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Spongelike domain structure in a two-dimensional model gel undergoing volume-phase transition

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We have studied the numerical model of a two-dimensional gel exhibiting the volumetric phase separation between the swollen and shrunken phases. We have found a peculiar percolating (spongelike) structure of the shrunken phase domain. A qualitative explanation for the appearance of such a structure is given and its relevance to the real gel system is discussed.

The spatial coexistence in bulk gels of the swollen and shrunken phase domains upon volume-phase transition[1-3] is just beginning to be understood.[4,5] A unique feature of the gel system is that each of these domains is neither isotropic nor homogeneous.[5,6] Here we report a new approach to the volume-phase transition of gels by numerical modeling.

We have constructed the two-dimensional model of a gel on the basis of the free-energy F similar to the Flory model[1,7] having the following functional form:

$$F=\int d^2\mathbf{x}[f(\lambda_1\lambda_2)+(v_0/2)(\lambda_1^2+\lambda_2^2)]\,, \tag{1}$$

where $d^2\mathbf{x}$ is the volume (area) element of the gel in its reference state,[6] which is uniform and isotropic but is arbitrary otherwise, and $\lambda_1^2\equiv[\lambda_1(\mathbf{x})]^2$ and $\lambda_2^2\equiv[\lambda_2(\mathbf{x})]^2$ with $\lambda_1,\lambda_2>0$ are the two principal values of the 2×2 matrix $\underline{M}^T(x)\underline{M}(x)$. Here the 2×2 matrix $\underline{M}(\mathbf{x})$ describes local deformation through $d\mathbf{X}(\mathbf{x})=\underline{M}(\mathbf{x})d\mathbf{x}$ with $\mathbf{X}(\mathbf{x})$ the position of the material point which was at $\mathbf{x}$ in the reference state. $f(\lambda_1\lambda_2)$ is a function of the local swelling ratio $s\equiv\lambda_1\lambda_2$ and represents, in the original Flory model,[1] the mixing free energy of polymer and solvent. The term $(v_0/2)(\lambda_1^2+\lambda_2^2)$ describes the elastic contribution. Here v_0 (>0) is the constant which corresponds to the quantity proportional to the cross-linking density in the original Flory model.[1] We note that according to the Rivlin's large deformation theory[7,8] we have

$$\lambda_1\lambda_2=[\det(\underline{M}^T\underline{M})]^{1/2}=\det(\underline{M})\,, \tag{2}$$

$$\lambda_1^2+\lambda_2^2=\mathrm{tr}(\underline{M}^T\underline{M})\,. \tag{3}$$

These quantities are known[8] to generate all the other quantities that are invariant under the symmetry transformation of isotropically and homogeneously fabricated materials in two dimension. In the isotropic states where $\lambda_1=\lambda_2=s^{1/2}$, the swelling pressure ω, which is conjugate to s, becomes $\omega=\omega(s)=-df(s)/ds-v_0$. We now choose $\omega(s)=-(s-s_1)(s-s_2)(s-s_3)$ with $0<s_1<s_2<s_3$, which can describe the isotropically shrunken (or swollen) state by taking $s=s_1$ (or $s=s_3$) for a freely suspended gel. To facilitate the computation we convert the above continuum model into the discrete one by making the following approximations: We regard the gel to consist of the material-attached finite elements (elementary triangles) which in the reference state form a regular triangular lattice with the lattice constant a. Next we assume that the deformation of the material within a given element is uniform. Thus we can show that if the vertices $\mathbf{X}$, $\mathbf{X}'$, and $\mathbf{X}''$ of an elementary triangle encircle this element counterclockwise in this order, the quantities in (2) and (3) for this element are given as follows:

$$\lambda_1\lambda_2=\frac{2}{\sqrt{3}a^2}(X'Y''-Y'X''+X''Y-Y''X+XY'-YX')\,, \tag{4}$$

$$\lambda_1^2+\lambda_2^2=\frac{2}{3a^2}(|\mathbf{X}'-\mathbf{X}''|^2+|\mathbf{X}''-\mathbf{X}|^2+|\mathbf{X}-\mathbf{X}'|^2)\,. \tag{5}$$

Here we have denoted $\mathbf{X}'=(X',Y')$, etc. Using (4) and (5) we can perform the integration in (1) element by element. We then obtain F as a function of the vertex positions $\{\mathbf{X}_\mu\}$, that is, $F=F\{\mathbf{X}_\mu\}$, where the suffix μ designates each vertex and the parameters (s_1,s_2,s_3,v_0) are suppressed. We sought the local minima (the "metastable" states) of $F\{\mathbf{X}_\mu\}$ with various parameter values and various initial conditions by applying the dissipative molecular dynamics[9-11] in which the νth vertex obeys the following evolution equation:

$$\frac{\partial\mathbf{X}_\nu}{\partial t}=-\frac{\partial F\{\mathbf{X}_\mu\}}{\partial\mathbf{X}_\nu}\,, \tag{6}$$

where t is the time.

Our model free energy (1) does not include the terms depending on the strain gradient. The strain gradient terms would give rise to the interfacial energy associated with the interfaces between the two coexisting phases. To distinguish F defined in (1) from this energy, we call F the bulk energy. In the usual model exhibiting phase separation, such as those of the (incoherent) binary alloys, we cannot discuss the optimal *shape* of domains without the gradient terms of order parameter since the interfacial energy dominates the variation of the free energy in the coexisting state. In contrast to this, the present system of our interest has the feature that the bulk energy (1) dominates in determining the *morphology* of the domain structures in gels. This is essentially due to the fact that the swelling ratio, which is the primary order parameter in a naive sense, is the quantity of geometrical nature, and couples to the shear deformation which strongly depends on the morphology of the domain. We will discuss this point in more detail below. Suppose here that we change the morphology of the domain whose linear dimension is $\sim l$. Then the change in the deformation energy is of the order of l^d (d is the spatial dimensionality) since the free-energy density in (1) contains no characteristic length scale.[6] On the other hand, the corresponding change in the interfacial energy would be of the order of l^{d-1}. This implies that if we consider the domain structure of phase coexistence whose characteristic length scale is sufficiently large (typically larger than the interface thickness), then the morphology, not the length scale, of the domain structure is predominated by the bulk deformation energy. We can show[6] that the integrand on the right-hand side of (1) is invariant under the similarity transformation $\mathbf{X}(\mathbf{x}) \rightarrow \theta\mathbf{X}(\theta^{-1}\mathbf{x})$ with $\theta > 0$. This implies that the bulk energy (1) does not give rise to the driving force for the growth of characteristic length l. We consider the case where l is very large, and we assume that the growth of l is very slow as compared with the equilibration of the morphology of domains. In such a case the "metastable" domain structure, which we will show below (or, more precisely, those which would be found in the three dimensional version of our model), can be compared with the *transient* or true metastable structure of domains of actual gels, and the relaxation Eq. (6) will describe the dynamics of fast process with possibly some modification due to the effect of volume fraction and flow of the solvent. A dynamical equation of this sort was proposed by Tanaka and Fillmore.[12]

Below we describe the results of our numerical computation for the system of $50\times50\times2$ elements subjected to the periodic boundary condition in both *horizontal* (X) and *vertical* (Y) directions. Figure 1(a) shows the initial ($t=0$) random configuration. This configuration has been constructed in two steps: First, we randomly displaced all the vertices from their positions in the regular triangular lattice using the computer generated uniform random numbers. Second, we smoothed the displacements by the process in which the displacement of every vertex is replaced by the average of displacements of the vertex itself and its six neighboring vertices. We have repeated this process ten times, and have thus introduced the characteristic length l which is of the order of ten times the lattice constant a. The size of the system of Figs. 1(a) and 1(b) has been chosen to coincide with that in the reference state ($\lambda_1=\lambda_2\equiv1$). Figure 1(b) shows the metastable phase-coexisting state which was obtained by relaxing the initial state of Fig. 1(a) with the parameters s_1, s_2, s_3, $\nu_0=0.49$, 1.0, 1.69, 0.34, respectively. Figure 2 shows another metastable state derived from that shown in Fig. 1(b) by the adiabatic application of external strain, which we simulated by the repetition of the small affine transformation $(X,Y)\rightarrow((4/5)^{1/10}X,(5/4)^{1/10}Y)$, followed by the relaxation procedure until the system dimension is changed into 80% and 125% of the starting system in the horizontal (X) and vertical (Y) directions, respectively. Figures 1 and 2 show that the shrunken phase forms a single percolating domain having a spongelike structure and that the strain inside that domain is varied locally and is highly anisotropic. Under the external strain (Fig. 2) the structural change occurs both through the deformations inside each domain and through the transformation of some elements from swollen phase into shrunken phase and vice versa. We have also performed computations with other choices of s_1, s_2, s_3, ν_0 and have checked that the percolation of shrunken-phase domain is not dependent on the volume fraction of that phase being large.

We propose a qualitative explanation for the appearance of the percolating shrunken-phase domain: First, we note that an isolated shrunken region, if it ever existed, stretches materials around it in the radial directions.[5] And if there were two such shrunken regions near each other, there will be a highly anisotropic stretching zone *along* the line connecting the centers of these regions. Conversely if there are a certain number of swollen regions separated from each other, the remaining region among them is more or less stretched in the directions *perpendicular* to the lines connecting the centers of the neighboring swollen regions. In any way it seems very

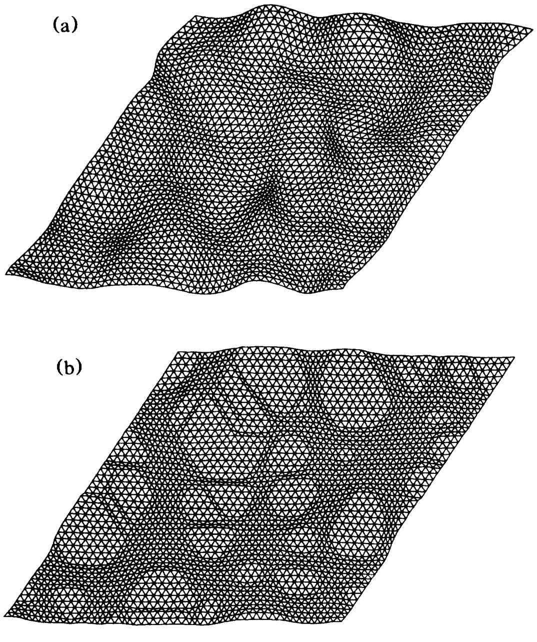

FIG. 1. (a) Randomly distorted initial state. (b) Relaxed state from the initial state.

FIG. 2. Relaxed state after adiabatic compression of the state shown in Fig. 1(b).

likely that the stretched zone forms a spatially connected structure involving all the shrunken regions. Next we note that in the neighborhood of a stretched zone, the strain, and therefore, the volume fraction, is constrained to change along the directions perpendicular to the boundaries of this zone. Therefore, we expect that the interface will be formed along the stretching direction(s) of the stretched zone, and the shrunken-phase domain percolates through the system. Srolovitz, Hassold, and Gayda[13] have done the Monte Carlo simulation that is relevant to our work. They have studied an Ising-spin system with elastic couplings. In their system they did not discuss the topology of domain structure.

Our findings of spongelike domain structure in a model gel system evokes many experimental and theoretical interests: Recent observation by optical micrograph[4] seems to exhibit the three-dimensional spongelike domain structure. The macroscopic storage and loss moduli and the macroscopic permeability of phase separated gels at high frequencies would reflect the existence and topology of percolating shrunken-phase domain. Moreover, the domain-structure dynamics may give rise to the low-frequency dispersion in the shear as well as bulk viscosities.[14] Finally the coarsening process of domains and the accompanying morphology change can be also studied.

The predominance of the deformation energy over the interfacial energy in determining the morphology of the coexisting domain structure will not be the feature unique to polymer gels. The systems undergoing martensitic transformation[15] in solids might be the other examples.

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