Volume Transitions, Phase Separation, and Anisotropic Surface Phases in Charged Gels

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ABSTRACT: Thermodynamic analysis of phase transitions in charged gels in poor solvents is presented. At sufficiently high degree of ionization, the gel undergoes a discontinuous volume transition to a new homogeneous and isotropic phase. When the two-phase coexistence line is reached under fixed volume conditions, the new phase forms a thin anisotropic layer on the surface of the gel. The concentration and the deformation of the surface phase are calculated and the results are generalized to the case of uniaxially deformed gels. The stability of the surface phase is studied and it is shown that a dilute surface phase is unstable against long wavelength fluctuations with wave vectors oriented along the surface of the gel. The connection between the theory and experiments on phase transitions in gels is discussed.

1. Introduction

The complex behavior of charged water-soluble polymer gels is the result of the interplay of long-range elastic and electrostatic forces and short-range hydrophobic interactions, hydrogen bonding, and van der Waals forces. Variation of thermodynamic conditions to which charged (and other, complex) gels are subjected can result in dramatic macroscopic effects on their volume, shape, and permeability and in the appearance of complex patterns on the gel surface.[1,2] Recent neutron scattering experiments[3] and theories[4] suggest the possibility that charged gels may undergo microphase separation, which leads to the reorganization of their density profile on microscopic length scales.

In this work we analyze the thermodynamics of phase transitions in charged gels in poor solvents. Our starting point (the thermodynamic free energy) is the same as that of ref 5 and we arrive at similar results concerning the homogeneous volume transition in gels. The difference between the present work and that of ref 5 stems from the different way phase separation in gels is described. While in the latter work phase separation is discussed in the same language as the coexistence of two phases of different compositions in a binary fluid, we take into account the fact that a gel is a solid and therefore obeys the condition of continuity of the displacement field at the interface between the two phases. This boundary condition leads to the breakdown of the usual thermodynamic rules (Maxwell rule and Gibbs phase rule[6]) and resuls in anisotropic deformation of the coexisting phases, even in the absence of external forces on the surface of the gel.[7]

The most important observation about phase transitions in gels is that, in general, two types of transitions are possible. A gel can undergo a phase transition into a new homogeneous and isotropic state by expelling the solvent and changing its volume. This type of a transition is intimately related to the fact that the gel is a solid which has a unique volume under given thermodynamic conditions and has no analogue in binary liquids. The second type of transition which can take place in gels, as well as in liquids, is phase separation into two coexisting phases of different compositions. However, the presence of elastic forces results in important differences between the thermodynamics and the kinetics of phase separation in gels and in binary liquids. Phase separation in liquids proceeds through nucleation or spinodal decomposition and results in the formation of coexisting bulk phases, each of which is isotropic and homogeneous. In gels, the nucleation of a new bulk phase is strongly suppressed by the fact that the formation of such a nucleus must be accompanied by the deformation of the surrounding elastic medium[8] and the gel remains stable against a volume transition until the spinodal is reached. Since, close to the coexistence line, phase separation proceeds through the formation of an anisotropic phase on the surface of the gel,[7] it is plausible that, for deeper quenches into the coexistence region, phase separation into two coexisting anisotropic bulk phases proceeds through the growth of surface instabilities.

There are several fundamental differences between neutral and charged gels. In the former, the coexistence line which defines the stability limit of the single phase state cannot be reached under conditions of equilibrium swelling. This line can be reached only by fixing the volume of the gel and reducing the solvent quality (exceptions to this rule are complex gels such as NIPA,[9] in which hydrophobic interactions play an important role). In charged gels, different scenarios are possible at swelling equilibrium, depending on the degree of ionization.[10] Weakly charged gels, like their neutral counterparts, change their volume continuously when the thermodynamic conditions are changed. At an intermediate degree of ionization, charged gels can undergo a discontinuous volume transition. At yet higher degree of ionization, the homogeneous gel can separate into two anisotropic and inhomogeneous phases.

In section 2 we present the thermodynamics of charged gels swollen to equilibrium in a poor solvent. Our analysis is based on the standard theory of elasticity of gels which was can be derived from a microscopic theory of Gaussian networks without topological entanglements,[11,12] rather than on the more general but less physically transparent approach based on a nonlinear variant of the theory of elasticity.[13] We study the volume transition between two homogeneous states of different monomer concentrations and find its spinodal and critical point. We show that at sufficiently high degrees of ionization the volume transition is preempted by phase separation into coexisting bulk and

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surface phases. The formation of an anisotropic surface phase which appears at the coexistence line is discussed and the monomer volume fractions in the two phases are calculated. We find that contrary to the standard situation in binary liquids, the compositions of the coexisting phases and their relative amounts cannot be simply read off the phase diagram.

In section 3 we consider phase separation in compressed gels. We derive the phase diagram of a uniaxially deformed cylindrical gel, calculate the spinodals of the volume transition and of phase separation, and show that when the gel is subjected to uniaxial compression, an anisotropic surface phase appears first on the flat surfaces of the cylinder. Biaxial compression results in the appearance of this phase on the curved surface of the cylinder. The corresponding spinodals and coexistence lines are calculated. We study the stability of the bulk and the surface phases and derive the spinodals at which these phases become unstable against long wavelength fluctuations. At the surface spinodal the instability occurs for density waves with wave vectors directed along the principal axis of deformation, which corresponds to the smallest deformation ratio λ (compression axis). We find that when a concentrated undeformed gel is brought to the vicinity of the coexistence line, the dilute phase formed on its surface is unstable against density fluctuations but that a dense surface phase formed on a dilute gel is stable.

In section 4 we summarize the main results of this work, discuss the connection with experimental studies of phase transitions in gels, and suggest new experiments which can test our predictions.

2. Equilibrium in Excess Solvent

Consider a charged gel with degree of ionization (fraction of charged monomers) f and average monomer volume fraction ϕ. The monomer volume fraction in the state of preparation (reference state) is ϕ_0, and the average number of monomers between neighboring cross-links is N. For simplicity, we consider the case of no added salt.

Assuming that the gel is electrically neutral (the volume V spanned by the gel contains an equal number of positive and negative charges), the thermodynamic free energy is given by the sum of the free energy of a neutral network and that due to the entropy of the mobile counterions. We distinguish between the case in which the volume of the gel is fixed by applying external forces to its surface (and preventing the evaporation of solvent) and one in which the gel swells to equilibrium in a solvent bath.

We begin with the thermodynamics of charged gels swollen to equilibrium in excess solvent. The equilibrium monomer volume fraction is obtained by minimizing the free energy with respect to ϕ. Using the Flory-Huggins expression for the osmotic part of the free energy, the total free energy *per monomer* can be written as

$$\frac{F_0\{\lambda_\alpha\}}{T} = \frac{1}{4N}\sum_\alpha {\lambda_\alpha}^2 - \chi\phi + \frac{1-\phi}{\phi}\ln(1-\phi) + f\ln\phi \tag{1}$$

Here, T is the temperature and χ is the Flory interaction parameter. The deformation ratios $\{\lambda_\alpha\}$ describe the swelling and the stretching in the observed state of the gel, measured with respect to the state of preparation. In the case of uniaxial extension, these deformation ratios parallel and perpendicular to the stretching axis are given by $(\phi_0/\phi)^{1/3}\lambda$ and $(\phi_0/\phi)^{1/3}(1/\lambda)^{1/2}$, respectively, where λ is the experimental stretching ratio measured with respect to the swollen state. Note that the above expression for the free energy differs from that of Flory and Rehner in which a factor of $^1/_2$ (instead of $^1/_4$) appears in front of the elastic term and which contains an additional term proportional to $\ln\phi$. Our expression can be derived from first principles for gels formed by instantaneous cross-linking of a polymer solution in a Θ solvent.[11,12] When the preparation is done in a good solvent, N should be replaced by ${\phi_0}^{1/4}N$ in eq 1.[12,14]

2.1. Volume Transition. Assuming that the equilibrium state of the gel is homogeneous and isotropic, we can substitute $\lambda_\alpha = (\phi_0/\phi)^{1/3}$ (for all α) into above free energy and obtain an expression which depends only on the volume fraction ϕ of monomers in the gel. Minimizing $F_0(\phi)$ with respect to ϕ, we obtain an equation for the equilibrium volume fraction of monomers in the gel:

$$\frac{1}{2N}\left(\frac{\phi_0}{\phi}\right)^{2/3} + \chi\phi + \frac{1}{\phi}\ln(1-\phi) + 1 - f|_{\mathrm{eq}} = 0 \tag{2}$$

Note that for small equilibrium monomer volume fractions ($\phi \ll 1$), the osmotic pressure due to the polymer counterions is opposed by the elastic entropy of the network and we recover the result of ref 15, $\phi \propto f^{-3/2}$. These predictions are at variance with recent experiments on swelling of polyelectrolyte gels[16] which report $\phi \propto f^{-2/3}$. The disagreement does not cast a serious doubt on the validity of the theory since these experiments were carried out at high degrees of ionization to which the present theory does not apply, because of the assumption of Gaussian statistics of network chains in our model.

Charged gels can undergo a volume phase transition[5] to a new homogeneous state with a different equilibrium concentration. We proceed to calculate the *spinodal of the volume transition* at which the gel becomes unstable with respect to change of its volume. This line is defined by the conditions of swelling equilibrium $\partial F_0/\partial\phi = 0$ and of vanishing osmotic bulk modulus $K \equiv \phi^2\,\partial^2 F_0/\partial\phi^2 = 0$, i.e., by eq 2 and the relation

$$\chi_{\mathrm{vsp}} = \frac{{\phi_0}^{2/3}}{3N\phi^{5/3}} + \frac{1}{\phi^2}\ln(1-\phi) + \frac{1}{\phi(1-\phi)}\Big|_{\text{volume spinodal}} \tag{3}$$

Note that the above expression for the spinodal does not contain explicitly the degree of ionization (f) and can be interpreted as the locus of the spinodal points obtained by considering gels with different values of f. The spinodal of the volume transition exists only for ionization degrees larger than a critical value, f_{v}.

The critical point of the above spinodal can be found from the condition $\partial^3 F_0/\partial\phi^3 = 0$. We will show in the following that at this point the gel is still stable with respect to phase separation into two coexisting phases and therefore it can be called *the critical point of the volume transition*. We obtain

$$\phi_v = \left(\frac{5{\phi_0}^{2/3}}{6N}\right)^{3/8} \qquad \chi_v = \frac{1}{2} + \frac{16}{15}\phi_{\mathrm{v}}$$

$$f_v = \frac{4}{3}{\phi_{\mathrm{v}}}^2 \tag{4}$$

The spinodal and the parameters of the critical point of the volume transition, ϕ_v, χ_v, and f_v, depend on the conditions of preparation of the gel (ϕ_0 and N). Since $\phi_0/\phi_v = (6N\phi_0{}^2/5)^{3/8}$, the critical concentration can be either smaller (for small degrees of cross-linking and large concentrations of preparation) or larger (in the opposite case) than the concentration of preparation. When the degree of ionization is smaller than f_v, the gel is always in the stable single-phase region of the phase diagram and each degree of ionization corresponds to a unique equilibrium concentration, i.e., to a unique gel volume. In particular, one concludes that there is no volume transition in neutral gels ($f = 0$) and that they undergo a continuous volume change when the solvent quality is changed into the poor solvent regime.

2.2. Anisotropic Surface Phase. We proceed to investigate the *coexistence line* at which a two-phase state of the gel first appears. On this line the new phase has a small but macroscopic volume. We denote the fraction of monomers in this phase by x and the corresponding volume fraction by ϕ'. In the following we will assume that *the new phase appears on the surface of the original bulk phase* (this will minimize the elastic energy of deformation which arises due to continuity of the displacement field along the interface[6]) and show that *this phase is anisotropically deformed.*[7] Experimental evidence for the existence of transient surface phases in gels undergoing swelling and deswelling transitions was reported in ref 17. Segregation into coexisting "bulk" phases, of the type which occurs in binary liquids, can only take place in long rodlike (quasi-one-dimensional) gels.[18,19]

The deformation ratios in the surface phase can be obtained from the continuity of the displacement field at the interface between the two phases. The deformation ratios along the tangents to the interface should be the same as in the undeformed bulk phase, i.e., $\lambda_t = 1$. Since the number of chain monomers in the gel does not change, we have $\phi' = \phi/(\lambda_t{}^2\lambda_n)$, where λ_n is the deformation ratio along the normal to the interface, and therefore, $\lambda_n = \phi/\phi'$. The free energy per monomer of the anisotropic two-phase system is given by the expression

$$\frac{F\,(\phi,\phi')}{T} = (1-x)\left[\frac{3}{4N}\left(\frac{\phi_0}{\phi}\right)^{2/3} - \chi\phi + \left(\frac{1}{\phi}-1\right)\ln(1-\phi) + f\ln\phi\right] + x\left\{\frac{1}{4N}\left(\frac{\phi_0}{\phi}\right)^{2/3}\left[2+\left(\frac{\phi}{\phi'}\right)^2\right] - \chi\phi' + \left(\frac{1}{\phi'}-1\right)\ln(1-\phi') + f\ln\phi'\right\} \quad (5)$$

The volume fractions of the two phases and the fraction of monomers in the surface phase can be found by minimizing the above free energy with respect to ϕ, x, and ϕ'. The condition $\partial F/\partial\phi = 0$ defines the equilibrium density of the bulk phase, and setting $x \to 0$ in the resulting expression in order to obtain the density of the bulk phase at the coexistence line, we recover eq 2. The condition $\partial F/\partial\phi' = 0$ (at $x \to 0$) defines the monomer volume fraction in the surface phase, $\phi' = \phi'(\phi)$. A plot of ϕ' vs ϕ is presented in Figure 1. Substituting $\phi'(\phi)$ into the relaxation $\chi = \chi_{cl}(\phi,\phi')$ obtained from the condition $\partial F/\partial x = 0$ yields the coexistence line $\chi = \chi_{cl}(\phi)$.

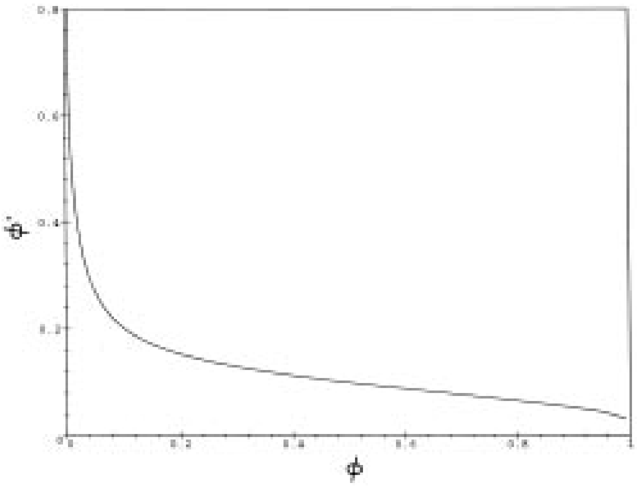

Figure 1. The volume fraction ϕ' of the anisotropic surface phase as a function of the volume fraction ϕ of the bulk phase, at coexistence. The network parameters are $N = 50$ and $\phi_0 = 0.05$.

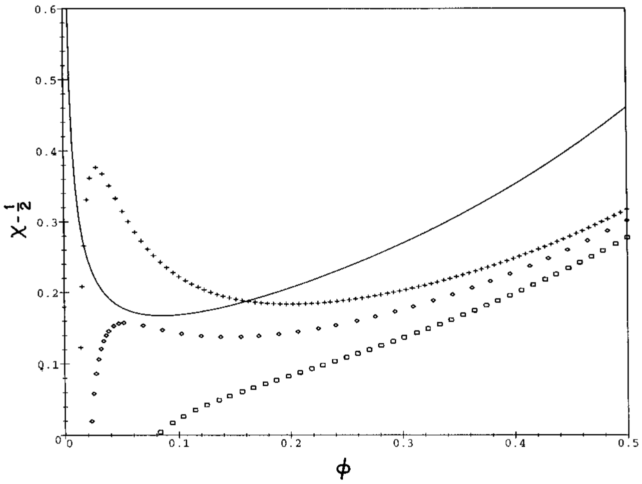

Figure 2. The coexistence line (solid line) and the equilibrium swelling curves in the ($\chi - 1/2,\phi$) plane. The equilibrium swelling lines correspond to degrees of ionization $f = 0.005$ (□), 0.017 (◇), and 0.025 (+). The network parameters are the same as in Figure 1.

The condition $\phi = \phi'$ defines the *critical point of the two-phase state* at which the longitudinal modulus $K + 4\mu/3$ vanishes and the gel becomes unstable against the spontaneous formation of large-scale small-amplitude inhomogeneities (μ is the shear modulus of the gel[5]). The critical parameters are:

$$\phi_c = \left(\frac{9\phi_0{}^{2/3}}{2N}\right)^{3/8} \qquad \chi_c = \frac{1}{2} + \frac{8}{9}\phi_c$$

$$f_c = \frac{2}{3}\phi_c{}^2 \qquad (6)$$

All the parameters of the critical point of the two-phase state are larger than those of the critical point of the volume transition given in eq 4. Combining the results of the previous and the present subsections, we can construct the phase diagram of charged gels in poor solvents: at very small degrees of ionization ($f < f_v$), the volume of the gel varies monotonically with the solvent quality (e.g., temperature) and there is no discontinuous volume transition (Figure 2, □). Note that at $f \le f_v$ the equilibrium swelling line always lies below the coexistence line.

At intermediate values of f ($>f_v$), the equilibrium swelling line develops two extrema (spinodal points; see Figure 2, ◇) and *a volume transition between two homogeneous phases takes place*. Since, as will be argued below, the transition can take place only at the limit of metastability, i.e., at the spinodal points, and since these two points have different values of χ, there is hysteresis between swelling and deswelling transitions.[7]

The kinetics of a first-order phase transition between two homogeneous states of the gel is determined by the probability of formation of a critical nucleus of the new phase. In the absence of long-range forces this probability is finite and the transition takes place by homogeneous nucleation. In gels, the main contribution to the free energy barrier associated with the formation of the critical nucleus comes from the energy of deformation of the surrounding elastic medium, due to the presence of long-range network forces. It was shown[8] that the probability of formation of this nucleus (and, therefore, the decay rate of the metastable state) is proportional to $\exp(-cKV/T)$, where V is the volume of the gel, K is the osmotic bulk modulus of the gel, and c is a numerical constant of order unity. This probability is vanishingly small for macroscopic three-dimensional gels and one concludes that a volume transition into a new homogeneous state takes place only when the spinodal (at which the osmotic bulk modulus vanishes) is reached. This result depends on the dimensionality of the problem and is valid in three and two dimensions. The argument does not apply in one dimension, with the result that a first-order volume transition from a metastable state, due to nucleation in the "bulk", can take place in one-dimensional gels, i.e., in thin rods.[18,19] In the following, we will only consider three-dimensional gels.

At higher f values, the equilibrium swelling line (Figure 2, +) intersects the coexistence line (Figure 2, solid line) and the volume of the gel varies continuously with χ until it reaches an intersection point. At this point the formation of a small amount of a daughter phase of volume fraction ϕ' is thermodynamically favored. Since the formation of a bulk daughter phase inside the majority phase is prohibited by the same arguments that lead to the suppression of nucleation in two- and three-dimensional gels, we conclude that at the coexistence line *an anisotropically deformed thin surface layer is formed on the surface of the gel*. This theoretical prediction is supported by experiments which report that anisotropic shrunken layers form on the surface of three-dimensional gel samples.[2] Upon further change in the quality of solvent, the surface layer will initially grow at the expense of the bulk phase, and this process will continue until both coexisting phases become strongly inhomogeneous. Although the analysis of this inhomogeneous state is beyond the scope of our thermodynamic approach, we expect that a volume transition induced by surface instabilities will eventually take place (such sequence of events was observed experimentally[17]), since the free energy minimum which corresponds to a homogeneous equilibrium phase is lower than that of the inhomogeneous two-phase state.

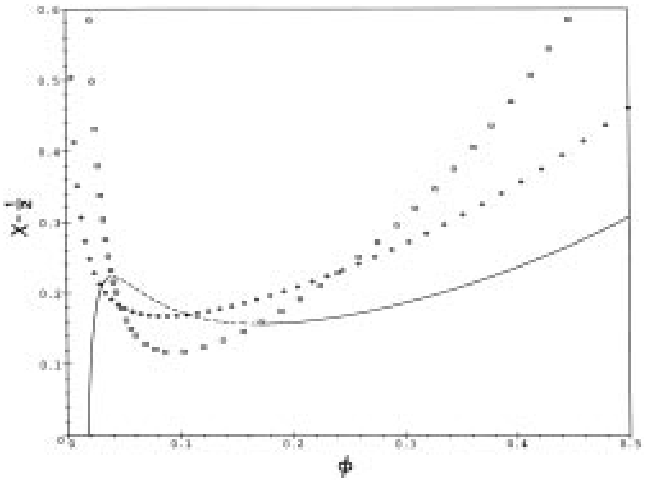

Figure 3. The equilibrium swelling line for $f = 0.02$ (solid line), the coexistence line (◇), and spinodal of the volume transition (□), in the ($\chi - {}^1/_2,\phi$) plane. The network parameters are the same as in Figure 1.

In Figure 3 we plot the equilibrium swelling line (calculated for $f = 0.02$), the spinodal of the volume transition, and the coexistence line. The latter two lines depend only on the degree of cross-linking and on the monomer volume fraction in the state of preparation (these lines should be interpreted as the loci of the points obtained for different values of f). The dashed portion of the equilibrium swelling curve (shown by the solid line in Figure 3), which lies between the spinodal points, corresponds to a maximum of the free energy and has no physical meaning. Consequently, the dilute (left-hand) branch of the coexistence line can only be reached by preparing the gel at a low concentration and moving upward along the equilibrium swelling line. The concentrated (right-hand) branch of the coexistence line can be approached from the high concentration side, by moving downward along the equilibrium swelling line.

In binary liquids, the volume fraction in the minority phase (ϕ') is found by passing a horizontal line through the point (χ, ϕ) and reading the value of ϕ' at the point where this line intersects the other branch of the coexistence line. Furthermore, since the total volume occupied by the two phases does not change during the process of phase separation in binary liquids, the relative amount of the two phases following a quench into the coexistence region is obtained by the Maxwell rule. These simple rules do not apply to gels, because the anisotropy of the surface phase formed when the mother phase reaches the coexistence curve results in a change of the volume of the gel at the transition. Instead, the volume fraction in the surface phase should be calculated using eq 5 (see Figure 1). Both coexisting phases are anisotropic and inhomogeneous in the case of a deep quench into the coexistence region.

3. Phase Transitions in Compressed Gels

Up to this point we discussed the equilibrium phase diagrams of charged gels in excess solvent. Because of the extremely long relaxation time to osmotic equilibrium, such experiments can be performed only on very small gel samples.[2,17] Experiments can also be done under conditions of fixed volume[20] or fixed osmotic pressure, e.g., by placing the gel in a polymer solution.[18] Furthermore, gels can be subjected to various deformations, the simplest of which are uniaxial ($\lambda < 1$) and biaxial ($\lambda > 1$) compression (note that compression, unlike stretching, does not require gluing the gel to a solid surface).

In order to describe the nonequilibrium state of a deformed gel with a given volume, we introduce the conjugate force (g) and the osmotic pressure (Π) which can be interpreted as Lagrange multipliers that fix the required values of λ and ϕ. For simplicity, we will assume that the gel is cylindrical and consider only uniaxial deformations (λ is the deformation ratio along the principal axis of deformation). The free energy F_g is obtained by adding the term $-\Pi/\phi - g\lambda(\phi_0/\phi)^{1/3}$ to the free energy F_0 defined in eq (1)

$$F_g = F_0 - \Pi/\phi - g\lambda(\phi_0/\phi)^{1/3} \tag{7}$$

Minimizing this free energy with respect to ϕ and λ gives

$$\Pi = \frac{\phi_0^{2/3}\phi^{1/3}}{2N\lambda} + \chi\phi^2 + \ln(1-\phi) + \phi - f\phi \tag{8}$$

and

$$g = \frac{1}{2N}\left(\frac{\phi_0}{\phi}\right)^{1/3}\left(\lambda - \frac{1}{\lambda^2}\right) \tag{9}$$

from which the particular case of equilibrium in excess solvent (eq 2) is obtained by substituting $\Pi = 0$ and $g = 0$. These equations can be solved to obtain the volume fraction and deformation ratio which minimize the free energy and therefore are the equilibrium values of ϕ and λ for given Π and g. The stability limit of the thermodynamic state characterized by Π and g (for which solutions of eqs 8 and 9 exist) is given by the condition that the free energy is stable under arbitrary small deviations from equilibrium, $\delta\phi$ and $\delta\lambda$. This condition can be expressed in the form

$$\frac{\partial\Pi}{\partial\phi}\frac{\partial g}{\partial\lambda} - \frac{\partial\Pi}{\partial\lambda}\frac{\partial g}{\partial\phi} < 0 \tag{10}$$

When the expression on the left-hand side of eq 10 vanishes, the gel becomes unstable with respect to a volume transition to a new homogeneous state with a different density and deformation, and we conclude that this point defines the spinodal of the volume transition in gels subjected to given osmotic pressure and force on their surface. This yields the following condition for the volume transition spinodal in the presence of external forces:

$$\chi_{\mathrm{vsp}} = -\frac{\phi_0^{2/3}}{4N\phi^{5/3}}\frac{1}{\lambda(2+\lambda^3)} + \frac{1}{2(1-\phi)} + \frac{f}{2\phi}\Big|_{\text{volume spinodal}} \tag{11}$$

In the limit $\Pi = g = 0$, this expression reduces to the equilibrium spinodal of an undeformed gel swollen to saturation in excess solvent (eq 3).

We proceed to calculate the coexistence line at which a thin anisotropic surface phase of volume fraction ϕ' coexists with a bulk phase of volume fraction ϕ in a thick cylindrical gel (the bulk phase is uniaxially deformed, with deformation ratios λ and $\lambda^{-1/2}$ along and normal to the axis of the cylinder, respectively). The surface phase can form on either the flat or the curved surfaces of the cylindrical gel and different boundary conditions apply in each case. The deformation ratios in the surface phase along the directions tangential to the interface between the bulk and the surface phase, coincide with those in the bulk phase. This geometry implies that the flat surface phase is uniaxially deformed with $\lambda' = (\phi/\phi')^{2/3}\lambda$ and that the deformation ratios along the three principal axes are all different in the curved surface phase. Which of the two phases is thermodynamically favored is determined by the value of χ on the corresponding coexistence lines (the phase with a smaller value of χ is favored). The coexistence line $\chi = \chi(\phi)$ is calculated by the same procedure as in equilibrium swelling case, using the expressions for Π and g from eqs 8 and 9 in the free energy F_g. This yields

$$\chi_{\mathrm{cl}} = \left\{\frac{\phi_0^{2/3}}{4N\phi^{2/3}\phi'}h(\lambda) + \frac{f}{\phi'-\phi}\left[\frac{\phi'}{\phi'-\phi}\ln\frac{\phi'}{\phi} - 1\right] - \frac{1}{\phi'-\phi}\left[\frac{1-\phi'}{\phi'-\phi}\ln\frac{1-\phi}{1-\phi'} - 1\right]\right\}\Big|_{\text{coexistence line}} \tag{12}$$

where $h(\lambda) = \lambda^2$ and $1/\lambda$ for the case of $\lambda < 1$ and $\lambda > 1$, respectively (flat and curved surface phases). The density of the surface phase is found from the condition $\partial F_g/\partial\phi' = 0$ (at $x \to 0$), which can be rewritten in the form $\partial\chi_{\mathrm{cl}}/\partial\phi' = 0$. Inspection of eq 12 shows that in the case of uniaxial compression ($\lambda < 1$), the surface phase appears on the flat surfaces. For biaxial compression ($\lambda > 1$), the surface phase grows on the curved surface of the cylinder (see Figure 4). The transition temperatures of the flat and the curved surface phases in undeformed ($\lambda = 1$) gels coincide, and it has been suggested[7] that the surface transition will start at the circular edges of the ends of the cylinder, where the deformations are less constrained.

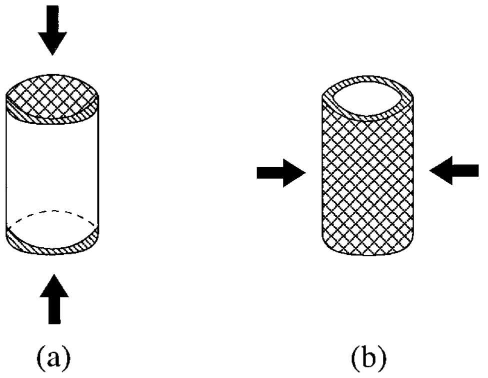

Figure 4. Schematic drawing of the surface (shaded region) and bulk phases in (a) uniaxially and (b) biaxially compressed gels. The surface phase corresponds to the shaded region and the compression axes are indicated by arrows.

In Figure 5 we show the volume transition spinodal and the coexistence line of a uniaxially compressed gel ($\lambda = 1/2$). The coexistence line of a biaxially compressed gel ($\lambda = 4$) is shown in Figure 6. The region between the coexistence line and the volume spinodal (in which the former lies above the latter) cannot be reached under conditions of fixed osmotic pressure and force on the surface, since in this region the gel is unstable against a volume transition. However, the entire coexistence line is accessible when the gel is deformed under conditions of fixed volume, which can be arranged by removing it from the solvent bath (as long as the evaporation of solvent is negligible). In the special case of no applied deformation ($\lambda = 1$), one can physically fix the volume of the gel by gluing its surfaces to a solid[21] and the gel will remain stable everywhere below the coexistence line.

In the above discussion we did not consider the possibility of mechanical (e.g., buckling) instabilities which may appear during uniaxial compression of cylindrical gels under conditions of vanishing bulk modulus. Although buckling instabilities in the single phase region can be suppressed by constraining the gel or by using platelike gel samples (so that the radius of

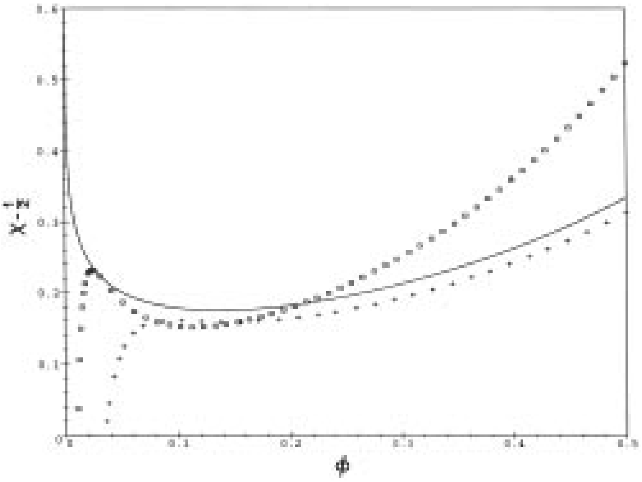

Figure 5. The equilibrium ($\Pi = 0$) swelling line (+), the spinodal of the volume transition (□), and the coexistence line (solid line) of a uniaxially compressed ($\lambda = 1/2$) gel, with degree of ionization $f = 0.025$. The network parameters are the same as in Figure 1.

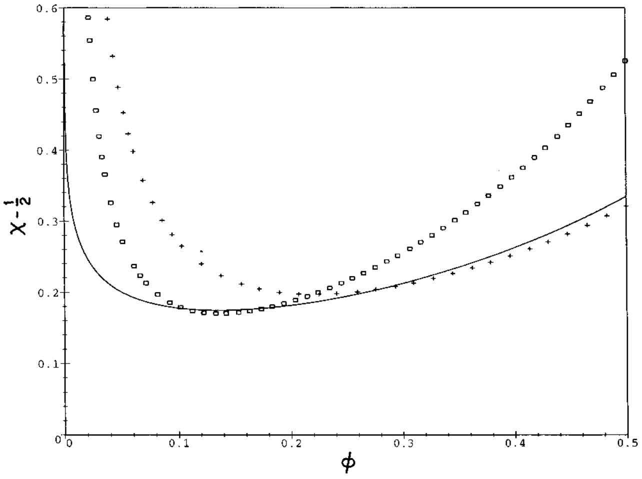

Figure 6. The equilibrium ($\Pi = 0$) swelling line (+), the spinodal of the volume transition (□), and the coexistence line (solid line) of a biaxially compressed ($\lambda = 4$) gel. All other parameters are the same as in Figure 5.

the cylinder is smaller than its length), such instabilities may appear in the swollen surface phase when the coexistence line is reached by swelling a collapsed gel.[22,23]

3.1. Stability of Bulk and Surface Phases. The analysis of the stability of the surface phases with respect to fluctuations with a finite wave vector **q** goes beyond the thermodynamic considerations used in this work. In the long wavelength limit such fluctuations involve elastic deformations of the medium, which can be described by the coordinate-dependent deformation coefficients λ_α. Therefore, the stability condition with respect to long wavelength fluctuations with wave vector **q** ($q \to 0$) directed along the principal axis of deformation α takes the form

$$\frac{\partial^2 F_{\rm g}\{\lambda_\beta\}}{(\partial\lambda_\alpha)^2}\bigg|_{\rm g} > 0 \qquad F_{\rm g}\{\lambda_\beta\} \equiv F_0\{\lambda_\beta\} - \sum_\alpha g_\alpha\lambda_\alpha \quad (13)$$

where F_0 is defined by eq 1 and where the forces $g_\alpha = \partial F_0/\partial\lambda_\alpha$ fix the values of the deformation coefficients λ_α in the phase under consideration. Using the relation

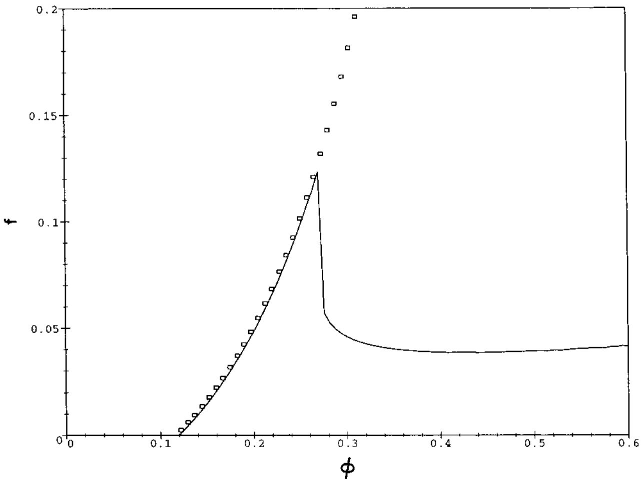

Figure 7. The line of the critical points at which the spinodal of the surface phase crosses the coexistence line (□), in the (f, ϕ) plane. The dependence of $f_{\rm int}$ on ϕ is shown by the solid line. The network parameters are the same as in Figure 1.

$\phi_0 = \lambda_x\lambda_y\lambda_z\phi$, the above condition can be rewritten in the form

$$\frac{\lambda_\alpha^{\ 2}}{2N} - 2\chi\phi + \frac{\phi}{1-\phi} + f > 0 \qquad (14)$$

When the quality of the solvent is changed, stability is first lost for fluctuations with wave vector **q** along the axis with the minimal value of λ_α, and the *macrophase separation spinodal* is obtained by equating to zero the right-hand side of eq 14 for this direction.

Using the above condition, we first find the macrophase separation spinodal of the bulk phase

$$\chi_{\rm sp} = \frac{\phi_0^{\ 2/3}}{4N\phi^{5/3}}h(\lambda) + \frac{1}{2(1-\phi)} + \frac{f}{2\phi} \qquad (15)$$

where $h(\lambda)$ was defined following eq 12.

Note that the macrophase separation spinodal of the bulk phase lies above the coexistence line ($\chi_{\rm cl} < \chi_{\rm sp}$) (eq 12) and touches it at the critical point, at which the densities of the bulk and surface phases coincide, $\phi_{\rm c} = \phi'_{\rm c}$. This critical point is defined by the equation

$$f = \left(\frac{\phi}{1-\phi}\right)^2 - \frac{3\phi_0^{\ 2/3}}{2N\phi^{2/3}}h(\lambda)\big|_{\text{critical point}} \qquad (16)$$

The line of critical points of an undeformed gel ($h(1) = 1$) is shown by the boxed curve in Figure 7.

Comparing expression 15 with eq 11 for the volume spinodal, we conclude that the stability of gel under given pressure Π and force g is first lost on the spinodal of the volume transition ($\chi_{\rm vsp} < \chi_{\rm sp}$), when the gel becomes unstable with respect to a homogeneous change of its volume. This process is very slow and can be prevented by fixing the volume of the sample instead of fixing the applied pressure and force. In this case the homogeneous phase remains stable (for $\chi < \chi_{\rm cl}$) or metastable (for $\chi_{\rm cl} < \chi < \chi_{\rm sp}$) until the macrophase separation spinodal is reached.

The surface phase can be destabilized by fluctuations with wave vector **q** directed along the principal axis of deformation with the smallest value of the stretching ratio λ, i.e., either normal to the surface (for a dense surface phase, with $\phi' > \phi_{\rm c}$) or parallel to it (for a dilute surface phase, with $\phi' < \phi_{\rm c}$). Such surface instabilities

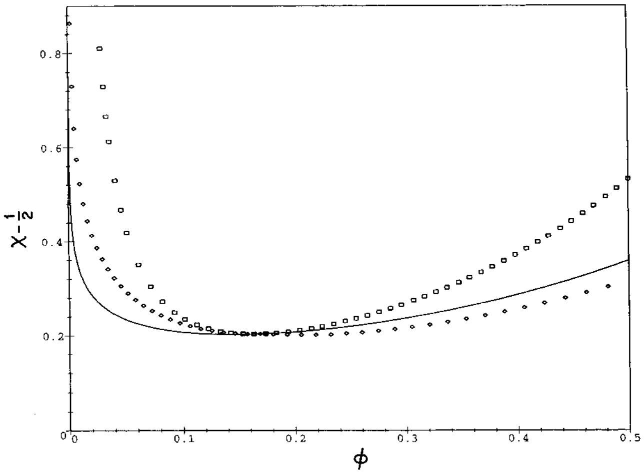

Figure 8. The coexistence line (solid line) and the corresponding spinodals of the bulk (□) and the anisotropic surface (◇) phases of a charged (f = 0.03) undeformed gel. The network parameters are the same as in Figure 1.

were observed in studies of phase transitions in NIPA gels.[17] The spinodal of the surface phase on the flat surfaces of the cylinder sample is given by

$$\chi_{\mathrm{sp}}^{\mathrm{surf}} = \frac{{\phi_0}^{2/3}}{4N(\phi')^{5/3}} h(\lambda') + \frac{1}{2(1-\phi')} + \frac{f}{2\phi'} \quad \lambda < 1 \qquad (17)$$

where $\lambda' = (\phi/\phi')^{2/3}\lambda$ is the coefficient of uniaxial deformation of this phase. This spinodal of the surface phase on the curved surfaces of the cylinder takes the form

$$\chi_{\mathrm{sp}}^{\mathrm{surf}} = \frac{{\phi_0}^{2/3}}{4N(\phi')^{5/3}\lambda} h\left[\left(\frac{\phi}{\phi'}\right)^{2/3}\right] + \frac{1}{2(1-\phi')} + \frac{f}{2\phi'} \quad \lambda > 1 \qquad (18)$$

Expressions 17 and 18 for the spinodal lines of surface phases are valid only on the coexistence line and slightly above it, when the volume of surface phase is small compared to that of the bulk phase. The spinodal of the surface phase crosses the coexistence line at the critical point (eq 16). A second intersection point exists only for small enough f, $f < f_{\mathrm{int}}$. The dependence of f_{int} on the volume fraction ϕ for an undeformed gel ($\lambda = 1$) is shown by the solid line in Figure 7. This line is continued in the region of small ϕ by the segment of the line of critical points. The area under the solid line in this figure corresponds to an unstable homogeneous dilute phase on the surface of the dense ($\phi > \phi_{\mathrm{c}}$) bulk phase. Above this solid line, the surface phase is stable with respect to small deformations of the gel.

The macrophase spinodals of the bulk (χ_{sp}) and the surface ($\chi_{\mathrm{sp}}^{\mathrm{surf}}$) phases and the coexistence line of an undeformed gel (χ_{cl}) are plotted in Figure 8 as a function of the volume fraction in the bulk phase, ϕ. Inspection of the spinodal of the surface phase (◇) shows that, at the coexistence line (solid line), a dense surface phase formed on top of a dilute bulk phase with $\phi < \phi_{\mathrm{c}}$ is always stable ($\chi_{\mathrm{sp}}^{\mathrm{surf}} > \chi_{\mathrm{cl}}$) with respect to monomer concentration fluctuations. A dilute surface phase formed on top of a dense bulk phase with $\phi > \phi_{\mathrm{c}}$ is unstable ($\chi_{\mathrm{sp}}^{\mathrm{surf}} < \chi_{\mathrm{cl}}$) against long wavelength fluctuations with wave vectors in the plane tangential to the surface of the gel. Both types of surface phases become unstable for sufficiently deep quenches into the coexistence region ($\chi > \chi_{\mathrm{sp}}^{\mathrm{surf}}$). Note that even though the bulk phase becomes unstable against long wavelength fluctuations only in the range $\chi > \chi_{\mathrm{sp}}$, surface instabilities can nucleate bulk instabilities and lead to phase separation in the bulk, already in the range $\chi_{\mathrm{sp}} > \chi > \chi_{\mathrm{sp}}^{\mathrm{surf}}$.

4. Discussion

We presented the thermodynamic analysis of the phase diagrams of charged gels in poor solvent. Unlike binary liquids in which only phase separation can take place, gels can undergo two types of phase transitions: a volume transition between two homogeneous states with different monomer concentrations and phase separation into two coexisting anisotropic phases. While the former transition can be prevented by fixing the volume of the gel, the latter will always take place in sufficiently poor solvents.

Analysis of the volume transition shows that while weakly charged gels change their volume continuously with decreasing quality of solvent, a discontinuous collapse or expansion of the gel takes place at intermediate degrees of ionization. Since nucleation of the new homogeneous phase is suppressed by long-range elastic forces, the gel remains stable against a homogeneous and isotropic change of its volume, until a spinodal point at which the osmotic bulk modulus vanishes is reached. For high degrees of ionization, the spinodal points lie inside the coexistence region in which the homogeneous gel is unstable against phase separation and the volume transition is preempted by segregation into two anisotropically deformed phases. The general analysis of this complex situation will be presented in a future publication and here we have restricted ourselves to the limiting case of an isotropic bulk phase which coexists with an anisotropic surface phase, when the gel is brought to the vicinity of the coexistence line. We have calculated the thermodynamic parameters (e.g., monomer volume fraction and deformation) of the anisotropic surface phase which appears when the gel is brought to the coexistence line by equilibrium swelling (or deswelling) in excess solvent. Since the gel is a solid, chain monomers cannot be freely exchanged between the two coexisting phases and, unlike the case of binary liquids, the monomer chemical potentials in the two phases do not have to be equal. The absence of this constraint leads the breakdown of the Maxwell rule, with the result that the monomer concentration in the surface phase and the volume occupied by this phase cannot be determined by examining the phase diagram and must be calculated by minimizing the total free energy of the gel.

The above analysis has been extended to the case of gels subjected to osmotic pressure and forces on their surface, and the corresponding phase diagrams were derived. The study of the surface phases which appear on the surface of a cylindrical gel subjected to uniaxial deformation shows that, under uniaxial compression, this phase appears first on the flat faces of the cylinder and that biaxial compression leads to the formation of this phase on the curved surface. Examination of the stability of the surface phase leads to the conclusion that in the vicinity of the coexistence line, a dense surface phase formed on top of a dilute undeformed gel is always stable with respect to arbitrary long-wavelength fluctuations. However, a dilute surface phase formed on top of a dense gel is unstable with respect to long-wavelength density fluctuations in the tangent plane (i.e., parallel to the surface).

We proceed to discuss the experimental ramifications of our results. The observation of enhanced light scattering from gels as the volume transition point is approached[24] can be interpreted as the result of scattering from macroscopic domains due to phase separation in gels quenched inside the coexistence region, since surface instabilities can nucleate bulk phase separation before the spinodal of the volume transition is reached. Direct comparison of our theory with experiments on phase separation in polymer gels faces the difficulty that, in most experimental studies, no attempt was made to fix the volume of the gel and, therefore, surface phases were observed only transiently, before the transition to a new homogeneous state took place.[17] An unambiguous study of equilibrium phase separation in gels must separate between phase separation and volume transition, by fixing the volume of the gel[21] or by using large gel samples, in which the duration of the experiment can be much shorter than the time scale over which a significant change of volume takes place.

A more serious problem which may hinder attempts to interpret experimental observations on phase transitions in gels in terms of thermodynamic theories is the possibility of the existence of extremely long-lived metastable states. For example, there are indications that two-phase states which arise during a quench to the coexistence region persist indefinitely even under conditions where one would expect that the true free energy minimum corresponds to a homogeneous collapsed state.[2] It is unknown at present whether such observations should be attributed to kinetic barriers or whether they reflect the predicted violation of the Gibbs phase rule in coherent solids.[6,25]

Another difficulty in making quantitative comparisons with experiment is that while our analysis applies only to charged gels in poor solvents, many of the experimental studies of phase transitions in polymer networks utilize neutral gels with hydrophobic and hydrogen-bonding interactions, which can be described by Flory-type models with concentration-dependent χ parameters.[2] We believe that while there is a quantitative difference between these cases, the qualitative trends predicted in this work apply equally well to the description of phase transitions in these complex gels.

The analysis presented in this work does not deal with microscopic phenomena such as the presence of static density inhomogeneities and microphase separation in charged gels. While the frozen inhomogeneous distribution of cross-links in randomly cross-linked gels has a profound effect on the density profiles and is essential for the interpretation of scattering experiments,[26] it has little effect on the thermodynamics of gels.[12] Evidence for microphase separation in charged swollen gels was reported in neutron scattering[3] and mechanical[20] experiments, and a theory of these phenomena was recently proposed by the present authors, based on the statistical mechanical analysis of thermal fluctuations and static inhomogeneities.[4] The phenomenon can take place in the bulk or in the surface phases, depending on the thermodynamic conditions.

A new generation of experiments which combine thermodynamic, mechanical, and scattering methods is clearly needed in order to test the new theories and to provide better understanding of the equilibrium and the kinetic aspects of phase transitions in charged polymer networks.

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