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Elastic Instability of Gels Upon Swelling

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1. Introduction

Gels are the deformable solids which consist of three-dimensional networks and the solvents saturating these networks. The networks are made, for example, of cross-linked polymers. Some of the gels exhibit the phase transition (so called the volume-phase transition) upon which the volume fraction of the monomers of the network (the network fraction, for short) changes discontinuously (1). The transition is due to the competition between the interaction energies among the molecules of the gel and the configurational entropy of the network and the solvent.

For the gel samples immersed in a pure solvent with no mechanical constraints the equilibrium network fraction is given as the function of the temperature (Fig. 1). On this curve, the condition for the osmotic equilibrium is satisfied between the

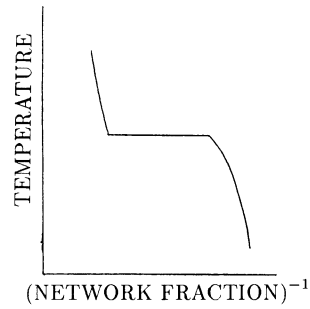

Fig. 1. A typical equation of state is shown schematically in the plane of the temperature and the inverse of the network fraction, or the envelope volume occupied by the gel sample.

solvent in the gel and the pure solvent surrounding the gel. If we attach the boundary of the gel sample (or, more precisely, the monomers on the surface part of the network of the gel) to the inner wall of a rigid container, then there can occur the spatial phase separation for a certain range of temperature. While phase separation seems like that observed in binary fluid mixtures, the situation is not so simple in the case of gels: Since the order parameter of the volume-phase transition is related to the elastic strain of the system, we always have to take into account the effect of the shear strain induced either by imposition of the boundary condition or by the occurrence of the phase separation (2). This point can be understood by the example shown in Fig. 2: Unlike in the case of binary fluid mixtures we cannot realize within a single gel sample the spatial phase coexistence between the isotropic swollen phase domain and the isotropic shrunken phase domain without introducing the cuts or the reconnections into the network. (Also for the phase separation in the binary alloys, it is known that the internal strain caused by the phase separation sometimes has important effects even if the strain itself is very small (3)).

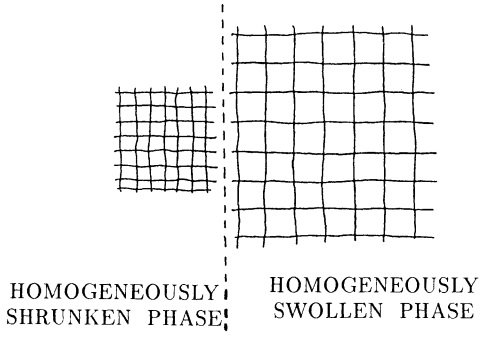

Fig. 2. Illustration of the fact that, if the topological defects in the networks are not allowed, the strong shear deformation must occur in the region between of the domains with different degrees of swelling.

Below, we describe the framework of the elasticity theory for the small distortion from the uniformly and finitely strained states of gels (Section 2 (2)). We then show in Section 3 the results of the simulation of the large distortion in a two-dimensional model gel (4).

2. Linear Stability

First we describe the linear stability of the uniformly strained gel whose boundary is attached to the inner walls of a rigid container. We define the reference state of a gel as the strain-free state at a certain temperature. Then imagine that we

stretch or squeeze the sample uniformly by the factors $\alpha_\perp$, $\alpha_\perp$ and $\alpha_\parallel$ in the directions, respectively, along x, y and z axes (Fig. 3). After that, we attach the sample to the walls of the containter without changing the shape of the sample. The free energy of the gel in this uniaxially deformed state is the function of $\alpha_\perp$ and $\alpha_\parallel$ as well as the temperature and the chemical composition of the solvent. In the continuum description, we denote by $\vec{u}(x, y, z)$ the small displacement of the network. Using the general theory of elasticity (5) the excess free energy F due to the displacement can be expressed up to the second order of $\vec{u}$ as follows:

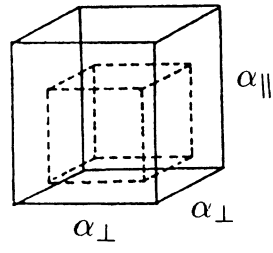

Fig. 3. The gel in the reference state (the unit cube shown by the dashed lines) is deformed uniaxially by the ratio $\alpha_\parallel$ along the z axis and by the ratio $\alpha_\perp$ the transverse directions. At this state the surfaces of the gel are attached to the inner walls of the rigid container. (Such a uniformly deformed state sometimes may be attained either by mechanical straining or by changing the temperature of the gel under an appropriate mechanical constraints.)

$$F = \int dxdydz \left(\frac{K}{2} \sum_i \left(\frac{\partial u_i}{\partial x_i} \right)^2 + \mu \sum_{ij} \left\{ \frac{1}{2} \left(\frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j} \right) - \frac{\delta_{ij}}{3} \sum_k \frac{\partial u_k}{\partial x_k} \right\}^2 \right.$$

$$+ L \sum_i \frac{\partial u_i}{\partial x_i} \left(\frac{\partial u_z}{\partial z} - \frac{1}{3} \sum_k \frac{\partial u_k}{\partial x_k} \right) + 2M \sum_i \left\{ \frac{1}{2} \left(\frac{\partial u_z}{\partial x_i} + \frac{\partial u_i}{\partial z} \right) - \frac{\delta_{iz}}{3} \sum_k \frac{\partial u_k}{\partial x_k} \right\}^2$$

$$+ \frac{N}{2} \left(\frac{\partial u_z}{\partial z} - \frac{1}{3} \sum_k \frac{\partial u_k}{\partial x_k} \right)^2 + S |\mathrm{rot}\, \vec{u}|^2$$

$$\left. + S' \left\{ \left(\frac{\partial u_z}{\partial x} - \frac{\partial u_x}{\partial z} \right)^2 + \left(\frac{\partial u_z}{\partial y} - \frac{\partial u_y}{\partial z} \right)^2 \right.$$

$$-2\left[\left(\frac{\partial u_z}{\partial x}\right)^2+\left(\frac{\partial u_z}{\partial y}\right)^2-\left(\frac{\partial u_x}{\partial z}\right)^2-\left(\frac{\partial u_y}{\partial z}\right)^2\right]\Bigg\} + \text{constant.}$$

The integral is done over the whole volume of the gel sample. The elastic constants K, μ, etc. are the functions of the temperature, $\alpha_\perp$ and $\alpha_\parallel$. Especially K and μ are, respectively, the bulk modulus and the shear modulus which also appear in the elasticity theory of isotropic media. Among the other moduli, L, M and N, are the moduli peculiar to the elastic media with uniaxial anisotropy. The last terms including the moduli S and S' are the terms which does not appear in the usual elasticity theory. These terms appear due to the fact that we have imposed the global strain on the system before we attach it to the containter wall. Even in the case of $\alpha_\perp = \alpha_\parallel$ the term $S\,|\mathrm{rot}\,\vec{u}|^2$ remains.

These terms including S and S' have the feature that, upon the rotation of the coordinate system which yields the apparent displacement $\vec{u}(\vec{r}) = \vec{\theta} \times \vec{r}$ (here $\vec{\theta}$ is the vector defining the rotation), these terms have contributions of the order of $|\vec{\theta}|^2$. Such contributions seems to be in contradiction with the natural requirement of the rotational invariance of the free energy to that order. The key to solve this paradox is in the constant term on the right hand side of the above expression of F. For example in the case of isotropically strained gel ($\alpha_\perp = \alpha_\parallel$), this term is the volume integral of the quantity $4S\,\mathrm{div}\vec{u}$, the integral which in fact vanishes due to the boundary conditions on the wall of the container. The presence of $O(\vec{u})$ terms is due to the fact that the system under mechanical constraint is not in the true equilibrium. Upon the rotation of the coordinate system by $\vec{\theta}$ these terms of $O(\vec{u})$ yields the contribution of the order of $|\vec{\theta}|^2$, which can be shown to exactly cancel point by point the above mentioned $\sim|\vec{\theta}|^2$ contributions from the $O(\vec{u}^2)$ terms. Thus the rotational symmetry is recovered locally upon addition of the last $O(\vec{u})$ terms, and this fact tells us that it is necessary to distinguish the expansion in powers of the displacements from the expansion in powers of the small angle rotation.

The $O(\vec{u}^2)$ terms of F determines the linear stability of the mechanically constrained gel, and to analyze this we decompose these terms using the normal modes of deformations. Neglecting tentatively the effects of the boundaries, we assume the following form of deformation:

$$\vec{u}(x,y,z) = \vec{u}_0 \exp(ikx + iqz)$$

Then the condition of the instability is defined as that, in the following eigenvalue problem

$$\begin{bmatrix} R_{xx}^{\parallel}k^2 + R_{xx}^{\perp}q^2 & R_{xz}kq \\ R_{xz}kq & R_{zz}^{\parallel}k^2 + R_{zz}^{\perp}q^2 \end{bmatrix} \begin{bmatrix} u_x \\ u_z \end{bmatrix} = \lambda \begin{bmatrix} u_x \\ u_z \end{bmatrix},$$

one of the eigenvalue vanishes for a certain value of k/q. Here the coefficients $R_{xx}^{\parallel}$, etc. depends on the temperature, $\alpha_{\perp}$ and $\alpha_{\parallel}$ through the combinations of the elastic moduli described above. (Here we disregarded the purely transversal modes, $\vec{u}_0 \parallel$ y-axis, which are stable.) The instability conditions are further reduced to that the instability occurs if in the parameter space (J_1, J_2, J_3) defined as

$$J_1 \equiv R_{xx}^{\parallel} R_{zz}^{\parallel}$$

$$J_2 \equiv R_{xx}^{\perp} R_{zz}^{\perp}$$

$$J_3 \equiv \left(R_{xx}^{\parallel} R_{zz}^{\perp} + R_{xx}^{\perp} R_{zz}^{\parallel} - R_{xz}^2 \right) / 2$$

either one of the inequalities $J_1 > 0, J_2 > 0$ and $J_3 > -(J_1 J_2)^{1/2}$ is violated. There are three types of the modes of the instability, according to which of these inequalities is violated, as shown in Fig. 4. These modes have, respectively, Ising, XY and

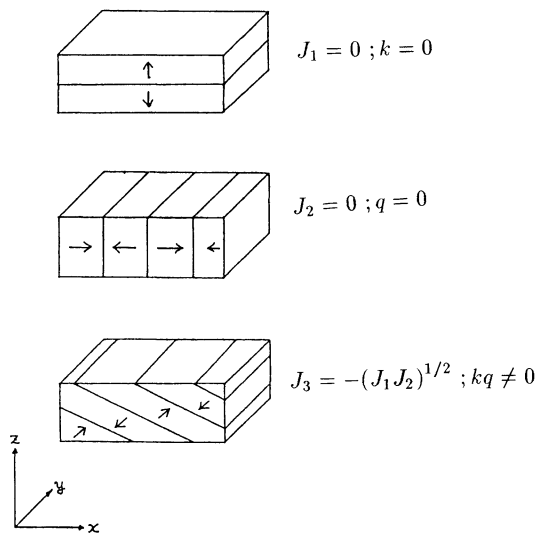

Fig. 4. The three modes of the mechanical instabilities in the infinite bulk of gel. The arrows in the figures schematically show the directions of the displacement field $\vec{u}$, and the solid lines show the instantaneous nodal planes of the displacement. All the directions within the xy-plane are equivalent.

"oblique" symmetry. The unstable fluctuations belonging to these modes will contribute to the anisotropic light scattering near the spinodal. We do not know, however, whether the oblique type of instability ($kq \neq 0$) can be realized in nature. For the model free-energy proposed by Flory (1), which is often used in analyzing the experiments and in theoretical calculations (1, 6), we can prove the inequality $(J_1+J_2)/2 \geq J_3 \geq (J_1 J_2)^{1/2}$, and therefore, the oblique type instability is not accessible by that model. The nonlinear or large amplitude fluctuation cannot be predicted from the above linear analyses alone.

Thus far we have ignored the effect of the boundaries of the container. This is justified by the following argument: In the present framework of elasticity theory, which does not include in F the higher derivatives of $\vec{u}$ than the first order, there are no characteristic length scale other than the dimensions of the integration volume. As the result, the eigenvalues λ (see above) in the case of infinitely large gels are the second order homogeneous function of $\vec{k}$. The destabilization, $\lambda(\vec{k}) = 0$, in the infinite bulk gel therefore occurs at a special direction of $\vec{k}$ with arbitrary magnitude, $|\vec{k}|$. On the other hand when the sample is bounded by the fixed boundaries separated at a distance, say L ($<\infty$) from each other, the eigenmodes are constructed from plane waves so as to satisfy the boundary conditions. And, among these modes, those with the wavelength larger than $\sim L$ are relatively stabilized by the presence of the rigid boundaries (2). Thus the instability in the finite system with fixed boundaries first occurs at those modes with infinitely short wavelengths and hence the condition of destabilization is not affected by the system boundaries.

The above argument must be modified when there are the stress-free boundaries. In the presence of the stress-free boundaries there appears the branch(es) of the "surface sound modes" which are localized near these boundaries. The short wavelength modes of this branch become unstable before all the other bulk modes. It is the undulation and partial folding of the stress-free surfaces, not the spinodal decomposition within the bulk, that are lead by the instability of the surface sound modes; even when the partial folding of the surface appears, the bulk modes can still be stable. This can be also seen in the numerical simulation (see the next section).

3. Model Simulation of Large Deformations

The model we have used in the simulation is as follows: By connecting the Hookean springs with the identical natural length l_0 we construct the two dimensional triangular network. The natural length l_0 is the important parameter of the system. The bottom array of the nodes joining the springs are fixed on the straight line with the separation between the neighboring nodes on this line being fixed to be unity. We impose the periodic boundary condition in the horizontal direction parallel to the bottom line. As for the topmost array of the nodes, we have considered (1) the case of the fixed boundary on which the nodes are fixed in the way similar to those nodes on the bottom line, (Fig. 5), and (2) the case of free nodes, simulating

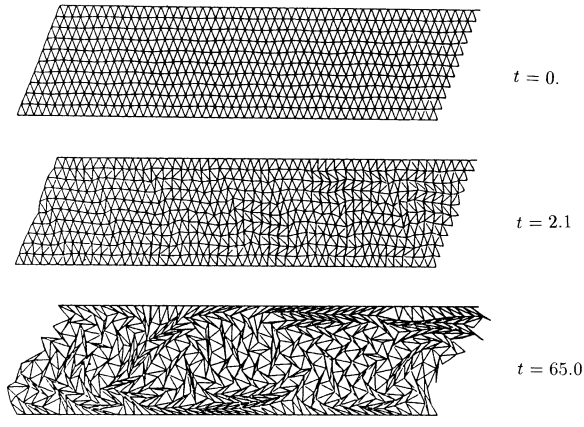

Fig. 5(a). The relaxation of the system with the fixed top and bottom boundaries. The unit of time t is of the order of the relaxation time of individual springs. The initial evolution is governed by the linear instability. The mesh size on the boundaries is taken to be unity.

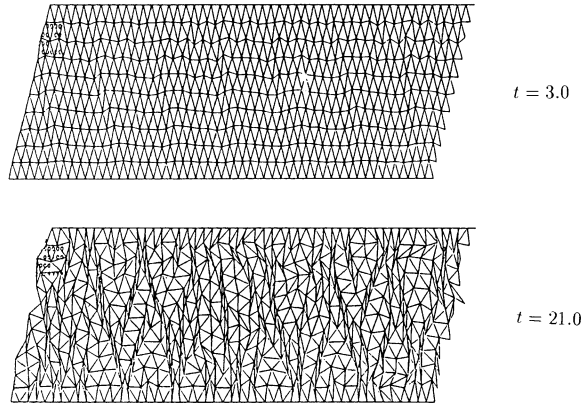

Fig. 5(b). The similar calculation to 5(a) with the wider gap between the fixed boundaries.

the stress-free surface (Fig. 6). Besides the Hookean springs we added the three body potentials for each angle between the adjacent springs joined to a node so that they exert strong repulsive forces when the angles become less than ≈ 0.01 rad. We let the system relax from the initial configuration to the final one which corresponds to the (local) minimum of the total energy, using the relaxational molecular dynamics method, in which every node is displaced at each timestep in a way that the displacement of the node is proportional to the sum of the forces acting on the

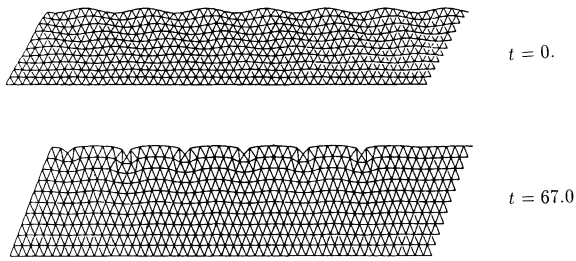

Fig. 6(a). The relaxation of the system with the stress-free boundary on the top. The natural length of each spring is $l_0 = 1.45$.

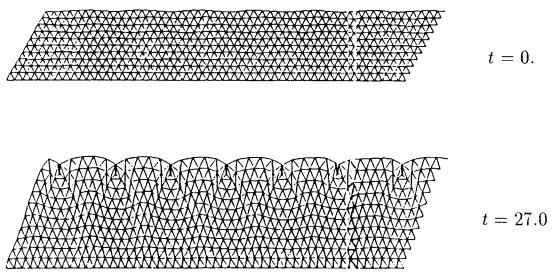

Fig. 6(b). The similar calculation to 6(a) with the natural length chosen as $l_0 = 1.60$.

node. The computation was carried out at the Institute of Plasma Physics of Nagoya University as the part of a joint research program of the Institute.

In Fig. 5 we have fixed both the top and the bottom boundaries and l_0 was set as $l_0 = 2.5$. In the case of the narrow gap between these boundaries (Fig. 5(a)) the short wavelength fluctuations in the initial linear stage evolve into the large distortion with some structures. The locally ordered structure in the mid part of the gap seems to be the artifact of the descretization employed in the present model. On the other hand in the case of the wider gap between the fixed boundaries (Fig. 5(b)) there appear the bands consisting of the strongly sheared triangular elements, and each of these bands connects the two horizontal boundaries. Between these strongly sheared bands, there are the domains of the swollen and fairy isotropic triangular elements. Unlike the domain wall of ferromagnets, these strongly sheared bands we observed are not the topological defects and thus have no homotopical characterizations. The new theoretical framework would be needed which could characterize (apparently) non-topological defects such as these sheared bands and the cusps on the stress-free surface which we describe below.

Figure 6 shows the cases with the stress-free top surface. The natural lengths

were chosen to be $l_0 = 1.45$ (Fig. 6(a)) and $l_0 = 1.60$ (Fig. 6(b)). In both cases, the initial condition is the nearly perfect regular triangular networks with the weak periodic modulation along the horizontal direction. The amplitude of the initial modulation was chosen to be an increasing function of the distance from the bottom surface. In the former case the cusps are formed in the long time while the bulk remains stable under the influence of the deformed surface. (We have also studied the case with $l_0 = 1.35$ which is not shown. In that case, the system converges to the uniaxially stretched uniform state.) For the larger values of l_0 (Fig. 6(b)) the cusps develops deeper into the bulk and the partial folding of the surface occurs. There is an analysis of the partial folding (6). Other simulation with the stress-free surfaces were also done starting from the regular triangular network with the minimal displacements due to cutoff errors. When the natural lengths were chosen to be the same as those in the above figures, an aperiodic array of the cusps have appeared, where the typical separation distances among them are the order of the distance between the top and the bottom surfaces. Such observation is in accordance with the experiments by the MIT group (1). When we choose much larger natural length, $l_0 = 2.50$, the instability occurred also within the bulk as well as at the stress-free surface, and complicated patterns of deformations appeared (7).

4. Conclusion

We have reviewed our study on the mechanical aspects of gels using the linear stability analysis and the model simulation of the nonlinear elastic deformations. The other aspects of the gel physics from the view points of the hydrodynamics, the statistical mechanics of polymer networks, the chemistry of solutions, the statistical mechanics of random systems, etc. also await further developments.

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