Theory of pattern formation in gels: Surface folding in highly compressible elastic bodies

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Gels are highly compressible elastic bodies near the volume phase transition. They undergo large elastic deformations that cannot be described within the usual elastic theory. A theoretical framework is proposed to incorporate a nonlinear elastic theory into the Ginzburg-Landau theory of phase transition. Then we analyze patterns emerging on the upper surface of uniaxially deformed gels whose lower surface is clamped to a substrate. On the upper surface a two-dimensional spinodal decomposition is shown to occur when the elongation ratio exceeds a critical value. If the gel is uniaxially stretched and sufficiently compressible, the surface eventually folds itself, yielding periodic cusps in the late stage of the coarsening process. The folded parts are singular surfaces like cracks in solids accompanied by large strains. Developing some mathematical techniques, we properly take into account a drastic change of the boundary conditions at the folded parts, but elastic deformations inside the gel are treated within a linear theory around uniaxial homogeneous states. We also find that the cusp pattern exists only in a limited region of the parameter space, outside which it is still an open question as to what kinds of patterns emerge in final stages of the spinodal decomposition. We expect corrugated surfaces without folding when the gel is uniaxially stretched and rather incompressible or when it is uniaxially compressed near the critical point.

I. INTRODUCTION

It is now well known that polymer gels can change their volume drastically as a first-order phase transition, through a small change of some external parameter.[1] As a striking observation, Tanaka found that transient patterns consisting of numerous line segments of cusps emerge on the surface in the course of swelling when the volume change is large.[2] Furthermore, he showed that the same patterns can be formed permanently in equilibrium gels whose lower surfaces are fixed to a substrate and whose upper surfaces are in contact with a solvent. In these cases, the gels are uniaxially stretched in the direction normal to the surface and compressed in the lateral directions. It may be expected that a mechanical instability should be triggered for sufficiently large lateral osmotic pressure producing some buckling of the outer surface. Tanaka tried to estimate the free-energy change due to emergence of periodic corrugations on the surface. Although his *theory* is questionable,[2] he could see that it can be negative if the system is compressed in the lateral directions. However, the essential aspect of the phenomenon is that the pattern observed in gels is not composed of mere corrugations, which are still in contact with the solvent, but consists of *cusps into the gel,* as Tanaka himself stated.[2] More precisely, it is periodically folded parts on the surface in contact with themselves, as recently found theoretically.[3] Therefore, it is now very desirable to develop mathematical theory to clarify the elastic structure of the pattern and the conditions of its observation. We expect that such an analysis should have a bearing on a number of patterns in elastic materials, such as those in phase-separating alloys.[4] We also notice that the pattern in gels closely resembles that of brain surfaces.

Initial theories have treated clamped gels, which are easier to study than swelling gels. Sekimoto and Kawasaki have shown that an elastic model system with uniaxial symmetry readily becomes linearly unstable against small sinusoidal perturbations if its lower surface is clamped and its upper surface is freely deformable.[5] The present author has incorporated a classical theory of nonlinear elasticity with the usual scheme of phase transition[6,7] where the order parameter is the deformation tensor of gels. The minimum condition of the free-energy functional then leads to equations for inhomogeneous patterns.[3] The free energy has been shown to be lowered below its value in the homogeneous state when the surface folds itself periodically. Details of these results will be explained in this paper. Interestingly, the mathematics for the pattern has turned out to be very similar to that for fractures in elastic bodies.[8] In both the cases, fundamental elements of the phenomena are surface singularities, folded parts or cracks, accompanied by large elastic strains. Their mathematical structure may be clarified by regarding them as superposition of dislocations (which will not be discussed here, however). Subsequent numerical simulations on simple elastic networks by Hwa and Karder,[9] and by Sekimoto and Kawasaki[10] have confirmed that the surface tends to touch and fold as surface corrugations grow. However, to realize the folding in simulation, new computation rules are required to assure the condition that the gel is not penetrable into itself. By this reason, the simulations so far seem to have not realized the folding unambiguously.

This paper is organized as follows. In Sec. II we explain a framework of nonlinear elasticity incorporated into the Ginzburg-Landau theory of phase transition. This framework is now giving rise to a number of new predictions unique to gel, and the pattern of our concern cannot be described by the usual elastic theory of isotropic bodies.[11,12] In Sec. III we will show that the upper surface of uniaxially clamped gels undergoes a spinodal decomposition if the elongation ratio $\alpha_\parallel$ exceeds a certain critical value. In Sec. IV we will calculate the cusp pattern which is the final equilibrium state after the onset of the instability in some parameter region. The approximation scheme used is a linear theory around uniaxial homogeneous states, although it is still inadequate. In Sec. V we will first calculate the free-energy change due to the periodic cusp formation in the linear theory. It can be surely negative, but the linear theory will turn out to be insufficient to determine both the depth of the folding d and the period $L_\perp$ as optimal values minimizing the free energy. To find d and $L_\perp$ we need to take into account nonlinear elastic effects. However, such calculations will not be presented in this paper due to great mathematical difficulties encountered. Instead, we will propose an expansion of the free energy in powers of $d/L_\perp$ and $L_\perp/L_\parallel$ where $L_\parallel$ is the gel thickness. Then we can derive some conjectural predictions on the behavior of d and $L_\perp$. In Sec. VI concluding remarks will be given.

II. ELASTIC MODEL FOR GELS

We are interested in gels swollen by a θ or poor solvent. Let ΔF be the Gibbs free-energy change after the mixing of the solvent and an initially pure, unstrained polymer network.[13] When the gel is isotropic and is immersed in a pure solvent, ΔF is a thermodynamic potential satisfying the thermodynamic relation $d(\Delta F) = -(\Delta S)dT + \Pi dV$ as a function of the temperature T and the volume V.[14] Here ΔS is the entropy change after the mixing and Π is the osmotic pressure. If ΔF is expressed as a function of T and V (or the polymer volume fraction $\phi \propto 1/V$), we can then examine the phase transition in which V is the order parameter. This has been the usual approach so far.[15,16]

However, if we are interested in phase transitions in anisotropically deformed gels or in inhomogeneous patterns, we must express ΔF more generally in terms of the deformation tensor

$$\Gamma_{ij} = \partial X_i / \partial x_j^0 \ . \tag{2.1}$$

Here $\mathbf{X} = (X_1, X_2, X_3)$ are the Cartesian coordinates of the deformed gel representing the real spatial position, while $\mathbf{x}_0 = (x_1^0, x_2^0, x_3^0)$ are those in some reference relaxed state representing the original position before deformation. The classical rubber theory suggests that the simplest form for ΔF in terms of Γ_{ij} is given by[17,18]

$$\Delta F = k_B T \int_V d\mathbf{X} \left[f(\phi, T) + \tfrac{1}{2}\nu_0 \left[\frac{\phi}{\phi_0} \right] I_1 \right] + \Delta F_{\text{inh}} \ , \tag{2.2}$$

where the integral is within the volume V of the deformed gel, and ϕ is related to the determinant of the deformation tensor by

$$\frac{\phi_0}{\phi} = \det \left[\frac{\partial X_i}{\partial x_j^0} \right] \ , \tag{2.3}$$

ϕ_0 being the volume fraction in the relaxed state. The function $f(\phi, T)$ is the ordinary mixing free energy plus the ionization free energy (if the network is ionized) per unit volume divided by $k_B T$.[13,16] Its dependence on ϕ and T will be suppressed for simplicity. The parameter ν_0 represents the effective chain density in the relaxed state.[13] We may introduce an effective polymerization index N by $\nu_0 v_0 = \phi_0 / N$, where v_0 is the volume of one polymer segment. The quantity I_1 is the so-called first invariant in the nonlinear elasticity theory:[18]

$$I_1 = \sum_{i,j} \left[\frac{\partial}{\partial x_j^0} X_i \right]^2 \ . \tag{2.4}$$

The last term ΔF_{inh} is the gradient free energy indispensable in describing short wavelength fluctuations and phase separation.[19] It will be neglected, however, in this paper for the purpose of presenting a first-simplest theory of the pattern. Here it is convenient for later variational calculations to rewrite ΔF as the integral over the original coordinates $\mathbf{x}_0$ as

$$\Delta F = k_B T \int_{V_0} d\mathbf{x}_0 \left[\frac{\phi_0}{\phi} f(\phi) + \tfrac{1}{2}\nu_0 I_1 \right] \ , \tag{2.5}$$

where use has been made of (2.3) and the integration region is within the volume V_0 of the relaxed state.

In any elastic theory the expression for the stress tensor Π_{ij} is of prime importance.[18] It can be obtained, once we have the free energy, as follows. We deform the gel infinitesimally as $X_i \to X_i + \delta X_i$. Then the resultant change in ΔF should be of the form

$$\begin{aligned} \delta(\Delta F) &= -\int_V d\mathbf{X} \sum_{i,j} \Pi_{ij} \left[\frac{\partial}{\partial X_j} \delta X_i \right] \\ &= -\int_{\partial V} d\sigma \sum_{i,j} n_j \Pi_{ij} \delta X_i + \int_V d\mathbf{X} \sum_{i,j} \left[\frac{\partial}{\partial X_j} \Pi_{ij} \right] \delta X_i \ . \end{aligned} \tag{2.6}$$

The first term on the second line is the work exerted from the outside on the surface, $d\sigma$ and n_i being the surface element and the outward unit normal vector, while the second term is the change within the elastic body due to mechanical disequilibrium. Note that the volume element $d\mathbf{X}$ is equal to $d\mathbf{x}_0(\phi_0/\phi)$ from (2.3). The variational change of ΔF can be readily obtained from (2.5) as

$$\begin{aligned} \delta(\Delta F) = k_B T \int_{V_0} d\mathbf{x}_0 \Bigg\{ &\left[\frac{\partial}{\partial \phi} \left[\frac{\phi_0}{\phi} f \right] \right] (\delta\phi) \\ &+ \nu_0 \sum_{l,m} \left[\frac{\partial X_m}{\partial x_l^0} \right] \left[\frac{\partial}{\partial x_l^0} \delta X_m \right] \Bigg\} \ . \end{aligned} \tag{2.7}$$

Here we use the following identity which directly follows from the definition[20] (2.3):

$$\delta\phi = -\phi \sum_l \frac{\partial}{\partial X_l} (\delta X_l) = -\phi \sum_{l,m} \left[\frac{\partial x_m^0}{\partial X_l} \right] \left[\frac{\partial}{\partial x_m^0} \delta X_l \right] \ , \tag{2.8}$$

where $\partial x_m^0/X_l$ is the derivative of x_m^0 with respect to X_l with the other X_n held fixed. Now substitution of (2.8) into (2.7) and some manipulations yield

$$\frac{\Pi_{ij}}{k_B T}=(\phi f'-f)\delta_{ij}-\nu_0\left[\frac{\phi}{\phi_0}\right]\sum_l\left[\frac{\partial X_i}{\partial x_l^0}\right]\left[\frac{\partial X_j}{\partial x_l^0}\right], \tag{2.9}$$

where $f'=\partial f/\partial\phi$. At this point we should note that the functional derivative of ΔF with respect to X_i and the divergence of the stress tensor are simply related by

$$\sum_j\frac{\partial}{\partial X_j}\Pi_{ij}=\left[\frac{\phi}{\phi_0}\right]\frac{\delta}{\delta X_i}\Delta F \tag{2.10}$$

$$=\phi f''\frac{\partial\phi}{\partial X_i}-\nu_0\frac{\phi}{\phi_0}\sum_l\left[\frac{\partial}{\partial x_l^0}\right]^2 X_i\ , \tag{2.11}$$

where $f''=\partial^2 f/\partial\phi^2$. To derive (2.11), use has been made of the relation

$$\sum_j\frac{\partial}{\partial X_j}\left[\phi\left[\frac{\partial X_j}{\partial x_i^0}\right]\right]$$

$$=\left[\frac{\partial}{\partial x_i^0}\phi\right]+\phi\sum\left[\frac{\partial x_m^0}{\partial X_j}\right]\left[\frac{\partial^2 X_j}{\partial x_m^0\partial x_i^0}\right]=0\ , \tag{2.12}$$

which can be obtained by differentiating (2.8) with respect to x_i^0. Equation (2.10) shows that in mechanical equilibrium the divergence of Π_{ij} vanishes and, simultaneously, F attains an extremum value as a functional of $\mathbf{X}(\mathbf{x}_0)$.

The simplest dynamic equation is given by[21]

$$\gamma\frac{\partial}{\partial t}X_i=-\sum_j\frac{\partial}{\partial X_j}\Pi_{ij}=-\left[\frac{\phi}{\phi_0}\right]\frac{\delta}{\delta X_i}(\Delta F)\ , \tag{2.13}$$

where γ is the friction coefficient (equal to f in Tanaka's notation) between the network and the solvent. The scaling theory for θ solvent[22] suggests $\gamma\propto\phi^2$. Note that the above form of the equation cannot correctly describe the transverse motion of the network (where $\delta\phi\cong 0$). They couple with the transverse velocity field and behave as transverse sound modes in the long-wavelength limit.[23] Furthermore, even on the longitudinal motion, the velocity field can have significant effects in easily deformable gels (or in gels with very small shear modulus), particularly near the spinodal point.[11] This aspect will be reported shortly.

Flory's results simply follow if we set $X_i=(\phi_0/\phi)^{1/3}x_i^0$, assuming that the gel is homogeneous and isotropic. Then,

$$\Delta F=k_B TV[f+\tfrac{3}{2}\nu_0(\phi/\phi_0)^{1/3}]\ , \tag{2.14}$$

$$\Pi/k_B T=\phi f'-f-\nu_0(\phi/\phi_0)^{1/3}\ , \tag{2.15}$$

where Π is the osmotic pressure [or the diagonal component of Π_{ij}, (2.9), in the isotropic case]. We may also calculate the small change in the stress tensor around an isotropic case due to infinitesimal deformations. The stress increment $\delta\Pi_{ij}$ can then be written in terms of the bulk and shear moduli in the standard form.[8] Our model leads to

$$K/k_B T=\phi(\partial\Pi/\partial\phi)_T/k_B T=\phi^2 f''-\tfrac{1}{3}\nu_0(\phi/\phi_0)^{1/3}\ , \tag{2.16}$$

$$\mu/k_B T=\nu_0(\phi/\phi_0)^{1/3}\ . \tag{2.17}$$

See (3.15)–(3.17) below for a derivation of (2.16) and (2.17). Here f'' decreases as the solvent quality decreases leading to phase transitions.[11,24] That is, if K becomes negative, a macroscopic mechanical instability is first triggered resulting in homogeneous expansion or shrinkage of the gel. If K is further decreased below $-4\mu/3$, then the gel undergoes spinodal decomposition and becomes opaque. This means that, in gels freely expandable in the solvent, the mechanical instability point $K=0$ and the cloud point $K+\frac{4}{3}\mu=0$ are separated due to finite shear modules. See Ref. 11 on this point.

III. SURFACE INSTABILITY OF UNIAXIAL GELS

We present a linear stability analysis of uniaxially clamped gels. Our approach is based on (2.2) or (2.5) and is less general than that of Sekimoto and Kawasaki,[5] but it leads to simpler and more analytic results. The average position in a uniaxial state is given by $(\alpha_\parallel x_0,\alpha_\perp y_0,\alpha_\perp z_0)$, where $\mathbf{x}_0=(x_0,y_0,z_0)$ is the original position in the relaxed state. We introduce new coordinates by

$$x=\alpha_\parallel x_0,\quad y=\alpha_\perp y_0,\quad z=\alpha_\perp z_0\ . \tag{3.1}$$

The vector (x,y,z) will be denoted by $\mathbf{x}$, and the displacement vector $\mathbf{u}=(u_x,u_y,u_z)=\mathbf{X}-\mathbf{x}$ will be assumed to be a small quantity. Furthermore we assume $u_z=0$ supposing only two dimensional deformations independent of z. Then, in terms of the new coordinates, ΔF is expressed as

$$\Delta F/k_B T=L_z\int\int dx\,dy\left[\frac{\phi_s}{\phi}f+\tfrac{1}{2}\nu_s\alpha_\parallel^2\left|\frac{\partial}{\partial x}\mathbf{X}\right|^2+\tfrac{1}{2}\nu_s\alpha_\perp^2\left|\frac{\partial}{\partial y}\mathbf{X}\right|^2\right], \tag{3.2}$$

where L_z is the linear dimension of the gel in the z axis and

$$\phi_s=\phi_0/(\alpha_\parallel\alpha_\perp^2),\quad \nu_s=\nu_0\phi_s/\phi_0\ . \tag{3.3}$$

The system is assumed to extend nearly to infinity in the y axis, while it has a finite depth $L_\parallel$ in the x axis. At the lower surface there is no displacement and

$$\mathbf{u}=\mathbf{0}\quad\text{for } x=0\ . \tag{3.4}$$

At the upper surface we have

$$\sum_j\Pi_{ij}n_j=\Pi_\parallel n_i\quad\text{for } x=L_\parallel\ , \tag{3.5}$$

where $\mathbf{n}$ is the normal vector and $\Pi_\parallel$ is the osmotic pressure acting on the gel from above. If we neglect the fluctuation, (3.5) becomes from (2.9)

$$\Pi_\parallel/k_B T=(\phi f'-f)_s-\nu_s\alpha_\parallel^2\ , \tag{3.6}$$

where $(\ )_s$ is the value at $\phi=\phi_s$. It should be noted that in the uniaxial state the osmotic pressure from the lateral boundaries $\Pi_\perp$ is different from $\Pi_\parallel$ as

$$\Pi_\perp/k_BT=(\phi f'-f)_s-\nu_s\alpha_\perp^2 . \qquad (3.7)$$

If the gel is clamped also at the lateral boundary walls or extends nearly to infinity with fixed lateral dimensions, thermodynamic equilibrium is described by the potential

$$\Delta G=\Delta F+V\Pi_\parallel=\Delta F+\int d\mathbf{x}\frac{\phi_s}{\phi}\Pi_\parallel . \qquad (3.8)$$

We notice that ΔG can be simply obtained if f in ΔF is replaced by $f+\Pi_\parallel$. Therefore, without loss of generality, we may set $\Pi_\parallel=0$ in the following.

A. Formulations of the linear scheme

Next we expand $(\phi_s/\phi)f$ in (3.2) in powers of the relative volume change $\phi_s/\phi-1=I+J$ where

$$I=\frac{\partial}{\partial x}u_x+\frac{\partial}{\partial y}u_y , \qquad (3.9)$$

$$J=\left[\frac{\partial}{\partial x}u_x\right]\left[\frac{\partial}{\partial y}u_y\right]-\left[\frac{\partial}{\partial x}u_y\right]\left[\frac{\partial}{\partial y}u_x\right] . \qquad (3.10)$$

Retaining the terms only up to second order we find

$$\mathcal{F}\equiv[\Delta F-(\Delta F)_s]/(k_BT\nu_s\alpha_\parallel^2L_z)$$
$$\equiv\int\int dx\,dy\left[-J+\frac{1}{2}\epsilon(I+J)^2+\frac{1}{2}\left|\frac{\partial}{\partial x}\mathbf{u}\right|^2+\frac{1}{2}\hat{\delta}^2\left|\frac{\partial}{\partial y}\mathbf{u}\right|^2\right] , \qquad (3.11)$$

where $(\Delta F)_s$ is the free energy in the absence of the fluctuations and

$$\epsilon=\phi_0\phi_sf''(\phi_s)/(\nu_0\alpha_\parallel^2) , \qquad (3.12)$$

$$\hat{\delta}=\alpha_\perp/\alpha_\parallel . \qquad (3.13)$$

The ϵ is the degree of incompressibility, as will be explained below, and $\hat{\delta}$ represents the degree of anisotropy. The terms linear in $\mathbf{u}$ vanish in (3.11) due to (3.6). In this section we will further replace $\frac{1}{2}\epsilon(I+J)^2$ by $\frac{1}{2}\epsilon I^2$ in (3.11), retaining only the bilinear terms. Then recombination of the terms in (3.11) yields another expression,

$$\mathcal{F}=\int\int dx\,dy\left[\frac{1}{2}\left[\frac{\partial}{\partial x}u_y+\frac{\partial}{\partial y}u_x\right]^2+\frac{1}{2}\left[\frac{\partial}{\partial x}u_x-\frac{\partial}{\partial y}u_y\right]^2+\frac{1}{2}\epsilon(\nabla\cdot\mathbf{u})^2-\frac{1}{2}(1-\hat{\delta}^2)\left|\frac{\partial}{\partial y}\mathbf{u}\right|^2\right] . \qquad (3.14)$$

This form shows that, if $\epsilon>0$, $\mathcal{F}$ can be negative (leading to an instability) only for the stretched case $\hat{\delta}<1$ [otherwise, all the terms in (3.14) are non-negative definite], whereas, if $\epsilon<0$, $\mathcal{F}$ can be negative even for $\hat{\delta}>1$, as will be shown below.

Now ΔF is characterized by essentially two dimensionless parameters, ϵ and δ. In Appendix A, we express them in terms of parameters in the Flory theory to make a connection with experiments. Physically, ϵ represents the degree of incompressibility and is a function of the temperature (usually decreasing with decreasing T). To see this, let us consider a small change in the stress tensor $\delta\Pi_{ij}$ due to small displacements u_i. Writing $\hat{\sigma}_{ij}=-\delta\Pi_{ij}/(k_BT\nu_s\alpha_\parallel^2)$ and using (2.9) we obtain to linear order in $\mathbf{u}$ in the two-dimensional case,

$$\hat{\sigma}_{xx}=\epsilon(\nabla\cdot\mathbf{u})+2\frac{\partial}{\partial x}u_x-\nabla\cdot\mathbf{u} , \qquad (3.15)$$

$$\hat{\sigma}_{yy}=\epsilon(\nabla\cdot\mathbf{u})+\hat{\delta}^2\left[2\frac{\partial}{\partial y}u_y-\nabla\cdot\mathbf{u}\right] , \qquad (3.16)$$

$$\hat{\sigma}_{xy}=\frac{\partial}{\partial x}u_y+\hat{\delta}^2\frac{\partial}{\partial y}u_x . \qquad (3.17)$$

For two-dimensionally isotropic deformations, $\partial u_i/\partial x_j\propto\delta_{ij}$, with $u_z=0$, $\hat{\sigma}_{xx}$ and $\hat{\sigma}_{yy}$ change by the same amount proportional to $\epsilon\nabla\cdot\mathbf{u}$. Particularly, for isotropic gels, $\hat{\delta}=1$, the elastic coefficients are given by (2.16) and (2.17), and $\epsilon=K/\mu+\frac{1}{3}$.

Then the linearized form of the boundary condition (3.5) will be calculated. The normal vector $\mathbf{n}$ on the upper surface is proportional to the vector $\partial x/\partial X_i$ at $x=L_\parallel$,[25] from which we can find $n_x\cong 1$ and $n_y\cong-\partial u_x/\partial y$ to linear order in $\mathbf{u}$. Noting that Π_{yy} is given by $\Pi_\perp$, (3.7), to zeroth order, we may rewrite (3.5) into the following two conditions at $x=L_\parallel$:

$$(1+\epsilon)\frac{\partial}{\partial x}u_x-(1-\epsilon)\frac{\partial}{\partial y}u_y=0 , \qquad (3.18)$$

$$\frac{\partial}{\partial x}u_y+\frac{\partial}{\partial y}u_x=0 . \qquad (3.19)$$

Notice that (3.18) is just the condition $\hat{\sigma}_{xx}=0$ and (3.19) does not involve $\hat{\delta}^2$ while $\hat{\sigma}_{xy}$ does. These coincide with the boundary conditions of free surfaces in the usual linear elastic theory if ϵ is replaced by $K/\mu+\frac{1}{3}$.

B. Dynamic equation and eigenvalue problem

The dynamic equation (2.13) can be linearized using (3.15)–(3.17) into

$$\frac{\partial}{\partial t}u_i=D\left[\epsilon\frac{\partial}{\partial x_i}(\nabla\cdot\mathbf{u})+\left[\frac{\partial^2}{\partial x^2}+\hat{\delta}^2\frac{\partial^2}{\partial y^2}\right]u_i\right] , \qquad (3.20)$$

where

$$D=k_BT\nu_s\alpha_\parallel^2/\gamma . \qquad (3.21)$$

The density deviation $\delta\phi=-\phi(\nabla\cdot\mathbf{u})$ then obeys

$$\frac{\partial}{\partial t}\delta\phi=D\left[(1+\epsilon)\frac{\partial^2}{\partial x^2}+(\hat{\delta}^2+\epsilon)\frac{\partial^2}{\partial y^2}\right]\delta\phi . \qquad (3.22)$$

The bulk instability can obviously be avoided under the conditions

$$\epsilon>-1, \quad \epsilon>-\hat{\delta}^2 . \qquad (3.23)$$

If $\epsilon < -1$ or $\epsilon < -\hat{\delta}^2$, spinodal decomposition occurs in the bulk and this is the subject in the future.[6,11]

The right-hand side of (3.20) suggests that we should examine the following eigenvalue problem:

$$\epsilon \frac{\partial}{\partial x_i}(\nabla \cdot \mathbf{u}) + \left[\frac{\partial^2}{\partial x^2} + \hat{\delta}^2 \frac{\partial^2}{\partial y^2} \right] u_i = -\lambda u_i \ , \qquad (3.24)$$

where the eigenvector $\mathbf{u}$ satisfies the boundary conditions (3.18) and (3.19). We can generally prove that the eigenvalue λ is real and there is an orthogonal complete set of eigenvectors $\{\mathbf{u}_p\}$ with eigenvalue λ_p where p is an appropriate subscript (see Appendix B). If we set $\mathbf{u} = \sum_p A_p \mathbf{u}_p$, the scaled free energy $\mathcal{F}$, (3.14), can be expressed as

$$\mathcal{F} = \frac{1}{2} \sum_p \lambda_p C_p A_p^2 \ , \qquad (3.25)$$

where the $C_p = \int \int dx\, dy \, |\mathbf{u}_p|^2$ are the normalization coefficients. If all the λ_p are positive, the variables A_p independently obey a Gaussian distribution near equilibrium. However, the system is unstable if some λ_p is negative. In the following we explicitly solve (3.24).

We assume that $\mathbf{u}$ depends on y as $\exp(iky)$. As will be shown in Appendix B, we may express $\mathbf{u}$ in the form

$$u_x = (k^2/\kappa_1)(W_+ e^{\kappa_1 x} - W_- e^{-\kappa_1 x}) - \kappa_2(\psi_+ e^{\kappa_2 x} - \psi_- e^{-\kappa_2 x}) \qquad (3.26)$$

$$u_y = ik(W_+ e^{\kappa_1 x} + W_- e^{-\kappa_1 x} - \psi_+ e^{\kappa_2 x} - \psi_- e^{-\kappa_2 x}) \ . \qquad (3.27)$$

The factor $\exp(iky)$ is not written explicitly and the wave numbers κ_1 and κ_2 are defined by

$$\hat{\kappa}_1 = \kappa_1 / k = (\hat{\delta}^2 - \hat{\lambda})^{1/2} \ , \qquad (3.28)$$

$$\hat{\kappa}_2 = \kappa_2 / k = [(\epsilon + \hat{\kappa}_1^2)/(1+\epsilon)]^{1/2} \ , \qquad (3.29)$$

where

$$\hat{\lambda} = \lambda / k^2 \ . \qquad (3.30)$$

Here we are assuming $\kappa_1 \neq \kappa_2$ or $\hat{\kappa}_1 \neq 1$ [since $\hat{\kappa}_1^2 - \hat{\kappa}_2^2 = \epsilon(\hat{\kappa}_1^2 - 1)/(1+\epsilon)$] (Ref. 26). The four boundary conditions, (3.4), (3.18) and (3.19), determine the ratios among the four coefficients, W_+, W_-, ψ_+, and ψ_-, and in addition they yield an equation for $\hat{\lambda}$,

$$(1+\hat{\kappa}_1\hat{\kappa}_2)[(1+\hat{\kappa}_1^2)^2 + 4\hat{\kappa}_1\hat{\kappa}_2]\{\cosh[(\kappa_1-\kappa_2)L_\parallel] - 1\} + 2(1-\hat{\kappa}_1^2)^2\hat{\kappa}_1\hat{\kappa}_2 = (1-\hat{\kappa}_1\hat{\kappa}_2)[(1+\hat{\kappa}_1^2)^2 - 4\hat{\kappa}_1\hat{\kappa}_2]\{\cosh[(\kappa_1+\kappa_2)L_\parallel] - 1\} \ . \qquad (3.31)$$

The wave number k and the thickness $L_\parallel$ appear only through the product $kL_\parallel$ in the hyperbolic functions and hence (3.31) determines $kL_\parallel$ as a function of $\hat{\kappa}_1$ and ϵ.[27]

We are interested in the unstable case $\hat{\lambda} < 0$, and hence may assume $\hat{\kappa}_1 > 0$ and $\hat{\kappa}_2 > 0$. [Note that (3.31) can also have solutions for $\hat{\lambda} > \hat{\delta}^2$ or for purely imaginary $\hat{\kappa}_1$.[27]] Then, because the left-hand side of (3.31) is positive definite, we readily notice a necessary condition,

$$(1-\hat{\kappa}_1\hat{\kappa}_2)[(1+\hat{\kappa}_1^2)^2 - 4\hat{\kappa}_1\hat{\kappa}_2] > 0 \ . \qquad (3.32)$$

This condition is also sufficient for the existence of a solution to (3.31). In fact, if (3.32) holds for given positive $\hat{\kappa}_1$ and $\hat{\kappa}_2$, (3.31) is always satisfied for some $kL_\parallel$ because the hyperbolic function on the right-hand side increases more rapidly with increasing $kL_\parallel$ than that on the left-hand side and the right-hand side vanishes for $kL_\parallel = 0$. In Appendix C it will be shown that (3.32) is just imposing an upper limit to $\hat{\kappa}_1$,

$$\hat{\kappa}_1 < \hat{\delta}_c \ , \qquad (3.33)$$

where $\hat{\delta}_c^2$ is a positive zero point of the following cubic polynomial:[28]

$$f_c(z) = z^3 + 5z^2 + \left[\frac{11\epsilon - 5}{\epsilon + 1} \right] z - 1 \ . \qquad (3.34)$$

In Fig. 1 we show curves of $\hat{\kappa}_1$ versus ϵ for $kL_\parallel = 0.6$, 1, 2, and ∞, the last one representing the marginal curve $\hat{\kappa}_1 = \hat{\delta}_c$. Here $\hat{\delta}_c(0) = 1$ and $\hat{\delta}_c(\infty) = 0.296$ as a function of ϵ. For $\hat{\kappa}_1$ less than $\hat{\delta}_c$ there is some $kL_\parallel$ which satisfies (3.31). Then $\hat{\lambda}$ is known to be bounded from below and its minimum is the right-hand side of the following inequality:

$$\hat{\lambda} = \hat{\delta}^2 - \hat{\kappa}_1^2 > \hat{\delta}^2 - \hat{\delta}_c^2 \ . \qquad (3.35)$$

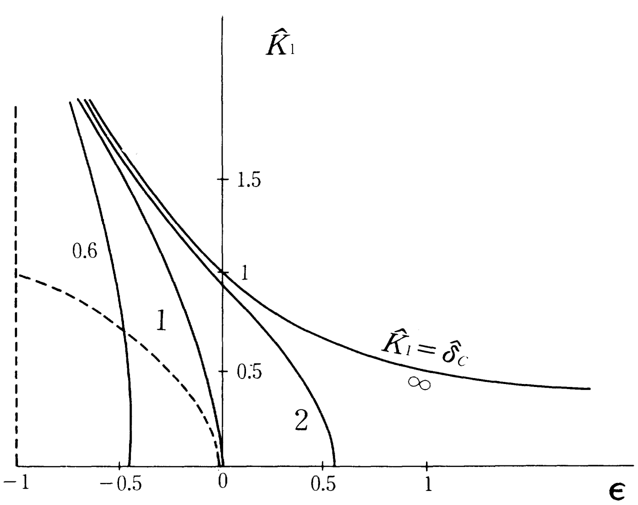

FIG. 1. Solutions to (3.31) are shown in the $\hat{\kappa}_1$-ϵ plane for fixed values of $kL_\parallel$, where $\hat{\kappa}_2$ is related to $\hat{\kappa}_1$ and ϵ by (3.29). The numbers attached to the curves represent the value of $kL_\parallel$. Below the dotted curve, $\epsilon + \hat{\kappa}_1^2 < 0$, $\hat{\kappa}_2$ becomes purely imaginary. The value of $\hat{\lambda}$, (3.30), can be obtained from $\hat{\lambda} = \hat{\delta}^2 - \hat{\kappa}_1^2$.

We have thus arrived at a very simple criterion: there are eigenmodes with negative $\hat{\lambda}$, and the system is unstable if

$$\hat{\delta} < \hat{\delta}_c \ . \tag{3.36}$$

Particularly in the isotropic case $\hat{\delta}=1$ the surface instability occurs for $\epsilon<0$. In Fig. 2 we show the phase diagram in the linear theory. See Secs. IV and V for an explanation of the regions II–IV.

Under (3.36) $\hat{\lambda}$ can be negative for k greater than a critical value k_c, which is determined by (3.31) by setting $\hat{\lambda}=0$. In particular, for small $\hat{\delta}_c-\hat{\delta}$, the coefficient in front of the hyperbolic function on the right-hand side of (3.31) is proportional to $\hat{\delta}_c^2-\hat{\kappa}_1^2=\hat{\delta}_c^2-\hat{\delta}^2-\hat{\lambda}$. Thus

$$k_c \simeq \frac{1}{2\hat{\delta}L_\parallel}\ln[A_c/(\hat{\delta}_c^2-\hat{\delta}^2)] \ , \tag{3.37}$$

$$\lambda=\hat{\lambda}k^2 \simeq -(\hat{\delta}_c^2-\hat{\delta}^2)\{1-\exp[-2\hat{\delta}(k-k_c)L_\parallel]\}k^2 \ , \tag{3.38}$$

where A_c in (3.37) is a function of ϵ.

C. Spinodal decomposition on the surface in clamped gels

Equation (3.38) shows that the $L_\parallel$ dependence of λ can soon be neglected once k considerably exceeds k_c (say, $k/k_c>2$), resulting in a simple relation, $\lambda \simeq -(\hat{\delta}_c^2-\hat{\delta}^2)k^2$. On the other hand, we should recall the presence of the gradient free energy ΔF_{inh} in (2.2), which is crucial in describing small-scale fluctuations. The scaling theory for θ solvent[19,22] suggests $\Delta F_{\text{inh}} \sim \int d\mathbf{X}(a\phi)^{-1}|\nabla\phi|^2$, where a is the microscopic monomer size. Thus, if we take into account ΔF_{inh}, λ should be modified to

$$\lambda \simeq -(\hat{\delta}_c^2-\hat{\delta}^2)k^2+bk^4 \ . \tag{3.39}$$

Here $b \sim Na^2 \sim R_G^2$, where $N=\phi_0/(v_0a^3)$ is the effective polymerization index and R_G is the gyration radius of one effective chain. This suggests that very fine surface perturbations should grow as a spinodal decomposition process, with the initial peak wave number given by

$$k_m=[(\hat{\delta}_c^2-\hat{\delta}^2)/2b]^{1/2} \sim (\hat{\delta}_c^2-\hat{\delta}^2)^{1/2}/R_G \ . \tag{3.40}$$

The corresponding initial maximum growth rate is

$$\Gamma_m=\tfrac{1}{4}Db^{-1}(\hat{\delta}_c^2-\hat{\delta}^2)^2 \sim DR_G^{-2}(\hat{\delta}_c^2-\hat{\delta}^2)^2 \ , \tag{3.41}$$

where D is defined by (3.21). The time scale $1/\Gamma_m$ is much faster than typical observation times, unless R_G is very large and $\hat{\delta}_c^2-\hat{\delta}^2$ is extremely small. Therefore, we will observe only very late stages of the process in most experiments.

As the fluctuations on the surface grow, some nonlinear mechanism should come into play serving to suppress the growth and thus leading to some final, stationary pattern. In this paper, the following are expected: (i) If the gel is sufficiently incompressible (or if ϵ is large), nonlinear terms in ΔF [such as the term $\frac{1}{2}\epsilon J^2$ in (3.11)] can stop the growth at a relatively small saturation level. (ii) However, if the gel is sufficiently compressible (or for small ϵ), such nonlinear terms are not effective enough, allowing the final folding of the surface. These aspects will be further discussed in the following sections.

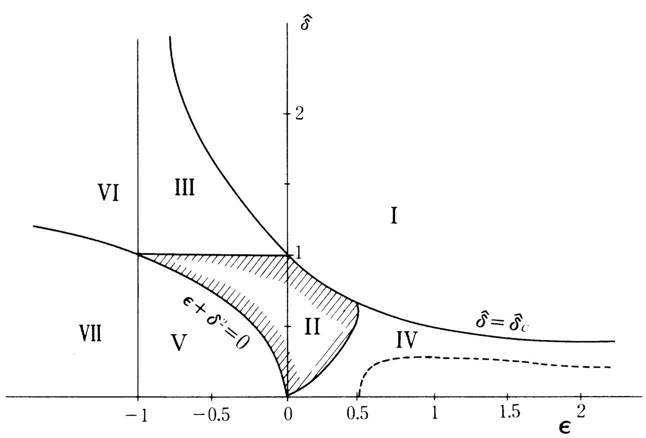

FIG. 2. Phase diagram from the linear theory. The system is stable in region I, while in regions II–IV it is unstable against surface perturbations, but still stable with respect to bulk instabilities. In region II we expect folding of the surfaces, as will be shown in Sec. III. In region III the folding is unstable in the sense that $\Pi_{yy}<0$ at the contact for $\hat{\delta}>1$. In region IV there are no meaningful solutions in the linear scheme representing periodic cusps. The dashed curve in region IV will be explained in Sec. V. In region V we expect anisotropic spinodal decomposition in the bulk with cylindrical domains, while in region VI that with lamellar domains. In region VII the gel is unstable against plane wave perturbations of any directions.

D. Instability of gel plates with free surfaces

When both the upper and lower surfaces are freely exposed to solvent, we find a very different instability. That is, if $\epsilon>0$, the gel plate bends macroscopically (without small-scale structures) for $\hat{\delta}<1$. This case corresponds to the usual elastic instability of plates or rods subject to compressional forces (Euler's problem).[8] Let us consider the eigenvalue problem (3.24) under the boundary conditions (3.18) and (3.19) at $x=L_\parallel/2$ and $-L_\parallel/2$. The system dimensions in the lateral directions are assumed to be fixed. Then, assuming (3.26) and (3.27), we find $W_+=-W_-$, $\psi_+=-\psi_-$, and the counterpart of (3.31),

$$(1+\hat{\kappa}_1^2)^2-4\hat{\kappa}_1\hat{\kappa}_2[\tanh(\tfrac{1}{2}\kappa_1L_\parallel)/\tanh(\tfrac{1}{2}\kappa_2L_\parallel)]=0 \ . \tag{3.42}$$

For $|k|L_\parallel \gg 1$, we obtain the same relation $\hat{\kappa}_1=\hat{\delta}_c(\epsilon)$ as in the clamped case, as it should be. For $|k|L_\parallel \ll 1$, on the other hand, (3.42) yields

$$\hat{\lambda}=\hat{\delta}^2-\hat{\kappa}_1^2=(\hat{\delta}^2-1)+\frac{1}{3}\left[\frac{\epsilon}{1+\epsilon}\right](kL_\parallel)^2+\cdots \ . \tag{3.43}$$

We can prove that eigenvectors with $\hat{\kappa}_1=1$ are nonexistent except for the special point $\epsilon=0$.

If $\epsilon>0$, the gel becomes unstable if $\hat{\delta}$ is lowered slightly below 1. The critical value of $\hat{\delta}^2$ is $1-\frac{1}{3}[\epsilon/(1+\epsilon)](\pi L_\parallel/L_y)^2+\cdots$ if the gel size in the y axis is given by L_y. In this case the instability occurs only at long wavelengths of order $L_\parallel$; the upper bound of k is

$$k_{\text{upper}} \simeq [3(1+\epsilon)(1-\hat{\delta}^2)/\epsilon]^{1/2}/L_\parallel \ . \tag{3.44}$$

Obviously, the gel plate will bend as a whole in the same manner as plates or rods bend under compression.

However, if $\epsilon<0$, an instability occurs for $\hat{\delta}<\hat{\delta}_c$, in which the system is unstable at short wavelengths, as in the clamped case. Further, if $\hat{\delta}>1$, there can be no macroscopic bending, since $\hat{\lambda}$ is positive at long wavelengths from (3.43). Thus, if $\epsilon<0$ and $\hat{\delta}>1$, fine patterns will appear on both the upper and lower surfaces. For $\hat{\delta}<1$ and $\epsilon<0$, the system is unstable at all wavelengths (if ΔF_{inh} is not taken into account).

Here we point out a great difference between the modes of instabilities in our system and those in usual isotropic elastic materials.[8] In the latter, since $\hat{\delta}=1$, plates or rods become unstable obviously only for variable system length (L_y in our notation) parallel to the compressional force. On the other hand, if the elastic coefficients are anisotropic as in our system, instabilities can occur even for fixed L_y. Notice that $\hat{\lambda}$ is positive-definite in (3.43) if $\hat{\delta}=1$ and $\epsilon=K/\mu+\frac{1}{3}>0$.

IV. FOLDING OF THE SURFACE

A. Boundary conditions in the folded region

For small ϵ, growing corrugations will eventually touch each other and then folded parts will form on the surface just because any parts of the gel are impenetrable into each other. Let a two-dimensionally folded part exist in the region, $-d<y<d$ and $x=L_\parallel$, where d is the depth of the folding. The boundary conditions here are different from those, (3.18) and (3.19), on the surface in contact with the solvent. First, the condition of contact is

$$Y=y+u_y=0 \quad \text{or} \quad \left[\frac{\partial}{\partial y}u_y\right]_b=-1 \quad \text{for } |y|<d \ . \tag{4.1}$$

Hereafter, $(\ )_b$ denotes the value at $x=L_\parallel$. Equation (2.3) means that the density at the folded part is written as

$$\frac{\phi_s}{\phi}=-\left[\frac{\partial}{\partial x}u_y\right]_b\left[\frac{\partial}{\partial y}u_x\right]_b \ . \tag{4.2}$$

In the region $0<y<d$ (or $-d<y<0$) the profile is meaningful only if $(\partial u_x/\partial y)_b$ is positive (or negative). The positivity of ϕ then requires that $(\partial u_y/\partial x)_b$ be negative for $0<y<d$ (or positive for $-d<y<0$). Second, if the surface is very smooth, the shear stress must vanish and (2.9) yields

$$\sum_l\left[\frac{\partial X}{\partial x_l^0}\right]\left[\frac{\partial Y}{\partial x_l^0}\right]=0 \quad \text{for } |y|<d \ , \tag{4.3}$$

where $x_1^0=\alpha_\parallel^{-1}x$ and $x_2^0=\alpha_\perp^{-1}y$ are the original coordinates. If $(\partial Y/\partial x)_b=(\partial u_y/\partial x)_b$ were zero, ϕ would be infinite for $|y|<d$ from (4.2). This will be shown to be not the case self-consistently, and therefore (4.3) becomes

$$\left[\frac{\partial}{\partial x}X\right]_b=0 \quad \text{or} \quad \left[\frac{\partial}{\partial x}u_x\right]_b=-1 \ . \tag{4.4}$$

Third, the osmotic pressure at the folded surface should be non-negative; otherwise, the contact will be pulled back from the inside of the gel. From (2.9) this condition is written as

$$\frac{\Pi_{yy}}{k_B T}=\phi f'-f+\nu_s\alpha_\parallel^2\left[\frac{\partial}{\partial x}u_y\right]_b\Big/\left[\frac{\partial}{\partial y}u_x\right]_b\geq 0 \quad \text{for } |y|<d \ , \tag{4.5}$$

where use has been made of (4.2). As in Sec. III we expand $(\phi_s/\phi)f$, in powers of $\phi_s/\phi-1=I+J$, to retain the terms up to second order. Then in the folded surface region we have

$$\frac{\Pi_{yy}}{k_B T}=\nu_s\alpha_\parallel^2\left[\left[\frac{\partial}{\partial x}u_y\right]_b+(1+2\epsilon)\left[\frac{\partial}{\partial y}u_x\right]_b-\epsilon\left[J\frac{\partial}{\partial y}u_x\right]_b\right]\Big/\left[\frac{\partial}{\partial y}u_x\right]_b \ , \tag{4.6}$$

where we have set $I=-2$ from (4.1) and (4.4). The quantity in the square brackets of (4.6) must be non-negative.

B. Single cusp in thick gels

We impose the boundary conditions (4.1) and (4.4) at the folded part, which cause strong nonlinear deformations in the bulk. Then the linear scheme in Sec. III should be a poor approximation, at least in the neighborhood of the cusp. However, solutions to the linearized equation in the bulk region do exist and can lower the free energy below the value for the homogeneous state in certain parameter regions. Therefore, these solutions can be a starting point for more complete theories. To be precise, our theory in this approximation is partly a nonlinear theory accounting for the great change of the boundary conditions at the folded parts. To the end of illustrating the mathematical structure of the folding, we first calculate a stationary single cusp in the limit $L_\parallel\to\infty$. Namely, we assume (3.20) with no time dependence in the bulk,

$$\epsilon\frac{\partial}{\partial x_i}(\nabla\cdot\mathbf{u})+\left[\frac{\partial^2}{\partial x^2}+\hat{\delta}^2\frac{\partial^2}{\partial y^2}\right]u_i=0 \ . \tag{4.7}$$

The boundary conditions are (4.1) and (4.4) for $|y|<d$ and $x=L_\parallel$, while (3.18) and (3.19) for $|y|>d$ and $x=L_\parallel$.

It is convenient to introduce two functions of y defined on the upper surface,

$$U(y)=\left[\frac{\partial}{\partial x}u_y+\frac{\partial}{\partial y}u_x\right]_b \ , \tag{4.8}$$

$$R(y)=\left[(1-\epsilon)\frac{\partial}{\partial y}u_y-(1+\epsilon)\frac{\partial}{\partial x}u_x\right]_b =2\epsilon\Theta(d-|y|) \ , \tag{4.9}$$

where $\Theta(p)$ is the step function being equal to zero for $p<0$ and to 1 for $p>0$. The second line of (4.9) has been derived from the boundary conditions. The two functions are nonvanishing only in the region $|y|<d$. In Appendix D we will derive the following integral equation on the upper surface (with y as its argument):

$$\left[\frac{\partial}{\partial y}u_y\right]_b=-\frac{1}{C}\hat{\delta}(1-\hat{\delta}^2)(\hat{H}U)+\frac{1}{C}C'R \ . \qquad (4.10)$$

Here $\hat{H}$ is the Hilbert transformation,[29,8]

$$(\hat{H}f)(y)=\pi^{-1}\int_{-\infty}^{\infty}dy'\frac{f(y')}{y'-y} \ , \qquad (4.11)$$

where the Cauthy principal value should be taken in the integration. The two coefficients C and C' are defined by

$$C=(1+\hat{\delta}^2)^2-4\hat{\delta}\hat{\kappa} \ , \qquad (4.12)$$

$$C'=1+\hat{\delta}^2-2\hat{\delta}\hat{\kappa} \ , \qquad (4.13)$$

where

$$\hat{\kappa}=[(\epsilon+\hat{\delta}^2)/(1+\epsilon)]^{1/2} \ . \qquad (4.14)$$

Equation (4.10) can be readily solved if we notice that the Hilbert transformation of the function $y\Theta(d-|y|)/(d^2-y^2)^{1/2}$ is equal to 1 for $|y|<d$ and to $1-|y|/(y^2-d^2)^{1/2}$ for $|y|>d$.[29] Because $(\partial u_y/\partial y)_b=-1$ for $|y|<d$ from (4.1), we obtain

$$U=U_0\left[\frac{y}{(d^2-y^2)^{1/2}}\right]\Theta(d-|y|) \ , \qquad (4.15)$$

with

$$U_0=(C+2\epsilon C')/[\hat{\delta}(1-\hat{\delta}^2)] \ . \qquad (4.16)$$

Substitution of U into (4.10) then yields

$$\left[\frac{\partial u_y}{\partial y}\right]_b=-1+\left[\left[1+2\epsilon\frac{C'}{C}\right]\frac{|y|}{(y^2-d^2)^{1/2}}-2\epsilon\frac{C'}{C}\right]\times\Theta(|y|-d) \ . \qquad (4.17)$$

Using (D1) in Appendix D we also find

$$\left[\frac{\partial u_x}{\partial y}\right]_b=\frac{C'}{C}U-\left[\frac{2\epsilon}{\pi C}\right]\hat{\kappa}(1-\hat{\delta}^2)\ln\left|\frac{d+y}{d-y}\right| \ . \qquad (4.18)$$

The surface profile can be obtained by integration of (4.17) and (4.18), with respect to y, and is meaningful only for $(\partial Y/\partial y)_s>0$ in the region $y>d$. This condition simply becomes $C>0$ because the quantity $C+2\epsilon C'$ is positive-definite if $\hat{\delta}\neq 1$. Then, the relation $(\partial u_x/\partial y)_b>0$ in the region $0<y<d$ is always satisfied (see Appendix D). In addition, the condition (4.5) must hold. In the linear scheme, we neglect the third term ($\propto J$) in the square brackets of (4.6) to find that Π_{yy} is equal to a positive quantity divided by $1-\hat{\delta}^2$ from (4.15) and (4.18). Thus we require the following two conditions to have a meaningful cusp:

$$C>0 \ \text{ and } \ \hat{\delta}<1 \ . \qquad (4.19a)$$

Because C is equal to $(\hat{\delta}^2-1)(\hat{\delta}^2-\hat{\delta}_c^2)$ multiplied by a positive quantity (Appendix C), these conditions are equivalent to

$$\hat{\delta}<\hat{\delta}_c \ \text{ for } \epsilon>0 \ \text{ and } \hat{\delta}<1 \ \text{ for } \epsilon<0 \ . \qquad (4.19b)$$

Just outside the folded region, $0<y-d\ll d$, we have $Y\propto(y-d)^{1/2}$ from (4.17), and a nearly parabolic profile, $X-X(d)\simeq \text{const}\times\epsilon Y^2\ln Y$, from (4.18). For $\epsilon>0$, the surface is mildly protuberant at the position of folding, while for $\epsilon<0$, it is shrinking inward (see Fig. 3 below). In more detail, we may calculate $\partial u_x(x,y)/\partial y$ and $\partial u_y(x,y)/\partial y$ as functions of x and y in the limit $L_\parallel\to\infty$. See (4.34) and (4.35) below. Also we notice that the constant term in u_x remains indefinite if the limit $L_\parallel\to\infty$ has been taken at the beginning. By this reason we defer the calculation of the free-energy change to Sec. V.

Finally, we remark that the line $\hat{\delta}=1$ is a singular line in the calculation. We may take the limit $\hat{\delta}\to 1$ in the above expressions, and we find $U_0\to 0$ from $C/(1-\hat{\delta}^2)\to -2\epsilon/(1+\epsilon)$ and $C'/(1-\hat{\delta}^2)\to 1/(1+\epsilon)$. The results of this limit are obviously those derivable from the usual linear elastic theory for isotropic bodies in which $\hat{\delta}=1$. In this case (4.6) shows $\Pi_{yy}/k_BT=2\epsilon v_s\alpha_\parallel^2$ in the linear order, leading to $\epsilon>0$. However, we notice that the periodic solution in the case $\hat{\delta}\to 1$ is meaningful only for $\epsilon<0$ [see (4.33) below in the region $p\lesssim a$]. Furthermore, the free-energy change due to the cusp formation can be negative only for $\epsilon<0$ if $\hat{\delta}=1$, as will become evident from (5.6) and (5.7) below. Therefore, the usual linear elastic theory cannot reproduce physically meaningful patterns.

C. Periodic cusps in thick gels

We proceed to the calculation of a two-dimensional periodic pattern with period $L_\perp$ in the y direction. The folding is assumed to take place in the regions, $nL_\perp-d<y<nL_\perp+d$, with $n=0,\pm1,\ldots$, on the upper surface. Within the linear scheme, use will be made of (4.7) in the bulk, (3.4) on the lower boundary, (3.18) and (3.19) in the free-surface regions, and (4.1) and (4.4) in the folded regions. For mathematical simplicity the calculation will be performed under the condition

$$2\pi L_\parallel/L_\perp\gtrsim 1 \ . \qquad (4.20)$$

We shall find that the thick-gel limit $L_\parallel\to\infty$ is quickly approached under the above condition.

It should not be overlooked that the total volume is changed for $\epsilon\neq 0$ due to the periodic cusp formation. Notice that the average of $u_x(x,y)$ over one period, $0<y<L_\perp$, is equal to const$\times x$ because its second derivative, with respect to x, vanishes from (4.7) and is zero at $x=0$. Then we integrate $(\partial u_x/\partial x)_b$ at $x=L_\parallel$ over one period; it is equal to -1 in the folded region from (4.4), and to

$$[(1-\epsilon)/(1+\epsilon)](\partial u_y/\partial y)_b$$

outside the folded region from (3.18). Further from

$$\int_0^{L_\perp}dy\left[\frac{\partial u_y}{\partial y}\right]_b=-2d+\int_d^{L_\perp-d}dy\left[\frac{\partial u_y}{\partial y}\right]=0 \ ,$$

we obtain

$$\bar{u}_x \equiv \frac{1}{L_\perp}\int_0^{L_\perp} dy\, u_x(L_\parallel, y) = -\frac{4\epsilon}{1+\epsilon}\frac{dL_\parallel}{L_\perp} . \tag{4.21}$$

For $0<x<L_\parallel$ the average is linear in x as

$$\frac{1}{L_\perp}\int_0^{L_\perp} dy\, u_x(x,y) = -\frac{4\epsilon}{1+\epsilon}\frac{d}{L_\perp}x . \tag{4.22}$$

The above quantity is just the zeroth component of the Fourier series of $u_x(x,y)$ with respect to y. The volume of the gel after the cusp formation is given in the linear approximation by

$$V\left[1+\frac{\bar{u}_x}{L_\parallel}\right] = V\left[1-\frac{4\epsilon}{1+\epsilon}\frac{d}{L_\perp}\right] . \tag{4.23}$$

The volume change divided by the initial volume V is determined by the ratio $d/L_\perp$ and is independent of $L_\parallel$ (however long $L_\parallel$ is). The boundary conditions (4.1) and (4.4) are, themselves, strong ones, causing large deformations near the surface and changing the total volume in this manner. On the other hand, we find $\int_0^{L_\perp} dy\, u_y = 0$ from the boundary conditions.

We can show that the derivative $\partial \mathbf{u}/\partial y$ tends to a well-defined limit as $L_\parallel \to \infty$, whereas the zeroth Fourier component of u_x is linear in x, as shown in (4.22). Then the counterpart of the integral Eq. (4.10) readily follows in the periodic case (Appendix D); in terms of U and R, (4.8) and (4.9), it reads

$$\left[\frac{\partial u_y}{\partial y}\right]_b = -\frac{1}{C}\hat{\delta}(1-\hat{\delta}^2)(\hat{\mathcal{H}}U) + \frac{1}{C}C'\left[R - 2\frac{\epsilon d}{L_\perp}\right] . \tag{4.24}$$

Here $\hat{\mathcal{H}}$ is an operator on periodic functions of y with period $L_\perp$,

$$\hat{\mathcal{H}}f = \frac{1}{L_\perp}\int_0^{L_\perp} dy' f(y')\cot[\tfrac{1}{2}k_\perp(y'-y)] , \tag{4.25}$$

where $k_\perp = 2\pi/L_\perp$ and the Cauthy principal value should be taken at $y'=y$. Note that each term in (4.24) vanishes if averaged over one period. The operator $\hat{\mathcal{H}}$ is in essence very simple if the variable y is changed to a new variable p defined by

$$p = \tan(\tfrac{1}{2}k_\perp y) . \tag{4.26}$$

Noting that p varies from $-\infty$ to ∞ in the one period, $-L_\perp/2 < y < L_\perp/2$, we may rewrite (4.25) as

$$\hat{\mathcal{H}}f = \frac{1}{\pi}\int_{-\infty}^{\infty} dp' \frac{1}{p'-p}\tilde{f}(p') - \frac{1}{L_\perp}\int_0^{L_\perp} dy' f(y')\tan(\tfrac{1}{2}k_\perp y') , \tag{4.27}$$

where $\tilde{f}(p) \equiv f(y) = f(2k_\perp^{-1}\tan^{-1}p)$. The first term is just the ordinary Hilbert transformation and the second term is simply a constant, the latter role being to ensure $\int_0^{L_\perp} dy\, \hat{\mathcal{H}}f = 0$.

Analogously to (4.15), we can solve (4.24) by setting

$$U = U_1 \frac{p}{(a^2-p^2)^{1/2}}\Theta(a-|p|) , \tag{4.28}$$

where

$$a = \tan(\tfrac{1}{2}k_\perp d) = \tan(\pi d/L_\perp) . \tag{4.29}$$

The coefficient U_1 has a little more complicated form than U_0, (4.16),

$$U_1 = [C + 2\epsilon C'(1-2d/L_\perp)]/[\hat{\delta}(1-\hat{\delta}^2)b] , \tag{4.30}$$

where

$$b = \cos(\tfrac{1}{2}k_\perp d) = \frac{1}{(1+a^2)^{1/2}} . \tag{4.31}$$

The factor b, in the denominator, stems from the second term on the right-hand side of (4.27). The functional form of the derivative $(\partial u_y/\partial y)_b$ is nearly the same as (4.17),

$$\left[\frac{\partial}{\partial y}u_y\right]_b = -1 + \left\{\frac{1}{b}\left[1+2\epsilon\left[1-\frac{2d}{L_\perp}\right]\frac{C'}{C}\right]\frac{|p|}{(a^2-p^2)^{1/2}} - 2\epsilon\frac{C'}{C}\right\}\Theta(|p|-a) . \tag{4.32}$$

On the other hand, $(\partial u_y/\partial y)_b$ is exactly of the form of (4.18), provided that d and y are replaced by a and p. Although re^dundant, we write it here,

$$\left[\frac{\partial}{\partial y}u_x\right]_b = \frac{C'}{C}U - (2\epsilon/\pi C)\hat{\kappa}(1-\hat{\delta}^2)\ln\left|\frac{a+p}{a-p}\right| . \tag{4.33}$$

As in the single cusp case, the condition (4.19a) [or (4.19b)] must again be required by the same reasons.

Moreover, the overall behavior of $\mathbf{u}(x,y)$ can be calculated, analytically in the limit $L_\parallel \to \infty$, in the forms (Appendix D)

$$\frac{\partial}{\partial y}u_x = C_{11}F_R(\zeta_1) + C_{12}F_R(\zeta_2) + C_{21}G_I(\zeta_1) + C_{22}G_I(\zeta_2) , \tag{4.34}$$

$$\frac{\partial}{\partial y}u_y = -1 + D_{11}F_I(\zeta_1) + D_{12}F_I(\zeta_2) + D_{21}G_R(\zeta_1) + D_{22}G_R(\zeta_2) . \tag{4.35}$$

Here C_{ij} and D_{ij} are coefficients defined by

$$C_{11}=-\frac{1}{\hat{\delta}}D_{11}=(1+\hat{\delta}^2)U_1/C\ ,$$
$$C_{12}=-\hat{\kappa}D_{12}=-2\hat{\delta}\hat{\kappa}U_1/C\ , \tag{4.36}$$
$$C_{21}=\frac{1}{\hat{\delta}}D_{21}=-4\epsilon\hat{\kappa}/C\ ,$$
$$C_{22}=\hat{\kappa}D_{22}=2\epsilon\hat{\kappa}(1+\hat{\delta}^2)/C\ ,$$

and ζ_1 and ζ_2 are complex variables defined by

$$\zeta_1=y+i\hat{\delta}(L_\parallel-x),\quad \zeta_2=y+i\hat{\kappa}(L_\parallel-x)\ . \tag{4.37}$$

The functions $F_R(z)$ and $F_I(z)$ are the real and imaginary parts of the following analytic function of ζ, defined in the upper plane $\mathrm{Im}\zeta>0$:

$$F(\zeta)=F_R(\zeta)+iF_I(\zeta)=\tan(\tfrac{1}{2}k_\perp\zeta)/[a^2-\tan^2(\tfrac{1}{2}k_\perp\zeta)]^{1/2}\ . \tag{4.38}$$

In the same manner $G_R(\zeta)$ and $G_I(\zeta)$ are defined by

$$G(\zeta)=G_R(\zeta)+iG_I(\zeta)=\frac{1}{i\pi}\ln\left[\frac{a-\tan(\frac{1}{2}k_\perp\zeta)}{a+\tan(\frac{1}{2}k_\perp\zeta)}\right]\ . \tag{4.39}$$

After some calculations we can also derive

$$\frac{\partial}{\partial x}u_x=-1+C_{11}\hat{\delta}F_I(\zeta_1)+C_{12}\hat{\kappa}F_I(\zeta_2)-C_{21}\hat{\delta}G_R(\zeta_1)-C_{22}\hat{\kappa}G_R(\zeta_2)\ , \tag{4.40}$$

$$\frac{\partial}{\partial x}u_y=-D_{11}\hat{\delta}F_R(\zeta_1)-D_{12}\hat{\kappa}F_R(\zeta_2)+D_{21}\hat{\delta}G_I(\zeta_1)+D_{22}\hat{\kappa}G_I(\zeta_2)\ . \tag{4.41}$$

Equations (4.34), (4.35), (4.40), and (4.41) cannot be explicitly integrated to give the deformed position $X=x+u_x$ and $Y=y+u_y$, except for the case $\epsilon=0$. For $\epsilon=0$, however, we obtain a simple result,

$$Y+i\hat{\delta}(L_\parallel-X)=(i\pi)^{-1}L_\perp\ln\{[\cos^2(\tfrac{1}{2}k_\perp\zeta)-b^2]^{1/2}+\cos(\tfrac{1}{2}k_\perp\zeta)\}\ , \tag{4.42}$$

where $\zeta=y+i\delta(L_\parallel-x)$ and $b=\cos(\frac{1}{2}k_\perp d)$.

The mapping $\zeta\to\omega=\tan(\frac{1}{2}k_\perp\zeta)$ is a conformal transformation, in which the one period, $-\frac{1}{2}L_\perp<\mathrm{Re}\zeta<\frac{1}{2}L_\perp$ and $0<\mathrm{Im}\zeta<\infty$, is mapped into the upper plane, $-\infty<\mathrm{Re}\omega<\infty$ and $\mathrm{Im}\omega>0$. As $\mathrm{Im}\zeta\to\infty$ we have $\omega\to i$, $F\to ib$, and $G\to 2d/L_\perp-1$. We can check the following mathematical details: (i) As $x\to L_\parallel$ or as ζ_1 and $\zeta_2\to y$, (4.34) and (4.35) surely reduce to (4.32) and (4.33) (see the last sentence of Appendix D). (ii) The right-hand side of (4.34) is odd and periodic in y, while that of (4.35) is even and periodic. Furthermore, the latter should vanish if integrated over one period. This can be proved from (4.30), and the relations $\int_0^{L_\perp}dyF=ibL_\perp$ and $\int_0^{L_\perp}dyG=2d-L_\perp$, which hold irrespectively of the value of x. (iii) From (4.40) we can derive

$$\int_0^{L_\perp}dy(\partial u_x/\partial x)=-4\epsilon d/(1+\epsilon)$$

in accord with (4.22), if we notice the relation

$$C_{11}\hat{\delta}b+C_{12}\hat{\kappa}b+(C_{21}\hat{\delta}+C_{22}\hat{\kappa})(1-2d/L_\perp)=1-4\epsilon d/(1+\epsilon)L_\perp\ .$$

(iv) Far from the upper surface we have $\partial u_x/\partial y\to 0$, $\partial u_y/\partial y\to 0$, $\partial u_x/\partial x\to -4\epsilon d/(1+\epsilon)L$, and $\partial u_y/\partial x\to 0$, the corrections being of order $\exp[-\hat{\delta}k_\perp(L_\parallel-x)]$ or $\exp[-\hat{\kappa}k_\perp(L_\parallel-x)]$. This justifies the criterion (4.20) for the thick-gel limit, if $\hat{\delta}$ and $\hat{\kappa}$ are assumed to be of order 1. (Our model will not be meaningful for $\hat{\delta}\ll 1$.)

Numerically integrating (4.34) and (4.35), we display one period of the gel pattern in Figs. 3(a)–3(d) for $L_\perp=1$ and $L_\parallel=0.8$. The other parameters are written in each figure. We notice the following from the figures: (i) The gel is strongly compressed just below the apex of the cusp. Our results imply $\phi_s/\phi\propto L_\parallel-x$ at $y=0$ as $x\to L_\parallel$. (ii) The surface $x=0.8$ and the curve of $x=0.796$ are noticeably separated at $y\cong\pm d$, indicating enormous and unphysical expansion here. In fact, on the folded part, (4.2) leads to $\phi_s/\phi\sim(d-y)^{-1}$ as y approaches d from below. More generally, (3.34) and (3.35) show that near the point $y=d$ and $x=L_\parallel$, u_x and u_y are expressed as constant terms plus linear combinations of $\rho_j^{1/2}\cos(\frac{1}{2}\theta_j)$ and $\rho_j^{1/2}\sin(\frac{1}{2}\theta_j)$ with $\rho_j e^{i\Theta_j}\equiv\zeta_j-a$, ζ_j being defined by (4.37). The points $y=\pm d$ correspond to tips of cracks in the fracture theory.[8] (iii) Use of (4.34) and (4.35) in writing the figures has been justified because the effect of the cusp has been confirmed to be very small at the bottom, even for the ratio $L_\parallel/L_\perp=0.8$ [except for the homogeneous change (4.22)].

We also note that the coefficients C_{ij} and D_{ij} diverge as $\hat{\delta}\to\hat{\delta}_c$ because C is of order $(1-\hat{\delta}^2)(\hat{\delta}_c^2-\hat{\delta}^2)$. The divergent parts of $\mathbf{u}$ are of order $|\epsilon||y^2-d^2|^{1/2}/(\hat{\delta}_c^2-\hat{\delta}^2)$ for $y\simeq d$ and $x\simeq L_\parallel$. The profile becomes deformed into meaningless shapes if we let $\hat{\delta}\to\hat{\delta}_c$ with d held fixed. Therefore to avoid unphysical profiles, we must require

$$|\epsilon|d/L_\perp\lesssim\hat{\delta}_c^2-\hat{\delta}^2\quad\text{as }\hat{\delta}\to\hat{\delta}_c\ , \tag{4.43}$$

where the proportionality constant is of order 1 and has been deleted. If (4.43) is not satisfied, unphysical overlapping occurs in the region $y\simeq L_\perp/2$ and $x\simeq L_\parallel$. Furthermore, for $\epsilon>1$, (4.34) and (4.35) result in overlapping [namely, $(\partial X/\partial x)<0$] just below the apex of the cusp in region IV of Fig. 2. From (4.40) we find for $y=0$, $L_\parallel-x\ll d$, and $d/L_\perp\ll 1$,

$$\frac{\partial X}{\partial x}\simeq\tfrac{1}{2}k_\perp(L_\parallel-x)a^{-1}\left[\hat{\delta}^2C_\parallel+\hat{\kappa}^2C_{12}+\frac{2}{\pi}(\hat{\delta}^2C_{21}+\hat{\kappa}^2C_{22})\right]\ . \tag{4.44}$$

The boundary between regions II and IV in Fig. 2 is obtained by setting the quantity in the large parentheses of (4.44) equal to 0. The maximum of ϵ in region II is given by 0.46 at $\hat{\delta}=0.57$. By writing profiles from (4.34) and (4.35), we find that the overlapping is small near the boundary curve, such that it seems to be remedied if nonlinear elastic effects are accounted for. However, for $\epsilon>1$, the overlapping is so destructive, indicating no cusp formation for $\epsilon>1$.

V. FREE-ENERGY CHANGE AND ITS MINIMIZATION

A. Free-energy change in the linear approximation

Here we estimate the free-energy change due to the pattern formation, on the basis of the results so far. We note that the scaled free energy $\mathcal{F}$, (3.11) or (3.14), in the bilinear approximation can be expressed in the form of a surface integral at $x=L_\parallel$. We denote its integral over one period by $L_\parallel L_\perp \mathcal{F}_1$. Then, from (3.11) and (3.14), we obtain

$$\mathcal{F}=(L_y L_\parallel)\mathcal{F}_1, \quad \Delta F-(\Delta F)_s=(k_B T v_s \alpha_\parallel^2)V\mathcal{F}_1 , \qquad (5.1)$$

where L_y is the linear dimension of the gel in the y axis assumed to be much longer than $L_\perp$, and V is the volume in the homogeneous state. If $\mathbf{u}$ is a stationary solution satisfying (4.7), we readily obtain

$$L_\parallel L_\perp \mathcal{F}_1=\tfrac{1}{2}\int_{-L_\perp/2}^{L_\perp/2} dy(u_y U-u_x R) . \qquad (5.2)$$

Here U and R are defined by (4.8) and (4.9), so that the integrand of (5.2) is nonvanishing only in the folded region $|y|<d$. We have found that $u_y=-y$, U is odd, and u_x is even in the region $|y|<d$. Therefore, decomposing u_x at $x=L_\parallel$ into the sum of $\bar{u}_x$, (4.21), and $u_x-\bar{u}_x$, we find

$$L_\parallel L_\perp \mathcal{F}_1=\left[\frac{8\epsilon^2}{1+\epsilon}\right](L_\parallel/L_\perp)d^2-\int_0^d dy\, yU -2\epsilon\int_0^d dy(u_x-\bar{u}_x)_b . \qquad (5.3)$$

The first term is an increase of the free energy due to

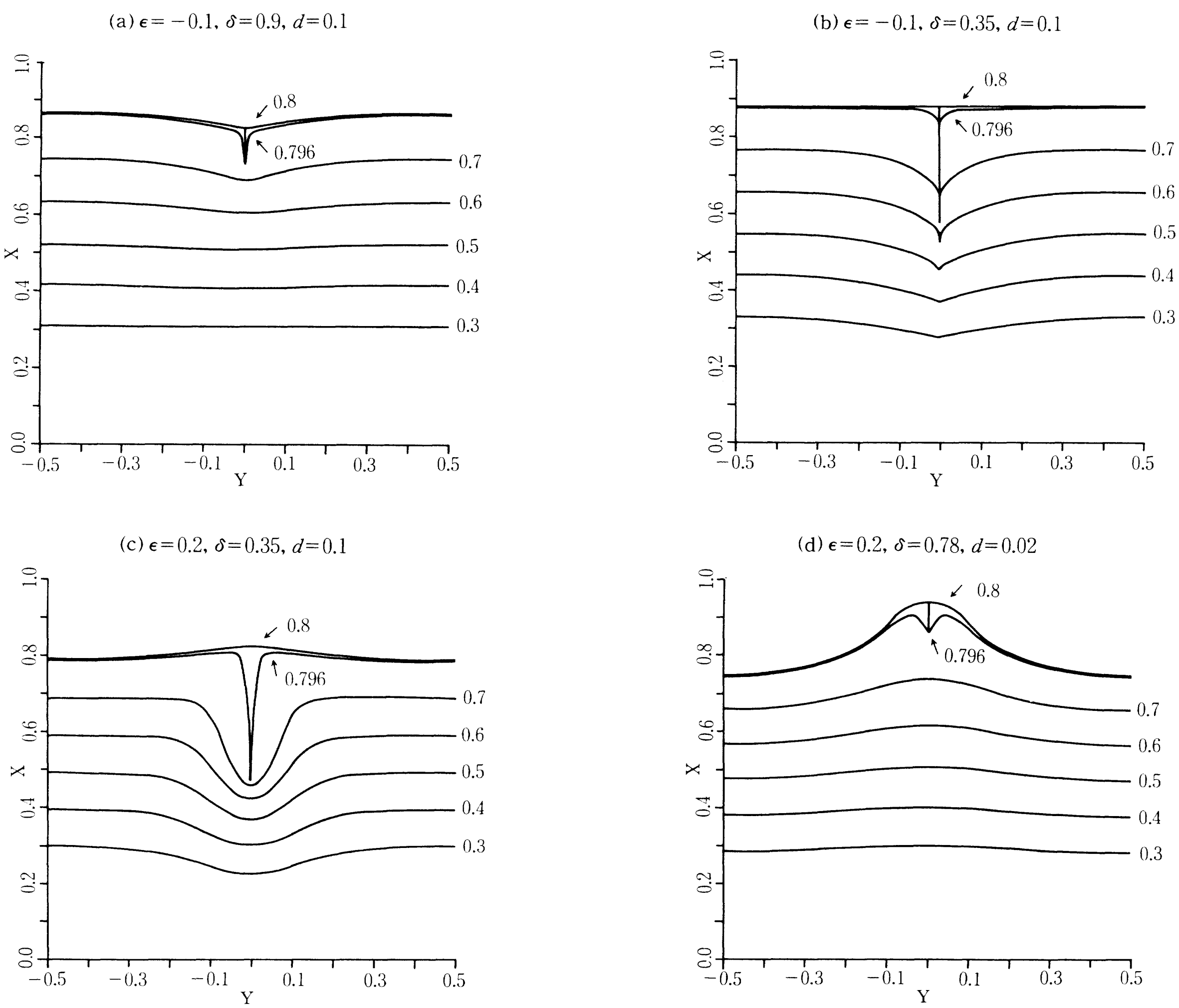

FIG. 3. Cusp profiles in one period for $L_\perp=1$ and $L_\parallel=0.8$ from (4.22), (4.34), and (4.35). Here, $\epsilon=-0.1$, $\hat{\delta}=0.9$, and $d=0.1$ in (a); $\epsilon=-0.1$, $\hat{\delta}=0.35$, and $d=0.1$ in (b); $\epsilon=0.2$, $\hat{\delta}=0.35$, and $d=0.1$ in (c); and $\epsilon=0.2$, $\hat{\delta}=0.78$, and $d=0.02$ in (d). The curves in each figure represent the initial heights $x=0.8$, 0.796, 0.7, 0.6, 0.5, 0.4, and 0.3 from above in the homogeneous state before the cusp formation. In (d) $\hat{\delta}$ is close to the critical value $\hat{\delta}_c=0.82$ at $\epsilon=0.2$, and deformations are large even for $d=0.02$. As stated below (4.19b), the surface is protuberant at the position of folding for $\epsilon>0$, while it is shrinking inward for $\epsilon<0$.

the overall volume change. In fact, if the volume of the system were homogeneously changed as (4.22) without any patterns, the resultant increase of $\mathcal{F}$ could be calculated from (3.14) exactly into the first term of (5.3). The other two terms in (5.3) are generally very complicated; however, they can be expressed as power series of the factors $\exp(-\hat{\delta}k_\perp L_\parallel)$ and $\exp(-\hat{\kappa}k_\perp L_\parallel)$. Assuming (4.20), and neglecting corrections of the order of these factors, we simply take the limit $L_\parallel \to \infty$ in the second and third terms. That is, we substitute (4.28) into the integrand of the second term of (5.3) and (4.33) into

$$(u_x-\bar{u}_x)_b=\int_0^y dy' F_1(y')-\frac{1}{L_\perp}A_1 \ , \tag{5.4}$$

where $F_1(y)\equiv(\partial u_x/\partial y)_b$ given in (4.33), and A_1 is the integral of the first term of (5.4) over one period. After some calculations, we find that $\mathcal{F}_1$ is proportional to d^2 in the limit $d/L_\perp \ll 1$ (as in the case of cracks[8]), so that we express $\mathcal{F}_1$ in the form

$$\mathcal{F}_1=\frac{8\epsilon^2}{1+\epsilon}(d/L_\perp)^2-(\sigma_n-\sigma_p)d^2/L_\perp L_\parallel \ , \tag{5.5}$$

where σ_n and σ_p are positive quantities written as

$$\sigma_n=J_1C/\hat{\delta}(1-\hat{\delta}^2)+[2\epsilon(1-2d/L_\perp)]^2J_2\hat{\kappa}(1-\hat{\delta}^2)/C \ , \tag{5.6}$$

$$\sigma_p=[2\epsilon(1-2d/L_\perp)C']^2J_1/[\hat{\delta}(1-\hat{\delta}^2)C] \ . \tag{5.7}$$

Here, J_1 and J_2 are positive quantities of order 1 only weakly dependent on the ratio $d/L_\perp$; $J_1\simeq\pi/4$ and $J_2\simeq(2/\pi)\ln(L_\perp/d)$ for small $d/L_\perp$, while they behave as $J_1\simeq J_2\simeq(2/\pi)\ln a$ for $a=\tan(\frac{1}{2}k_\perp d)\gg 1$ (see Appendix E).

To estimate σ_n and σ_p we recall the relations $C\sim(\hat{\delta}^2-\hat{\delta}_c^2)(\hat{\delta}^2-1)$ and $C'\sim 1-\hat{\delta}^2$, where the proportionality coefficients are positive quantities of order 1 (see Appendix C). Then we can estimate each term in σ_n and σ_p: the first term in $\sigma_n\sim(\hat{\delta}_c^2-\hat{\delta}^2)/\hat{\delta}$, the second term in $\sigma_n\sim\epsilon^2/(\hat{\delta}_c^2-\hat{\delta}^2)$, and $\sigma_p\sim\epsilon^2/\hat{\delta}(\hat{\delta}_c^2-\hat{\delta}^2)$, where $1-2d/L_\perp$ is assumed to be not close to 0. Each term changes its sign across the curve $\hat{\delta}=\hat{\delta}_c$, and the cusp has a meaningful shape only for $\hat{\delta}<\hat{\delta}_c$ as found in (4.19b) and in the sentence below (4.33). From these estimates we notice that there are two limiting cases: If $\hat{\delta}$ is not close to $\hat{\delta}_c$, such that $\hat{\delta}_c^2-\hat{\delta}^2\gtrsim|\epsilon|$, we find

$$\sigma_n-\sigma_p\simeq J_1C/\hat{\delta}(1-\hat{\delta}^2)\sim(\hat{\delta}_c^2-\hat{\delta}^2)/\hat{\delta} \ . \tag{5.8}$$

On the other hand, if $0<\hat{\delta}_c^2-\hat{\delta}^2\lesssim|\epsilon|$ (namely, if close to the curve $\hat{\delta}=\hat{\delta}_c$), we find

$$\begin{aligned}\sigma_n-\sigma_p&\simeq 4\epsilon^2(J_2-J_1)(1-2d/L_\perp)^2\hat{\kappa}(1-\hat{\delta}^2)/C\\&\sim\epsilon^2/(\hat{\delta}_c^2-\hat{\delta}^2) \ ,\end{aligned}\tag{5.9}$$

where J_2-J_1 is positive-definite. Note that $\sigma_n-\sigma_p$ diverges as $\hat{\delta}\to\hat{\delta}_c$ in the second case. This requires that the optimal value of d, which minimizes $\mathcal{F}$, must goes to 0 as $\hat{\delta}\to\hat{\delta}_c$, consistently with (4.43). We can numerically check $\sigma_n>\sigma_p$ everywhere in region II of Fig. 2. On the other hand, in region IV of Fig. 2 there appears a region of $\sigma_n<\sigma_p$, below the dotted curve in region IV, where the profile itself is meaningless, containing unphysical overlapping as found below (4.44).

B. Free-energy minimum and nonlinear contributions

The next step of the theory is to minimize $\mathcal{F}$ as a function of $L_\perp$ and d, and to determine their optimal values. However, this procedure is not possible within the linear theory. To show this, we rewrite $\mathcal{F}_1$, (5.5), in terms of new dimensionless variables

$$r=L_\perp/L_\parallel, \quad s=d/L_\perp \ . \tag{5.10}$$

Then,

$$\mathcal{F}_1=\alpha_0 s^2-(\sigma_n-\sigma_p)s^2r \ , \tag{5.11}$$

where $\alpha_0=8\epsilon^2/(1+\epsilon)$. The right-hand side can surely be negative for $\sigma_n>\sigma_p$ with increasing r, but there can be no upper limit of r in this form (even if we take into account the r dependence of $\sigma_n-\sigma_p$).

Here we should recall that the gel is strongly deformed near the cusp of the gel, as shown in Fig. 3. This nonlinear effect should give rise to a positive contribution to $\mathcal{F}_1$. Also, the effect of finite thickness should be taken into account. However, I have not yet succeeded in calculating these effects at present. Instead of tackling these tough calculations, we tentatively present a phenomenological approach to determine r and s. Let r and s both be considerably smaller than 1. Then we assume that $\mathcal{F}_1$ may be expanded as

$$\mathcal{F}_1=\alpha_0 s^2-(\sigma_n-\sigma_p)s^2r+\alpha_1 s^3+\beta_1 s^2r^2+\cdots \ . \tag{5.12}$$

The coefficients $\alpha_1, \beta_1, \ldots$, should be able to be calculated by perturbation calculations starting with the linear solution given in Sec. IV C. This suggests that these coefficients are functions of $\Lambda=\epsilon/(\hat{\delta}_c^2-\hat{\delta}^2)$, since $\epsilon C'/C\sim\Lambda$, which appear in (4.32) and (4.33). They will tend to some limits as $|\Lambda|\to 0$ and grow with some powers of Λ for $|\Lambda|\to\infty$. Note that $\sigma_n-\sigma_p$ behaves in this manner, as shown in (5.8) and (5.9). If $\alpha_1>0$, $\beta_1>0$, and $(\sigma_n-\sigma_p)^2>4\alpha_0\beta_1$, $\mathcal{F}_1$ can attain a minimum with only the two additional terms written in (5.12). The optimal values are

$$r=(\sigma_n-\sigma_p)/2\beta_1, \quad s=\tfrac{2}{3}[(\sigma_n-\sigma_p)^2-4\alpha_0\beta_1]/4\alpha_1\beta_1 \ . \tag{5.13}$$

We assume $\beta_1\sim 1$ for $|\Lambda|<1$. Then,

$$r\sim\hat{\delta}_c^2-\hat{\delta}^2 \quad \text{for } |\epsilon|\lesssim\hat{\delta}_c^2-\hat{\delta}^2 \ . \tag{5.14}$$

Namely, even if $\epsilon\to 0$, r should remain finite. The value of s should also be of the order of some power of $\hat{\delta}_c^2-\hat{\delta}^2$. On the other hand, let $\beta_1\sim\Lambda^{2n}\to\infty$ as $|\Lambda|\to\infty$; then, $r\sim(\hat{\delta}_c^2-\hat{\delta}^2)\Lambda^{2(1-n)}$ and s remains positive only for $4\geq 2+2n$. These lead to $n=1$. As regards s, we can determine the upper bound from (4.42). Thus

$$r\sim\hat{\delta}_c^2-\hat{\delta}^2, \quad s\lesssim(\hat{\delta}_c^2-\hat{\delta}^2)/|\epsilon| \quad \text{for } \hat{\delta}_c^2-\hat{\delta}^2\lesssim|\epsilon| \ . \tag{5.15}$$

These results are consistent with the initial assumptions, $r<1$ and $s<1$.

The above results have no firm theoretical basis and must be highly conjectural. We need to calculate $\alpha_1, \beta_1, \ldots$ explicitly. In some cases, more higher-order terms might be necessary, and the optimal value of r might not satisfy (4.20). Nevertheless, we propose (5.14) and (5.15) as guiding predictions for future measurements of r and s in various conditions. Such experiments should be very informative even if they would contradict (5.14) and (5.15).

VI. SUMMARY AND CONCLUDING REMARKS

We give a summary of our results together with comments. In Sec. II we have presented our phenomenological model of gels near the phase transition. This model will be useful also to study a number of other interesting problems involving anisotropy and inhomogeneities, such as phase transitions in affinely deformed gels[6,27] or spinodal decomposition in gels.

In Sec. III we have developed the linear scheme around uniaxial homogeneous states, and have focused our attention on the stability of the upper surface of uniaxially clamped gels for two given parameters, $\hat{\delta}=\alpha_\perp/\alpha_\parallel$ and ϵ (the degree of incompressibility), which are defined in (3.12) and (3.13) and examined in Appendix A. When the gel is stretched in the region $\hat{\delta}<\hat{\delta}_c(\epsilon)$, it becomes unstable against surface perturbations in an intermediate wave-number region. The lower bound arises from the fact that the lower surface is fixed and is of order $\ln[1/(\hat{\delta}_c^2-\hat{\delta}^2)]/L_\parallel$. The upper bound arises from the gradient term in the free energy and is of order $(\hat{\delta}_c^2-\hat{\delta}^2)^{1/2}/R_G$. Here $L_\parallel$ and R_G are the gel thickness and the gyration radius. As stated at the end of Sec. III C, the growth of surface corrugations will saturate, resulting in some final patterns on the surface. However, nothing is virtually known at present on effects of nonlinear terms (higher than quadratic in the displacement $\mathbf{u}$) in the free energy ΔF, (2.2). It is natural to expect that, if such nonlinear contributions to ΔF increase greatly against large corrugations, their growth will be stopped before folding. Then the final pattern will be some corrugated surface without folding. This seems to be the case, particularly for large ϵ; indeed, if ϵ is large, there is no reason for neglecting the term $\frac{1}{2}\epsilon J^2(\propto u^4)$ in (3.11). In this paper, however, we have not examined such a possibility. Instead, we have assumed from the beginning that corrugations grow until they touch to form folding. This should be the case, of course, for $|\epsilon|\lesssim 1$, in view of the actual observation of the cusp pattern. In Sec. III D, to clarify the special nature of the instability in clamped gels, we have examined the stability of gel plates whose lower and upper surfaces are both in contact with solvent. In the latter case, if $\epsilon>0$, the plate simply bends for $\hat{\delta}<1$ without small-scale fluctuation enhancement. However, if $\epsilon<0$ and $\hat{\delta}>1$, the nature of the instability remains similar to that of clamped gels in region III of Fig. 2.

In Sec. IV A we have shown that the boundary conditions at the folded part, (4.1) and (4.4), are very different from those of the surface in contact with the solvent, (3.18) and (3.19). That is, the folded parts press each other. In Sec. IV B a single cusp in thick gels has been calculated as an illustrative example. There, we have derived the integral Eq. (4.10) involving the Hilbert transformation for the strain $\partial u_x/\partial y+\partial u_y/\partial x$ on the upper surface. The analytic solution is similar to that of cracks,[8] and the upper points $y=\pm d$ corresponds to tips of cracks. Then in Sec. III C, the analytic solutions representing periodic roll patterns have been obtained in the thick-gel case (4.20). The gradients of the displacement, $\partial u_i/\partial x_j$, are expressed as (4.34), (4.35), (4.40), and (4.41) in terms of the analytic functions $F(\zeta)$ and $G(\zeta)$ defined in (4.38) and (4.39). The coefficients in these expressions, (4.36), diverge as $1/(\hat{\delta}_c^2-\hat{\delta}^2)$ in the limit $\hat{\delta}\to\hat{\delta}_c$, which then leads to (4.43): the ratio of the depth of the folding to the period $d/L_\perp$ must be, at most, of order $(\hat{\delta}_c^2-\hat{\delta}^2)/|\epsilon|$ as $\hat{\delta}\to\hat{\delta}_c$.

In Sec. V, the free-energy change due to the periodic cusp formation has been calculated as (5.5) in the linear scheme, which can be surely negative if $\sigma_n>\sigma_p$. Unfortunately, however, to determine the optimal values of d and $L_\perp$, which minimize the free energy, we must further take into account the nonlinear elastic effect near the cusp and the finite thickness effect. In this paper, deferring this task to the future, we have proposed the expansion (5.12) of the free energy in powers of $r=L_\perp/L_\parallel$ and $s=d/L_\perp$, assuming that r and s are considerably smaller than 1. Then the estimations of r, (5.14) and (5.15), have followed. The thick-gel assumption, (4.20), seems to be supported at least near the marginal curve $\hat{\delta}=\hat{\delta}_c$. The contents of this section are very insufficient and further efforts are required.

Final comments are as follows: (i) Our solutions to the cusp patterns give extremum to the free energy as a functional of the displacement. However, they do not give the minimum. Hence there should be some coarsening of the pattern and gradual increase of d, until $L_\perp$ and d minimize the free energy. This process has indeed been observed, and a coarsening law, $L_\perp(t)\propto t^\alpha$, has been found.[2,30] Some insight into the coarsening can be obtained from the simulation by Hwa and Kardar,[9] and simulation on a two-dimensional cell pattern by Nagai *et al.*[31] (ii) In the experiment[2] hexagonal patterns were observed. However, roll patterns will also appear when the linear dimension L_z in the z axis is not large. (iii) As argued above, the cusp formation for large ϵ is very improbable. We also stress that nothing is known about the pattern formation in regions III and IV in Fig. 2. Therefore, observation of the pattern, with changing external parameters such as the temperature, is strongly needed. Experiments can be compared with our theory if use will be made of the results in Appendix A, where ϵ and $\hat{\delta}$ are expressed in terms of the usual parameters in the literature. (iv) Matsuo and Tanaka have reported their finding of intriguing patterns in shrinking gels.[32] Hirotsu also observed a network pattern on the surface of a gel slightly shrinking near the critical point.[30] Such a corrugated pattern will appear permanently for $\hat{\delta}>1$ and $\epsilon<0$ (region III in Fig. 2) as long as the lateral dimensions are fixed (even if the lower surface is not clamped as shown in Sec. III D). (v) If the system is situated very close to the curve $\hat{\delta}=\hat{\delta}_c(\epsilon)$ in Fig. 2, the amplitude of the surface inhomogeneities will be small and cubic, and quartic terms in the free energy will suffice to describe the patterns. Here, the transition can well be of first-order due to the general presence of the cubic terms. To see such a discontinuity, we propose experiments on a clamped gel in the presence of a temperature gradient in the lateral direction. (vi) Indeed, we encounter a rich variety of new phenomena emerging when networks undergo phase transitions.

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APPENDIX A

We consider uniaxial homogeneous gels whose lower surface is clamped, and express $\hat{\delta}$ and ϵ in terms of parameters in the Flory theory.[13,16,33] For simplicity we assume that the osmotic pressure from above $\Pi_\parallel$ vanishes. The free-energy density f in (2.2) is given by

$$f=a^{-3}[(1-\phi)\ln(1-\phi)+\chi\phi(1-\phi)] + \nu_0(\tfrac{1}{2}+f_i)(\phi/\phi_0)\ln(\phi/\phi_0) , \quad \text{(A1)}$$

where a is the monomer size, χ is the interaction parameter representing the solvent quality with respect to the polymer, and f_i is the degree of ionization per effective chain. The χ may be assumed to depend on the temperature T by

$$u\equiv 1-2\chi=A(T-T_\theta) , \quad \text{(A2)}$$

where A is a constant and T_θ is the θ temperature.[13,19] Here we fix the elongation ratio $\alpha_\perp$ in the perpendicular directions. Then $\phi=(\phi_0/\alpha_\perp^2)/\alpha_\parallel$ or $\alpha_\parallel$ should be determined by the minimum condition of the total free energy.[33] Defining $g=\Delta F/(V_0\phi_0k_BTa^{-3})$, we obtain

$$g=u\phi+\tfrac{1}{6}\phi^2+\gamma\ln\phi+\tfrac{1}{2}\alpha\phi^{-2}+\text{const} , \quad \text{(A3)}$$

where we have expanded $\ln(1-\phi)$ in (A1) in powers of ϕ assuming $\phi \ll 1$ and

$$\gamma=\nu_0a^3(f_i+\tfrac{1}{2})/\phi_0, \quad \alpha=\nu_0a^3\phi_0/\alpha_\perp^4 . \quad \text{(A4)}$$

The condition $\Pi_\parallel=0$ is equivalent to the condition $\partial g/\partial\phi=0$ [see (3.6)], which yields

$$u=-\tfrac{1}{3}\phi-\gamma\phi^{-1}+\alpha\phi^{-3} . \quad \text{(A5)}$$

On the other hand, ϵ defined by (3.12) becomes

$$\epsilon+1=\alpha^{-1}\phi^3(\tfrac{1}{3}\phi-\gamma\phi^{-1}+3\alpha^{-3}) = -\alpha^{-1}\phi^4(du/d\phi) . \quad \text{(A6)}$$

The second line has been derived using (A5). The ratio $\hat{\delta}=\alpha_\perp/\alpha_\parallel$ is written as

$$\hat{\delta}=(\alpha_\perp^3/\phi_0)\phi . \quad \text{(A7)}$$

Note that the critical point under $\Pi_\parallel=0$ can be obtained from $du/d\phi=d^2u/d\phi^2=0$. More general cases with $\Pi_\parallel\neq 0$ are discussed in Ref. 33. The critical value of γ (for given α) and the critical volume fraction are given by

$$\gamma_c=2\alpha^{1/2}, \quad \phi_c=3^{1/2}\alpha^{1/4} . \quad \text{(A8)}$$

For $\gamma<\gamma_c$ there occurs a first-order phase transition, and two phases can coexist with a sharp planar interface. In this case, there are no shear deformations because the system is allowed to change its shape in only one direction. The phase change will occur from the upper surface like the melting of ice into water. Let u_1 be the value of u at the two-phase coexistence, and ϕ_1 and ϕ_2 be the volume fractions in the two phases. Then from $g(\phi_1)=g(\phi_2)$, we find the Maxwell rule $\int_{\phi_1}^{\phi_2}d\phi[u(\phi)-u_1]=0$. In particular, when γ/γ_c-1 is a small positive number, we find near the critical point,

$$u/\phi_c\simeq\tfrac{2}{3}(\gamma/\gamma_c-1)(\phi/\phi_c-1)-\tfrac{8}{9}(\phi/\phi_c-1)^3+\text{const} . \quad \text{(A9)}$$

If the system is stable (neither metastable nor unstable), ϵ assumes a minimum at the two-phase coexistence in our model. It is equal to $\epsilon=-1+12(\gamma/\gamma_c-1)+\cdots$ near the critical point.

APPENDIX B

First, to find some general relations, we introduce a Hermitian form $\langle \mathbf{v},\mathbf{u}\rangle$ for two two-dimensional vectors $\mathbf{v}(\mathbf{x})$ and $\mathbf{u}(\mathbf{x})$ by

$$\langle \mathbf{v},\mathbf{u}\rangle=\int\int dx\,dy\left[\left[\frac{\partial}{\partial x}v_x-\frac{\partial}{\partial y}v_y\right]\left[\frac{\partial}{\partial x}u_x-\frac{\partial}{\partial y}u_y\right]+\left[\frac{\partial}{\partial y}v_x+\frac{\partial}{\partial x}v_y\right]\left[\frac{\partial}{\partial y}u_x+\frac{\partial}{\partial x}u_y\right]+\epsilon(\nabla\cdot\mathbf{v})(\nabla\cdot\mathbf{u})+(\hat{\delta}^2-1)\left[\frac{\partial}{\partial y}\mathbf{v}\right]\cdot\left[\frac{\partial}{\partial y}\mathbf{u}\right]\right] . \quad \text{(B1)}$$

The integration region is given by $0<x<L_\parallel$ and $-\infty<y<\infty$, and $\mathbf{u}$ and $\mathbf{v}$ satisfy the boundary conditions (3.18) and (3.19). Then we readily obtain

$$\langle \mathbf{v},\mathbf{u}\rangle=\langle \mathbf{u},\mathbf{v}\rangle=-\int\int dx\,dy\,\mathbf{v}\cdot\left[\epsilon\nabla(\nabla\cdot\mathbf{u})+\left[\frac{\partial^2}{\partial x^2}+\hat{\delta}^2\frac{\partial^2}{\partial y^2}\right]\mathbf{u}\right] . \quad \text{(B2)}$$

Hence any eigenvalue λ of (3.24) must be real, and different eigenfunctions, $\mathbf{u}_1$ and $\mathbf{u}_2$, with different eigenvalues are orthogonal in the sense that $\int dx\, dy \mathbf{u}_1 \cdot \mathbf{u}_2 = 0$.

Next, assuming $\mathbf{u} \propto \exp(iky)$ we find from (3.24),

$$\left[(1+\epsilon)\frac{\partial^2}{\partial x^2} - (\epsilon + \hat{\delta}^2)k^2 + \lambda\right](\nabla \cdot \mathbf{u}) = 0 , \quad \text{(B3)}$$

$$\left[\frac{\partial^2}{\partial x^2} - \hat{\delta}^2 k^2 + \lambda\right]\left[\frac{\partial}{\partial x}u_y - \frac{\partial}{\partial y}u_x\right] = 0 . \quad \text{(B4)}$$

This shows that $\mathbf{u}$ can be expressed as a linear combination of $e^{\pm\kappa_1 x}$ and $e^{\pm\kappa_2 x}$ if $\kappa_1 \neq \kappa_2$, and we obtain (3.26) and (3.27), where κ_1 and κ_2 are defined by (3.28) and (3.29). The boundary condition (3.4) leads to

$$W_+ + W_- = \psi_+ + \psi_- , \quad \text{(B5)}$$

$$W_+ - W_- = \hat{\kappa}_1 \hat{\kappa}_2 (\psi_+ - \psi_-) , \quad \text{(B6)}$$

while (3.18) and (3.19) yield

$$\tilde{W}_+ + \tilde{W}_- = \tfrac{1}{2}(1+\hat{\kappa}_1^2)(\tilde{\psi}_+ + \tilde{\psi}_-) , \quad \text{(B7)}$$

$$\tilde{W}_+ - \tilde{W}_- = [2\hat{\kappa}_1\hat{\kappa}_2/(1+\hat{\kappa}_1^2)](\tilde{\psi}_+ - \tilde{\psi}_-) . \quad \text{(B8)}$$

Here $\tilde{W}_\pm \equiv W_\pm \exp(\pm\kappa_1 L_\parallel)$, and $\tilde{\psi}_\pm \equiv \psi_\pm \exp(\pm\kappa_2 L_\parallel)$. From these equations we can derive (3.31).

Finally we consider the eigenvalue problem for $\hat{\kappa}_1 = \hat{\kappa}_2 = 1$. From (3.4) and (3.24), $\hat{\lambda}$ is uniquely equal to $\hat{\delta}^2 - 1$ and u_x and u_y are expressed as

$$u_x = A_1[\sinh(kx) - \alpha kx \cosh(kx)] - i\alpha A_2 kx \sinh(kx) , \quad \text{(B9)}$$

$$u_y = A_2[\sinh(kx) + \alpha kx \cosh(kx)] - i\alpha A_1 kx \sinh(kx) , \quad \text{(B10)}$$

where A_1 and A_2 are coefficients and $\alpha = \epsilon/(2+\epsilon)$. Then imposing (3.18) and (3.19) we obtain

$$\tanh^2(kL_\parallel) = 1 + \epsilon(2+\epsilon)/[1+\epsilon^2(kL_\parallel)^2] . \quad \text{(B11)}$$

This has a solution only for $\epsilon < 0$ (since $2+\epsilon > 0$) and $kL_\parallel$ is a monotonically decreasing function of $\epsilon' = |\epsilon|$ in the region $0 < \epsilon' < 1$. We find $kL_\parallel \simeq \frac{1}{2}\ln(2/\epsilon')$ for $\epsilon' \ll 1$ and $kL_\parallel \to 0$ as $\epsilon' \to 1$.

APPENDIX C

The equivalence of (3.32) and (3.33) follows from the relations

$$1 - \hat{\kappa}_1\hat{\kappa}_2 = (1-z)(z+1+\epsilon)/[(1+\epsilon)(1+\hat{\kappa}_1\hat{\kappa}_2)] , \quad \text{(C1)}$$

$$(1+\hat{\kappa}_1^2)^2 - 4\hat{\kappa}_1\hat{\kappa}_2 = (z-1)f_c(z)/[(1+\hat{\kappa}_1^2)^2 + 4\hat{\kappa}_1\hat{\kappa}_2] , \quad \text{(C2)}$$

where $\hat{\kappa}_1^2$ is written as z, and $f_c(z)$ is defined in (3.34). Thus the left-hand side of (3.32) is equal to $-(1-z)^2 f_c(z)$ multiplied by a positive quantity. Elementary calculations show that $f_c(z)$ has a unique positive root and $f_c(z)$ is equal to $(z - \hat{\delta}_c^2)$ multiplied by a positive quantity for $z > 0$.

The coefficient C, defined by (4.12), is just equal to the quantity in (C2) if we replace $\hat{\kappa}_1$ and $\hat{\kappa}_2$ by $\hat{\delta}$ and $\hat{\kappa}$, respectively. Thus C divided by $(\hat{\delta}^2 - 1)(\hat{\delta}^2 - \hat{\delta}_c^2)$ is positive-definite. Next, the positivity of the factor $C + 2\epsilon C'$ will be shown, which appears in U_0, (4.16). By writing $z = \hat{\delta}^2$, we have from (4.12)~(4.14),

$$C + 2\epsilon C' = [(1+z)(1+z+2\epsilon) + 4\hat{\delta}\hat{\kappa}(1+\epsilon)]^{-1}(1-z)^2 \times [(2\epsilon + z + 1)^2 + 4z] . \quad \text{(C3)}$$

This also indicates that U_0 vanishes in the limit $\hat{\delta} \to 1$.

Third, we show the positivity of $(\partial u_x/\partial y)_b$, (4.18), in the region $0 < y < d$. A manipulation like (C1) leads to $C'(1-\hat{\delta}^2) > 0$ for any $\hat{\delta}$, so that the first term in (4.18) is positive-definite. We then examine whether or not the second logarithmic term can cancel the first term. For this purpose, we may assume $\epsilon > 0$ and $\hat{\delta} < \hat{\delta}_c < 1$ to find $\hat{\kappa} < 1$ and $C' > (1-\hat{\delta}^2)^2$. The last inequality, if substituted into (4.18), assures the positivity.

APPENDIX D

1. Single cusp in the limit $L_\parallel \to \infty$

It is convenient to introduce $x' = L_\parallel - x$ (>0 in the gel). Let $(\ )_k$ denote the Fourier transform with respect to y. In the limit $L_\parallel \to \infty$, $(U_x)_k$ and $(U_y)_k$ depend on x' as $f_1 = \exp(-\hat{\delta}|k|x')$ or $f_2 = \exp(-\hat{\kappa}|k|x')$, where $\hat{\kappa}$ is defined by (4.14), and the coefficients in front of f_1 and f_2 can be written in terms of the Fourier transforms of U, (4.8), and R, (4.9). Some calculations yield

$$\left[\frac{\partial}{\partial y}u_x\right]_k = \frac{1}{C}[(1+\hat{\delta}^2)U_k + 2i\hat{\kappa}(\mathrm{sgn}k)R_k]f_1 - \frac{1}{C}\hat{\kappa}[2\hat{\delta}U_k + i(1+\hat{\delta}^2)(\mathrm{sgn}k)R_k]f_2 , \quad \text{(D1)}$$

$$\left[\frac{\partial}{\partial y}u_y\right]_k = \frac{1}{C}\hat{\delta}[i(1+\hat{\delta}^2)(\mathrm{sgn}k)U_k - 2\hat{\kappa}R_k]f_1 + \frac{1}{C}[-2i\hat{\delta}(\mathrm{sgn}k)U_k + (1+\hat{\delta}^2)R_k]f_2 , \quad \text{(D2)}$$

where $\mathrm{sgn}k$, the sign of k, appears from derivatives with respect to x. Then (4.10) follows with the aid of the following relation for arbitrary function $f(x)$:

$$\hat{H}f = i(2\pi)^{-1}\int dk(\mathrm{sgn}k)f_k e^{iky} , \quad \text{(D3)}$$

where $\hat{H}$ is the Hilbert transformation defined by (4.11).

2. Periodic case in the limit $L_\parallel \to \infty$

If $f(y)$ is a periodic function with period $L_\perp$, it can be expressed as $f(y) = \sum_n f_n \exp(ik_n y)$, where $k_n = 2\pi n/L_\perp$. Here $(\cdots)_n$ denotes the Fourier component. Then (D1) and (D2) still hold for $\partial u_x/\partial y$ and $\partial u_y/\partial y$, provided that the lower subscript k is replaced by n, $\mathrm{sgn}k$ by $\mathrm{sgn}n$, and $|k|$ in the definitions of f_1 and f_2 by $|k_n|$. Equation (4.24) can be obtained from the relation

$$\hat{\mathcal{H}}f = \sum_{n(\neq 0)} i(\mathrm{sgn}n)f_n e^{ik_n y} . \quad \text{(D4)}$$

Equations (4.34) and (4.35) can be calculated as follows. Note that the following function is an analytic function of z in the upper complex plane:

$$F(z)=2\sum_{n(>0)} f_n e^{ik_n z} , \tag{D5}$$

where z is a complex variable, and $f_n(=f^*_{-n})$ is the Fourier component of any real periodic function $f(y)$. Then the real and imaginary parts of F are expressed as

$$F_R(z)=\sum_{n(\neq 0)} f_n \exp(ik_n z_R-|k|z_I) , \tag{D6}$$

$$F_I(z)=-\sum_{n(\neq 0)} i(\mathrm{sgn}\,n)f_n \exp(ik_n z_R-|k|z_I) , \tag{D7}$$

where $z_R=\mathrm{Re}(z)$ and $z_I=\mathrm{Im}(z)$. Let z approach the real axis as $z_R \to y$ and $z_I \to 0$; then,

$$F_R \to f(y)-f_0, \quad F_I \to -(\hat{\mathcal{H}}f)(y) . \tag{D8}$$

These theorems can now give rise to (4.34) and (4.35), if use is made of (D1) and (D2). On approaching the real axis, we have $F_R \to p\Theta(a-|p|)/(a^2-p^2)^{1/2}$, $F_I \to |p|\Theta(|p|-a)/(p^2-a^2)^{1/2}$, $G_R \to -\Theta(|p|-a)$, and $G_I \to \pi^{-1}\ln|(a+p)/(a-p)|$ with $p=\tan(\frac{1}{2}k_\perp y)$.

APPENDIX E

Here Eqs. (5.6) and (5.7) will be derived. The terms proportional to J_1 in (5.6) and (5.7) are contributions from U, (4.28), and the first term of (4.33). The J_1 reads

$$J_1=\frac{1}{bd^2}\int_0^d dy\, yp/(a^2-p^2)^{1/2} , \tag{E1}$$

where p, a, and b are defined in (4.26), (4.29), and (4.31). The second term in (5.6) is the contribution from the second logarithmic term in (4.33). The J_2 is defined by

$$(1-2d/L_\perp)^2 J_2=\frac{1}{\pi d}\int_0^{L_\perp} dy[1-2y/L_\perp-\Theta(d-y)(1-y/d)]\ln\left|\frac{a+p}{a-p}\right| . \tag{E2}$$

We can examine the behaviors of J_1 and J_2 in detail by changing the integration variable y to appropriate ones. Numerical analysis shows $J_2>J_1>0$ for any $d/L_\perp$.

[1]T. Tanaka, Physica A **140**, 261 (1986).

[2]T. Tanaka *et al.*, Nature **325**, 26 (1987); in *Molecular Conformation and Dynamics of Macromolecules in Condensed Systems,* edited by M. Nagasawa (Elsevier, New York, 1988). He introduced a bending energy in the usual form for a thin plate (see Ref. 8). However, this analogy does not hold if the lower surface is fixed as in clamped gels. Detailed comments can be found in Sec. III D. Note also that the analogy is based on the assumption $k_\perp L_\parallel \lesssim 1$, where $k_\perp$ is the wave vector of the corrugations and $L_\parallel$ is the thickness. On the contrary, our theory of the cusp pattern will be based on the reverse assumption $k_\perp/L_\parallel \gtrsim 1$ [see (4.20) in this paper], which is valid at least for fine patterns in initial stages of swelling, and for slightly unstable gels in which $\hat{\delta} \simeq \hat{\delta}_c$ (see the text). Tanaka also introduced a free-energy increase due to vertical stretching. Analogously, our theory will show the presence of such a term [the first term of (5.3)], but it will arise only after the surface has folded.

[3]A. Onuki, J. Phys. Soc. Jpn. **57**, 703 (1988).

[4]See, for example, F. C. Larché and J. W. Cahn, Acta Metall. **33**, 331 (1985).

[5]K. Sekimoto and K. Kawasaki, J. Phys. Soc. Jpn. **56**, 2977 (1987).

[6]A. Onuki, J. Phys. Soc. Jpn. **57**, 699 (1988).

[7]A. Onuki, in *Dynamics of Ordering Processes in Condensed Matter,* edited by S. Komura and H. Furukawa (Plenum, New York, 1988).

[8]L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon, New York, 1973); M. F. Kanninen and C. H. Popelar, *Advanced Fracture Theory* (Oxford University Press, New York, 1985).

[9]T. Hwa and M. Kardar, Phys. Rev. Lett. **61**, 106 (1988). However, it is not clear whether or not the boundary conditions assumed by them are consistent with their free-energy expression (which is rather unnatural). Note that the stress tensor is uniquely determined once the free energy is given in terms of the deformation tensor.

[10]K. Sekimoto and K. Kawasaki, J. Phys. Soc. Jpn. **57**, 2594 (1988).

[11]A. Onuki, Phys. Rev. A **38**, 2192 (1988); in *Space-Time Organization in Macromolecular Fluids,* Proceedings of the 11th Taniguchi International Conference, Kyoto, 1988 (unpublished).

[12]K. Sekimoto and K. Kawasaki, J. Phys. Soc. Jpn. **57**, 2591 (1988); Physica A **154**, 384 (1989).

[13]P. J. Flory, *Principles of Polymer Chemistry* (Cornell University, Ithaca, NY, 1953).

[14]We assume that the system of a network and a solvent is incompressible, and the pressure of the surrounding solvent p_0 is fixed. Then $d(\Delta F)=-(\Delta S)dT+(\Delta\mu_s)dN_s$, where N_s is the solvent particle number inside the gel, and $\Delta\mu_s$ is the difference of the solvent chemical potential $\mu_s(p,T,N_s)$ in the gel and that of pure solvent $\mu_s^0(p,T)$. From the incompressibility we have $\Pi=p-p_0=\Delta\mu_s/v_0$ and $dV=v_0 dN_s$, where v_0 is the volume per solvent particle.

[15]K. Dušek and K. Patterson, J. Polym. Sci., Part A-2 **6**, 1209 (1968).

[16]T. Tanaka, D. Fillmore, S-T. Sun. I. Nishio, G. Swislow, and A. Shah, Phys. Rev. Lett. **45**, 1636 (1980).

[17]R. Kubo, J. Phys. Soc. Jpn. **3**, 312 (1948).

[18]R. S. Rivlin, in *Rheology,* edited by F. Eirich (Academic, New York, 1956), Vol. 1.

[19]P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1980).

[20]Let D be the determinant of a matrix $\{A_{ij}\}$. Then we have the

identity $\partial D/\partial A_{ij}=DA^{ji}$, where $\{A^{ji}\}$ is the inverse matrix of $\{A_{ij}\}$. If we use this theorem setting $D=\phi_0/\phi$ and $A_{ij}=\partial X_i/\partial x_j^0$, (2.3) readily leads to (2.8).

[21]T. Tanaka, L. O. Hocker, and G. B. Benedek, J. Chem. Phys. **59**, 5151 (1973).

[22]A.-M. Hecht and E. Geissler, J. Phys. (Paris) **45**, 309 (1984).

[23]J. C. Bacri, J. Dumas, and A. Levelut, J. Phys. (Paris) Lett. **40**, L-231 (1979).

[24]Usually K is supposed to be positive in elastic theories. In gels, K can be made negative transiently because the time scale of swelling is very slow due to the friction between the network and the solvent. In principle, K/μ can be negative with no instability in any materials if deformations are allowed in only one or two directions (see Ref. 33).

[25]This is because the vector $\partial x/\partial X_i$ is orthogonal to the tangential vector $\partial X_i/\partial y$.

[26]For $\hat{\kappa}_1=1$ each term in (3.31) vanishes and we need to examine this case separately. In Appendix B we see that, if $\hat{\kappa}_1=1$, there is a class of eigenvectors with $\hat{\lambda}=\hat{\delta}^2-1$ in the region $\epsilon<0$, and that $kL_\parallel$ is uniquely determined by negative ϵ. These eigenvectors can also be obtained by taking the limit $\hat{\kappa}_1\rightarrow 1$ in (3.26) and (3.27). Note that the curves in Fig. 1 cross the line $\hat{\kappa}_1=1$ for $\epsilon<0$.

[27]Equation (3.31) can be solved explicitly only for $\epsilon=0$ in the form $kL_\parallel=(2\hat{\kappa}_1)^{-1}\ln[(1+\hat{\kappa}_1)/(1-\hat{\kappa})]$. This shows that $kL_\parallel$ is real for $0\le\hat{\kappa}_1<1$ or for $\hat{\delta}^2\ge\hat{\lambda}>\hat{\delta}^2-1$, and that $\hat{\kappa}_1$ is purely imaginary for $\hat{\lambda}>\hat{\delta}^2$.

[28]Interestingly, the equation $f_c(z)=0$ coincides with the equation to determine the propagation velocity c_R of the surface (Rayleigh) wave (Ref. 8) in isotropic elastic bodies if z is replaced by $1-(c_R/c_t)^2$, c_t being the transverse sound velocity. The ratio of the longitudinal sound velocity c_l to c_t is given by $c_l/c_t=(1+\epsilon)^{1/2}$. Thus we find $c_R/c_t=(1-\hat{\delta}_c^2)^{1/2}$.

[29]H. Bateman, *Tables of Integral Transforms* (McGraw-Hill, New York, 1954), Vol. II, Chap. 15.

[30]S. Hirotsu (private communication).

[31]T. Nagai, K. Kawasaki, and K. Nakamura, J. Phys. Soc. Jpn. **57**, 222 (1988).

[32]E. S. Matsuo and T. Tanaka, J. Chem. Phys. **89**, 1695 (1988).

[33]A. Onuki, J. Phys. Soc. Jpn. **57**, 1868 (1988).