence gel can change its volume only by absorbing a solvent. This gives some unique features for the mathematical structures of gel dynamics.

Thirdly, gels can undergo a phase transition: a small change of external parameters causes a very large change in volume. In the process of phase transitions, gels show many unusual and interesting behaviors.

Gel dynamics has been constructed by several groups,<sup>3,9–13)</sup> each studying different problems with different objectives. Accordingly, although there is a general consensus on the physics underlying the model, the equations proposed by these authors are not exactly the same. In this article, the discussion is restricted to slow phenomena in gels, i.e., the problems illustrated in Fig. 2. Fast phenomena such as wave propagation or density fluctuations are not discussed here.

The discussion is also restricted to the continuum mechanics of gels. The molecular aspects of gels, on which many studies have been done,<sup>1,14)</sup> are not discussed. In continuum mechanics, it does not matter whether the gel is a polymer gel or a colloidal gel. However, the present discussion is mostly suited for polymer gels since we are making two assumptions that are generally satisfied for polymer gels but not for colloidal gels.

- (1) The network of gels is purely elastic: the network is not broken and does not undergo plastic deformation. This condition is usually satisfied for strong chemical gels

made of polymers but not for weak physical gels or colloidal gels.

- (2) The specific density  $\rho_p$  of the network component is equal to that of the solvent  $\rho_s$ , and is a constant independent of temperature and pressure.

$$\rho_p = \rho_s = \rho = \text{constant} \quad (1)$$

The second assumption, which is commonly made for polymer solutions, can be stated as follows. Let  $\phi$  be the volume fraction of the polymer network, then the mass density of the polymer  $m_p$ , and that of the solvent  $m_s$  are given by

$$m_p = \rho\phi, \quad m_s = \rho(1 - \phi). \quad (2)$$

The total mass density of the gel  $m_p + m_s$  is constant independent of temperature and pressure.

Since we are focusing on polymer gels, we shall refer to the network component as the polymer network.

## 2. Equilibrium Theory for Soft Elastic Materials

### 2.1 Swelling equilibrium

Let us start the discussion with the equilibrium state of gels. A gel placed in a solvent changes its volume by absorbing or desorbing the solvent and eventually reaches thermodynamic equilibrium. The equilibrium state of a gel can also be defined when the gel is subject to an external force [as shown in Fig. 2(b)]. In this case, the swelling is not uniform but the final state is at thermodynamic equilibrium.

Equation (1) indicates that gels can change their volume only by absorbing or desorbing a solvent. Note that when we discuss the volume of gels, we are referring to the volume of the region surrounded by the material points that move with the polymer network. Also note that the deformation of gels actually means the deformation of the polymer network. The swelling of a gel can therefore be regarded as the deformation of the polymer network constituting the gel.

The mathematical framework describing the deformation of a polymer network is the same as that developed for rubber elasticity. Rubber is made of a polymer network and can be regarded as a special case of a gel in which there is no solvent (or the flow of solvent can be ignored). The continuum theory of rubber elasticity has been discussed in many literatures,<sup>15,16)</sup> and the following section is a brief summary.

### 2.2 Description of deformation

Let us consider the deformation of a soft elastic material (rubber or gel) that is isotropic and homogeneous when all external forces are removed. We shall use the force-free state as the reference to describe the deformation. We label each point on the material (or more precisely the points that move together with the polymer network) by its position  $X$  in the reference state. The deformation of the whole material is characterized by the function  $\tilde{x}(X)$  which denotes the position of the material point  $X$  after deformation.

Although the deformation of the material is described by some complex nonlinear function  $\tilde{x}(X)$ , the local deformation is always simple and can be represented by a linear transformation. The vector  $dX$  joining two nearby material points in the reference state is transformed to

$$dx = dX \cdot \frac{\partial}{\partial X} \tilde{x}(X), \quad (3)$$

or in terms of components,

$$dx_i = F_{ij} dX_j, \quad (4)$$

where  $i$  and  $j$  are the  $x, y, z$  components of the vector, and  $F_{ij}$  is defined by

$$F_{ij}(X) = \frac{\partial \tilde{x}_i}{\partial X_j}. \quad (5)$$

(In this article, we use the standard summation convention in which summation is taken over the repeated indices.) The quantity  $F_{ij}$  is called the deformation gradient. Locally, the material can be regarded as undergoing a linear transformation from  $X_i$  to  $F_{ij}X_j$ .

The linear transformation  $X_i \rightarrow F_{ij}X_j$  changes a sphere in the reference state to an ellipsoid in the deformed state. Let  $\lambda_1, \lambda_2$ , and  $\lambda_3$  be the lengths of the principal axes of the ellipsoid. It is easy to show that the  $\lambda_i^2$  are equal to the eigenvalues of the symmetric tensor  $C_{ij} = F_{ik}F_{jk}$  and are the solutions of the following equation:<sup>15)</sup>

$$\det(C_{ij} - \delta_{ij}\lambda^2) = 0. \quad (6)$$

Thus the  $\lambda_i$  are functions of  $F_{ij}$ . From this equation it is easy to show the following relations:<sup>15)</sup>

$$\lambda_i^2 = F_{ij}F_{ij} \quad (7)$$

$$\lambda_1\lambda_2\lambda_3 = \det(F_{ij}). \quad (8)$$

### 2.3 Stress tensor

The equilibrium state of the elastic material is completely determined by the free energy functional  $\mathcal{A}[\tilde{x}]$  which denotes the free energy of the material in the deformed state characterized by the function  $\tilde{x}(X)$ . The free energy  $\mathcal{A}$  is the sum of the local free energy which is entirely determined by the local deformation characterized by  $F_{ij}$ . Let  $\tilde{A}(F_{ij})$  be the free energy density of the material subject to the deformation  $F_{ij}$ , then the total free energy of the system can be written as

$$\mathcal{A} = \int dX \tilde{A}(F_{ij}(X)). \quad (9)$$

Here  $\tilde{A}(F_{ij})$  is the free energy density referring to the reference state, i.e., the free energy of deformation per unit volume in the *reference state*.

Note that in the case of gels,  $\tilde{A}(F_{ij})$  is the difference in the free energy of the two states shown in Fig. 3. Figure 3(a) is the reference state, where a gel of unit volume is immersed in a solvent. Figure 3(b) is the deformed state, where the point  $X$  is displaced to the point  $\tilde{x} = F \cdot X$ . If the volume of the gel in state (b) is larger than that in state (a), the gel absorbs some of the surrounding solvent. Therefore,  $\tilde{A}(F_{ij})$  includes not only the work needed to deform the polymer network but also the work needed to mix the polymer network with the solvent.

The equilibrium state is determined by the condition  $\delta\mathcal{A}/\delta\tilde{x}_i = 0$ , i.e., the variation of  $\mathcal{A}$  with respect to  $\delta\tilde{x}_i$  is equal to zero. Since

$$\delta\mathcal{A} = \int dX \frac{\partial \tilde{A}}{\partial F_{ij}} \frac{\partial \tilde{x}_i}{\partial X_j}$$

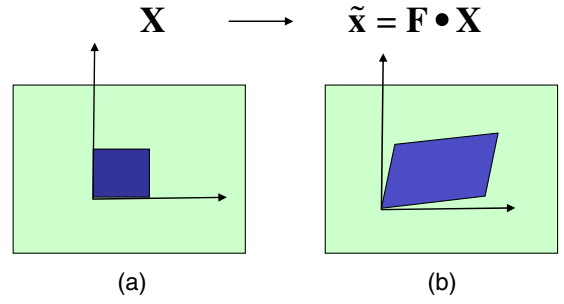


Fig. 3. (Color online) Definition of the free energy density for gels: (a) Reference state and (b) current state.

$$= - \int dX \frac{\partial}{\partial X_j} \left( \frac{\partial \tilde{A}}{\partial F_{ij}} \right) \delta\tilde{x}_i + \int dS N_j \frac{\partial \tilde{A}}{\partial F_{ij}} \delta\tilde{x}_i, \quad (10)$$

( $N_i$  being the unit vector normal to the boundary), the condition  $\delta\mathcal{A}/\delta\tilde{x}_i = 0$  requires that

$$\frac{\partial \tilde{\sigma}_{ij}}{\partial X_j} = 0, \quad (11)$$

where

$$\tilde{\sigma}_{ij} = \frac{\partial \tilde{A}(F_{ij})}{\partial F_{ij}}. \quad (12)$$

Equation (11) is the force balance equation written in the frame of the reference state:  $\tilde{\sigma}_{ij}$  is the stress in the reference frame. For a given external force applied on the surface, the solution of eqs. (11) and (12) under a suitable boundary condition determines the deformation of the material in mechanical equilibrium. The swelling equilibrium and volume transition of gels under an external force have been discussed in this manner.<sup>13)</sup>

The above formulation, which uses the coordinate  $X$  in the reference state, has a disadvantage that all physical quantities such as stress and volume fraction are for the point in the reference state, not the actual point in the current state. It is convenient to use the coordinate in the current state. This can be done as follows.

Let  $A(F_{ij})$  be the free energy density with reference to the *current state*, i.e., the free energy of deformation per unit volume in the current state. Since the volume change of the material is given by  $\det(F_{ij})$ ,  $A$  and  $\tilde{A}$  are related to each other by

$$A(F_{ij}) = \frac{\tilde{A}(F_{ij})}{\det(F_{ij})}. \quad (13)$$

The total free energy of the material is then written as

$$\mathcal{A} = \int dx A(F_{ij}(x)), \quad (14)$$

where the deformation gradient  $F_{ij}$  is expressed as a function of  $x$ , and the integral is evaluated over the volume of the material in the deformed state.

To obtain the equilibrium condition, let us consider a hypothetical small deformation that displaces the material point  $x$  to  $x + \delta u(x)$ . For this deformation, the deformation gradient changes by

$$\delta F_{ij} = \frac{\partial \delta u_i}{\partial X_j} = \frac{\partial \delta u_i}{\partial x_k} \frac{\partial \tilde{x}_k}{\partial X_j} = \frac{\partial \delta u_i}{\partial x_k} F_{kj}. \quad (15)$$

Also, let us assume that the gel is subject to some external force  $f_{\text{ext}}$  acting on the surface. The change of the free energy is then given by

$$\begin{aligned}\delta\mathcal{A} &= \int d\mathbf{x} \frac{\partial A}{\partial F_{ij}} \delta F_{ij} - \int dS f_{\text{ext},i} \delta u_i \\ &= \int d\mathbf{x} \frac{\partial A}{\partial F_{ij}} \frac{\partial \delta u_i}{\partial x_k} F_{kj} - \int dS f_{\text{ext},i} \delta u_i.\end{aligned}\quad (16)$$

By integration by parts, we have

$$\delta\mathcal{A} = - \int d\mathbf{x} \frac{\partial \sigma_{ij}}{\partial x_j} \delta u_i + \int dS (\sigma_{ij} n_j - f_{\text{ext},i}) \delta u_i, \quad (17)$$

where  $n_i$  is the unit vector normal to the surface of the gel and  $\sigma_{ij}$  is defined by

$$\sigma_{ij} = \frac{\partial A}{\partial F_{ik}} F_{jk}. \quad (18)$$

Therefore the condition for the system to be in equilibrium is

$$\frac{\partial \sigma_{ij}}{\partial x_j} = 0, \quad (19)$$

and at the boundary

$$\sigma_{ij} n_j = f_{\text{ext},i}. \quad (20)$$

Equations (19) and (20) indicate that  $\sigma_{ij}$  is the stress tensor in the gel. Equation (19) represents the force balance in the bulk and eq. (20) represents the force balance at the surface.

#### 2.4 Expression for the free energy density

Before proceeding further, we briefly discuss the explicit form of the free energy density  $A(F_{ij}; T)$ . (Here the temperature dependence of the free energy is written explicitly since we will discuss the swelling or shrinking induced by the temperature change.) Note that for isotropic materials, the free energy of deformation does not depend on which direction the material is stretched; it depends on the magnitude of the stretch. Therefore, the free energy density  $A$  depends on  $F_{ij}$  only through  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$ , and can be written as

$$A = A(\lambda_1, \lambda_2, \lambda_3; T). \quad (21)$$

The function  $A(\lambda_1, \lambda_2, \lambda_3; T)$  can, in principle, be determined by experiments. In practice, this is difficult, and has only been carried out for limited systems.<sup>17)</sup> Conventionally, the functional form of the free energy density has been determined on the basis of some molecular or phenomenological theories. Since this subject has been discussed extensively in textbooks of polymer physics,<sup>2,14,18)</sup> we shall discuss about it very briefly.

Let us take the dry state (the state without a solvent) as the reference state of the gel. Since the unit volume in the reference state occupies the volume  $\det(F_{ij})$  in the deformed state swollen with the solvent, the volume fraction of the polymer  $\phi$  is given by

$$\phi = \frac{1}{\det(F_{ij})} = \frac{1}{\lambda_1 \lambda_2 \lambda_3}. \quad (22)$$

The free energy density of a gel consists of two terms:

$$A(\lambda_1, \lambda_2, \lambda_3; T) = A_{\text{el}}(\lambda_1, \lambda_2, \lambda_3; T) + A_{\text{mix}}(\phi; T), \quad (23)$$

where  $A_{\text{el}}$  is the free energy associated with the elastic deformation of the polymer network and  $A_{\text{mix}}$  is the mixing free energy.

The elastic term  $A_{\text{el}}$  has been studied both theoretically and experimentally in polymer physics. The simple Gaussian chain network model gives<sup>2,18)</sup>

$$A_{\text{el}}(\lambda_1, \lambda_2, \lambda_3; T) = \frac{1}{2} C_1(\phi) \left( \sum_i \lambda_i^2 - 3 \right), \quad (24)$$

where  $C_1(\phi)$  is given by, according to molecular theory,

$$C_1(\phi) = \frac{k_B T \phi}{2w N_x}, \quad (25)$$

where  $N_x$  is the mean number of segments in the polymer chain connecting the neighboring junctions and  $w$  is the volume of a segment.

The mixing term  $A_{\text{mix}}$  is a function of the polymer volume fraction  $\phi$  only. A simple model for  $A_{\text{mix}}$  is to use the expression for the mixing energy for a polymer solution:<sup>2)</sup>

$$A_{\text{mix}}(\phi, T) = \frac{k_B T}{w} [(1 - \phi) \ln(1 - \phi) + \chi(T) \phi(1 - \phi)], \quad (26)$$

where  $\chi(T)$  is a temperature-dependent dimensionless parameter (called the chi parameter), which represents the dis-affinity between the polymer and solvent. If  $\chi$  is increased, solvent molecules are expelled from the gel and the gel shrinks, while if  $\chi$  is decreased, the gel swells.

#### 2.5 Swelling equilibrium in stress-free state

Given the expression for the free energy  $A$ , it is easy to calculate the equilibrium state for isotropic free swelling. In this case,  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$  are all equal to  $\phi^{-1/3}$  [see eq. (22)]. The free energy density is written as

$$A(\phi; T) = A_{\text{el}}(\lambda_1 = \lambda_2 = \lambda_3 = \phi^{-1/3}; T) + A_{\text{mix}}(\phi; T). \quad (27)$$

Since the total free energy of the system (per unit volume in the reference state) is  $A(\phi; T)/\phi$ , the equilibrium value  $\phi_{\text{eq}}$  is determined by  $\partial(A(\phi; T)/\phi)/\partial\phi = 0$  or

$$\phi \frac{\partial A}{\partial \phi} - A = 0. \quad (28)$$

For the free energy density given by eqs. (24) and (26), the equilibrium condition of eq. (28) is written as

$$\frac{\partial}{\partial \phi} \left[ \frac{(1 - \phi) \ln(1 - \phi)}{\phi} + \chi(T)(1 - \phi) + \frac{3}{2N_x} \phi^{2/3} \right] = 0 \quad \text{at } \phi = \phi_{\text{eq}}. \quad (29)$$

This equation determines the equilibrium swelling of a force-free gel. For  $\chi < 0$  and  $N_x \gg 1$ ,  $\phi_{\text{eq}}$  has been shown to be small; thus eq. (29) can be solved as

$$\phi_{\text{eq}} = \left[ \left( \frac{1}{2} - \chi \right) N_x \right]^{-3/5}. \quad (30)$$

The equilibrium volume fraction  $\phi_{\text{eq}}$  can be very small if  $N_x$  is large, i.e., if the gel is made of long weakly cross-linked polymers.

#### 2.6 Free energy for small deformation

In general, it is difficult to determine the explicit form of the free energy density  $A(\lambda_1, \lambda_2, \lambda_3; T)$  as a general nonlinear function of the deformation. For a small deformation,

however, it can be determined generally using the symmetry argument as it is done in the linear theory of elasticity.

Let  $u_i(\mathbf{x})$  be the displacement of the material point at  $\mathbf{x}$ . We assume that  $u_i(\mathbf{x})$  is small and consider only the lowest order term. For an isotropic material, the free energy density is written as<sup>19)</sup>

$$A = \frac{1}{2}K \left( \frac{\partial u_k}{\partial x_k} \right)^2 + \frac{1}{4}G \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial u_k}{\partial x_k} \right)^2, \quad (31)$$

where  $K$  and  $G$  are material constants called the osmotic modulus and the shear modulus respectively.  $G$  stands for the restoring force for a deformation that does not involve a volume change (such as a shear). On the other hand,  $K$  stands for the restoring force when the volume of the gel is changed. It should be noted that the osmotic modulus  $K$  is different from the bulk modulus, which we are assuming to be infinitely large:  $K$  is the restoring force for the swelling deformation (i.e., the gel volume increases by absorbing solvent).

Given the expression for free energy density, it is easy to show that  $K$  and  $G$  are given by

$$K = \phi^2 \frac{\partial^2}{\partial \phi^2} \left( \frac{A(\phi)}{\phi} \right) \quad \text{at } \phi = \phi_{\text{eq}}, \quad (32)$$

$$G = \frac{\partial^2}{\partial \epsilon^2} A(\lambda_1 = \lambda_{\text{eq}}(1 + \epsilon), \lambda_2 = \lambda_3 = \lambda_{\text{eq}}(1 - \epsilon/2)) \quad \text{at } \epsilon = 0, \quad (33)$$

where  $\lambda_{\text{eq}} = \phi_{\text{eq}}^{-1/3}$ . Note that the shear modulus  $G$  has a contribution from  $A_{\text{el}}$  only, while the osmotic modulus  $K$  has contributions from both  $A_{\text{mix}}$  and  $A_{\text{el}}$ .

Equation (31) must be modified if the temperature of the gel is changed. Consider that the temperature is changed from  $T_0$  to  $T$ . The volume of the gel changes by  $\alpha_{\text{eq}}(T) = [V_{\text{eq}}(T) - V_{\text{eq}}(T_0)]/V_{\text{eq}}(T_0)$ , where  $V_{\text{eq}}(T)$  is the equilibrium volume of the gel at temperature  $T$ . In this case, the free energy density is written as

$$A = A_0 + \frac{1}{2}K \left[ \frac{\partial u_k}{\partial x_k} - \alpha_{\text{eq}}(T) \right]^2 + \frac{1}{4}G \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial u_k}{\partial x_k} \right)^2, \quad (34)$$

and the stress tensor is

$$\sigma_{ij} = K \left( \frac{\partial u_k}{\partial x_k} \right) \delta_{ij} - K \alpha_{\text{eq}}(T) \delta_{ij} + G \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial u_k}{\partial x_k} \right). \quad (35)$$

The term  $-K \alpha_{\text{eq}}(T) \delta_{ij}$  corresponds to the thermal stress in the standard theory of elasticity. One might think that the swelling of a gel is a phenomenon similar to the thermal expansion of metals. Although this analogy is useful, there is an important difference between gels and metals.

In the case of metals, the equilibrium is attained as soon as the temperature is changed since the thermal expansion of metals is basically caused by the change of the inter atomic distance. On the other hand, in the case of gels, the volume change occurs as a result of the permeation of the solvent. (There is, of course, a change of the specific volume of the solvent due to thermal expansion, but this effect is very small and is ignored in this article.) Consequently, the

swelling equilibrium of gels is attained very slowly since the relaxation time is basically determined by the permeation speed of the solvent.

## 2.7 Constraint for solvent permeation

So far, the solvent in the gel has played no or a minor role. The solvent is important in calculating the free energy, but it does not appear explicitly in the governing equations: the equations governing the equilibrium shape, such as eqs. (19), (20), and (35), are the same as those in the theory of elasticity. We now show that the solvent in gels can affect the equilibrium shape.

Consider that a weight is placed on top of a gel as it is shown in Fig. 4(a). The equilibrium shape of the gel can be calculated, in the case of a small deformation, by solving eqs. (19) and (35) under the boundary condition given by eq. (20). These equations are precisely the same as those in the theory of elasticity.

Now let us consider the hypothetical situation shown in Fig. 4(b), where the whole gel is surrounded by a flexible thin film that can deform freely but blocks the permeation of the solvent. In such a situation, the volume of the gel cannot change. In this case, the equilibrium shape is determined by minimizing the free energy under the constraint that the total volume is unchanged. Therefore, in the variational calculation, we need to take into account of the constraint that the volume change  $\delta V$  caused by the deformation  $\delta u_i$  is equal to zero:

$$\delta V = \int d\mathbf{x} \frac{\partial \delta u_i}{\partial x_i} = 0. \quad (36)$$

Therefore the variational calculation as illustrated in eq. (16) now reads

$$\delta \mathcal{A} = \int d\mathbf{x} \frac{\partial A}{\partial F_{ij}} \delta F_{ij} - \int dS f_{\text{ext},i} \delta u_i - p \int d\mathbf{x} \frac{\partial \delta u_i}{\partial x_i} = 0, \quad (37)$$

where  $p$  is a Lagrangian multiplier for the constraint given by eq. (36).

Equation (37) gives the following equations for the bulk and the boundary:

$$\frac{\partial}{\partial x_j} (\sigma_{ij} - p \delta_{ij}) = 0 \quad \text{in the bulk}, \quad (38)$$

$$(\sigma_{ij} - p \delta_{ij}) n_j = f_{\text{ext},i} \quad \text{at the boundary}. \quad (39)$$

The Lagrangian multiplier  $p$  is determined by the condition that the total volume of the gel is  $V$ . Equation (39) indicates that the stress tensor is now given by  $\sigma_{ij} - p \delta_{ij}$ , and that  $p$  represents the pressure created by the constraint that the total volume of the gel cannot change.

The situation shown in Fig. 4(b) is rather artificial, but it suggests an important consequence of the constraint of the volume change. As we have discussed, the permeation of the solvent takes place very slowly. If the permeation of the solvent cannot take place, the gel must deform keeping its local volume unchanged; thus the variation must be calculated under the constraint

$$\frac{\partial \delta u_i}{\partial x_i} = 0, \quad (40)$$

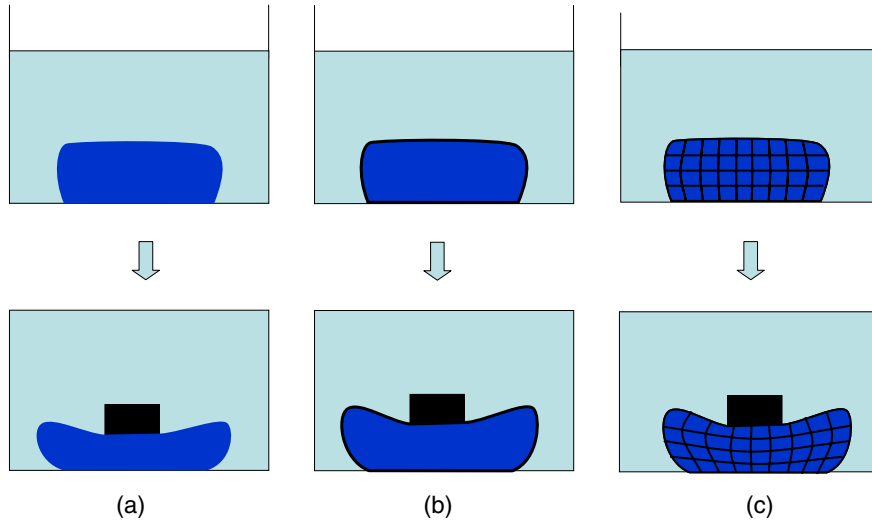


Fig. 4. (Color online) (a) When a weight is placed on a gel in a solvent, the gel is deformed and eventually reaches an equilibrium configuration. (b) The gel is now wrapped by a flexible membrane, which prevents the solvent from permeating through it. The equilibrium configuration of such a gel is different from that of the unwrapped gel since the volume of the gel is conserved. (c) Schematic picture of the gel in which the permeation of the solvent is blocked.

which must be satisfied at all points. This gives the following condition for the variational calculation:

$$\delta\mathcal{A} = \int d\mathbf{x} \frac{\partial\mathcal{A}}{\partial F_{ij}} \delta F_{ij} - \int dS f_{\text{ext},i} \delta u_i - \int d\mathbf{x} p(x) \frac{\partial\delta u_i}{\partial x_i} = 0. \quad (41)$$

The equilibrium condition is

$$\frac{\partial}{\partial x_j} (\sigma_{ij} - p\delta_{ij}) = 0, \quad \text{in the bulk,} \quad (42)$$

$$(\sigma_{ij} - p\delta_{ij})n_j = f_{\text{ext},i} \quad \text{at the boundary.} \quad (43)$$

Note the difference between eqs. (38) and (42). In eq. (38),  $p$  is a constant independent of position, while in eq. (42)  $p$  is a function of  $\mathbf{x}$ . This situation is schematically illustrated in Fig. 4(c). Suppose that the gel is divided into compartments by a hypothetical flexible membrane which prevents the solvent from permeating. The pressure  $p$  in eq. (42) can be regarded as the pressure in each compartment.

The effect of solvent permeation can be seen more quantitatively by the following example (see Fig. 5). Suppose that a rod-like specimen of a gel of length  $L$  and radius  $a$  immersed in a solvent is stretched at time  $t = 0$  from  $L$  to  $L + \Delta L$ . Such an experiment was first performed by Takigawa *et al.*,<sup>20</sup> and they observed the following phenomena.

When the gel is stretched, it is deformed keeping its volume constant since there is no time for the surrounding solvent to permeate into the gel. Therefore, the initial change of the gel radius  $\Delta a_0$  is given by the condition  $(L + \Delta L)(a + \Delta a_0)^2 = La^2$ , i.e.,

$$\frac{\Delta a_0}{a} = -\frac{1}{2} \frac{\Delta L}{L}. \quad (44)$$

As time goes on, the solvent permeates through the gel, and the equilibrium radius is given by the Poisson ratio  $\nu$  which can be expressed by  $K$  and  $G$ :

$$\frac{\Delta a_\infty}{a} = -\nu \frac{\Delta L}{L}, \quad (45)$$

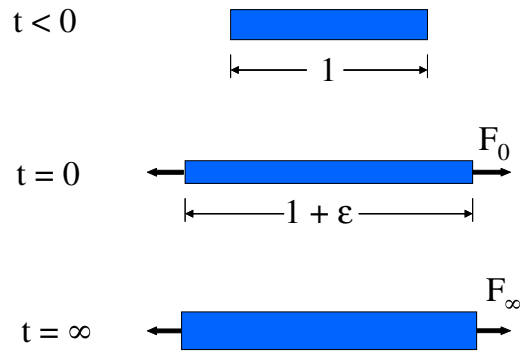


Fig. 5. (Color online) Experiment on stretching a gel in solvent. A gel in swollen equilibrium is stretched at time  $t = 0$  and kept at a constant length. The force needed to maintain the gel at the length changes with time because the stretching induces the permeation of the solvent.

where  $\nu$  is given by, according to the theory of elasticity,

$$\nu = \frac{K - (2/3)G}{2[K + (1/3)G]}. \quad (46)$$

Thus the diameter of the gel increases by a factor of  $-\nu + (1/2) = (G/2)/[K + (1/3)G]$ .

As the diameter of the gel changes with time, the restoring force  $F$  also changes. Since the gel behaves as an incompressible material, the initial restoring force is given by

$$F_0 = 3G \frac{\Delta L}{L} S \quad (47)$$

( $S = \pi a^2$  is the area of the cross section). On the other hand, the equilibrium restoring force is given by

$$F_\infty = \frac{3G}{1 + (G/3K)} \frac{\Delta L}{L} S. \quad (48)$$

Thus the stress decreases by a factor of  $(1 + G/3K)^{-1}$  as time goes on. Such behavior has indeed been observed.<sup>20</sup>

### 3. Basic Equations for Gel Dynamics

#### 3.1 Slow dynamics in gels

Having discussed the equilibrium state of gels, we now consider the dynamics and discuss how to model the phenomena illustrated in Fig. 2.

Our objective here is to determine the velocity field of the polymer network  $\mathbf{v}_p(\mathbf{x}, t)$  and that of the solvent fluid  $\mathbf{v}_s(\mathbf{x}, t)$ . The velocity field  $\mathbf{v}_p(\mathbf{x}, t)$  is equal to the time derivative of the displacement field  $\tilde{\mathbf{x}}(\mathbf{X}, t)$ , i.e.,

$$\mathbf{v}_p(\mathbf{x}, t) = \frac{\partial}{\partial t} \tilde{\mathbf{x}}(\mathbf{X}, t) \quad \text{at } \mathbf{x} = \tilde{\mathbf{x}}(\mathbf{X}, t). \quad (49)$$

For simplicity, we assume that the temperature is constant throughout the system. Such an assumption is allowed since the thermal diffusivity is  $10^3$  to  $10^4$  times larger than the diffusion constant of the solvent.

In the following, we derive the equations for  $\mathbf{v}_p$  and  $\mathbf{v}_s$  by two ways. One is based on a simple physical argument, and the other is based on Lagrangian mechanics.<sup>11)</sup> The second derivation is rather formal, but it is convenient for deriving equations for more general cases such as multicomponent fluids.<sup>21)</sup>

#### 3.2 Derivation of gel dynamics equation 1

As we have discussed, the permeation of the solvent is a slow process. Let us consider the limit at which the solvent permeation is infinitesimally slow. At this limit, the local volume of the gel element cannot change with time. This is equivalent to the situation shown in Fig. 4(c), where the permeation of the solvent is prohibited by the hypothetical membrane. In such a case, the stress tensor is given by  $\sigma_{ij} - p\delta_{ij}$  and the mechanical equilibrium equation is given by

$$\nabla \cdot (\boldsymbol{\sigma} - p\mathbf{I}) = 0. \quad (50)$$

Now let us consider the effect of solvent permeation. Suppose that the hypothetical membrane is removed. Then the solvent will permeate from the high-pressure region to the low-pressure region. The permeation speed is represented by the velocity of the solvent relative to that of polymer network,  $\mathbf{v}_s - \mathbf{v}_p$ , and we can assume that this speed is proportional to the gradient of the pressure:

$$\mathbf{v}_s - \mathbf{v}_p = -\kappa_0 \nabla p. \quad (51)$$

Equation (51) is the empirical relation known as Darcy's law for porous materials. In general,  $\kappa_0$  is a tensor and can be a function of the deformation gradient of the polymer network. However, to simplify the analysis, we assume that  $\kappa_0$  is a scalar and depends on  $\phi$  only.

The mass conservation law is expressed by

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot (\phi \mathbf{v}_p), \quad (52)$$

and the incompressible condition is written as

$$\nabla \cdot [\phi \mathbf{v}_p + (1 - \phi) \mathbf{v}_s] = 0. \quad (53)$$

Equations (50)–(53) are the basic set of equations in gel dynamics.<sup>22)</sup> Given the free energy functional  $A(F_{ij}, T)$  and the Darcy constant  $\kappa_0(\phi)$ , one can calculate, in principle, the time evolution of the gel by solving this set of equations. At this point, it may not be clear how the above set of equations

are sufficient to solve the problem. The mathematical structure of the basic equations of gel dynamics is slightly peculiar, but we will show that the above equations are the complete set of equations in later sections.

To solve the partial differential equation, we need boundary conditions. There are two sets of boundary conditions; for the mechanical condition and for the permeation condition of the solvent.<sup>22,23)</sup>

- (1) Mechanical condition: This is essentially the same as the boundary condition for the theory of elasticity. Let  $\mathbf{f}_{\text{ext}}$  be the force acting at the outer surface of the gel per unit area. Then the force balance at the boundary gives the following equation:

$$(\boldsymbol{\sigma} - p\mathbf{I}) \cdot \mathbf{n} = \mathbf{f}_{\text{ext}}. \quad (54)$$

If the boundary is constrained geometrically, other conditions are imposed. For example, if the polymer network is glued to a wall,  $\mathbf{v}_p$  must be equal to the velocity of the wall.

- (2) Permeation condition: If the solvent can permeate freely through the boundary, the pressure  $p$  in the gel must be equal to the solvent pressure  $p_{\text{out}}$  outside of the gel at the boundary. On the other hand, if the solvent cannot permeate through the boundary, the pressure gradient normal to the boundary must be zero. These conditions are expressed by the following equations:

$$p = p_{\text{out}}, \quad \text{permeable boundary}, \quad (55)$$

$$\mathbf{n} \cdot \nabla p = 0, \quad \text{no permeable boundary}, \quad (56)$$

where  $p_{\text{out}}$  is the pressure in the outer solvent.

#### 3.3 Derivation of gel dynamics equation 2

We now give another derivation for the above set of equations.<sup>11)</sup> This derivation is based on the Lagrangian mechanics for dissipative systems. The derivation is more formal, and maybe less transparent, but it is more powerful for solving problems.

Consider a dynamical system with  $f$  degrees of freedom, described by the coordinates  $q_1, q_2, \dots, q_f$ . Let  $K(q_i, \dot{q}_i)$  be the kinetic energy of the system and  $U(q_i)$  be the potential energy. The equation of motion of the system is given by the following Euler equation:

$$\frac{d}{dt} \left( \frac{\partial K}{\partial \dot{q}_i} \right) = \frac{\partial K}{\partial q_i} - \frac{\partial U}{\partial q_i}. \quad (57)$$

Equation (57) does not involve any dissipative force. Rayleigh showed that if there is a dissipative force  $f_i$  that is proportional to the velocity  $\dot{q}_i$ , i.e.,

$$f_i = -\zeta_{ij} \dot{q}_j, \quad (58)$$

the equation of motion can be written as<sup>24,25)</sup>

$$\frac{d}{dt} \left( \frac{\partial K}{\partial \dot{q}_i} \right) = \frac{\partial K}{\partial q_i} - \frac{\partial U}{\partial q_i} - \frac{\partial W}{\partial \dot{q}_i}, \quad (59)$$

where  $W(q_i, \dot{q}_i)$  is given by

$$W = \frac{1}{2} \zeta_{ij} \dot{q}_i \dot{q}_j, \quad (60)$$

and is called Rayleigh's dissipation function. The dissipation function is equal to half of the energy dissipated in the system per unit time.

If the inertia effect is negligibly small, one may set the kinetic energy term  $K$  in eq. (59) equal to zero. This gives

$$\frac{\partial U}{\partial q_i} + \frac{\partial W}{\partial \dot{q}_i} = 0. \quad (61)$$

It is convenient to write eq. (61) in the following form:

$$\frac{\partial}{\partial \dot{q}_i} (\dot{U} + W) = 0, \quad (62)$$

where  $\dot{U}$  is defined by

$$\dot{U} = \sum_i \frac{\partial U}{\partial q_i} \dot{q}_i, \quad (63)$$

which represents the change of the potential energy. Equation (62) can be written in a variational form.<sup>26,27</sup> Let  $\mathcal{R}$  be defined by

$$\mathcal{R} = \dot{U} + W, \quad (64)$$

then the variational principle states that the actual velocity is determined by  $\delta \mathcal{R} / \delta \dot{q}_i = 0$ . This variational principle is a simple rewriting of the force balance equation  $-\partial U / \partial q_i + f_i = 0$ . However the variational form gives us a convenient tool for deriving the equation of motion, particularly for systems with constraints.

Now let us use this principle to derive the kinetic equation for gels.<sup>11</sup> The time evolution of a gel is entirely characterized by the two velocity fields  $\mathbf{v}_p(\mathbf{x})$  and  $\mathbf{v}_s(\mathbf{x})$ . The energy dissipation in the system is mostly caused by the relative motion between the polymer and solvent. [In a fluid–fluid mixture, the energy dissipation has two origins; one arises from the relative motion and the other arises from the viscosity of the fluid. In the fluid–solid mixture, the latter mechanism is negligibly small, and the energy dissipation function is given by eq. (65).] Thus,  $W$  can be written as

$$W = \frac{1}{2} \int d\mathbf{x} \zeta(\phi) (\mathbf{v}_p - \mathbf{v}_s)^2, \quad (65)$$

where  $\zeta(\phi)$  is the friction constant per unit volume of the gel.

The free energy of the system is given by eq. (14); thus, its time derivative is calculated as

$$\delta \dot{\mathcal{A}} = \int d\mathbf{x} \frac{\partial A}{\partial F_{ij}} \dot{F}_{ij}. \quad (66)$$

Using the relation,  $\dot{F}_{ij} = (\partial v_{pi} / \partial x_k) F_{kj}$  [see eqs. (15) and (18)], we have

$$\delta \dot{\mathcal{A}} = \int d\mathbf{x} \sigma_{ij} \frac{\partial v_{pi}}{\partial x_j}. \quad (67)$$

In performing the variational calculation for  $\delta \mathcal{R}$ , we need to take into account the constraint that  $\mathbf{v}_p$  and  $\mathbf{v}_s$  must satisfy the incompressible condition given by eq. (53). Thus, the functional  $\mathcal{R}$  to be minimized is

$$\mathcal{R} = \int d\mathbf{x} \left\{ \frac{1}{2} \zeta(\phi) (\mathbf{v}_p - \mathbf{v}_s)^2 + \boldsymbol{\sigma} : \nabla \mathbf{v}_p - p \nabla \cdot [\phi \mathbf{v}_p + (1 - \phi) \mathbf{v}_s] \right\}. \quad (68)$$

The equations  $\delta \mathcal{R} / \delta \mathbf{v}_p = 0$  and  $\delta \mathcal{R} / \delta \mathbf{v}_s = 0$  give

$$\zeta(\phi) (\mathbf{v}_p - \mathbf{v}_s) = \nabla \cdot \boldsymbol{\sigma} - \phi \nabla p, \quad (69)$$

$$\zeta(\phi) (\mathbf{v}_s - \mathbf{v}_p) = -(1 - \phi) \nabla p. \quad (70)$$

Adding eqs. (69) and (70), we obtain eq. (50). Equation (70) gives the Darcy law [eq. (51)], where

$$\kappa_0(\phi) = \frac{1 - \phi}{\zeta(\phi)}. \quad (71)$$

Thus, the set of equations in the previous subsection have been derived from the variational principle.

### 3.4 Gel dynamics for small deformation

The above set of equations can be written explicitly in the case that the deformation of the polymer network is small. Let  $\mathbf{u}(\mathbf{x}, t)$  be the displacement of the polymer network at point  $\mathbf{x}$ . The network velocity  $\mathbf{v}_p(\mathbf{x}, t)$  is equal to  $\dot{\mathbf{u}}(\mathbf{x}, t) (= \partial \mathbf{u} / \partial t)$ . The expression for the stress tensor is given by eq. (35), and therefore the force balance equation [eq. (50)] can be written as

$$\left( K + \frac{G}{3} \right) \nabla \nabla \cdot \mathbf{u} + G \nabla^2 \mathbf{u} = \nabla p. \quad (72)$$

For a small deformation,  $\phi$  and  $\kappa$  can be regarded as constant. Therefore, the incompressible condition in eq. (53) can be written as

$$\phi \nabla \cdot \dot{\mathbf{u}} + (1 - \phi) \nabla \cdot \mathbf{v}_s = 0. \quad (73)$$

Equation (73) and the Darcy law [eq. (51)] give

$$\nabla \cdot \dot{\mathbf{u}} = \kappa \nabla^2 p, \quad (74)$$

where

$$\kappa = (1 - \phi) \kappa_0 = \frac{(1 - \phi)^2}{\zeta(\phi)}. \quad (75)$$

Equations (72) and (74) are the linearized form of the gel dynamics.

Note that in the above set of equations, the time derivative  $\dot{\mathbf{u}}$  is not given explicitly, rather it appears in a spatial differential equation. It is possible to derive a more familiar equation. For example, if one defines the volume change  $\alpha(\mathbf{x}, t)$  by

$$\alpha = \nabla \cdot \mathbf{u}, \quad (76)$$

one can easily prove from eqs. (72) and (74) that  $\alpha$  satisfies the following diffusion equation:

$$\frac{\partial \alpha}{\partial t} = D \nabla^2 \alpha, \quad (77)$$

where  $D$  is defined by

$$D = \left( K + \frac{4}{3} G \right) \kappa. \quad (78)$$

Although eq. (77) is simple, it is not useful for solving problems. This is because the boundary conditions for  $\alpha$  are not given in usual problems, and we must go use eqs. (72) and (74) as we shall see in later examples.

From eq. (77), one might think that the swelling process of a gel is the simple diffusion process of a solvent through a gel network. This is not correct. Although the diffusion of the solvent is a key factor in swelling kinetics, it is not the only factor. In the following we shall show examples which demonstrate that such an understanding is too naive and can lead to the wrong conclusion.



### 3.5 Tanaka–Filmore equation

In the special case that the average velocity  $\phi \mathbf{v}_p + (1 - \phi) \mathbf{v}_s$  is equal to zero, the above set of equations can be simplified. In this case,  $\mathbf{v}_s = -\phi/(1 - \phi) \mathbf{v}_p$ , and eqs. (70) (72) give

$$\frac{\zeta}{(1 - \phi)^2} \mathbf{v}_p = \left( K + \frac{G}{3} \right) \nabla \nabla \cdot \mathbf{u} + G \nabla^2 \mathbf{u}, \quad (79)$$

or

$$\frac{\partial \mathbf{u}}{\partial t} = D [\nabla \nabla \cdot \mathbf{u} + \mu \nabla^2 \mathbf{u}], \quad (80)$$

where  $D$  is given by eq. (78) and

$$\mu = \frac{G}{K + (4/3)G}. \quad (81)$$

Equation (80) is called the Tanaka–Filmore (TF) equation. The TF equation<sup>4)</sup> was proposed to describe the swelling of spherical gels. In the case of the isotropic swelling of spherical gels, the average velocity is zero and the TF equation is valid. However, in the general case, such as the swelling of cylindrical or sheetlike gels, the average velocity is nonzero, and the TF equation is not valid. The TF equation cannot describe the phenomena of squeezing and filtration.

## 4. Examples of Analysis

In this section, we solve the linear kinetic equations given in the previous section for some typical situations, and discuss the characteristic features of gel dynamics.

### 4.1 Gel dynamics in one dimension

We first consider a simple one-dimensional problem. This is realized in a thin gel glued to a rigid wall as shown in Fig. 6. In Fig. 6, the dark block indicates an impermeable wall, while the patterned block indicates a permeable wall made of a porous material. In this article, we assume that the solvent permeates through the porous wall freely (i.e., the pressure drop across the porous wall is zero).

If the gel is thin, the displacement vector  $\mathbf{u}$  has a component normal to the wall only. We take the  $x$  coordinate

normal to the wall, the origin of which is taken to be at the wall boundary. Then

$$u_x = u(x, t), \quad u_y = u_z = 0. \quad (82)$$

The  $xx$ -component of the stress tensor in eq. (35) is given by

$$\sigma_{xx} = \left( K + \frac{4}{3}G \right) \frac{\partial u}{\partial x} - K\alpha_{\text{eq}}. \quad (83)$$

Therefore the basic equations (72) and (74) become

$$\left( K + \frac{4}{3}G \right) \frac{\partial^2 u}{\partial x^2} = \frac{\partial p}{\partial x}, \quad (84)$$

$$\frac{\partial^2 u}{\partial x \partial t} = \kappa \frac{\partial^2 p}{\partial x^2}. \quad (85)$$

The boundary condition depends on the situation and will be discussed in the following sections.

#### 4.1.1 Swelling of a constrained gel sheet

Consider the case that a gel in swelling equilibrium is glued to an impermeable wall as shown in Fig. 6(a). Assume that the temperature is changed at time  $t = 0$  and the gel starts to swell for  $t > 0$ . We consider the kinetic process of swelling.

Since the left wall is fixed and impermeable for the solvent, the boundary condition at  $x = 0$  is

$$u(x, t) = 0, \quad (86)$$

$$\frac{\partial p}{\partial x} = 0. \quad (87)$$

On the other hand, the right end of the gel is free. Let  $p_{\text{out}}$  be the pressure of the solvent outside the gel. Then eqs. (54) and (55) give the following boundary conditions at  $x = h$ .

$$\sigma_{xx} - p = -p_{\text{out}}, \quad (88)$$

$$p = p_{\text{out}}. \quad (89)$$

From eq. (84) and the boundary condition (88),  $p$  is obtained as

$$p = p_{\text{out}} + \sigma_{xx} = p_{\text{out}} + \left( K + \frac{4}{3}G \right) \frac{\partial u}{\partial x} - K\alpha_{\text{eq}}. \quad (90)$$

Eliminating  $\partial u / \partial x$  from eqs. (85) and (90), we find that  $p$  satisfies the following diffusion equation

$$\frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial x^2}, \quad (91)$$

where  $D$  is given by eq. (78). Equation (91) can be solved for  $p(x, t)$ : the boundary condition is given by eqs. (87) and (89), and the initial condition is  $p(x, 0) = p_{\text{out}} - K\alpha_{\text{eq}}$ . [This follows from the initial condition  $\partial u / \partial x = 0$  and eq. (90).] The solution is given by

$$p(x, t) = p_{\text{out}} - K\alpha_{\text{eq}} \sum_{n=0}^{\infty} \frac{4}{(2n+1)\pi} \sin \left[ \frac{(2n+1)\pi x}{h} \right] \times \exp \left[ -\frac{(2n+1)^2 t}{\tau} \right], \quad (92)$$

where

$$\tau = \frac{h^2}{D\pi^2}. \quad (93)$$

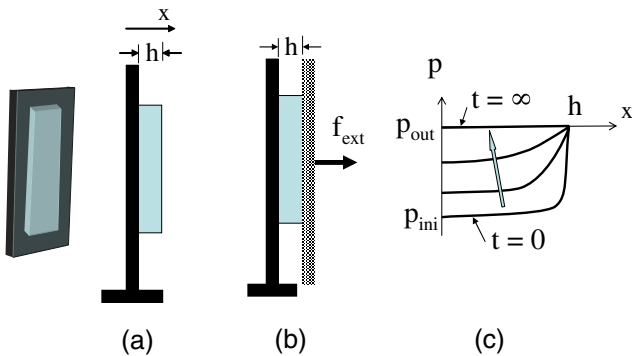


Fig. 6. (Color online) (a) Swelling of a constrained gel: a thin gel sheet of thickness  $h$  is glued to a rigid wall and is allowed to swell. (b) Negative squeezing: the other side of the same gel is glued to a porous wall which is pulled by external force  $f_{\text{ext}}$  (c) Time evolution of the pressure distribution. In case (a),  $p_{\text{ini}} = p_{\text{out}} - K\alpha_{\text{eq}}$  and in case (b),  $p_{\text{ini}} = p_{\text{out}} - f_{\text{ext}}$ .

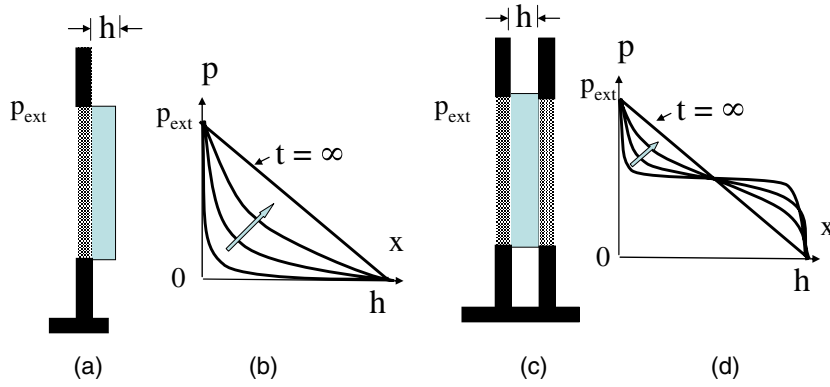


Fig. 7. (Color online) (a) The left side of the gel sheet is glued to a porous wall, and the solvent is pumped into the gel by the pressure difference between the left and right compartments. (b) Time evolution of the pressure distribution. (c) The same situation as in (a) except that the right side is also glued to a porous wall whose position is fixed. (d) Time evolution of the pressure distribution.

Figure 6(c) shows a schematic diagram of the time evolution of  $p(x, t)$ . When the temperature is changed, the pressure inside the gel drops suddenly from  $p_{out}$  to  $p_{out} - K\alpha_{eq}$ , and a large pressure gradient is created near the free surface of the gel. This causes the solvent to diffuse into the gel and the gel to swell. Equilibrium is attained when the pressure becomes equal to  $p_{out}$  everywhere in the gel. Note that in the present problem the pressure  $p_{out}$  appears only as the reference of the pressure and does not affect the swelling behavior; the swelling behavior is unaffected even if the solvent pressure is changed during the swelling process.

The variation of the gel thickness  $\Delta h(t)$  is given by  $u(h, t)$ , which is calculated from  $p(x, t)$  by integrating eq. (90):

$$\begin{aligned} \Delta h(t) &= u(h, t) = \int_0^h dx \frac{\partial u}{\partial x} \\ &= \frac{1}{K + (4/3)G} \int_0^h dx [p(x, t) - p_{out} + K\alpha_{eq}]. \end{aligned} \quad (94)$$

This gives the equilibrium thickness

$$\Delta h(\infty) = \frac{K}{K + (4/3)G} h\alpha_{eq}. \quad (95)$$

Note that the equilibrium swelling ratio  $\Delta h(\infty)/h$  is not equal to  $\alpha_{eq}$  in this case. This is because the gel is constrained in the  $x$ - and  $y$ -directions.

#### 4.1.2 Squeezing of a gel sheet

Next, let us consider the case shown in Fig. 6(b), where the right side of the gel is glued to a permeable wall upon which an external force  $f_{ext}$  (per unit area) starts to be applied at time  $t = 0$ . The boundary conditions at  $x = h$  now become

$$\sigma_{xx} - p = f_{ext}, \quad \text{and} \quad p = 0, \quad \text{at} \quad x = h, \quad (96)$$

where we have set  $p_{out}$  equal to zero. This problem can be solved by the same method as that described in the previous example. The analysis indicates that  $p$  satisfies the same diffusion equation, and the initial condition is  $p(x, 0) = -f_{ext}$ . Thus the behavior is precisely the same as that of the swelling: the only difference is that  $K\alpha_{eq}$  is now replaced by  $f_{ext}$ . At equilibrium, the volume of the gel changes by a factor of

$$\frac{\Delta h(\infty)}{h} = \frac{f_{ext}}{K + (4/3)G}. \quad (97)$$

#### 4.1.3 Filtration through a gel sheet

We now consider the situation shown in Fig. 7(a). The left side of the gel is glued to a porous wall. At time  $t = 0$ , the pressure in the left compartment is increased to  $p_{ext}$  while the pressure in the right compartment is kept at zero; the pressure  $p_{out}$  is taken to be zero. Then the solvent will permeate from left to right. If the right side of the gel is set free as in the case shown in Fig. 7(a), the process causes the swelling of the gel. An experimental and theoretical study of this situation was performed by Takigawa *et al.*<sup>28)</sup>

The boundary conditions at  $x = 0$  are

$$u = 0 \quad \text{and} \quad p = p_{ext} \quad \text{at} \quad x = 0. \quad (98)$$

On the other hand, the boundary conditions at  $x = h$  are

$$\sigma_{xx} - p = 0 \quad \text{and} \quad p = 0 \quad \text{at} \quad x = h, \quad (99)$$

where  $\sigma_{xx}$  is now given by eq. (83) with  $\alpha_{eq} = 0$ . Equations (84) and (99) are solved for  $p$ :

$$p = \left( K + \frac{4}{3}G \right) \frac{\partial u}{\partial x}. \quad (100)$$

Hence  $p$  satisfies the same diffusion equation as before. The boundary conditions are now  $p(0, t) = p_{ext}$  and  $p(h, t) = 0$ , and the initial condition is  $p(x, 0) = 0$ .

The solution of the equation is shown in Fig. 7(b). In this case, the final state is not an equilibrium state, but a steady state in which the solvent flows with constant speed. In the steady state, the pressure drops linearly with  $x$  across the gel:

$$p(x, \infty) = p_{ext} \left( 1 - \frac{x}{h} \right), \quad (101)$$

and the velocity of the solvent is  $v_s = \kappa p_{ext}/h$ . The flow exerts a constant force on the polymer network, and the gel swells accordingly.

$$\frac{\partial u}{\partial x} = \frac{p_{ext}}{K + (4/3)G} \left( 1 - \frac{x}{h} \right) \quad \text{for} \quad t \rightarrow \infty \quad (102)$$

The volume change of the gel is given by

$$\frac{\Delta h}{h} = \frac{1}{h} \int_0^h dx \frac{\partial u}{\partial x} = \frac{p_{ext}}{2[K + (4/3)G]}. \quad (103)$$

This can be compared with the volume change in the squeezing case [eq. (97)]. There is a difference of factor 1/2, which originates from the fact that in the case of squeezing, the external force acts at the surface only, while in the case of filtration, the pressure drop acts as a force on the body of the polymer network.

If the right side of the gel is constrained by a porous wall fixed in space as shown in Fig. 7(c), the pressure distribution changes as shown in Fig. 7(d). This situation has been studied experimentally by Tokita *et al.*,<sup>29</sup> but a theoretical analysis has not been carried out. The pressure and solvent velocity approach the same values as those for (a) in the steady state, but their transient behaviors are different. In particular, the relaxation time in situation (c) is one-quarter of that in (a).

#### 4.1.4 Swelling of a spherical gel

The swelling of a spherical gel is a classical problem studied by Tanaka and Filmore.<sup>4</sup> Since the average velocity is zero, the swelling can be analyzed by the TF equation [eq. (80)], but here we derive it using the variational principle.

Let  $u(r, t)$  be the displacement of an element at point  $r$ . In the swelling of a sphere, the polymer network is locally deformed uniaxially; the strain  $\epsilon_{\parallel}$  in the radial direction and the strain  $\epsilon_{\perp}$  normal to it are given by

$$\epsilon_{\parallel} = \frac{\partial u}{\partial r}, \quad \epsilon_{\perp} = \frac{u}{r}. \quad (104)$$

Substituting these into eq. (34), we have

$$\begin{aligned} \mathcal{A} = \int_0^a dr 4\pi r^2 \left[ \frac{1}{2} K \left( \frac{\partial u}{\partial r} + 2 \frac{u}{r} - \alpha_{\text{eq}} \right)^2 \right. \\ \left. + \frac{2}{3} G \left( \frac{\partial u}{\partial r} - \frac{u}{r} \right)^2 \right], \end{aligned} \quad (105)$$

where  $a$  is the radius of the gel. Equation (105) gives

$$\begin{aligned} \dot{\mathcal{A}} = \int_0^a dr 4\pi r^2 \left[ K \left( \frac{\partial u}{\partial r} + 2 \frac{u}{r} - \alpha_{\text{eq}} \right) \left( \frac{\partial \dot{u}}{\partial r} + 2 \frac{\dot{u}}{r} \right) \right. \\ \left. + \frac{4}{3} G \left( \frac{\partial u}{\partial r} - \frac{u}{r} \right) \left( \frac{\partial \dot{u}}{\partial r} - \frac{\dot{u}}{r} \right) \right]. \end{aligned} \quad (106)$$

On the other hand, the energy dissipation function can be written as

$$\mathcal{W} = \frac{1}{2} \int_0^a dr 4\pi r^2 \zeta (\dot{u} - v_s)^2 = \frac{1}{2} \int_0^a dr 4\pi r^2 \frac{1}{\kappa} \dot{u}^2, \quad (107)$$

where we have used  $v_s = -\phi/(1-\phi)\dot{u}$ . The variational condition  $\delta(\mathcal{W} + \dot{\mathcal{A}})/\delta\dot{u} = 0$  gives the following time evolution equation for  $u$ :

$$\frac{\partial u}{\partial t} = D \left( \frac{\partial^2 u}{\partial r^2} + \frac{2}{r} \frac{\partial u}{\partial r} - \frac{2}{r^2} u \right), \quad (108)$$

where  $D$  is given by eq. (78). Equation (108) can be derived directly from the TF equation [eq. (80)].

The boundary condition can also be obtained from the variational principle:

$$K \left( \frac{\partial u}{\partial r} + 2 \frac{u}{r} - \alpha_{\text{eq}} \right) + \frac{4}{3} G \left( \frac{\partial u}{\partial r} - \frac{u}{r} \right) = 0 \quad \text{at } r = a. \quad (109)$$

Tanaka and Filmore solved the above boundary value problem for the case of  $K \gg G$  and showed that the longest relaxation time  $\tau$  is given by

$$\tau = \frac{a^2}{\pi^2 \kappa K} \quad \text{for } K \gg G. \quad (110)$$

Studies of the general case were carried out,<sup>30,31</sup> and it has been shown that at the other limit  $K \ll G$  the longest relaxation time diverges as

$$\tau = \frac{a^2}{15\kappa K} \quad \text{for } K \ll G. \quad (111)$$

The longest relaxation time is proportional to  $1/K$  at both limits of  $K/G \rightarrow \infty$  and 0. This behavior is observed for all gels as we shall see later.

#### 4.2 Coupling effect of elastic deformation and swelling

The problems discussed so far are one-dimensional in the sense that the displacement of the polymer network takes place only in a certain fixed direction (normal to the wall or in the radial direction). We now discuss cases where it is essential to take into account the displacement in two or three dimensions. The examples shown here again demonstrate the characteristic features of gel dynamics different from simple diffusion.

##### 4.2.1 Swelling of a free gel sheet

The swelling of a free gel sheet is a simple example that requires analysis in two dimensions. The reason for this is illustrated in Fig. 8. When the diffusion starts, the elements near the surface start to swell, while the inner part remains unswollen [see Fig. 8(b)]. The elements near the surface tend to extend the inner elements laterally, while the inner elements resist this. Therefore, a lateral extension is attained by their balance.

Again we take the  $x$ -direction to be normal to the sheet. If the gel is thin, the deformation in the  $y$ - and  $z$ -directions may be assumed to be uniform. Therefore, if we take the origin of the  $y$ - and the  $z$ -coordinates to be at the center of the sheet, the displacement of the material point  $(x, y, z)$  can be written as follows:

$$u_x = u(x, t), \quad u_y = \epsilon(t)y, \quad u_z = \epsilon(t)z. \quad (112)$$

The stress tensor for such a deformation is given by

$$\sigma_{xx} = \left( K + \frac{4}{3} G \right) \frac{\partial u}{\partial x} + \left( 2K - \frac{4}{3} G \right) \epsilon - K\alpha_{\text{eq}}, \quad (113)$$

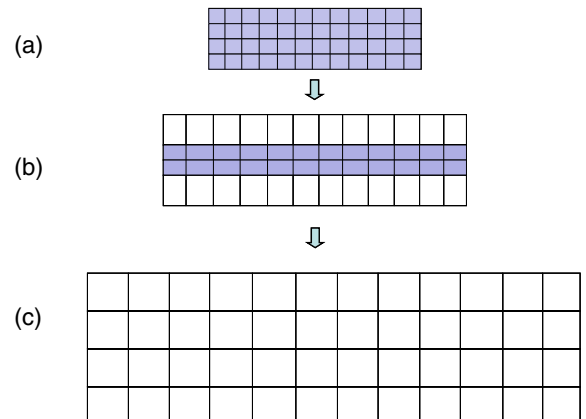


Fig. 8. (Color online) Time evolution of the swelling of a gel sheet. (a) Initial state. (b) Intermediate state, where the outer part is swollen, while the inner part is unswollen. (c) Final equilibrium state.

$$\sigma_{yy} = \sigma_{zz} = \left(K - \frac{2}{3}G\right) \frac{\partial u}{\partial x} + \left(2K + \frac{2}{3}G\right) \epsilon - K\alpha_{\text{eq}}. \quad (114)$$

Since there is no external force acting in the  $x$ -direction,  $\sigma_{xx} - p$  must be zero. Therefore,

$$p = \left(K + \frac{4}{3}G\right) \frac{\partial u}{\partial x} + \left(2K - \frac{4}{3}G\right) \epsilon - K\alpha_{\text{eq}}. \quad (115)$$

Note that the pressure  $p$  depends only on  $x$ , and does not depend on  $y$  or  $z$ .

Equation (74) is then written as

$$\frac{\partial \dot{u}}{\partial x} + 2\dot{\epsilon} = \kappa \frac{\partial^2 p}{\partial x^2}. \quad (116)$$

Eliminating  $\partial u/\partial x$  from eqs. (115) and (116), we have

$$\frac{\partial p}{\partial t} + 4G\dot{\epsilon} = D \frac{\partial^2 p}{\partial x^2}. \quad (117)$$

Note that there is an unknown term  $\dot{\epsilon}$ . This is determined by the force balance condition in the  $y$ - and  $z$ -directions. The total force acting across the plane normal to  $y$ - and  $z$ -must zero, i.e.,

$$\int_{-h/2}^{h/2} dx(\sigma_{yy} - p) = 0. \quad (118)$$

If  $\partial u/\partial x$  is expressed in terms of  $p$  using eq. (115), eq. (118) is written as

$$\int_{-h/2}^{h/2} dx p = Kh(3\epsilon - \alpha_{\text{eq}}). \quad (119)$$

Equations (117) and (119) give a coupled equation for  $p(x, t)$  and  $\epsilon(t)$ . The initial condition is

$$p(x, 0) = -K\alpha_{\text{eq}}, \quad \epsilon(0) = 0, \quad (120)$$

and the boundary condition is

$$p(h/2, t) = p(-h/2, t) = 0. \quad (121)$$

If eq. (115) is substituted for  $p$  in eq. (119), one gets the following equation

$$u(h/2, t) - u(-h/2, t) = \epsilon h. \quad (122)$$

The right-hand side is the change of the gel thickness  $\Delta h(t)$ . Equation (122) indicates that

$$\frac{\Delta h(t)}{h} = \epsilon(t), \quad (123)$$

i.e., during the swelling process, the aspect ratio of the gel remains unchanged: the gel swells keeping its original shape. This result is highly nontrivial since the shape of the gel is determined by a subtle balance of forces as illustrated in Fig. 8. Surprisingly, the same conclusion holds for the swelling of a cylindrical gel.

The above set of equations can be solved by the standard method of eigen function expansion. Let  $\tau$  be the longest relaxation time. For  $t \geq \tau$ , the solution can be written as

$$p(x, t) = f(x) \exp(-t/\tau), \quad \epsilon(t) = \frac{\alpha_{\text{eq}}}{3} + A \exp(-t/\tau). \quad (124)$$

Substituting eq. (124) into eq. (117), we have

$$\frac{\partial^2 f}{\partial x^2} = \frac{f + 4AG}{D\tau}. \quad (125)$$

The solution of this equation can be written as

$$f(x) = B \cos(\beta x) + B' \sin(\beta x) - 4GA, \quad (126)$$

where  $\beta = (D\tau)^{-1/2}$ . From eqs. (119) and (121), it can be shown that  $B' = 0$  and  $\beta$  is the solution of the equation

$$\chi \cot(\chi) = \frac{4G}{3K + 4G}, \quad (127)$$

where

$$\chi = \frac{\beta h}{2}. \quad (128)$$

Let  $\chi$  be the smallest positive solution of eq. (127), then  $\tau$  is given by

$$\tau = \frac{h^2}{4D\chi^2}. \quad (129)$$

If  $K/G \gg 1$ , the smallest solution of eq. (127) is  $\chi = \pi/2$  and

$$\tau = \frac{h^2}{\pi^2 \kappa K}. \quad (130)$$

In this case, eq. (130) agrees with eq. (93), the relaxation time of the constrained gel. On the other hand, if  $K/G \ll 1$ , the smallest solution of eq. (127) becomes  $\chi = (3/2)\sqrt{K/G}$  and the longest relaxation time is

$$\tau = \frac{h^2}{12\kappa K}. \quad (131)$$

Therefore, in the limit of  $K \rightarrow 0$ , the relaxation time  $\tau$  goes to infinity. This is different from the result for the constrained gel. In the case of the constrained gel, the relaxation time is proportional to  $1/[K + (4/3)G]$ , which does not diverge in the limit of  $K \rightarrow 0$ . Note that for both constrained gel and the free gel, the swelling is governed by the permeation of the solvent normal to the sample. However, the relaxation time is different. This example demonstrates that the swelling process cannot be described by the diffusion equation [such as eq. (80)] alone.

#### 4.2.2 Swelling of a cylindrical gel

The swelling of a long cylindrical gel can be analyzed by a method similar to that given above. This case is important since swelling experiments are usually performed for cylindrical gels. On the other hand, the development of theoretical analysis has been rather slow. In early analysis,<sup>32)</sup> the TF equation was used and the effect of stretching in the axial direction was ignored. The failure of the TF equation was corrected by Li and Tanaka,<sup>5)</sup> who proposed a method of accounting for the axial stretching. They proposed the physical mechanism, but did not express it in mathematical equations, and they solved the problem in an intuitive (and approximate) way. A more accurate calculation was performed by Wang *et al.*,<sup>33)</sup> but the analysis still involved approximation. A rigorous result has been obtained only recently.<sup>34)</sup> Leaving the detail to,<sup>34)</sup> we here summarize the main result.

As the cylindrical gel swells, both the radius  $a(t)$  and the

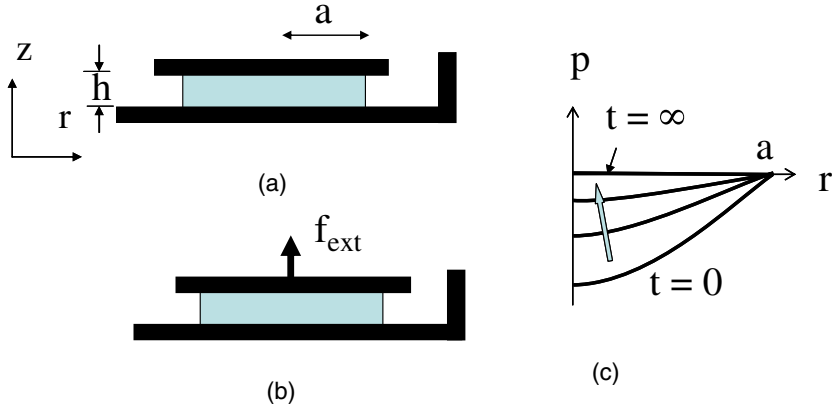


Fig. 9. (Color online) (a) The top and bottom sides of a disklike gel are glued to a rigid impermeable wall, and the gel is allowed to swell. (b) The same situation as in (a), but now the swelling of the gel is caused by an external force applied on the top wall. (c) Time evolution of the pressure distribution.

length  $L(t)$  increase with time, but it can be shown that the gel swells keeping its aspect ratio constant.

$$\frac{a(t)}{a(0)} = \frac{L(t)}{L(0)} \quad (132)$$

The longest relaxation time  $\tau$  for the swelling process is given by

$$\tau = \frac{a^2}{\chi^2 D}, \quad (133)$$

where  $\chi$  is the smallest positive solution of the equation.

$$\chi J_1'(\chi) + \frac{K - (4/3)G}{K + (4/3)G} J_1(\chi) = 0. \quad (134)$$

Here  $J_1(\chi)$  is the Bessel function of the first kind. Analysis of the equation gives the following expression for the relaxation time

$$\tau = 0.1730 \frac{a^2}{\kappa K} \quad \text{for } K \gg G \quad (135)$$

and

$$\tau = 0.125 \frac{a^2}{\kappa K} \quad \text{for } K \ll G. \quad (136)$$

The relaxation time is proportional to  $1/K$  at the two limits of  $K/G \rightarrow 0$  and  $\infty$ .

The above asymptotic behavior of the relaxation time at the limits of  $G/K \rightarrow 0$  and  $\infty$  is common to gels with sheetlike or spherical shapes. In fact, this is a general result; it has been proved<sup>35)</sup> that the relaxation time of an unconstrained gel always has the following characteristic behavior:

$$\tau = \begin{cases} C_1 \frac{L^2}{\kappa K} & \text{for } K \gg G, \\ C_2 \frac{L^2}{\kappa K} & \text{for } K \ll G, \end{cases} \quad (137)$$

where  $C_1$  and  $C_2$  are constants that depend on the shape of the sample and  $L$  is the characteristic size of the sample. (The divergence of  $\tau$  at the limit of  $K \rightarrow 0$  was first proposed by Onuki<sup>31)</sup> but his derivation was based on the TF equation, which is not correct for gels with a general shape.)

Analysis can be performed for a cylindrical gel stretched in the axial direction (see Fig. 5), and the time dependence of the stress and the radius of the gel can be calculated explicitly.<sup>34)</sup>

#### 4.2.3 Gel confined by rigid plate

As the final example, we analyze the situation shown in Fig. 9, the swelling of a gel slab whose top and bottom are glued to impermeable walls. For the gel to swell, the solvent must permeate sideways. Therefore, the relaxation time is determined not by the thickness  $h$  but by the lateral size  $a$  of the gel. An experiment for such a system was first performed by Suzuki *et al.*,<sup>36)</sup> and theoretical analysis was carried out in ref. 37.

We assume that the gel is a disk of thickness  $h$  and radius  $a$ . We take cylindrical coordinates  $(r, \theta, z)$ , the origin of which is at the center of the bottom circle. For a thin gel ( $h \ll a$ ), we may assume that the pressure is independent of  $z$ , i.e.,  $p = p(r, t)$ , and that the displacement in the  $z$  direction is uniform:

$$u_z(z, t) = \epsilon(t)z. \quad (138)$$

The volume change of the polymer network is

$$\nabla \cdot \mathbf{u} = \frac{\partial u_z}{\partial z} + \frac{1}{r} \frac{\partial(ru_r)}{\partial r} = \epsilon + \frac{1}{r} \frac{\partial(ru_r)}{\partial r}. \quad (139)$$

The second term on the right-hand side of eq. (139) is much smaller than the first term and can be ignored. Therefore, eq. (74) is written as

$$\dot{\epsilon} = \kappa \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial p}{\partial r} \right), \quad (140)$$

which is solved for  $p$  using the boundary condition  $p = 0$  at  $r = a$ :

$$p(r, t) = \frac{\dot{\epsilon}}{4\kappa} (r^2 - a^2). \quad (141)$$

The force acting on the top plate is given by

$$\sigma_{zz} - p = \left( K + \frac{4}{3}G \right) \epsilon - K\alpha_{\text{eq}} - p. \quad (142)$$

Since there is no force acting on the top plate, the force balance equation is written as

$$\int_0^a dr 2\pi r \left[ \left( K + \frac{4}{3}G \right) \epsilon - K\alpha_{\text{eq}} - p \right] = 0. \quad (143)$$

Using eqs. (141) and (143) we have

$$\dot{\epsilon} = \frac{1}{\tau} (\epsilon - \epsilon_{\text{eq}}), \quad (144)$$

where

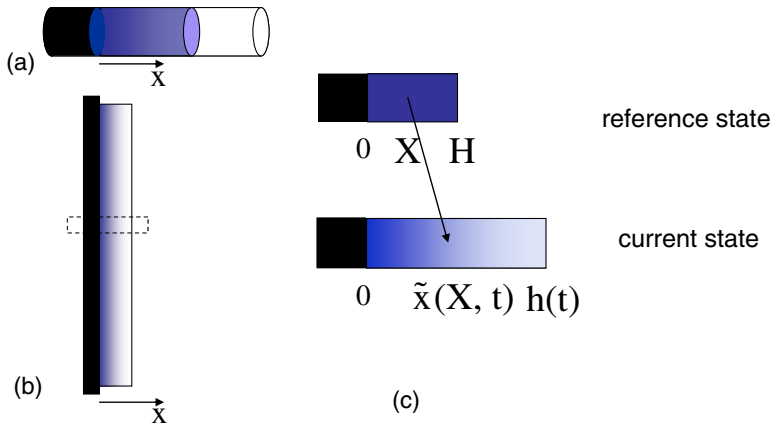


Fig. 10. (Color online) (a) An Examples realizing volume transition in one dimension. A cylindrical gel is allowed to swell in a tube. (b) Another example. A thin gel slab with one side glued to a rigid wall is allowed to swell. (c) The coordinate system used to describe the the kinetics of the gel.

$$\epsilon_{eq} = \frac{K}{K + (4/3)G} \alpha_{eq}, \quad (145)$$

and

$$\tau = \frac{a^2}{8D}. \quad (146)$$

Equation (145) is the same as eq. (95); the equilibrium swelling ratio of the gel constrained at one side (Fig. 6) is equal to that constrained at both sides (Fig. 9). On the other hand, their relaxation times are different: the relaxation time of the gel constrained at both sides is much larger than that of the gel constrained at one side. This is because in the case of Fig. 9, the solvent cannot enter the gel from the top and must diffuse into the gel over the long distance  $a$ .

A similar analysis can be performed for the situation that swelling is induced by an external force acting on the rigid plate.<sup>38)</sup> In this case, eq. (143) is replaced by

$$\int_0^a dr 2\pi r \left[ \left( K + \frac{4}{3}G \right) \epsilon - p \right] = \pi a^2 f_{ext}. \quad (147)$$

This gives

$$\dot{\epsilon} + \tau \epsilon = \frac{f_{ext}}{K + (4/3)G}. \quad (148)$$

This corresponds to a mechanical model in which a spring and dashpot are connected in parallel (this model is called the Voigt model in rheology).

## 5. Volume Transition

### 5.1 Specific features of volume transition

We now consider a problem that cannot be handled by the linearized equation. Specifically, we shall discuss the phenomenon called the volume transition. The volume transition is a phenomenon that the equilibrium volume of a swollen gel changes enormously (typically by a factor of hundreds) with a small change of external parameters such as temperature or solvent composition.<sup>1,39)</sup> This phenomenon is a type of phase transition, the phase having the large volume is called the swollen phase and that having the small volume is called the shrunken phase.

The volume transition of gels has often been discussed using the analogy of the gas–liquid transition of fluids since the order parameter of the transition is the volume (or the density), and there is no symmetry change associated with

the transition. However, it must be noted that there is a fundamental difference between the two transitions: the gas–liquid transition is a phase transition taking place in a fluid, while the volume transition of gels is a transition taking place in elastic materials. In this section we shall discuss the kinetics of volume transitions of gels, focusing on the similarities and differences between the two transitions.

### 5.2 Analysis of one dimensional case

#### 5.2.1 Kinetic equation

We shall first discuss the kinetics of volume transitions taking place in one dimension, i.e., the situation that the gel can expand in only one direction.<sup>40,41)</sup> This is the situation where the analogy between the volume transition and the gas–liquid transition is justified. However, it must be noted that this is a rather idealized situation. The situation may be realized by constraining a cylindrical gel in a tube as shown in Fig. 10(a), or by gluing a thin gel sheet on a rigid wall [Fig. 10(b)]. Both setups have some technical difficulties. In the former case, one must ensure that there is sufficient lubrication between the gel and the tube wall. In the latter case, one must ensure that the displacement can take place only normal to the wall, which is not easy since the gel is subject to buckling instability as we shall discuss later.

We take the  $x$  coordinate along the direction that the gel can move and let  $\tilde{x}(X, t)$  be the  $x$ -coordinate at time  $t$  of a point on the gel located at  $X$  in the reference state. We assume that the gel is fixed to an impermeable wall at  $X = 0$ . We also assume that the the gel is free at the other end at  $X = H$  and can absorb the solvent [see Fig. 10(c)]. The thickness of the gel at time  $t$  is given by

$$h(t) = \tilde{x}(H, t), \quad (149)$$

and the apparent (or overall) volume change is given by  $h(t)/h(0)$ . The local volume change at  $X$  is given by

$$\lambda(X, t) = \frac{\partial \tilde{x}(X, t)}{\partial X}. \quad (150)$$

If the reference state is taken to be the dry state, the polymer volume fraction  $\phi$  is given by  $1/\lambda$ .

To derive the kinetic equation, it is convenient to use the Rayleighian formulation described in §3.3 Let  $v_s(X, t)$  be the solvent velocity at position  $\tilde{x}(X, t)$  at time  $t$ . Since the polymer velocity is given by  $v_p = \dot{\tilde{x}}$ , the energy dissipation function [eq. (65)] can be written as

$$\mathcal{W} = \frac{1}{2} \int_0^H dX \tilde{\zeta}(\lambda) (\dot{\tilde{x}} - v_s)^2 = \frac{1}{2} \int_0^H dX \frac{\tilde{\zeta}}{(1-\phi)^2} \dot{\tilde{x}}^2, \quad (151)$$

where we have used the fact that the average velocity  $\phi \dot{\tilde{x}} + (1-\phi)v_s$  is zero. [Note that the average velocity  $\phi \dot{\tilde{x}} + (1-\phi)v_s$  is zero only when the one end of the gel is fixed to an impermeable wall. If the right end of the wall in Fig. 10(c) is permeable, the average velocity is nonzero.]

On the other hand, the free energy  $\mathcal{A}$  is written as

$$\mathcal{A} = \int_0^H dX \tilde{A}(\lambda). \quad (152)$$

Therefore,  $\dot{\mathcal{A}}$  is calculated as

$$\begin{aligned} \dot{\mathcal{A}} &= \int dX \frac{\partial \tilde{A}}{\partial \lambda} \dot{\lambda} \\ &= \int dX \frac{\partial \tilde{A}}{\partial \lambda} \frac{\partial \tilde{x}}{\partial X} \\ &= - \int dX \frac{\partial \sigma}{\partial X} \dot{\tilde{x}}, \end{aligned} \quad (153)$$

where

$$\sigma(\lambda) = \frac{\partial \tilde{A}}{\partial \lambda} \quad (154)$$

and integration by parts has been used.

Thus, the Rayleighian is written as

$$\mathcal{R} = \int dX \left( \frac{1}{2} \zeta \dot{\tilde{x}}^2 - \frac{\partial \sigma}{\partial X} \dot{\tilde{x}} \right), \quad (155)$$

where

$$\zeta = \frac{\tilde{\zeta}}{(1-\phi)^2}. \quad (156)$$

Minimizing eq. (155) with respect to  $\dot{\tilde{x}}$ , we have

$$\zeta \dot{\tilde{x}} = \frac{\partial \sigma}{\partial X} = \frac{\partial \sigma}{\partial \lambda} \frac{\partial \lambda}{\partial X} \quad (157)$$

or

$$\frac{\partial \tilde{x}}{\partial t} = D(\lambda) \frac{\partial^2 \tilde{x}}{\partial X^2}, \quad (158)$$

where

$$D(\lambda) = \frac{1}{\zeta(\lambda)} \frac{\partial \sigma}{\partial \lambda}. \quad (159)$$

At  $X = H$ , the gel is allowed to swell freely. Therefore, the boundary condition at  $X = H$  is  $\sigma = 0$ . This gives the following boundary condition:

$$\frac{\partial \tilde{x}}{\partial X} = \lambda_{\text{eq}} \quad \text{at } X = H, \quad (160)$$

where  $\lambda_{\text{eq}}$  is the solution of  $\sigma(\lambda) = 0$ . On the other hand, at  $X = 0$ , the gel is fixed to a rigid wall, i.e.,

$$\tilde{x} = 0, \quad \text{at } X = 0. \quad (161)$$

Equation (158) and the boundary conditions in eqs. (160) and (161) determine the free swelling in one dimension.

The kinetic equation [eq. (158)] can be rewritten in a more familiar form. By differentiating both sides of eq. (158) with respect to  $X$ , we have

$$\frac{\partial \lambda}{\partial t} = \frac{\partial}{\partial X} \left[ D(\lambda) \frac{\partial \lambda}{\partial X} \right]. \quad (162)$$

Thus,  $\lambda$  satisfies the usual nonlinear diffusion equation. However, eq. (162) is not very useful since the boundary condition for  $\lambda$  is not known.

### 5.2.2 Scaling property

An important feature of the equations given above is that the material property is entirely characterized by  $\sigma(\lambda)$  and  $\zeta(\lambda)$ , and there is no material parameter with the dimension of length or time. Therefore, for a given problem, the time scale and length scale are set by the boundary conditions such as the size of the specimen. This gives the following scaling property.<sup>10</sup> Let  $\tilde{x}(X, t)$  be the solution to eq. (158) for a gel of length  $H$ , then  $\xi \tilde{x}(\xi X, \xi^2 t)$  is the solution of the same equation for a gel having length  $\xi H$ .

To understand the implications of the scaling property, consider the swelling of two gels having the same shape, one being larger than the other by a factor of  $\xi$ . The scaling property indicates that the shape of the larger gel at time  $\xi^2 t$  is the same as that of the smaller gel at time  $t$ . Especially, the relaxation times of the two gels differ by a factor of  $\xi^2$ ; i.e., the relaxation time is proportional to the square of the gel size. Such a scaling relation is known for phenomena governed by a linear diffusion equation, but the scaling relation actually holds for the nonlinear case as well. This scaling relation is a general property of gel dynamics and it holds not only for the one-dimensional case discussed here but also for the three-dimensional case.

### 5.2.3 Coexistence condition

We now consider the time dependence of the volume transition. Suppose that the gel slab shown in Fig. 10(a) was initially in the shrunken state and that the temperature has been changed so that the equilibrium state of the gel is now in the swollen state. We discuss how the shrunken state transforms to the swollen state.

Figure 11 shows how the transformation takes place. Since the solvent can diffuse into the gel from the right, the swollen phase appears at the right end and expands toward the left. Let  $X_I(t)$  be the position of the interface between the swollen phase and shrunken phase. At  $X_I(t)$ ,  $\lambda$  changes discontinuously.

The discontinuity in  $\lambda$  at the interface can be determined by the condition that the system is in local equilibrium.<sup>40,41</sup> Consider a small region across the interface. Let  $\Delta X$  be the size of this region in the reference state and  $\Delta x$  be the size in the current state. Let us assume that, within this region, the fraction  $w$  is in the shrunken state and the rest,  $1-w$ , is in the swollen state. Let  $\lambda_{\text{sh}}$  and  $\lambda_{\text{sw}}$  be the respective values of  $\lambda$  in these states. They satisfy the condition

$$\Delta x = [w \lambda_{\text{sh}} + (1-w) \lambda_{\text{sw}}] \Delta X. \quad (163)$$

The local free energy of this region is given by

$$\tilde{\mathcal{A}}_{\text{local}} = [w \tilde{A}(\lambda_{\text{sh}}) + (1-w) \tilde{A}(\lambda_{\text{sw}})] \Delta X. \quad (164)$$

The position of the interface is determined by minimizing eq. (164) with respect to  $\lambda_{\text{sh}}$ ,  $\lambda_{\text{sw}}$ , and  $w$  under the constraint in eq. (163), i.e., they are given by

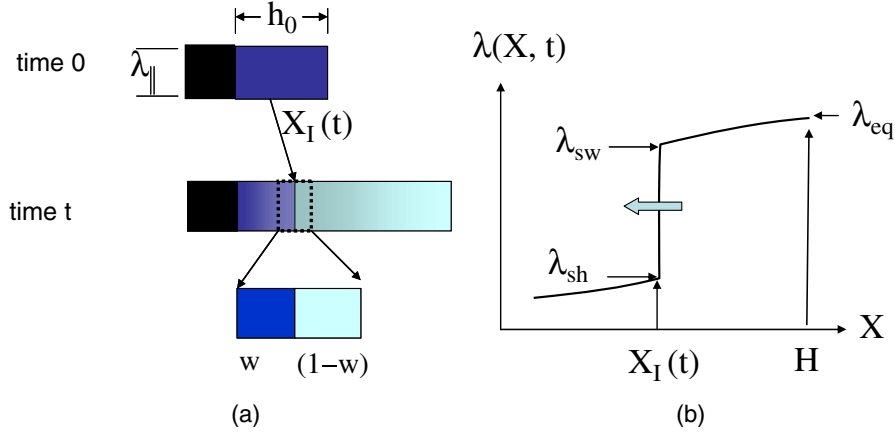


Fig. 11. (Color online) Intermediate state of volume transition. (a) The gel is initially in a shrunken phase, and the swollen phase appears at the right end. The boundary between the swollen phase and the shrunken phase moves to the left.  $X_I(t)$  is the coordinate (in the reference frame) of the boundary at time  $t$ . (b) Typical behavior of the function  $\lambda(X, T)$  for the state where the swollen phase and shrunken phase coexist at point  $X_I$ .

$$\frac{\partial \tilde{\mathcal{A}}_{\text{local,p}}}{\partial \lambda_{\text{sh}}} = 0, \quad \frac{\partial \tilde{\mathcal{A}}_{\text{local,p}}}{\partial \lambda_{\text{sw}}} = 0, \quad \frac{\partial \tilde{\mathcal{A}}_{\text{local,p}}}{\partial w} = 0, \quad (165)$$

where

$$\tilde{\mathcal{A}}_{\text{local,p}} = \mathcal{A}_{\text{local}} - p[w\lambda_{\text{sh}} + (1-w)\lambda_{\text{sw}}]\Delta X. \quad (166)$$

Equations (165) and (166) give

$$\sigma(\lambda_{\text{sh}}) = \sigma(\lambda_{\text{sw}}) = \frac{\tilde{\mathcal{A}}(\lambda_{\text{sh}}) - \tilde{\mathcal{A}}(\lambda_{\text{sw}})}{\lambda_{\text{sh}} - \lambda_{\text{sw}}}, \quad (167)$$

where  $\sigma(\lambda)$  is given by eq. (154).

Equation (167) indicates that  $\lambda_{\text{sh}}$  and  $\lambda_{\text{sw}}$  are obtained by constructing the common tangent in the plot of  $\tilde{\mathcal{A}}$  against  $\lambda$  as shown in Fig. 12(a). The construction of the common tangent is equivalent to the Maxwell construction in the gas–liquid transition. Thus, the coexistent condition in gels is very similar to that in the gas–liquid transition.

The above argument indicates that if the solution  $\lambda(X, t)$  of eq. (158) or (162) satisfies  $\lambda_{\text{sh}} < \lambda(X, t) < \lambda_{\text{sw}}$  in a certain region, the solution must be replaced by the discontinuous solution in the region. Alternatively, one can formulate the problem as a problem with a moving boundary condition:

$$\frac{\partial \tilde{x}}{\partial t} = D_1(\lambda) \frac{\partial^2 \tilde{x}}{\partial X^2} \quad \text{for } X < X_I(t), \quad (168)$$

$$\frac{\partial \tilde{x}}{\partial t} = D_2(\lambda) \frac{\partial^2 \tilde{x}}{\partial X^2} \quad \text{for } X > X_I(t), \quad (169)$$

where  $D_1(\lambda)$  and  $D_2(\lambda)$  denote the function  $D(\lambda)$  in the regions of  $\lambda < \lambda_{\text{sh}}$  and  $\lambda > \lambda_{\text{sw}}$ , respectively. The swelling ratio  $\partial \tilde{x} / \partial X$  is discontinuous at the interface;

$$\frac{\partial \tilde{x}}{\partial X} = \lambda_{\text{sh}} \quad \text{at } X = X_I(t) - 0, \quad (170)$$

$$\frac{\partial \tilde{x}}{\partial X} = \lambda_{\text{sw}} \quad \text{at } X = X_I(t) + 0. \quad (171)$$

The interface velocity  $\dot{X}_I(t)$  can be determined by the condition that the velocity of the polymer network at the interface  $d\tilde{x}[X_I(t), t]/dt$  must be continuous at  $X = X_I(t)$ :

$$\lambda_{\text{sh}} \dot{X}_I(t) + \left( \frac{\partial \tilde{x}}{\partial t} \right)_{X=X_I(t)-0} = \lambda_{\text{sw}} \dot{X}_I(t) + \left( \frac{\partial \tilde{x}}{\partial t} \right)_{X=X_I(t)+0}. \quad (172)$$

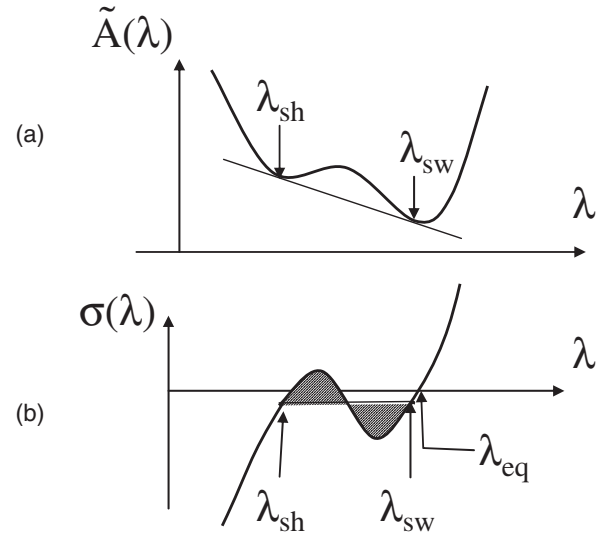


Fig. 12. (a) Free energy density per unit volume of the reference state plotted against the swelling ratio  $\lambda$ . (b) Stress is plotted against  $\lambda$ .  $\lambda_{\text{eq}}$  is the solution of  $\sigma(\lambda) = 0$ , and  $\lambda_{\text{sh}}$  and  $\lambda_{\text{sw}}$  are determined by eq. (167).

Using  $\partial \tilde{x} / \partial t = D \partial \lambda / \partial X$  [see eq. (158)], we have<sup>40)</sup>

$$\dot{X}_I(t) = - \frac{\left[ \left[ D(\lambda) \frac{\partial \lambda}{\partial X} \right] \right]}{[[\lambda]]}, \quad (173)$$

where  $[[F]]$  is the jump of  $F$  at the interface, i.e.,  $[[F]] = F(X_I + 0) - F(X_I - 0)$ .

Equation (173) allows us to estimate the velocity of the interface. The velocity  $\partial \tilde{x} / \partial t = D \partial \lambda / \partial X$  is much larger in the swollen state than that in the shrunken state. Hence,  $[[D \partial \lambda / \partial X]]$  can be approximated by  $D \partial \lambda / \partial X$  at  $X = X_I + 0$ . Furthermore, this value can be approximated by  $D(\lambda_{\text{sw}})(\lambda_{\text{eq}} - \lambda_{\text{sw}}) / (H - X_I)$  [see Fig. 11(b)]. Hence, eq. (173) gives<sup>41)</sup>

$$\dot{X}_I = D(\lambda_{\text{sw}}) \frac{\lambda_{\text{eq}} - \lambda_{\text{sw}}}{(H - X_I)(\lambda_{\text{sw}} - \lambda_{\text{sh}})}. \quad (174)$$

The equation is easily solved to give



$$X_1(t) = H - \sqrt{D_1 t}, \quad (175)$$

where

$$D_1 = D(\lambda_{sw}) \frac{(\lambda_{eq} - \lambda_{sw})}{\lambda_{sw} - \lambda_{sh}} \simeq D(\lambda_{sw}) \frac{\lambda_{eq} - \lambda_{sw}}{\lambda_{sw}}, \quad (176)$$

and we have used the relation  $\lambda_{sw} \gg \lambda_{sh}$ . Thus, the motion of the interface is essentially determined by the parameters in the swollen state, and the time needed for the interface to move from the left end to the right end is estimated as

$$\tau = \frac{H^2}{D_1}. \quad (177)$$

The time is proportional to  $H^2$  in accordance with the scaling property.

### 5.3 Complications in volume transitions

We have seen that the volume transition of gels has some similarity to the gas–liquid phase transition in the one-dimensional case. This is, however, a special situation. In fact, the similarity between the volume transition in gels and the gas–liquid transition is superficial: there are more differences than similarities. In this section, we shall discuss the differences.

#### 5.3.1 Volume transition of a spherical gel

Let us consider the volume transition of a spherical gel. Let us assume that each point of the gel can move only in the radial direction. Thus, the swelling of the gel is completely described by the function  $\tilde{r}(R, t)$  which denotes the radial coordinate at time  $t$  of the gel element that was at  $R$  in the reference state. This assumption reduces the problem to a one-dimensional partial differential equation. Even if such a simplifying assumption is made, the kinetics of the volume transition of spherical gels is complex and is quite different from that of the one-dimensional case.<sup>42,43</sup> This is because the deformation mode is different. In the one-dimensional case, the deformation takes place in the  $x$  direction only, and there is no deformation in the  $y$ - and  $z$ -directions, while in the swelling spheres, the deformation takes place in the radial direction as well as in the tangential direction. The deformation in the radial direction is given by

$$\lambda_{\parallel}(R, t) = \frac{\partial \tilde{r}(R, t)}{\partial R}, \quad (178)$$

and the deformation in the tangential direction is given by

$$\lambda_{\perp}(R, t) = \frac{\tilde{r}(R, t)}{R}. \quad (179)$$

The time evolution equation for  $\tilde{r}(R, t)$  can be obtained by the same method as that described in §5.2.1. The equation is different from eq. (158). Particularly, the condition at the interface between the swollen phase and shrunken phase is different. Note that  $\tilde{A}$  in eq. (167) is a function of  $\lambda_{\perp}$ , the stretch in the direction normal to the  $x$ -axis. In the one-dimensional case,  $\lambda_{\perp}$  is fixed. Therefore,  $\lambda_{sh}$  and  $\lambda_{sw}$  are constant and do not change as the interface moves. On the other hand, in the spherical gel,  $\lambda_{\perp}$  varies with time as the gel swells. Therefore  $\lambda_{\parallel,sh}$  and  $\lambda_{\parallel,sw}$  also change with time. This gives a complication to the problem.

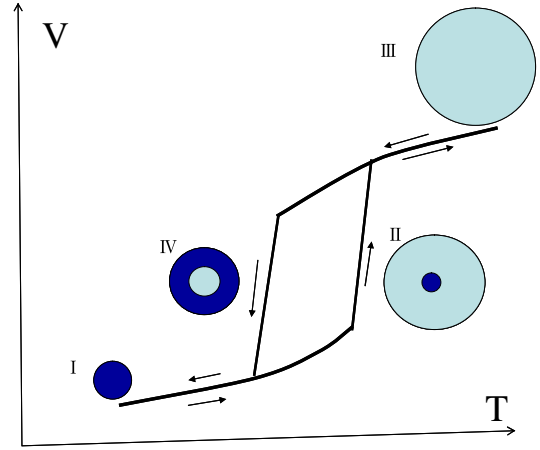


Fig. 13. (Color online) Hysteresis effect in the volume transition of spherical gels.

Suppose that the swollen phase and shrunken phase coexist as shown in Fig. 13. The condition for the two phases to coexist depends on whether the swollen phase occupies the outer part or inner part of the sphere. Suppose at some temperature  $T_1$ , the gel is in the shrunken state (state I in Fig. 13). As the temperature is increased, a swollen phase starts to appear near the surface (since the solvent must diffuse into the gel from the surface), and moves toward the center (state II). Eventually the whole sphere becomes in the swollen phase (state III). If the temperature is then decreased, the shrunken phase starts to appear near the surface (since the solvent must diffuse out of the gel through the surface), and moves toward the center. The temperature at which the shrunken phase starts to appear will be different from the temperature at which the swollen phase starts to appear: there is a hysteresis when the temperature is changed cyclically.

#### 5.3.2 Hysteresis

The hysteresis explained in the previous section is a result of the gel being an elastic material. If the material is a fluid, it does not matter whether the swollen phase (or the large-volume phase) occupies the outer part or inner part of the gel. On the other hand, if the material is elastic, it matters, since the free energy of the system involves the energy of deformation. This is the basic difference between the gas–liquid transition and the volume transition in gels.

The volume transition in elastic materials must exhibit hysteresis. This is explained in Fig. 14. Consider the temperature at which the free energy of the shrunken state (the small volume state) is equal to that of the swollen state (the large volume state). Figure 14 shows the free energy of the material at this temperature plotted against the volume of the material. The dashed line denotes the free energy of the homogeneous state and the solid line is the free energy of the state in which two phases coexist with each other.

For the fluid [Fig. 14(a)], the free energy in the coexistence region is flat; thus, the gas state can be transformed to the liquid state without any extra work. [The free energy discussed here is the Gibbs free energy  $G(V; T, p) = F(V, T, p) + pV$ , where  $F(T, V)$  is the Helmholtz free energy.] On the other hand, for elastic materials [Fig. 14(b)],

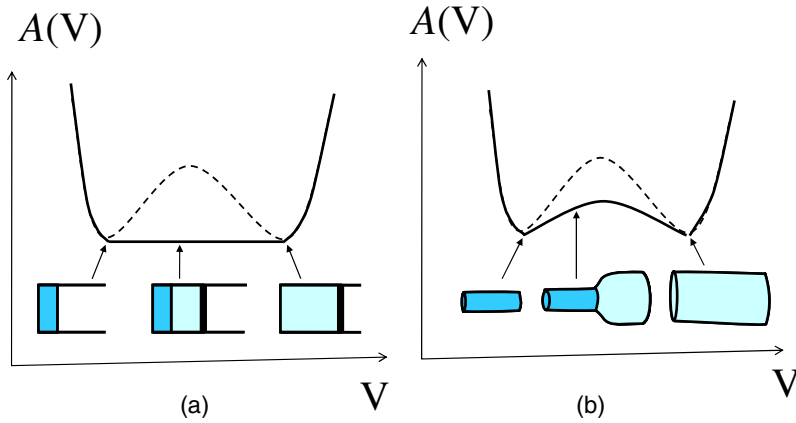


Fig. 14. (Color online) Free energy curve of a system undergoing a volume transition for fluid system (a) and elastic system (b). The free energy is drawn as a function of the total volume of the system at the temperature at which the free energy of the shrunken state (or small volume state) is equal to that of the swollen state (or large volume state). In the fluid system, the free energy of the fluid is flat in the coexistence region since the cost of coexistence is negligible. On the other hand, in the elastic system, the free energy has a peak in the coexistence region since the elastic energy of deformation contributes to the free energy cost of coexistence.

the free energy in the coexistence region has a peak in the middle of the region. The peak originates from the elastic energy of deformation required for the two phase to coexist. In fluids, the cost of the coexistence of the gas phase and liquid phase is the inter-facial tension, which is negligibly small compared with the bulk energy. On the other hand, in elastic materials, the cost of the coexistence of the swollen phase and shrunken phase is the elastic energy of deformation, which is a bulk energy and cannot be neglected.<sup>44)</sup> In order to cause the spontaneous transformation of the shrunken phase to the swollen phase, the temperature must be changed so that there is no bump in the free energy curve. This temperature will be different from the temperature at which the swollen phase transforms spontaneously to the shrunken phase. Therefore, the transition must have a hysteresis effect.

It has been shown<sup>43,45)</sup> that the kinetics of the volume transition can be quite complex; the volume change does not take place monotonically with time; occasionally there is an incubation period before a large volume change occurs, or the volume change stops for a while in the middle of the shrinking process and then starts again. Such behavior has indeed been observed experimentally.<sup>39,46)</sup>

### 5.3.3 Mechanical instability

The elasticity of gels complicates the kinetics of volume transitions as we have discussed. There are other complications which make the problem even more difficult: the buckling effect.

The buckling effect can be seen in the simple situation shown in Fig. 15(a). Consider the swelling of a gel fixed to a substrate [see Fig. 15(a)].<sup>47)</sup> Since the bottom of the slab is fixed, the slab cannot expand in the plane parallel to the substrate. If the equilibrium volume change is small, the gel swells homogeneously as discussed in §4.1. If the volume change is large (either due to a large temperature change, or a volume transition), the gel will buckle as shown in Fig. 15(b). The buckling occurs since the gel volume can increase [therefore reducing the bulk modulus term in eq. (35)] by sacrificing the shear modulus term.

Analytical calculations and computer simulations have been performed for the buckled state.<sup>48,49)</sup> It is clear by the scaling property discussed in §5.2.2 that the characteristic size of the wrinkles  $\ell$  is of the order of the thickness of the gel slab  $h$ .

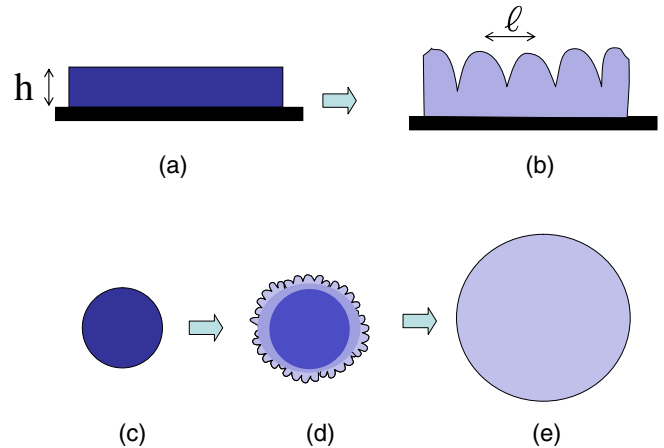


Fig. 15. (Color online) (a) and (b) Buckling of a swollen gel fixed on a substrate. (c)–(e) Wrinkles seen at the surface of spherical gels in the intermediate stage of the transition from the shrunken state to the swollen state.

Buckling can take place in a gel that is not subject to any constraints. Consider the swelling of a spherical gel. An element of the gel near the surface is in a situation similar to that of the constrained gel. The surface of the gel is swollen, while the inner core is not swollen. If the volume change near the surface is rapid, the gel elements near the surface buckle, and wrinkles appear on the surface of the sphere [see Figs. 15(c) and 15(d)]. The wrinkles disappear eventually when the whole gel reaches the equilibrium state [see Fig. 15(e)]. In the case of a spherical gel, the wrinkles appear in the intermediate state; the initial and final states are a smooth sphere. The characteristic size of the wrinkles is determined by time. By the scaling property, the size of the wrinkles can be estimated by

$$\ell \simeq \sqrt{Dt}. \tag{180}$$

There are other types of mechanical instabilities, and various patterns such as bamboo like patterns and bubble-like patterns have been observed in the transition state of volume phase transition.

## 6. Conclusion

In this article, we have proposed a continuum mechanical theory that describes the dynamics of gels. The characteristic feature of gels is that the permeation of a solvent (or its

diffusion) is coupled with the elastic deformation of the gel. This may be compared with a fluid mixture in which the diffusion and fluid flow are coupled with each other. The basic equations of gels can be constructed in the same way as those for a fluid mixture, but the difference is that one component of the gel is an elastic material. This results in unique features in the kinetics of gels.

- (1) Although the diffusion of the solvent in the gel can be described by diffusion equations such as eq. (77), the dynamics can be markedly different due to the elasticity. This is clearly demonstrated in the relaxation time of the free swelling of gels: the relaxation time diverges in the limit of  $K \rightarrow 0$ , even though the diffusion constant remains finite.
- (2) The elasticity gives specific kinematics in the phase transition of gels. When the swollen phase and shrunken phase coexist with each other, there is a very large cost of free energy. This causes the strong hysteresis and unusual kinematics in the volume transition of gels.

In this article, we restricted the discussion to problems that can be treated by analytical calculation. As gel dynamics generally requires the solution of coupled non-linear equations, numerical calculation is important. In early works, the coupling between the gel deformation and solvent permeation was not treated properly. Simulations based on proper models will have value for both scientific study and industrial applications.

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