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Dynamics of interface of gels undergoing volume phase transition

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Abstract. — The dynamics of interface of chemical gels undergoing volume phase transition is studied for one-dimensional geometry Permeation of solvent through the interface is taken into account It is shown that the rate determining process of motion of interface is the permeation of solvent through the bulk domains Generalization to three-dimensional case is also discussed.

1. Introduction.

Gels have been known to exhibit various peculiar phenomena as distinguished from conventional solids. A notable example is the volume phase transition When the temperature or solvent are varied, the equilibrium volume of a certain gel changes dramatically, typically by a factor of thousand Many intriguing phenomena have been reported associated with the kinetics of this transition Tanaka *et al.* [1, 2] observed that, during the swelling and shrinking process, instability takes place on the surface of the gel, resulting in curious wrinkled surface patterns. This has been analyzed in detail by Hayashi *et al* [3]. Hirotsu [4] observed that the swollen and the shrunken phases coexist in a gel of cylindrical shape [5]. From the theoretical side, the hydrodynamic equations of gels have been given [7] for a single phase based on the local equilibrium assumption. On the other hand the boundary between the swollen phase and the shrunken phase *in equilibrium* has been studied [6]

In order to analyze the experimental phenomena mentioned above, one needs, however, a basic set of equations that describe the deformation of the gel network and permeation of solvents *in the presence* of the interface between the swollen and the shrunken phases, and also an equation which describes the motion of the interface itself The purpose of the present paper is to give such a set of equations by combining the results of the previous two papers [6, 7].

The organization of this paper is as follows. In section 2, we briefly summarize the results of hydrodynamics and thermodynamics of gels [7] in order to introduce several notations. In

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section 3, we show an explicit calculation in the one-dimensional case, the situation which may be realized by experiment of permeation through a cylindrical gel in the two-phase coexistence region. We also discuss the range of applicability of our theory In section 4, we discuss the generalization to the three-dimensional case The final section (Sect. 5) is for conclusion.

2. Summary of thermodynamics and hydrodynamics of gels [7].

Results of [7] is summarized in order to introduce various notations We assume that solvent and polymer molecules are incompressible. We denote the specific volume of solvent and polymer molecules by $\bar{V}_f$ and $\bar{V}_m$ respectively. We also assume that the temperature T is kept constant throughout the gel. In such a situation, hydrodynamic equation of gels has also been proposed by other people [8-10]. See [7] for more general cases. We arbitrarily choose an isotropic and homogeneous state of gel, and define this state as a reference state. Each polymer molecule (in a sense of continuum) is distinguished by its position **X** in the reference state We denote the volume fraction of polymer molecules in this state by ϕ_0. Note that a given reference volume, say V', includes a constant mass of polymer molecules, $M_m = \phi_0 V'/\bar{V}_m$, regardless of actual deformation of gel.

In a deformed state the position **x** of a polymer molecule is a function of **X**, the position of the molecule in the reference state. We introduce the distortion matrix (**F**) as follows

$$(\mathbf{F})^{\mu}_{p} \equiv F^{\mu}_{p} \equiv \frac{\partial x^{\mu}}{\partial X^{p}}. \tag{2.1}$$

Hereafter we use Greek indices for the Cartesian components in actual space, latin indices for the Cartesian components in the reference space

The determinant of the distortion matrix

$$J \equiv \det(\mathbf{F}) \tag{2.2}$$

is the dilation ratio of gel, so that the polymer volume fraction in the deformed state, ϕ is given by

$$\phi = \phi_0/J. \tag{2.3}$$

We denote the free energy of the homogeneous gel by A. Under an isothermal condition, the change of the free energy is caused either by the change of polymer mass M_m or by the change of deformation **F**. We define $\tilde{\mu}_m$ and $\mathbf{\Pi}^R$ by

$$dA = \tilde{\mu}_m \, dM_m + \frac{\bar{V}_m M_m}{\phi_0} (\mathbf{\Pi}^R)^{p}_{\nu} \, dF^{\nu}_{p}, \tag{2.4}$$

where we adopted Einstein's convention for repeated indices.

If we introduce free energy per unit reference volume $\alpha \equiv A/V'$, where $V' = M_m \bar{V}_m/\phi_0$, we have the relations

$$d\alpha = (\mathbf{\Pi}^R)^{p}_{\nu} \, dF^{\nu}_{p}, \tag{2.5}$$

$$\tilde{\mu}_m = \frac{\bar{V}_m}{\phi_0} \alpha \tag{2.6}$$

The reversible stress $\mathbf{\Pi}$ due to deformation of gel is given by the following relation

$$(\Pi^{R})^{p}_{\nu} F^{\lambda}_{p} = J\Pi^{\lambda}_{\nu} \tag{2.7}$$

The pressure p is not included in $\mathbf{\Pi}$. Due to the incompressibility of the system, p is determined by hydrodynamics, not by thermodynamics The conservation of the mass of polymer molecules is written as

$$\partial_t \phi = -\nabla . [\phi \dot{\mathbf{x}}] , \tag{2.8}$$

where $\dot{\mathbf{x}}(= \partial \mathbf{x}(\mathbf{X}, t)/\partial t)$ is the velocity of the polymer molecules, and ∇ denotes the gradient operator in the real space Let $\mathbf{u}_f$ be the velocity of the solvent molecules The volume flux, i.e. the volume average velocity $\mathbf{j}_v$ is

$$\mathbf{j}_v = (1 - \phi)\, \mathbf{u}_f + \phi \mathbf{x} . \tag{2.9}$$

Since the system is incompressible, $\mathbf{j}_v$ has to satisfy

$$\nabla . \mathbf{j}_v = 0 . \tag{2.10}$$

We assume that a mechanical balance is always attained. This condition is expressed by

$$\nabla . (\mathbf{\Pi} - p\mathbf{1}) = 0 , \tag{2.11}$$

where $\mathbf{1}$ is a unit matrix. The Gibbs-Duhem relation under isothermal and incompressible condition becomes equivalent to a geometrical identity and is therefore not shown. The rate of irreversible production of entropy per unit (actual) volume, S_{irr}, which is calculated under the assumption of local equilibrium is given as

$$TS_{irr} = -(1 - \phi)(\mathbf{u}_f - \dot{\mathbf{x}}) . \nabla p . \tag{2.12}$$

Assuming a linear relation between thermodynamic force and irreversible flux, we have the following relation (Darcy's law),

$$(1 - \phi)(\mathbf{u}_f - \mathbf{x}) = -\mathbf{L} . \nabla p , \tag{2.13}$$

where $\mathbf{L}$ is the Onsager kinetic coefficient matrix with pertinent symmetry properties. In (2.12) and (2 13) $(1 - \phi)(\mathbf{u}_f - \mathbf{x})$ is the volume flux of solvent that passes through the gel network moving at the velocity $\dot{\mathbf{x}}$. Thus (2.13) means that this flux is driven by the pressure gradient in gel.

Finally, the following formula [7] will be used later

$$\partial_\sigma Q^{\sigma}_{\lambda} = \frac{1}{J} \frac{\partial}{\partial X^{p}} [J(\mathbf{F}^{-1})^{p}_{\nu} Q^{\nu}_{\lambda}] , \tag{2.14}$$

where Q is an arbitrary tensor.

3. Solvent permeation in one-dimensional geometry.

3.1 STEADY STATE. — We shall now consider the kinetics of the system which involves the interface between the swollen and the shrunken phases. First we consider the following-one dimensional problem (see Fig. 1). Consider a gel of cylindrical shape placed in a tube. The left side of the gel is free On the right side of the gel, we put a solid porous membrane so that the

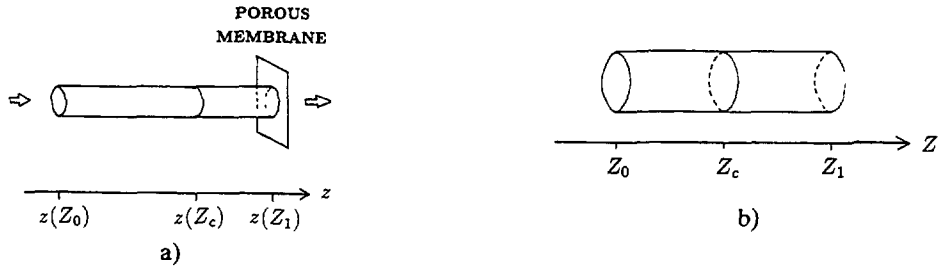

Fig. 1 — A state of gel is shown schematically in the actual coordinate (z) space (Fig 1a), and in the reference coordinate (Z) space (Fig. 1b) Permeation flow is in the positive z, or Z, direction as shown by arrows Solvent enters into the gel from the free surface at $z(Z_0)$ and goes out through the opposite surface at $z(Z_1)$, where the gel is supported by a porous membrane as shown in the figure. $z = z(Z_c)$ denotes the position of the interface in z-space, which separates the gel monomers into those belonging to the swollen phase domain ($Z < Z_c$) and those to the shrunken phase domain ($Z > Z_c$)

gel is not pushed out of the tube to the right. We assume that the solvent can flow freely through this membrane. Now suppose that the pressure p_0 and p_1 ($p_0 > p_1$) are applied for the solvent at the left and the right end of the tube, respectively. Due to the pressure difference $p_0 - p_1$, the solvent will flow through the gel, and compress the gel along the tube axis. Accordingly the volume of the gel will decrease and eventually the system will reach a new stationary state with constant flow of solvent. The problem we shall consider here is the dynamics of this process in the situation that the swollen and the shrunken phases coexist with each other

For simplicity, we assume that the equilibrium diameter of the freely suspended gel is always larger than the tube diameter so that the gel diameter is fixed at the value of the tube diameter, while the gel can slip freely at the tube wall (Experimentally there might be a difficulty in preventing the solvent flow along the inner wall of the tube, but our purpose here is to consider a situation which is convenient for theoretical analysis).

First we focus our attention to the stationary state in which the polymer velocity x is zero We choose the Z-axis parallel to the axis of the tube. Then by symmetry, the distortion components $F^x_X = F^y_Y$ are determined by the ratio between the tube diameter and the gel diameter in the reference state, and the off-diagonal components are all zero ; $F^x_Y = \cdots = 0$. The only unknown component of distortion is F^z_Z.

The basic equations are the mechanical balance equation (2.11) and Darcy's law (2 13), which are respectively written as

$$\partial_z \Pi^z_z = \partial_z p \tag{3.1.1}$$

and

$$J_v = - L \, \partial_z p \,, \tag{3 1 2}$$

where

$$J_v = (1 - \phi) \, u^z_f \tag{3.1.3}$$

is the volume flux of the solvent, which is constant in the stationary state, and $L \equiv L^{zz}$. (3 1.1) indicates that the pressure drop is counter-balanced by the increase of inner compressive stress of gel network. By equations (2.14) and (2.7), (3.1.2) is rewritten as

$$J_v = - \frac{L(W)}{J(W)} \frac{\mathrm{d}}{\mathrm{d}Z} \Pi(W) \,, \tag{3 1 4}$$

where we have denoted $W \equiv F_Z^z = \mathrm{d}z/\mathrm{d}Z$ and $\Pi \equiv (\mathbf{\Pi}^R)_z^Z$. Hereafter, we will not explicitly write the dependence of L, J, and Π on the other components of distortion F_X^x or F_Y^y, which are known parameters. The actual form of $L(W)$ and $\Pi(W)$ are given by constitutive equations: they may be measured by experiments, or obtained by molecular theories In any case, we shall proceed our argument assuming that the functional forms of $L(W)$ and $\Pi(W)$ are known. Thus equation (3.1.4) is a first-order differential equation for $W(Z)$

First we consider the case that the gel is in a single phase To solve the equation, we need boundary conditions at the ends of the gel. At each end there are two conditions;

(a) Continuity of the stress. The (zz) component of the stress in the gel is given by $\Pi_z^z - p$, which must be equal to the external stress at the boundary.

(b) Continuity of the solvent chemical potential: For an isothermal, incompressible fluid, p corresponds to the chemical potential of the solvent. Thus p has to be continuous at the interface

Now in the present problem, these conditions are written as follows.

i) The boundary at the left end $(Z = Z_0)$: Since the pressure of the solvent is p_0 (where we have neglected the pressure drop in the pure solvent region), the boundary condition becomes;

$$\Pi_z^z - p = -p_0 \qquad \text{and} \qquad p = p_0 \tag{3 1.5}$$

i.e., $\Pi_z^z = 0$ at $Z = Z_0$.

ii) The boundary at the right end $(Z = Z_1)$ Due to the mechanical balance of the gel, the pressure acting on the gel is p_0, while the chemical potential of the solvent is p_1. Thus

$$\Pi_z^z - p = -p_0 \qquad \text{and} \qquad p = p_1 . \tag{3 1 6}$$

Using $\Pi_z^z = W/J(W)\,\Pi$ (see Eq. (2.7)), we can rewrite these conditions as

$$\Pi(W) = 0 \qquad \text{at} \qquad Z = Z_0 \tag{3.1.7}$$

and

$$\Pi(W) = -\frac{J(W)}{W}(p_0 - p_1), \qquad \text{at} \qquad Z = Z_1 . \tag{3 1.8}$$

If $W(Z)$ is a continuous function of Z, then equation (3.1.4) can be integrated for $W(Z)$. The initial condition is $W(Z_0) = W_0$, where W_0 is a solution of $\Pi(W_0) = 0$. Hence

$$Z - Z_0 = -\frac{1}{J_v}\int_{W_0}^{W(Z)} \frac{L(W')}{J(W')}\frac{\partial \Pi(W')}{\partial W'}\,\mathrm{d}W' \tag{3.1 9}$$

From (3.1 6) and (3.1 9), we have

$$Z_1 - Z_0 = -\frac{1}{J_v}\int_{W_0}^{W_1} \frac{L(W')}{J(W')}\frac{\partial \Pi(W')}{\partial W'}\,\mathrm{d}W' , \tag{3 1 10}$$

where W_1 is a solution of

$$\Pi(W_1) = -\frac{J(W_1)}{W_1}(p_0 - p_1) . \tag{3.1.11}$$

Equations (3.1.10) and (3.1.11) give a relation between the pressure difference $p_0 - p_1$ and the solvent flux J_v in the steady state. In a special case of $p_0 = p_1$, i e., in equilibrium, there is no permeation current ($J_v = 0$), and we require $\Pi(W) = 0$ everywhere (cf. (3.1.7)) Then the system has a homogeneous distortion, $W(Z) = W_0$.

Next we consider the case that there is a phase coexistence between the shrunken phase and the swollen phase. In equilibrium with a free boundary condition (3.1 7), the phase transition can occur only at the phase transition temperature T_{tr} [11, 6]. This situation is summerized in figure 2a. If, however, we apply an external osmotic force ($-\Pi^{ext}$) on the movable boundary at $Z = Z_0$, we can induce the phase transition even at the temperature $T \neq T_{tr}$ (see Fig. 2b). On the other hand, in the presence of the permeation current $J_v > 0$, the friction between solvent and gel network causes nonzero and inhomogeneous osmotic force within the gel Thus the phase coexistence between the shrunken phase and the swollen phase may occur with an interface at $Z = Z_c$, where the distortion jumps form $W = W_-$ to $W = W_+$ (see Fig. 2c).

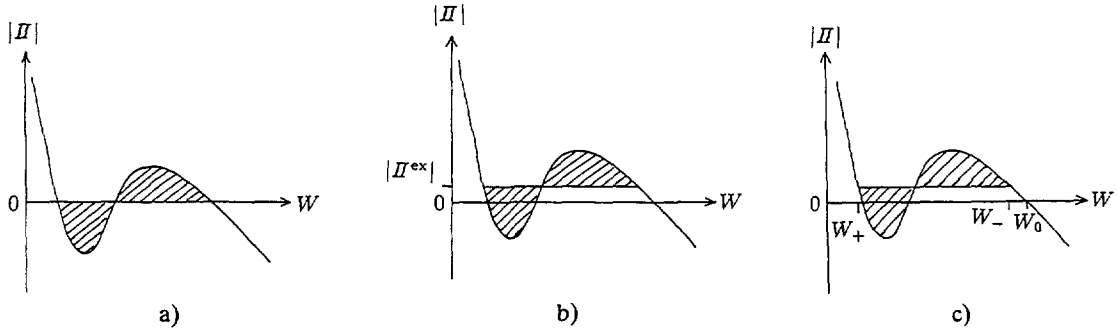

Fig 2 — The osmotic force *vs* the distortion is shown in three situations of phase coexistence in a cylindrical gel (a) Global equilibrium coexistence with a stress-free boundary condition By the Maxwell's construction rule, the two shaded regions are of the same area. (b) Global equilibrium coexistence under an externally applied osmotic force ($-\Pi^{ext}$) (c) Local equilibrium coexistence under the permeation flow J_v The values of distortion, W_- and W_+, are such that the two shaded regions are of the same area The interface is situated where the internal osmotic force is equal to the corresponding value $|\Pi(W_\pm)|$ The distortion at the free boundary, W_0, is determined such that $\Pi(W_0) = 0$

Below we shall describe in detail how we can determine the position of the interface, as well as the boundary values of W at both sides of the interface.

In our treatment of gel from the macroscopic viewpoint, the interface is regarded as an infinitely thin object. First we assume that in the presence of such interface the local equilibrium assumption is still a good assumption. (The validity of this assumption will be discussed afterwards in this subsection) Let us consider a very thin hypothetical layer which includes the interface. Under the local equilibrium assumption we claim that the thermodynamic quantities characterizing the state of this thin layer obey the relations in equilibrium. It means that the values of W on both sides of the interface, W_- and W_+, is determined by the equilibrium coexistence condition [6], which is given as follows in the present notation,

$$\frac{d\alpha(W_-)}{dW_-} = \frac{d\alpha(W_+)}{dW_+} = \frac{\alpha(W_-) - \alpha(W_+)}{W_- - W_+}, \tag{3.1.12}$$

or by using $\Pi = \mathrm{d}\alpha/\mathrm{d}W$ (see (2 5) and the definition of Π given just below (3.1.4)),

$$\Pi(W_-) = \Pi(W_+)\,, \tag{3.1.13}$$

$$\int_{W_-}^{W_+} [\Pi(W) - \Pi(W_\pm)]\,\mathrm{d}W = 0\,. \tag{3.1.14}$$

Equations (3 1 13) and (3.1.14) correspond to the Maxwell construction for the coexistence condition of the two phases. W_+ and W_- correspond to the specific volumes of the swollen and shrunken phases (except for a common constant factor). Since our equilibrium condition is *local*, we do not require W_- to satisfy $\Pi(W_-) = 0$ (cf. (3.1.7)). The boundary condition at the interface between the swollen and the shrunken phase becomes :

$$W(Z = Z_c - 0) = W_-\,; \qquad W(Z = Z_c + 0) = W_+\,. \tag{3 1 15}$$

It is important to note that, as long as we adopt the local equilibrium assumption up to the interface region, there is no room for the flux J_v to play a role In other words we have neglected the effect of finite permeation current on the interface region.

Now we summarize the recipe by which $W(Z)$ is calculated in the system with the interface between the shrunken phase and the swollen phase. First we assume that the temperature T is chosen such that the gel is in the swollen phase in equilibrium This assures that even under the permeation flow the swollen phase with $W = W_0$ is established *at* the free surface (see, (3.1.7)) Under the permeation current, the profile of $W(Z)$ in the swollen region $(Z_0 < Z < Z_c)$ is determined implicitly by (3.1.9). The coordinate Z_c of the interface is determined from (3 1 9) and (3.1.15), giving the result :

$$Z_c - Z_0 = -\frac{1}{J_v}\int_{W_0}^{W_-} \frac{L(W')}{J(W')}\frac{\partial \Pi(W')}{\partial W'}\,\mathrm{d}W'\,. \tag{3 1 16}$$

If the calculated value of Z_c exceeds Z_1, the Z-coordinate of the fixed end of the sample, it indicates that the whole sample of gel is still in the swollen phase. Once we found the value $Z_c(< Z_1)$, the profile in the shrunken region $(Z_c < Z < Z_1)$ is given by

$$Z - Z_c = -\frac{1}{J_v}\int_{W_+}^{W} \frac{L(W')}{J(W')}\frac{\partial \Pi(W')}{\partial W'}\,\mathrm{d}W'\,. \tag{3.1 17}$$

The value of W at the fixed boundary at $Z = Z_1$, which we denote by W_1, is then given by substituting $W = W_1$ and $Z = Z_1$ into the above equation (3.1.7) with $W(Z_0) = W_0$, and (3.1 12) ~ (3 1.17) are summarized in figure 3 The values of W and $|\Pi| = -(\boldsymbol{\Pi}^R)_z^Z$ at the same coordinate Z are related *via* the equilibrium thermodynamic relation $\Pi = \Pi(W)$, which has been shown in figure 2c. Once the distortion W is determined as a function of reference coordinate Z, the actual position of polymer molecules is given by integrating the relation $\mathrm{d}z = W(Z)\,\mathrm{d}Z$.

Two remarks are in order

i) In the above formulae, the coordinate Z is always accompanied by the flux J_v. Thus if the relation $J_v(Z_1 - Z_0) = \bar{J}_v(\bar{Z}_1 - \bar{Z}_0)$ is satisfied for the two setups, say (J_v, Z_0, Z_1) and $(\bar{J}_v, \bar{Z}_0, \bar{Z}_1)$, then the distortions $W(Z)$ and $\bar{W}(Z)$ are related as

$$W(Z_0 + (Z_1 - Z_0)\,\theta) = \bar{W}(\bar{Z}_0 + (\bar{Z}_1 - \bar{Z}_0)\,\theta)\,, \tag{3.1.18}$$

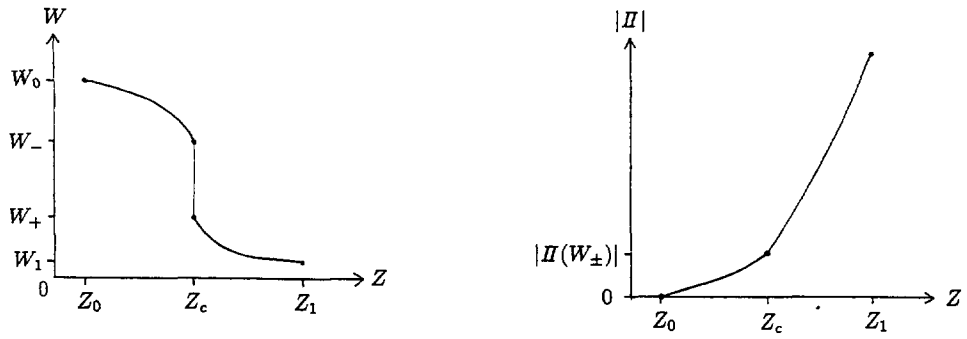

Fig 3 — Distortion W (a) and longitudinal osmotic force $|\Pi| = -(\Pi^R)_z^Z$ (b) are schematically shown as functions of reference coordinate Z

where θ is an arbitrary parameter between 0 and 1. Also the pressure drop $p_0 - p_1$ is the same in the two setups. In the other way to describe this similarity relationship, we can show that for a given pressure drop $p_0 - p_1$, distortion is written $W(Z) = \tilde{W}((Z - Z_0)/(Z_1 - Z_0))$, where $\tilde{W}(\theta)$ is a function of a dimensionless variable θ. If, for example, we prepare two gel rods with lengths L and $2L$ otherwise under the same condition, and if we perform an experiment under the same pressure drop $p_0 - p_1$, then the permeation current in the shorter rod will be twice as large as that in the longer one, while the partition ratio into the two phases will be the same for both samples

ii) If the temperature is made very close to the volume phase transition temperature T_{tr} of the present geometry, the difference $W_- - W_0$ becomes very small Then we can show that we have

$$W_- - W_0 \simeq A(T - T_{tr}), \qquad \text{as} \qquad |T - T_{tr}| \to 0, \tag{3.1.19}$$

where the proportionality constant A depends on the partial derivatives of Π with respect to W and T in a complicated way, since W_- and W_+ are determined through implicit equations (3 1 13) and (3.1 14). We will not show the explicit expression of A Only we note that the above asymptotic linear relation holds either under the fixed permeation current (j_v) or under the fixed pressure drop ($p_0 - p_1$). Since the integrand of (3 1 16) is a non-singular function of its argument near $W = W_-$, we expect that the following approximate relationship among $Z_c - Z_0$, j_v and $T - T_{tr}$,

$$Z_c - Z_0 \propto \frac{1}{j_v} |T - T_{tr}|, \qquad \text{as} \qquad |T - T_{tr}| \to 0 \tag{3 1.20}$$

Since $dz = W(Z)\, dZ \simeq W_0|_{T = T_{tr}}\, dZ$ in this swollen region, the actual length of the swollen region is also proportional to $|T - T_{tr}|$ near the phase transition temperature. Experimentally this relationship may be tested Especially if the thickness of the swollen phase region $Z_c - Z_0$ becomes extremely thin as $|T - T_{tr}| \to 0$, the free surface of gel may not be actually in a swollen phase, and our macroscopic description cannot be applied

The above formalism was based on the local equilibrium assumption. Here we shall examine the validity of this assumption following the van der Waals theory of the interface. We shall regard the interface as a small region of finite thickness across which W varies continuously from W_- to W_+ Since the osmotic compressibility $(\partial\Pi/\partial W)$ becomes negative

between W_- and W_+, such a structure can be stabilized only when an additional nonlocal term is assumed in the free energy density [12]. The nonlocal term depends on the distortion gradient dW/dZ. With this term the free energy is now given by

$$\tilde{\alpha} = \alpha(W) + \xi_{eq}^2 \frac{K(W)}{2} \left(\frac{dW}{dZ} \right)^2, \tag{3.1.21}$$

where $\xi_{eq}^2 K(W)$ is a coefficient related to the second order elasticity of gel network, and we have explicitly factored out the equilibrium thickness of the interfacial region, ξ_{eq}, which acts as smallness parameter. The total free energy A is given as the integral $A = \int \tilde{\alpha} \, dV'$ over the reference volume of gel (It is assumed in (3.1.21) that the higher order gradients of the distortion field $W(Z)$ are negligible. This is not unconditionally acceptable assumption partly because in the interface region this term is not smaller than the bulk term (α), and partly because ξ_{eq} may be of the order of the typical screening length of concentration fluctuation of gel network. Here, however, as a case study, we shall adopt the above model and draw only qualitative conclusions from it.) From (2.5) Π^R is now defined as the functional derivative $\delta A/\delta F$. In the one-dimensional case, this gives

$$\begin{aligned} \Pi &= \frac{\delta}{\delta W} \int dZ \left[\alpha(W) + \xi_{eq}^2 \frac{K(W)}{2} \left(\frac{dW}{dZ} \right)^2 \right] \\ &= \frac{d}{dW} \left[\alpha(W) - \xi_{eq}^2 \frac{K(W)}{2} \left(\frac{dW}{dZ} \right)^2 \right], \end{aligned} \tag{3.1.22}$$

where integration by parts has been performed once and a chain-rule $(dW/dZ)^{-1} \, d/dZ = d/dW$ has been used. (Note that the procedure is similar to that one obtains with Euler-Lagrange equation from Lagrangian [13], and also note that d/dW and d/dZ are usually not interchangeable since $W(Z)$ is generally a nonlinear function of Z)

Hence in place of equation (3 1.4) we have

$$J_v = - \frac{L(W)}{J(W)} \frac{d}{dZ} \frac{d}{dW} \left[\alpha(W) - \xi_{eq}^2 \frac{K(W)}{2} \left(\frac{dW}{dZ} \right)^2 \right] \tag{3.1.23}$$

This second order differential equation with respect to Z determines the profile of $W(Z)$ across the interface.

Slemrod [14] analyzed a somewhat similar problem in the case of liquid-gas interface In the liquid-gas system there is no counterpart of the permeation current, but the mass current through the interface drives off the system from equilibrium He proved that there exists a nonequilibrium interface profile, which tends smoothly to the equilibrium profile as the mass current through the interface goes to zero We assume that this tendency of the interface profile is also the case in our problem of gel permeation, and that, if the permeation current J_v is *sufficiently* small, the profile of $W(Z)$ in the interface region is nearly the same as that of the equilibrium state and that, therefore, the thickness of the interface is $O(\xi_{eq})$.

Now we shall seek for the characteristic magnitude of the permeation current $J_v = J_v^*$ below which the relations (3.1.12) ~ (3 1.15) are a good approximation for the macroscopic description of interface :

First we argue that the above assumption for ξ_{eq} is consistent with our macroscopic boundary condition (3.1 12) ~ (3 1 15) If the interface thickness is $O(\xi_{eq})$, we can neglect the ξ_{eq}^2-term on the right hand side of (3 1 23) as long as we are far from the interface, and thus we find that $J_v = O(\xi_{eq}^0)$. On the other hand in the interface region, we find that the right hand side of (3.1.23) is $O(\xi_{eq}^{-1})$ (note that $d/dZ \sim \xi_{eq}^{-1}$ in this region), while the left hand side

is $O(\xi_{eq}^0)$. Thus the balance must be established basically between the two terms on the right hand side of (3.1.23) in the interface region. This means that in the dominant order of ξ_{eq} the interface profile obeys the equilibrium equation with $j_v = 0$ in (3.1.23). For $j_v = 0$ it is easy to show [14] that (3.1.23) yields the relations (3 1.12) ~ (3.1.15) as the condition for *W far* from the interface as measured in the length scale of ξ_{eq}.

The above argument does not hold if the interface thickness is large (or, alternatively, the current j_v is large) so that the left hand side of (3.1 23) becomes comparable to the right hand side even in the interface region. The magnitude of the right hand side of (3.1.23) in the interface region can be estimated by the contribution from the first term in the square bracket ·

$$-\frac{L(W)}{J(W)}\frac{d}{dZ}\frac{d\alpha(W)}{dW} \sim \frac{L(W)}{\xi_{eq}}\frac{d^2\alpha(W)}{dW^2} \sim \frac{D_{coop}}{\xi_{eq}}. \tag{3.1.24}$$

Here D_{coop} is the cooperative diffusion constant of gel network [15] and we have noted that $d^2\alpha(W)/dW^2$ is proportional to the osmotic compressibility of gel and that $L(W)$ is related to the friction constant between solvent and monomer.

Thus we obtained the characteristic current $j_v^* = D_{coop}/\xi_{eq}$ If the permeation current exceeds j_v^*, the interfacial profile is substantially influenced by the permeation current and, consequently, the boundary condition (3.1.12) ~ (3.1.15) is not applicable. If we admit the scaling relation $D_{coop} \sim T/\xi_{eq}$ [15], we have $j_v^* \propto \xi_{eq}^{-2}$ near the critical point of the volume phase transition Under a permeation flow $j_v > j_v^*$ the interface thickness, however, may not become indefinitely large, because the spatial gradient of W imposed by the mutual friction between solvent and gel monomers will suppress the equilibrium density fluctuation.

3.2 MOVING INTERFACE. — We shall now consider the nonsteady state. Bearing in mind the discussion in the last part of the previous subsection, we here consider only the case where the permeation current j_v is sufficiently smaller than j_v^*. In the bulk region of each phase, the motion of polymer is governed by Darcy's law (2.13),

$$(1-\phi)(u_f^z - \partial_t z(Z,t)) = -L\,\partial_z p\,. \tag{3.2.1}$$

In the one-dimensional case, the volume flux

$$j_v(t) = (1-\phi)\,u_f^z + \phi\,\partial_t z \tag{3.2.2}$$

is independent of Z due to the incompressibility constraint (2.10). Using equation (3.2.2) and the mechanical balance equation (3 1 1), we have

$$j_v(t) - \partial_t z = -\frac{L(W)}{J(W)}\frac{\partial}{\partial Z}\Pi(W)\,. \tag{3.2.3}$$

Since $W = \partial z(Z,t)/\partial Z$, equation (3 2 3) is a parabolic partial differential equation for $z(Z,t)$ If $W(Z,t)$ is a continuous function of Z, this equation can be, in principle, solved under given external conditions such as equations (3 1.7) and (3.1.8) If there is an interface of the swollen phase and the shrunken phase, $W(Z,t)$ becomes discontinuous at $Z_c(t)$, and a special consideration is needed for the motion of the interface.

In general, the motion of the interface involves (a) the local volume change of the gel at the interface, and (b) the solvent permeation toward the interface. Generally the first process (a)

accompanies a mutual friction among the gel monomers and might be a cause of the violation of our assumption of local equilibrium. Below, however, we simply neglect this additional friction at the interface by the following reason . the process (a) is a local process, and its speed is independent of the gel size $Z_1 - Z_0$. On the other hand the process (b) involves the transport of the solvent over the length of the gel size, and becomes very slow for a macroscopic gel. Thus as long as the gel is not extremely small, we may assume that the motion of the gel is limited by the bulk permeation of solvent, and that the molecular conformations at the interface are the same as those in the steady state, which are in turn the same as those in the equilibrium state as we assumed $j_v \ll j_v^*$

Hence we have the boundary condition

$$W(Z_c(t) - 0, t) = W_- ; \qquad W(Z_c(t) + 0, t) = W_+ , \tag{3.2.4}$$

where W_+ and W_- are defined by equations (3.1.12), (3.1 13) and (3.1.14).

Now for a moving boundary, another condition is needed to determine the position of $Z_c(t)$. This is obtained by the condition that the gel is not ruptured at the interface. Notice that at the interface, the deformation $W(Z, t) = \partial z(Z, t)/\partial Z$ and the velocity of a gel point $\partial z(Z, t)/\partial t$ are generally discontinuous (For example if the swollen region in $Z < Z_c(t)$ moves towards the shrunken region in $Z > Z_c(t)$, $W(Z_c(t) - 0, t) > W(Z_c(t) + 0, t)$, and $\partial z(Z, t)/\partial t|_{Z = Z_c(t) - 0} < \partial z(Z, t)/\partial t|_{Z = Z_c(t) + 0}$) The velocity of the interface $dz(Z_c(t), t)/dt$, however, must be common to both phases, and the derivative $dz(Z_c(t), t)/dt = W\, dZ_c(t)/dt + \partial z/\partial t$ evaluated on each side of the interface must agree. Hence

$$W_- \frac{dZ_c(t)}{dt} + \frac{\partial z}{\partial t}\bigg|_{Z = Z_c(t) - 0} = W_+ \frac{dZ_c(t)}{dt} + \frac{\partial z}{\partial t}\bigg|_{Z = Z_c(t) + 0} \tag{3.2.5}$$

or

$$\frac{dZ_c(t)}{dt} = - \frac{\left[\!\left[\dfrac{\partial z}{\partial t} \right]\!\right]}{[\![W]\!]} , \tag{3.2.6}$$

where the double square bracket $[\![Q]\!]$ denotes the difference across the interface ;

$$[\![Q]\!] = Q|_{Z = Z_c(t) + 0} - Q|_{Z = Z_c(t) - 0} . \tag{3.2.7}$$

Using equations (3.2.3) and (3 2 4), we can rewrite equation (3.2.6) as

$$\frac{dZ_c}{dt} = - [\![W]\!]^{-1} \left[\!\!\left[\frac{L(W)}{J(W)} \frac{\partial \Pi}{\partial W} \frac{\partial W}{\partial Z} \right]\!\!\right] , \tag{3.2.8}$$

where we have noted that $j_v(t)$ is continuous at the interface Since the values of W at both sides of the interface are fixed at W_+ and W_-, equation (3 2 8) is written as

$$\frac{dZ_c}{dt} = - K_+ \frac{\partial W}{\partial Z}\bigg|_{Z = Z_c(t) + 0} + K_- \frac{\partial W}{\partial Z}\bigg|_{Z = Z_c(t) - 0} , \tag{3.2.9}$$

where

$$K_+ = \frac{1}{W_+ - W_-} \left(\frac{L(W)}{J(W)} \frac{\partial \Pi}{\partial W} \right)_{W = W_+} \tag{3 2.10}$$

and

$$K_- = \frac{1}{W_+ - W_-} \left(\frac{L(W)}{J(W)} \frac{\partial \Pi}{\partial W} \right)_{W = W_-} . \tag{3.2.11}$$

Equations (3.2.4) and (3.2.9) are the boundary conditions for the moving interface. In the steady state of $dZ_c(t)/dt = 0$, this condition of course reduces to the condition of (3 2.4). The velocity of the interface in the real space is written as

$$\frac{dz(Z_c(t), t)}{dt} = J_v - W_- K_+ \frac{\partial W}{\partial Z}\bigg|_{Z = Z_c(t)+0} + W_+ K_- \frac{\partial W}{\partial Z}\bigg|_{Z = Z_c(t)-0} . \quad (3.2.12)$$

4. Moving interface in the three-dimensional geometry.

4.1 BOUNDARY CONDITIONS AT THE INTERFACE. — Having seen the basic physics, we shall now discuss the boundary conditions in the general three-dimensional case.

First it should be noted that in the three-dimensional case, a new problem may arise due to the curvature of the interface. It is known that in a system of liquids, the curvature of the interface generally affects the chemical potential of the molecules, and changes the coexistence condition. As it was argued, however, in the previous paper [16], the driving force for the morphological change of gels predominantly comes from the bulk energy, and the interfacial energy is negligible unless the gel is extremely small. We shall therefore neglect the effect of curvature of the interface and the interfacial energy in the subsequent discussion.

Consider a point $\mathbf{X}_c$ on the interface in the reference space. Since the distortion near the interface can be regarded as locally one-dimensional with an arbitrary shear deformation, the distortion $\mathbf{x}(\mathbf{X})$ of a point $\mathbf{X}$ near $\mathbf{X}_c$ can be written as (time argument is temporarily suppressed) :

$$\mathbf{x} = \mathbf{x}(\mathbf{X}_c) + \tilde{\mathbf{x}}(\hat{\mathbf{N}} \cdot (\mathbf{X} - \mathbf{X}_c)) + \mathbf{F}_c^{\perp} \cdot (\mathbf{1} - \hat{\mathbf{N}}\hat{\mathbf{N}}) \cdot (\mathbf{X} - \mathbf{X}_c) , \quad (4\ 1)$$

where $\hat{\mathbf{N}}$ is the unit vector normal to the interface in the reference space, and $\tilde{\mathbf{x}}(\eta)$ is a function describing a sharp change of distortion across the interface. For simplicity we have defined $\tilde{\mathbf{x}}(0) \equiv 0$ $\mathbf{F}_c^{\perp}$ is a constant matrix which describes constant distortion on the interface (Fig. 4) (In the next order approximation $\mathbf{F}_c^{\perp}$ will be replaced by a function $\mathbf{F}_c^{\perp}(\eta)$, which varies smoothly at $\eta = 0$.)

From (4 1) the distortion $\mathbf{F}$ is given as

$$\mathbf{F} = \frac{d\tilde{\mathbf{x}}}{d\eta} \hat{\mathbf{N}} + \mathbf{F}_c^{\perp} \cdot (\mathbf{1} - \hat{\mathbf{N}}\hat{\mathbf{N}}) \quad (4.2)$$

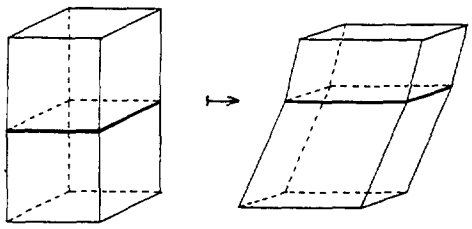

Fig 4 — Distortion of gel near the interface is shown schematically both in the reference space (a) and in the actual space (b). The interface position is denoted by a plane bounded by thick lines The cross sections parallel to the interface does not change their shape across the interface This corresponds to the continuity of $\mathbf{F}_c^{\perp}$ across the interface in the next

Since the argument given in section 3.1 should also be valid in the three-dimensional case, the boundary condition at the interface is the same as for the equilibrium case [6] In the present notation, it is written as ·

$$[\![\hat{\mathbf{N}} \cdot \boldsymbol{\Pi}^{\mathrm{R}}]\!] = \mathbf{0}\,, \tag{4.3}$$

$$\left[\!\!\left[\alpha - \hat{\mathbf{N}} \cdot \boldsymbol{\Pi}^{\mathrm{R}} \cdot \frac{\mathrm{d}\tilde{\mathbf{x}}}{\mathrm{d}\eta} \right]\!\!\right] = 0\,, \tag{4 4}$$

where $[\![Q]\!]$ denotes the jump of Q across the interface, i.e.,

$$[\![Q]\!] = Q|_{\eta = +0} - Q|_{\eta = -0}\,, \tag{4.5}$$

and α and $\boldsymbol{\Pi}^{\mathrm{R}}$ have been defined in the previous section. $\hat{\mathbf{N}} \cdot \boldsymbol{\Pi}^{\mathrm{R}}$ and $\mathrm{d}\tilde{\mathbf{x}}/\mathrm{d}\eta$ respectively correspond to Π and W in the one-dimensional geometry. If we introduce the notation $\mathbf{P} \equiv \hat{\mathbf{N}} \cdot \boldsymbol{\Pi}^{\mathrm{R}}$ and $\mathbf{W} \equiv \mathrm{d}\tilde{\mathbf{x}}/\mathrm{d}\eta$, (4.3) and (4.4) can be rewritten in a way that corresponds to (3.1.13) and (3.1.14),

$$\mathbf{P}(\mathbf{W}_+) = \mathbf{P}(\mathbf{W}_-)\,, \tag{4 6a}$$

$$\int_{W_-}^{W_+} [\mathbf{P}(\mathbf{W}) - \mathbf{P}(\mathbf{W}_\pm)] \,.\, \mathrm{d}\mathbf{W} = 0\,, \tag{4 6b}$$

where $\mathbf{W}_\pm$ denotes $\mathbf{W}|_{\eta = \pm 0}$ This may be regarded as the vector version of Maxwell construction, and the integral in (4.6b) can be shown to be path-independent.

4.2 INTERFACE VELOCITY. — The bulk of the domains of each phase obeys equations (2.8), (2.10), (2.11) and (2.13) supplemented with the boundary conditions (4.3) and (4.4). The interface velocity is determined in the manner similar to that in the one-dimensional case

Suppose that in the reference space, $\mathbf{X}_{\mathrm{c}}(t)$ is a moving point which stays on the interface The local velocity of interface V_{int} is given as

$$V_{\mathrm{int}} = \hat{\mathbf{N}} \cdot \dot{\mathbf{X}}_{\mathrm{c}}(t)\,, \tag{4 7}$$

where $\hat{\mathbf{N}}$ is the unit normal at time t. Using the condition that the time derivative $\mathrm{d}\mathbf{x}_{\mathrm{c}}(t)/\mathrm{d}t \equiv \mathrm{d}\mathbf{x}(\mathbf{X}_{\mathrm{c}}(t), t)/\mathrm{d}t$ must be the same in both phases, we have

$$[\![\mathbf{F}]\!] \cdot \dot{\mathbf{X}}_{\mathrm{c}}(t) + [\![\dot{\mathbf{x}}]\!] = \mathbf{0} \tag{4.8}$$

If we denote by $\hat{\mathbf{n}}$ the unit normal vector of the interface in the actual space, $\hat{\mathbf{N}}$ can be expressed as

$$\hat{\mathbf{N}} = \frac{\hat{\mathbf{n}} \cdot \mathbf{F}}{|\hat{\mathbf{n}} \cdot \mathbf{F}|} \tag{4.9}$$

(Here $\mathbf{F}$ must be evaluated on either one side of the interface.) Thus from (4 7), (4.8) and (4 9), we obtain the interface velocity V_{int},

$$V_{\mathrm{int}} = -\frac{[\![\hat{\mathbf{n}} \cdot \dot{\mathbf{x}}]\!]}{[\![\,|\hat{\mathbf{n}} \cdot \mathbf{F}|\,]\!]} \tag{4 10}$$

5. Conclusion.

We have discussed the dynamics of interface of gels undergoing volume phase transition. Permeation of solvent through the interface has been taken into account. It was shown that the rate determining process of motion of interface is the permeation of solvent through the bulk domains and, consequently, that an equilibrium phase coexistence condition applies to the interface region as long as the permeation current is sufficiently small. The threshold current is estimated to be $J_v^* \equiv D_{coop}/\xi_{eq}$, where D_{coop} is the cooperative diffusion constant of gel network and ξ_{eq} is the equilibrium thickness of the interface. We found that, near the equilibrium phase transition temperature T_{tr} (but still in the side of the swollen phase), the thickness of the swollen phase region under permeation current should behave like $\propto \frac{1}{J_v} |T - T_{tr}|$ This prediction may be tested experimentally Generalization to three-dimensional case is also discussed.

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