Phase Equilibria of Swollen Nematic Elastomers

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ABSTRACT: We calculate the phase diagram of a nematic network of covalently bonded semiflexible polymers swollen by isotropic solvent. At lower temperatures a nematic gel coexists with excess solvent; at high temperatures the coexisting gel is isotropic. In addition, coexistence is predicted between nematic and isotropic gel phases. There is an associated triple point. Possible elastic problems arise when different phases coexist in one gel sample.

1. Introduction

We show that covalently bonded networks composed of nematic-forming semiflexible chains can exhibit more complex phase equilibria when swollen than can their nonnematogenic counterparts. In addition to the usual isotropic gel/solvent coexistence and the expected nematic gel/solvent coexistence, there can be a nematic gel/isotropic gel coexistence. One thus has a triple point. In addition, a biphasic chimney, reminiscent of that found in solutions of nematic rods,[1] is also exhibited. We emphasize that here we are concerned with cross-linked systems that in their neat form display rubber elasticity, albeit modified by nematic effects. This is in contrast to systems of associative rods that also form nematic gels.

In this first section we give some background to nematic networks, conventional swelling, and the differences to be expected of nematic gels. Second, we explain the theory of nematic gels and show our principal results. We conclude by looking to the future problems this work has raised.

Otherwise flexible polymer chains can be made nematic by the addition to their structure of rodlike elements. This can be achieved by incorporating rods in the backbone (so-called main-chain (MC) polymers) or by attaching them as pendants to the backbone (so-called side-chain (SC) polymers). In a MC system when a nematic phase forms, the effect of orientational order is to distort a chain from its initially spherical conformation to a prolate spherical shape. In addition, certain of the SC systems are of prolate symmetry when nematic; see Wang and Warner[2] for a classification of possible uniaxial SC phases. For concreteness we shall consider phases of prolate symmetry, that is, where the order parameter associated with the backbone is positive. This implies the backbone has an extended, prolate shape. Thus, semiflexible polymer liquid crystals have a new element beyond their simple rod counterparts—when aligned the component molecules of the nematic change shape, here spherical to prolate, in a way not open to rods. Molecular-shape change is central to many polymer problems, none more so than in the physics of rubber networks where resistance to external stress is from the entropy drop associated with the molecular-shape change it imposes. Molecules that can spontaneously change shape will therefore give remarkable networks, as envisaged by de Gennes.[3]

A molecular explanation of the underlying order–shape–stress processes in such nematic networks has been given[4-6] in terms of the effectively anisotropic Gaussian shape of chains between cross-links in a nematic network. These are basically classical theories[7] of rubber. However, the constraint that the chains are in a network causes a shift in the free energy even when there is no applied stress: the chains in their nematic state cannot adopt the anisotropic shape that would be that natural in a nematic melt at the same temperature since the distortion from the isotropic state must be volume conserving. Thus, although anisotropic, the chains are still distorted in their nematic state and their entropy is correspondingly reduced. Predictions are of a spontaneous elongation of a sample (by λ_m), nonlinear stress–strain relations, and strong stress-optical effects. Experimentally these effects are seen[8,9] with the need for a mechanical or magnetic guiding field to eliminate the polydomains that mask the observation of λ_m. In the swelling case the volume-conserving constraints need not be applied, the volume fraction of polymer being able to change by solvent exchange.

Swelling of conventional networks is driven by the increase of entropy when mixing with the solvent occurs and, if the mixing parameter χ is less than $^1/_2$, by the favorable solvent/network interaction. Large χ limits the indefinite uptake of solvent. For small χ the ultimate limitation is the elastic energy required to continue expanding the network.

Gels in their nematic phase have a further driving force to solvent uptake—the relaxation of the constant-volume constraint, thus allowing chains to more closely adopt their natural anisotropic shape. However, as they swell nematic forces become diluted and it is found that an isotropic gel phase can intercede with a free energy lower than the nematic gel. For a solvent fraction fixed higher than that of this isotropic phase one can accordingly have nematic gel/isotropic gel coexistence across a phase gap. This phenomenon of two coexisting phases in a gel, and the concomitant discontinuous uptake of solvent, is the principal result of this paper. To focus discussion on this new driving force for solvent uptake, we shall make two simplifying assumptions concerning other aspects of the swelling problem which should have no effect on the *qualitative* aspects of the gel phase diagram. We assume that the mixing and elastic parts of the free energy are additive. Also we assume that the isotropic part of the interaction parameter χ is temperature independent. Thus, the shape of the isotropic gel phase diagram is temperature independent and of the simple Flory form.[7]

Gels that have unusual nematic or solvent properties are known in other contexts as well. One example is that of associating rigid-rod gels, for instance, those formed by PBLG.[10] Our discussion does not touch on this problem since we are concerned with polymer liquid crystal molecules with internal degrees of freedom (flexibility) analogous to that found in conventional polymers. The role of the concomitant shape changes thereby possible has been discussed above. Clearly the elastic mechanism in the two cases is entirely different. We also limit

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ourselves to covalently bonded systems, thus also ruling out such rigid-rod networks.

Another example of unusual solvent effects is where a change in solvent quality causes a collapse in the chain dimensions and hence solvent expulsion.[11] Again this gel behavior is very different from that envisaged by us, its origin being the appearance of the globular state rather than, as in our case, being due to nematic effects. However, such work raises problems of phase coexistence because of elastic strains set up between phases of different solvent volume fraction. We return to this question later.

Liquid crystalline elastomers have been swollen by solvent in order to study interesting macroscopic shape changes in response to applied electric fields. Zentel[12] used nematic solvents for this purpose. He was able to show for the first time that macroscopic sample shape follows the shape of the network polymers, the idea expounded above.

2. Theory

The free energy *per site* is (with our above assumptions)

$$F = F_{mix} + F_{el} + F_{nem} \tag{1}$$

The mixing free energy is[7]

$$F_{mix}/k_BT = (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi) \tag{2}$$

where ϕ is the volume fraction of polymer.

The elastic free energy[4-6] is

$$F_{el}/k_BT = \frac{\phi}{2L}\left[\left(\lambda_z^2\frac{l_0}{l_z} + 2\lambda_p^2\frac{l_0}{l_p}\right) - \ln\left(\frac{l_0^3}{l_z l_p^2}\right)\right] \tag{3}$$

where there are L sites associated with a chain strand between cross-links. The persistence length of the worm chain at the conditions of cross-linking is l_0. We thus assume that the network was formed in the isotropic state, an assumption that is easy to generalize.[4] We assume that, compared with changes in persistence due to nematicity, l_0 is a constant when it is used to reduce lengths. It is given by $l_0 = 2\beta\epsilon$ where ϵ is the bend constant of a chain and $\beta = 1/k_BT$, and in taking it to be constant we are assuming that this temperature dependence is weak. In the nematic state, the persistence lengths are anisotropic, being l_z and l_p, respectively, along and perpendicular to the director. These depend upon the current state of nematic order, $Q = \langle P_2(\cos\theta)\rangle$, where θ is the angle the chain makes with the director. Here we define l_0, and l_z, l_p as the number of sites associated with these persistence lengths.

The elongations are λ_z and λ_p, respectively. They are related to the swelling by

$$\lambda_z\lambda_p^2 = 1/\phi \tag{4}$$

We can retain λ_z and ϕ as variables, writing λ for λ_z, by taking $\lambda_p^2 = 1/\lambda\phi$ in all that follows.

Since λ only appears in F_{el}, we can find $\partial F/\partial\lambda)_{\phi,Q} \equiv \partial F_{el}/\partial\lambda)_{\phi,Q}$ which determines the equilibrium elongation of the gel, λ_m:

$$\left.\frac{1}{k_BT}\frac{\partial F_{el}}{\partial\lambda}\right|_{\phi,Q} = \frac{\phi}{L}\left(\lambda\frac{l_0}{l_z} - \frac{l_0}{l_p}\frac{1}{\lambda^2\phi}\right) = 0 \tag{5}$$

Hence, solving this equation for λ, the spontaneous distortion is

$$\lambda_m(\phi,Q) = \left(\frac{l_z}{l_p\phi}\right)^{1/3} \tag{6}$$

It remains to determine ϕ and Q.

The nematic free energy will be calculated for a worm model[4,6] and is

$$F_{nem}/k_BT = -\frac{\phi}{L}\ln Z + \frac{1}{2k_BT}\phi^2 v Q^2 \tag{7}$$

where Z is the partition function of the nematic worm, $Z = \exp(-\lambda_0 L/l_0)$, given in terms of the lowest eigenvalue λ_0 of the spheroidal wave equation. v is the nematic coupling per site, and the second term is the correction when using mean-field theory to correct for overcounting. The latter ϕ^2 term has one power of ϕ for the reduction to an energy per site and one power from $v\phi$ being the diluted nematic interaction. Rearrangement of (7) yields

$$F_{nem}/k_BT = \frac{\phi}{l_0}\left\{\lambda_0 + \frac{\phi Q^2}{T'^2}\right\} = \frac{\phi}{l_0}\frac{\tilde{F}_{nem}}{k_BT} \tag{8}$$

where $\tilde{F}_{nem}/k_BT$ is defined by $\{...\}$ and is the nematic free energy per persistence length previously used in melt problems. It is now a function of the combination $\Delta^2 = -3\phi Q/T'^2$.[13] The reduced temperature T' is $k_BT/(v\epsilon)^{1/2}$. The nematic free energy, $\tilde{F}_{nem}$, is equal to either of the equivalent expressions $\lambda_0(\Delta^2) - Q\Delta^2/3$ or $\lambda_0(\Delta^2) - (1/2)-(\Delta^2/3)^2T'^2/\phi$, depending on whether Q or T' is used as a variable. It can be given by simple perturbative expressions,[6] asymptotics, or numerics.[6,15]

The nematic order appears, via Δ^2, only in F_{el} and F_{nem}. Thus, to find its equilibrium value, we must minimize F, yielding the condition

$$\left.\frac{\partial(F_{nem} + F_{el})}{\partial\Delta^2}\right|_{\phi,\lambda} = 0 \tag{9}$$

The minimization results in the self-consistency equation, writing $l_0/l_z = \alpha_z$ and $l_0/l_p = \alpha_p$:

$$\frac{1}{3}\Delta^2T'^2/\phi = Q_N(\Delta^2) + \frac{3}{4}\frac{l_0}{L}\left(\lambda^2\alpha_z' + \frac{2}{\lambda\phi}\alpha_p' - \frac{\alpha_z'}{\alpha_z} - 2\frac{\alpha_p'}{\alpha_p}\right) \tag{10}$$

where the function $Q_N(\Delta^2) = (3/2)\,\partial\lambda_0/\partial\Delta^2$ from differentiating the first part of $\tilde{F}_{nem}$ is the only contributor when there is no cross-linking (the melt case); that is, for melts a given value of the coupling constant Δ^2 produces a chain order parameter $Q = Q_N(\Delta^2)$. $\alpha_i' \equiv \partial\alpha_i/\partial\Delta^2$ arises from differentiating F_{el}.

The extent of solvent uptake is governed by equality of the chemical potential (μ) of solvent in the gel either with μ for the solvent reservoir (for gel/solvent equilibrium) or with μ for solvent in another gel phase (for gel/gel equilibrium). The potential is

$$\mu = F - \phi(dF/d\phi) \tag{11}$$

which simplifies since the total derivative is

$$\frac{dF}{d\phi} = \left.\frac{\partial F}{\partial\phi}\right|_{\Delta^2,\lambda} + \left.\frac{\partial F}{\partial\lambda}\right|_{\Delta^2,\phi}\frac{d\lambda}{d\phi} + \left.\frac{\partial F}{\partial\Delta^2}\right|_{\lambda,\phi}\frac{d\Delta^2}{d\phi} \tag{12}$$

We evaluate at λ and Δ^2 determined above such that $\partial F/\partial\lambda)_{\Delta^2,\phi} = \partial F/\partial\Delta^2)_{\lambda,\phi} = 0$, thereby eliminating the latter terms in (12). Thus, the total derivative in (11) becomes $\partial F/\partial\phi)_{\Delta^2,\lambda}$ instead and yields

$$\frac{\mu}{k_BT} = \phi + \ln(1-\phi) + \chi\phi^2 + \frac{\alpha_p}{L\lambda} + \frac{1}{l_0}\frac{\phi^2Q^2}{T'^2} = 0 \tag{13}$$

Thus, the complete solution of the problem is the simultaneous solution of (5), (9), and, in (13), $\mu = 0$ or $\mu(\phi_1) = \mu(\phi_2)$ (as explained above (11)). Numerical solutions will be shown below, but the problem is not as formidable as it seems.

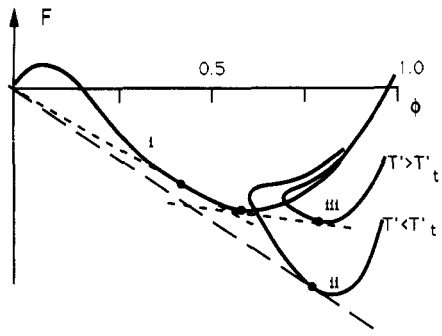

Figure 1. Free energy per site $F(\phi)$ against volume fraction ϕ for (i) an isotropic gel (ii) a nematic gel at low temperature ($T' < T'_t$, T'_t being the triple-point temperature), and (iii) a nematic gel at intermediate temperature. Common tangents are drawn in. They give the coexisting pairs of phases, being (ii) nematic gel/solvent (long dashed line) and (iii) isotropic gel/solvent and isotropic gel/nematic gel (short dashed lines).

The optimum value $\lambda_m(\phi,\Delta^2)$ for distortions (6) can be put into (10) and into (13). Writing $\lambda_m = (\alpha_p/\alpha_z\phi)^{1/3}$, λ can be eliminated from μ to give

$$\frac{\mu}{k_B T} = \phi + \ln(1-\phi) + \chi\phi^2 + \frac{(\alpha_z\alpha_p^2\phi)^{1/3}}{L} + \frac{T'^2}{l_0}\left(\frac{\Delta^2}{3}\right)^2 = 0 \quad (14)$$

Likewise the condition $\partial F/\partial\Delta^2 = 0$ (eq 10) can be simplified by employing $\lambda_m(\Delta^2,\phi)$ and assuming $W = (l_0^3/l_z l_p^2)^{1/3}$:

$$\frac{1}{3}\Delta^2 T'^2/\phi = Q_N(\Delta^2) + \frac{9}{4}\frac{l_0}{L}\left(\phi^{-2/3} - \frac{1}{W}\right)\frac{\partial W}{\partial\Delta^2} \quad (15)$$

The gel/gel equilibrium requires the common tangent condition on the F–ϕ plot which must be satisfied not only by equal chemical potential but also by equal exchange potential, i.e., $\partial F/\partial\phi$. A qualitative understanding of why new phase equilibria are possible can then be seen from a plot of F_N with such a common tangent drawn on; see Figure 1. The free energy is evaluated at the optimum λ_m and Δ^2_m corresponding to $\partial F/\partial\lambda)_{\Delta^2,\phi} = \partial F/\phi\Delta^2)_{\lambda,\phi} = 0$ and hence is a function of ϕ only. The motivation of why $F_N(\phi)$ is the shape shown in Figure 1 is given in an appendix where the simple method of solution of the self-consistency equation is also discussed. The basic idea is that cross-linking and swelling change the phase behavior very little and the qualitative aspects of the melt results can be taken over.

3. Results and Discussion

The phase diagram for a representative selection of parameters ($L = 50$, $l_0 = 5$, $\chi = 0.4$) has been calculated (Figures 2 and 3) in order to illustrate the phenomena we expect when a nematic elastomer is swollen. At low temperatures nematic gel coexists with excess solvent. Above a triple point T_t' excess solvent coexists with an isotropic gel. Also above this temperature one can have isotropic and nematic phases of gel coexisting. Beyond the phase gap a single nematic phase exists. The I/N biphasic region terminates at the $\phi = 1$ axis. This is at $T_{NI}^{(x)\prime}$, the transition temperature of the undiluted network, which in turn is close to T_{NI}', the transition temperature of the melt. This termination is of course the only possible outcome since the alternative of a critical point would allow one to go continuously from nematic to isotropic gel, states that are distinct in their quadrupolar symmetry.

Nematic order is not expected for any ϕ for T' above $T_{NI}^{(x)\prime}$, which is the limit of stability for even the undiluted case.

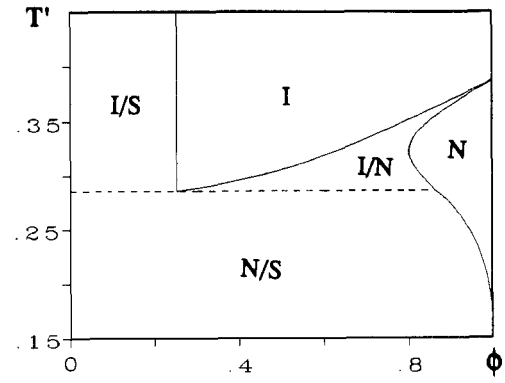

Figure 2. Reduced temperature, T', plotted against volume fraction, ϕ, of polymer in the network. One-phase regions of the nematic network are denoted by N. Two-phase coexistences are denoted by S/N (solvent/nematic gel), I/N (isotropic gel/nematic gel), and S/I (solvent/isotropic gel). There is a triple point S/I/N.

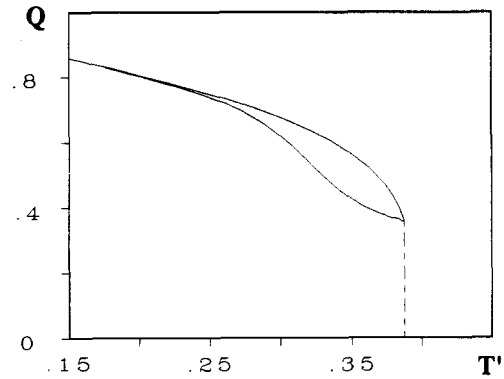

Figure 3. Order parameter, Q, as a function of reduced temperature, T'. For a given T' there is a range of Q, shown between two curves, depending on volume fraction, ϕ; the latter takes the values allowed in the region N of Figure 2.

4. Summary and Discussion

The above is an illustration of what can arise when nematic networks are swollen. Many interesting questions for the future are raised.

The addition of nematic solvent yields more complex possibilities, depending on the relationship between $T_{NI}^{(solvent)}$ to $T_{NI}^{(rubber)}$. Clearly, if the former is higher than the latter, then the biphasic region will swing around to the $\phi = 0$ axis. The intermediate interval $T_{NI}^{(solvent)} \sim T_{NI}^{(rubber)}$ yields greater complexity. Zentel[12] achieved a wide range of swellings with nematic solvent. His study was principally of shape and orientation effects. He did not report coexistence phenomena.

Another complexity can be introduced by cross-linking the network in its nematic phase. A memory of its nematic genesis is preserved, and the calculation is simply modified[4] to take account of this. A systematic experimental study of nematic rubbers (that is, networks without solvent) cross-linked in the nematic phase now exists and finds strong memory effects.[14]

As explained, nematic order and molecular shape follow each other closely and in networks applied stress couples to shape. Thus, the phase diagram of a nematic gel can be distorted by applied stress. All the above issues will be addressed in a later paper.

Other problems with interesting experimental ramifications are raised by the possibility of phase coexistence within a gel. It is well-known from conventional gels that as swelling or deswelling proceeds there are interfacial problems.[11] The mismatch in volume fraction between

swollen and, as yet, unswollen regions means that large elastic distortions can occur. The concomitant stresses involved can sometimes even lead to failure of the gel. They certainly affect the uptake process since they shift the local chemical equilibrium. These transient effects are encountered in the steady state here when we are in the I/N phase gap where nematic and isotropic gel coexist. Having different volume fractions, there must be an elastic interfacial energy of volume mismatch. Elastic fields, being of long range, can have a strong effect on the volume of sample. Do small samples then fail to exhibit N/I coexistence? What is then the form of the overall interfacial energy? How does microphase separation eventually coarsen and grow? Also intresting is the question of how this additional effect on elastic energy influences the stability of domains and defects. These problems are also under investigation.

Another interesting consequence of swelling is the possible plasticizing of the polymer by solvent. Thus, for example, the time scale for response of nematic elastomers to external fields (mechanical, electrical, etc.) could be strongly reduced, making conventional rheological investigations more straightforward.

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Appendix

Equation 9 (and its explicit forms (10) and (15)) is a self-consistency equation for Q (actually couched in terms of Δ^2) to be solved in order that $\partial F/\partial\Delta^2)_{\phi,\lambda} = 0$ be satisfied. Since cross-linking shifts the transition temperature and transition order parameter rather little, then we can discuss this condition qualitatively by ignoring elastic effects. Instead of solving a self-consistency condition at a given temperature, one can instead select a value of Δ^2, insert it into the function $Q_N(\Delta^2)$, and get the order parameter

$$Q = Q_N(\Delta^2) \tag{A1}$$

In the melt case one had $\Delta^2 = -Q/3T'^2$; hence, post hoc one can obtain T'

$$T'^2 = -\frac{Q}{3\Delta^2} \equiv -\frac{Q_N(\Delta^2)}{3\Delta^2} \tag{A2}$$

Thus to each Δ^2 there corresponds, at self-consistency, a T'^2 given by (A2). By this means $Q(T')$ can be mapped out without the explicit solution of any self-consistency equation: As Δ^2 increases from $-\infty$, Q diminishes until it reaches Q_{NI}. At the nematic–isotropic temperature, T_{NI}, the nematic free energy $F_N = 0$ and $\Delta^2 = \Delta^2_{NI}$. For larger Δ^2, $F_N > 0$ and the nematic phase is thus unstable. T' goes through a maximum at $T' = T'_{max}$ with $\Delta^2 = \Delta^2_0$, say, whereupon it again diminishes (Figure 4).

For the case of solvent the procedure is exactly the same: select a Δ^2, obtain $Q = Q_N(\Delta^2)$. Now at fixed T'^2 we obtain ϕ from $\Delta^2 = -3\phi Q/T'^2$; hence

$$\phi = -\frac{T'^2}{3}\frac{\Delta^2}{Q_N(\Delta^2)} \tag{A3}$$

Now ϕ at self-consistency is a function of Δ^2 and, since the same function $Q_N(\Delta^2)/\Delta^2$ is involved (but inverted), it has a minimum at $\phi = \phi_0$.

One can now take over the numerics of the melt problem to qualitatively analyze the swelling problem. The minimum of $\phi(\Delta^2)$ is at Δ^2_0; hence, from (A3) the minimum value of ϕ is $\phi_0 = -T'^2\Delta^2_0/3Q_N(\Delta^2_0)$ which can be rearranged to give $\phi_0 = T'^2/T'^2_{max}$ on applying (A2) at this value of

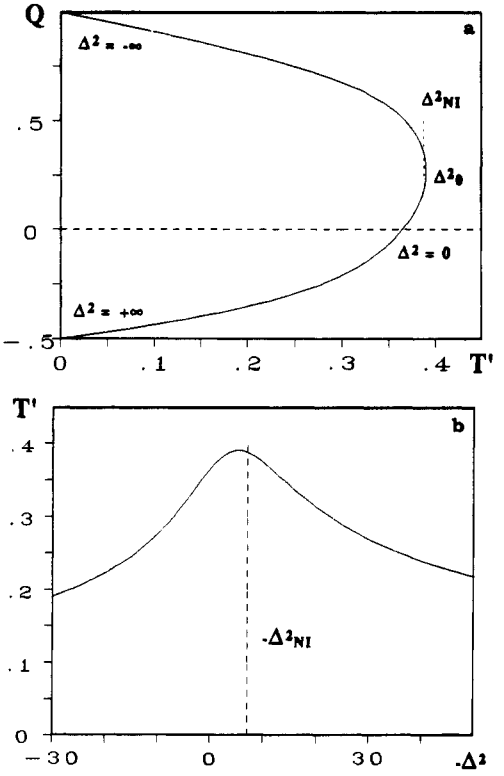

Figure 4. (a) Order parameter Q versus reduced temperature T' for a nematic melt. $Q(T')$ is drawn as a trajectory of Δ^2 increasing from $-\infty$ to $+\infty$. (b) The reduced temperature versus the nematic coupling Δ^2. Important values of Δ^2 are indicated: Δ^2_{NI} where F_N changes sign and Δ^2_0 where T' is a maximum.

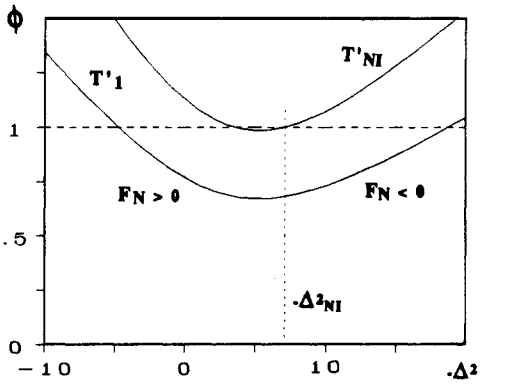

Figure 5. Volume fraction, ϕ, versus nematic coupling Δ^2. This plot corresponds to Figure 4b. Two different reduced temperatures T'_1 and T'_{NI} are shown. The nematic free energy $F_N(\phi)$ changes sign at $\Delta^2 = \Delta^2_{NI}$. For $T' = T'_{NI}$ this point is elevated to $\phi = 1$, and none of the curves associated with temperature above T'_{NI}, which leads to the unphysical $\phi > 1$, corresponds to a stable nematic phase.

Δ^2. Another constraint also acts: ϕ must be <1. For a stable nematic phase at all there must be a region of $\Delta^2 < \Delta^2_{NI}$ with $\phi(\Delta^2) < 1$. This region is indicated by $F_N < 0$ on Figure 5 for the T'_1 plot. At higher temperatures, the $\phi(\Delta^2) < 1$ region is only of a metastable nematic phase ($F_N > 0$). A curve corresponding to $T'_{NI}{}^{(x)}$, the temperature of intersection of the phase gap with $\phi = 1$, crosses $\phi = 1$ at Δ^2_{NI}. The form of $F(\phi)$ in Figure 1 can now be understood: as Δ^2 is increased from $-\infty$, a value of Δ^2 ($<\Delta^2_{NI}$) is reached where $\phi = 1$ and the $F(\phi)$ curve starts at a value $F(\phi=1)$ which is below the F curve for the isotropic gel. ϕ continues to decrease and $F(\phi)$ for the nematic gel crosses $F(\phi)$ for the isotropic gel when ϕ corresponds to $\Delta^2 = \Delta^2_{NI}$. At ϕ corresponding to $\Delta^2 = \Delta^2_{NI}$ there is a cusp in $F(\phi)$ since ϕ reverses its variation with

Δ^2. $F(\phi)$ continues to be above that of the isotropic gel until ϕ reaches $\phi = 1$. This latter observation is important since it precludes the possibility of forming any common tangents other than that shown. When the system is crosslinked, there is little shift from these conclusions. The values of Q, Δ^2, and T' relevant to the above can be found in ref 15 and are as follows: $Q_{NI} = 0.3564$, $\Delta^2_{NI} = -7.094$, $T'_{NI} = 0.3878$, $Q_{max} = 0.269$, $\Delta^2_0 = -5.29$, $T'_{max} = 0.391$.

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