Phase transitions in lyotropic nematic gels

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Abstract. In this paper, we discuss the equilibrium phases and collapse transitions of a lyotropic nematic gel immersed in an isotropic solvent. A nematic gel consists of a cross-linked polymer network with rod-like molecules embedded in it. Upon decreasing the quality of the solvent, we find that a lyotropic nematic gel undergoes a discontinuous volume change accompanied by an isotropic-nematic transition. We also present phase diagrams that these systems may exhibit. In particular, we show that coexistence of two isotropic phases, of two nematic phases, or of an isotropic and a nematic phase can occur.

PACS. 61.30.-v Liquid crystals – 81.40.Jj Elasticity and anelasticity, stress-strain relations – 83.80.Va Elastomeric polymers

1 Introduction

A polymer gel consists of flexible polymer chains that are cross-linked to form a three-dimensional network [1] whose volume in response to solvent changes can swell by factors as great as 1000 or more and undergo discontinuous changes along a coexistence line terminating in a liquid-gas–like critical point [2]. Dispersions of long rigid rods undergo a transition from an isotropic to a lyotropic nematic phase with increasing rod volume fraction [3,4]. In this paper, we will explore the possibility of creating lyotropic nematic phases in polymer gels with rigid rods either dispersed in their open spaces or forming parts of their constituent polymer chains. Our basic premise is that decreases in solvent quality contract the gel, thereby increasing rod volume fraction and inducing a transition to a nematic phase. A lyotropic nematic gel has the same spontaneous broken rotational symmetry and macroscopic elastic properties as a thermotropic nematic or elastomer [5–8]. As a result, it will exhibit the characteristic "soft" elasticity [8–11] of a nematic gel whereby the shear modulus for shears in planes containing the anisotropy axis vanishes and stresses up to critical distortions vanish for certain elongational and compressional strains. This "soft" elasticity along with unusually large coefficients of thermal expansion suggest interesting technological applications for thermotropic nematic or other liquid crystalline gels including artificial muscles [12,13], actuators [14], and electro-optical devices [15]. Lyotropic nematic gels might

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find use in similar applications. It is also imaginable that nature has found ways to use biological versions of these materials to control elastic properties of cells.

A theory for lyotropic nematic gels should be sophisticated enough to treat both the volume-collapse transition [16,17] of an isotropic gel and the development of nematic order. Tanaka [2] explained the former phenomena using Flory's theory for gels [1,18,19], which combines the Flory-Huggins theory of polymer solutions with the Flory theory for the entropic elasticity of isotropic elastomers. Brochard [20] considered gels in thermotropic liquid crystal solvents and concluded that a gel cross-linked in the isotropic phase of the solvent collapses when the solvent undergoes a transition from the isotropic to the nematic phase. Warner and Wang [21] modified Flory's theory to treat anisotropic gels using the neoclassical theory [11] for the elasticity of anisotropic rather than isotropic elastomers. They then used the phenomenological Maier-Saupe theory [22] to describe the development of nematic order. Coupling between elasticity and nematic order is provided by the dependence of anisotropic step lengths in the neoclassical elasticity theory on the nematic order parameter. They found a rich phase diagram, with temperature as a control parameter, in which coexistence of nematic and isotropic phases and a discontinuous uptake of solvent are possible. In this paper, we follow Warner and Wang's treatment of gel elasticity, but we use the Onsager theory [3], which provides a quantitatively accurate description for the isotropic-to-nematic (I-N) transition in dispersions of hard rods [4], rather than Maier-Saupe theory to describe the development of nematic order. Our theory provides a more accurate treatment of the strongly first-order I-N transition of dispersions of
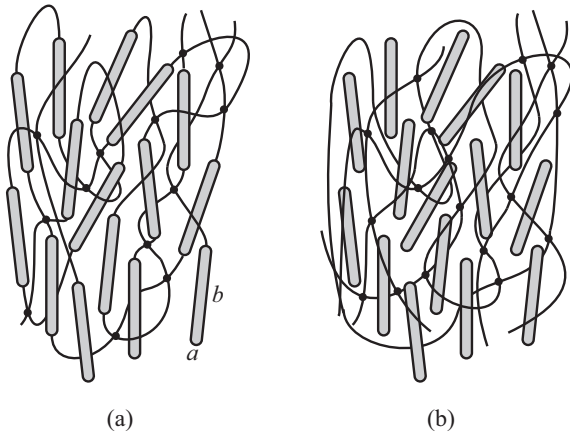
Fig. 1. Representation of the nematic gels referred to as (a) model 1 and (b) model 2. In both cases, rods of diameter a and length b are embedded in a cross-linked polymer network. In model 1, the rods are part of the network which consists of cross-linked polymer chains composed of rigid rods and flexible spacers. The thickness of the spacers is equal to the diameter of the rods, and the rods are much smaller than the average distance between cross-links. In model 2, the independent rigid rods are dispersed in the free spaces of a cross-linked flexible polymer network. There is no particular constraint on the distance between cross-links and on the size of the chains which constitute the network.

hard-rods than does one based on the phenomenological Maier-Saupe theory, which is best suited for a description of the vicinity of the transition in thermotropic systems.

We consider two models depicted schematically in Figure 1: model 1 in which the polymer chains constituting the gel consist of rigid rods connected by flexible segments and model 2 in which rigid rods are dispersed in the fluid volume between polymer segments. Though we introduce certain not completely controlled approximations to be discussed below, we believe that these models provide a realistic semi-quantitative description of lyotropic nematic gels. In both models, we find, as expected, a first-order I-N transition accompanied by a discontinuous change in volume. As in the systems considered by Brochard [20], the development of nematic order is accompanied by a decrease in the gel volume. In model 2, we also find lines along which either two isotropic or two nematic phases of differing densities coexist. These lines terminate in mean-field liquid-gas–like critical points, which are expected to retain their mean-field character even when fluctuations beyond mean-field theory are included because of effective long-range forces induced by a non-vanishing shear modulus [9].

This paper is organized as follows: In the next section (Sect. 2), we develop the model free energy for both models 1 and 2 including the orientational free energy of rods described by the Onsager theory. In Section 3, we construct the phase diagrams for models 1 and 2. We conclude with a brief summary.

2 Free energy of nematic gels

In this section, we will derive the free energy for nematic gels. This free energy includes entropic and enthalpic contributions that are present in uncross-linked polymer solutions, elastic contributions arising from cross-linking, and contributions arising from orienting rigid rods, and it depends on the volume fractions of polymer, solvent, and rods. We denote by ϕ the total volume fraction of the network, which contains flexible polymers of volume fraction ϕ_P and rods of volume fraction ϕ_R, so that

$$\phi = \phi_P + \phi_R. \tag{1}$$

The solvent volume fraction is thus $1 - \phi$. Under the assumption that the rods are confined within the network as it deforms, the ratio of the concentration of the rods to that of the network must be a constant, which we denote by

$$\beta = \frac{\phi_R}{\phi}. \tag{2}$$

In model 2, we have not considered the possibility of an equilibrium of the mobile rods between the inside and the outside of the gel as done in reference [20] for flexible rods chemically identical to the polymer chains of the network. Instead by using equation (2) with a fixed β, we have assumed that a constant number of rods stay trapped within the gel as the gel changes its volume. It is possible that the rods stay confined in the polymer network either for kinetic reasons or because of entanglements within the network.

To describe nematic gels immersed in a solvent, we assume that the total free energy can be written as a sum of three contributions:

$$\mathcal{F} = \mathcal{F}_{mix} + \mathcal{F}_{el} + \mathcal{F}_{rod}, \tag{3}$$

where $\mathcal{F}_{mix}$ is the free energy of mixing of the gel with its solvent, $\mathcal{F}_{el}$ is the elastic free energy of the gel network, and $\mathcal{F}_{rod}$ is the free energy of the rods. Within the Flory-Huggins theory, $\mathcal{F}_{mix}$ may be written as [1,2,21]

$$\mathcal{F}_{mix} = \frac{V k_B T}{v_c} f_{mix}, \tag{4}$$

where V is the volume of the gel and v_c is the volume of a lattice site, which is assumed to be $v_c = a^3$, where a is the monomer diameter. f_{mix} is the free energy per lattice site given by

$$f_{mix} = (1 - \phi) \ln(1 - \phi) + \chi \phi_P (1 - \phi) + \chi_R \phi_R (1 - \phi) + \chi_P \phi_R \phi_P, \tag{5}$$

where χ, χ_R, and χ_P are the Flory-Huggins parameters that characterize, respectively, the polymer-solvent, the rod-solvent, and the rod-polymer interactions at the level of the second virial approximation. The first term in equation (5) represents the entropy of the solvent. Note that the translational entropies of the polymers, $\phi_P \ln \phi_P$, and rods, $\phi_R \ln \phi_R$, are absent in equation (5) because the

chains, which include the rods, are attached to the network [18]. In order for the Onsager theory to be valid, the solvent quality must be good for the rods so that their mutual interactions are well described by the excluded-volume interaction. For simplicity, we assume that $\chi_R = \chi_P = 0$ corresponding to an athermal solvent for the rods and absence of a direct rod-polymer interactions. Thus, the single parameter χ, which measures the strength of interaction between polymer and solvent, controls the solvent quality. It is expected to vary with temperature as $\Theta/2T$, where Θ is the theta-temperature separating good-solvent ($T > \Theta$) from poor-solvent ($T < \Theta$) behavior.

The elastic free energy $\mathcal{F}_{el}$ introduced by Warner *et al.* [11] describes the energy change associated with a deformation of a nematic elastomer characterized by homogenous strains parallel $\lambda_\parallel$ and perpendicular $\lambda_\perp$ to the director (along which the rods are aligned). It may be written as

$$\mathcal{F}_{el} = \frac{1}{2} k_B T N_c \left[\lambda_\parallel^2 \frac{\ell_0}{\ell_\parallel} + 2 \lambda_\perp^2 \frac{\ell_0}{\ell_\perp} + \ln \left(\frac{\ell_\parallel \ell_\perp^2}{\ell_0^3} \right) \right], \quad (6)$$

where N_c is the total number of network strands, ℓ_0 is the step length of the polymer in the isotropic phase in which we assume the system was cross-linked, and $\ell_\parallel$ and $\ell_\perp$ are, respectively, the step lengths parallel to and perpendicular to the director in the nematic phase. Strains λ arise spontaneously due to the anisotropy of the network, and they are measured with respect to an isotropic state characterized by ℓ_0. Note that $\ell_\parallel$ and $\ell_\perp$ are, in general, functions of the de Gennes-Maier-Saupe [22] order parameter Q_{ij}, which describes the orientational ordering of the rods, and they reduce to ℓ_0 if $Q_{ij} = 0$. Equation (6) is based on the following assumptions: i) all chains are sufficiently long that their end-to-end vectors may be described by an anisotropic Gaussian distribution, and ii) this distribution transforms affinely under macroscopic deformation. Equation (6) has been used to account for many properties of nematic elastomers [7,11,23].

Equation (6) differs from the Flory expression for the elastic free energy of a gel [1,19], which contains an additional strain-dependent term of the form $\ln \left(\lambda_\parallel^2 \lambda_\perp \right)$. While Tanaka *et al.* [2] and Matsuyama *et al.* [24] have used the Flory theory with this term included to explain the collapse of isotropic gels, we believe (and later check) that this term does not play a significant role in nematic gels. Therefore, we do not include this term in the discussion that follows [21,18,25]. It is, nevertheless, interesting to note that this term is expected to be absent in the so-called phantom model of rubber elasticity [25]. This model essentially ignores the effect of entanglements of the chains and thermal fluctuations of the junctions points and is believed to be valid in the dilute regime. In more refined models, however, where these effects are properly taken into account, there may be additional strain-dependent terms contributing to equation (6) [26].

Unlike thermotropic nematic elastomers, which are essentially incompressible, lyotropic nematic gels can undergo large volume changes because of their ability to take up solvent [27]. We measure volume changes by the swelling ratio $V/V_0 = \phi_0/\phi$, where V_0 is the network volume (and ϕ_0 its volume fraction) in the reference state, and V is the network volume (and ϕ its volume fraction) in any particular state of gel. The strains are related to the swelling ratio by

$$\lambda_\parallel \lambda_\perp^2 = \frac{V}{V_0} = \frac{\phi_0}{\phi}. \quad (7)$$

This relation allows us to express the elastic free energy equation (6) in terms of $\lambda_\parallel$ only. Minimizing equation (6) with respect to $\lambda_\parallel$, we obtain

$$\lambda_\parallel = \left(\frac{\phi_0 \ell_\parallel}{\phi \ell_\perp} \right)^{1/3} \quad (8)$$

and

$$f_{el} = \frac{\mathcal{F}_{el} v_c}{k_B T V} = \frac{3}{2} \nu_c \left(\frac{\phi}{\phi_0} \right)^{1/3} \left[\frac{\ell_0}{\left(\ell_\parallel \ell_\perp^2 \right)^{1/3}} \right. \\ \left. - \left(\frac{\phi}{\phi_0} \right)^{2/3} \ln \frac{\ell_0}{\left(\ell_\parallel \ell_\perp^2 \right)^{1/3}} \right], \quad (9)$$

where $\nu_c = N_c v_c / V_0$. Note that equation (9) is slightly more general than the one used by Warner *et al.* [21], where the particular case of $\phi_0 = 1$, *i.e.* a dry gel, is considered. As pointed out in reference [2], in order for an isotropic gel to undergo collapse it is crucial that $\phi_0 \ll 1$, and we expect a similar conclusion to apply to nematic gels.

The free energy $\mathcal{F}_{rod}$ describes the physics of the rods embedded in the gel. Unlike previous treatments of nematic elastomers and gels, which focus mostly on thermotropic systems, our current treatment focusses on lyotropic gels. We employ the Onsager theory [3] to describe the isotropic-nematic transition that occurs upon increasing rod volume fraction *via* osmotic compression of the gel. The free energy obtained by Onsager is [3]

$$\frac{\mathcal{F}_{rod}}{k_B T} = N_R \int d^2\mathbf{u} \, \Psi(\mathbf{u}) \ln \left[\frac{4\pi \Psi(\mathbf{u}) N_R}{V e} \right] \\ + \frac{ab^2 N_R^2}{V} \int d^2\mathbf{u} \, d^2\mathbf{u}' \, \Psi(\mathbf{u}) \Psi(\mathbf{u}') |\mathbf{u} \times \mathbf{u}'|, \quad (10)$$

where $\mathbf{u}$ is the unit vector specifying rod direction, N_R is the number of rods in the network with length b and diameter a and $\Psi(\mathbf{u})$ is the orientational distribution function. The first term in equation (10) is the entropy of the rods, and the second takes into account the excluded-volume interaction between the rods at the level of the second virial approximation, which becomes exact in the limit of infinitely long rods. Equation (10) is the Onsager free energy for rods in an isotropic solvent, and not for rods either attached to or dispersed in a network. It clearly overestimates both rotational and translational entropy of rods since the network will introduce steric constraints whose effects are difficult to estimate. Using the Onsager free energy for the rods rather than one that takes full account

of constraints imposed by the network is the principal approximation of our theory. As discussed below, we will treat the rod translational entropy differently in models 1 and 2.

Even in the absence of the coupling between the strains and nematic order, minimizing the free energy $\mathcal{F}_{\mathrm{rod}}$ yields an intractable integral equation for $\Psi(\mathbf{u})$. We, therefore, follow Onsager [3,28] and introduce a trial distribution function of the form

$$\Psi(\mathbf{u}) = \frac{\alpha \cosh(\alpha \mathbf{u} \cdot \mathbf{c})}{4\pi \sinh \alpha}, \tag{11}$$

where α is a variational parameter and $\mathbf{c}$ is an arbitrary unit vector. Thus, the two integrals in equation (10) can be performed analytically:

$$\sigma(\alpha) = \int \mathrm{d}^2\mathbf{u}\,\Psi(\mathbf{u}) \ln\left[4\pi\Psi(\mathbf{u})\right] =$$
$$\ln\left(\alpha \coth \alpha\right) - 1 + \frac{\arctan\left(\sinh \alpha\right)}{\sinh \alpha}, \tag{12}$$

$$\rho(\alpha) = \frac{4}{\pi} \int \mathrm{d}^2\mathbf{u}\,\mathrm{d}^2\mathbf{u}'\,\Psi(\mathbf{u})\Psi(\mathbf{u}')|\mathbf{u} \times \mathbf{u}'| =$$
$$\frac{2 I_2(2\alpha)}{\sinh^2 \alpha}, \tag{13}$$

where $I_2(x)$ is a modified Bessel function.

Using these results and equation (2), we can calculate the rod free energy per site. In model 1, the rods are locked to the network, and there is no independent translational entropy associated with them, although there is rod translational entropy in f_{el} arising from fluctuations of the polymer-rod segments constituting the network. In model 2, rods are not attached to the network, and we assume for simplicity that they are free to diffuse throughout the volume of the gel not occupied by polymer segments and that they therefore have a translational entropy per site of $\phi_{\mathrm{R}} \ln \phi_{\mathrm{R}}$. In real systems, rods may be sterically confined to finite regions of the gel in which case, our model overestimates the rod translational entropy. The free energies f_{rod}^1 and f_{rod}^2 are thus, respectively,

$$f_{\mathrm{rod}}^1 = \frac{\mathcal{F}_{\mathrm{rod}} v_c}{k_{\mathrm{B}} T V} = \frac{4a}{\pi b} \phi\beta\sigma(\alpha) + \frac{4}{\pi}\phi^2\beta^2\rho(\alpha), \tag{14}$$

$$f_{\mathrm{rod}}^2 = f_{\mathrm{rod}}^1 + \frac{4a}{\pi b}\phi\beta \ln \phi, \tag{15}$$

up to an irrelevant constant in the chemical potential. Note that the term proportional to $\phi \ln \phi$ represents the translational entropy of the rods. The order parameter of the I-N transition is defined by the tensor [29]

$$Q_{ij} = \int \mathrm{d}^2\mathbf{u}\,\Psi(\mathbf{u})\left[u_i u_j - \frac{1}{3}\delta_{ij}\right]. \tag{16}$$

This tensor can be diagonalized to yield

$$Q = \mathrm{Diag}\left[-S/3, -S/3, 2S/3\right],$$

where S is the scalar order parameter given by

$$S(\alpha) = \frac{1}{2} \int \mathrm{d}^2\mathbf{u}\,\Psi(\mathbf{u})\left[3(\mathbf{u} \cdot \mathbf{c})^2 - 1\right] =$$
$$1 - \frac{3}{\alpha}\left(\coth \alpha - \frac{1}{\alpha}\right). \tag{17}$$

Note that $S(\alpha)$ vanishes in the isotropic phase when $\alpha = 0$ and that $S(\alpha) > 0$ in the nematic phase when $\alpha > 0$.

To complete our description of nematic gels, we must specify the relation between the anisotropy of the polymer chains and the nematic order. We define a step length tensor by $\ell_{ij} = \langle R_i R_j\rangle/N\ell_0$, which conveniently represents the anisotropy of the chains, where $\mathbf{R}$ is the end-to-end vector of the chains between two cross-links [30] and N is the total number of elements in these chains. The eigenvalues of ℓ_{ij} are $\ell_\parallel$ and $\ell_\perp$, which enter into the elastic free energy equation (6). In general, ℓ_{ij} is some unknown function of the nematic order parameter Q_{ij}, which may be model dependent. The simplest form of this function allowed by symmetry is [7,8]

$$\frac{\ell_{ij}}{\ell_0} = \delta_{ij} + \frac{1}{2}\eta\, Q_{ij}, \tag{18}$$

with an unknown coupling parameter η, which depends on the network structure and which will be different for models 1 and 2. Such a linear relationship is well verified experimentally for nematic elastomers [31].

In the case of model 1, we assume that there are γN rods of length b and volume $\pi a^2 b/4$, and $(1-\gamma)N$ spacers of size a and volume a^3, which are distributed randomly in a polymer chain, forming a main-chain liquid crystalline polymer [30]. Using the freely jointed chain (FJC) model [21,24], we find that

$$\eta = \eta_1 = \frac{6\gamma(b/a)^2}{1 - \gamma + \gamma(b/a)^2}, \tag{19}$$

where γ is related to β for model 1 in the following way:

$$\beta = \frac{\pi b\gamma}{4a\left(1 - \gamma\right) + \pi b\gamma}. \tag{20}$$

Note that equation (19) is exact for the FJC model and is valid for any form of the distribution function $\Psi(\mathbf{u})$.

For model 2, on the other hand, the FJC result is not expected to apply since the rods are not physically connected to the network chains. However, it is reasonable that for a sufficiently low concentration of the rods, equation (18) should still hold with an unknown coefficient η, which we take arbitrarily to be $\eta = \eta_2 = 6$ (the maximum value of η in model 1). Using equations (17) and (18), we have

$$\frac{\ell_\parallel(\alpha)}{\ell_0} = 1 + \frac{\eta}{3}S(\alpha), \tag{21}$$

$$\frac{\ell_\perp(\alpha)}{\ell_0} = 1 - \frac{\eta}{6}S(\alpha). \tag{22}$$

In both models $S > 0$ in equilibrium in the nematic phase, $\ell_\| > \ell_\perp$, and the gel adopts a prolate shape. Generalizations to allow an oblate phase are not difficult but will be left for another study. Our final free energy per site for model 1 is $f_{\mathrm{mix}} + f_{\mathrm{el}} + f_{\mathrm{rod}}^1$ with the parameter η given by equation (19) while that for model 2 is $f_{\mathrm{mix}} + f_{\mathrm{el}} + f_{\mathrm{rod}}^2$ with $\eta = \eta_2 = 6$. We analyze the phase diagrams arising from these free energies in the next section.

3 Equilibrium swelling of a nematic gel

In this section, we discuss the equilibrium properties of a nematic gel. The orientational order of the nematic gel is controlled by the parameter α, which is determined by the condition that the total free energy per site $f = f_{\mathrm{mix}} + f_{\mathrm{el}} + f_{\mathrm{rod}}$ is a minimum at $\alpha = \alpha^*(\phi)$. The constraint $\phi \leq 1$ implies that $\alpha^*(\phi) \leq \alpha_{\mathrm{max}}$, where α_{max} is the value of α^* obtained for $\phi = 1$. At $\alpha = \alpha_{\mathrm{max}}$ the maximum possible value of scalar order parameter S is reached. Note that the orientational order is governed only by f_{rod} and f_{el} and not by f_{mix}. The elastic free energy couples to the nematic order through $\ell_\|(\alpha)$ and $\ell_\perp(\alpha)$ as given in equations (21) and (22). As pointed out in reference [21], although the contribution from f_{el} is not negligible, the presence of the cross-linked network does not qualitatively alter the nematic properties of the rods. In particular, if the volume fraction ϕ is small, f has only one minimum at $\alpha = 0$, which corresponds to the isotropic state. If $\phi > \phi_1$, another minimum appears at positive α, which corresponds to the nematic state. If $\phi > \phi_2$, the minimum at $\alpha = 0$ disappears and there is only one minimum at a positive α. Therefore, the isotropic state is only possible for $0 \leq \phi < \phi_2$ and the nematic state for $\phi_1 < \phi \leq 1$. These features are also found in the Onsager theory for lyotropic liquid crystals. However, in nematic gels, the equilibrium phases are more interesting due to the coupling of elastic strains and nematic order.

The chemical potential μ and the osmotic pressure Π are two quantities characterizing a nematic gel. They are respectively, given by

$$\mu = \partial f / \partial \phi |_{\alpha = \alpha^*(\phi)}, \tag{23}$$

$$\Pi = -\frac{\partial \mathcal{F}}{\partial V} = -\frac{k_{\mathrm{B}} T}{v_{\mathrm{c}}} \left[f - \phi \frac{\partial f}{\partial \phi} \right]_{\alpha = \alpha^*(\phi)}. \tag{24}$$

In the nematic phase, their dependence on ϕ includes contribution from the dependence of $\alpha^*(\phi)$ on ϕ. The chemical potential governs the uptake of the solvent molecules and the osmotic pressure the mechanical stability of the gel. If $\Pi \geq 0$, the gel is stable with the surrounding solvent. If $\Pi < 0$ the gel becomes unstable in the absence of an external applied stress, and, consequently, it shrinks and separates itself from its fluid until it reaches $\Pi = 0$. Thus, the equilibrium swelling of the gel follows the volume curve $\phi^*(\chi)$ defined by the condition $\Pi = 0$, which is equivalent to minimizing the total free energy $\mathcal{F}$ with respect to ϕ. Note that in analogy with the phase diagram

of the liquid-gas model, it is interesting to consider isobars $\phi^*(\chi; \Pi_0)$ describing a gel to which a constant pressure Π_0 is applied [1]. In the following, we focus mainly on the situation with no applied stress $\Pi_0 = 0$, and we will not consider situations in which $\Pi_0 < 0$, which can only be reached by attaching the outer surfaces of the gel to movable walls that can be subjected to tension. In order to reach an equilibrium state of the gel, the external condition, such as the temperature, must change very slowly. On the other hand, if the temperature, and thus χ, changes rather rapidly, the gel does not have time to relax, and its concentration and volume are thus fixed. In this case, macroscopic phase separation [16] may take place if $\phi_A < \phi < \phi_B$, which means that an isotropic (or nematic) phase of volume fraction ϕ_A coexists with an isotropic (or nematic) phase of volume fraction ϕ_B within the same gel, where ϕ_A and ϕ_B are determined by the common tangent construction [32]: i) the osmotic pressure in the two phases are equal: $\Pi(\phi_A) = \Pi(\phi_B)$ and ii) the chemical potential are equal: $\mu(\phi_A) = \mu(\phi_B)$. We emphasize that in the Onsager theory, the I-N transition is independent of temperature and depends only on the volume fraction of the rods. Therefore, in our model for nematic gels, χ is the only parameter that depends on the temperature ($\chi \sim 1/T$). This is in contrast to previous studies [21] where the temperature dependence comes from the Maier-Saupe interaction parameter and χ is consequently assumed to be a constant independent of temperature. We present in what follows the phase diagrams for models 1 and 2 in the coordinates ϕ *vs.* χ or Π *vs.* χ for fixed values of the parameters ν_{c}, β, b/a, and ϕ_0.

## 3.1 Nematic gels with rods linked to the network: model 1

In model 1, the rods are part of the network in which a polymer chain consists of rigid rods and flexible spacers. Note that the parameters $\phi_0, \nu_{\mathrm{c}}, \beta, b/a$ and ℓ_0 are not all independent. This is because we have assumed that the deformation of the network is affine in deriving the elastic free-energy equation (3). This in turn implies that there is only one characteristic length scale of the network, the end-to-end separation of its constituent chains, and this length must be of the order of the average distance between cross-links [33]. This condition imposes that $\nu_{\mathrm{c}} \sim (a/\ell_0)^3 N^{-3/2}$ and $\phi_0 \sim (a/\ell_0)^2 N^{-1/2}$, where N is the total number of elements (spacers + rods) in the chains between cross-links [2]. Note that only when $N \gg 1$, the average distance between cross-links is larger than the rod length, which is required to justify *a posteriori* equation (2). For example, for $b/a = 50$, $\beta = 0.284$ and $N = 100$, we find that $\nu_{\mathrm{c}} \simeq 7 \cdot 10^{-6}$ and $\phi_0 \simeq 5 \cdot 10^{-3}$. These values are used below to construct the phase diagram.

In Figure 2 the phase diagram of the gel is given in two sets of coordinates: in (a) in terms of ϕ *vs.* χ and (b) in terms of the osmotic pressure Π *vs.* χ. Thick solid lines are isobars of constant osmotic pressure for $\Pi = 0.005$, and $\Pi = 0$. The most remarkable feature of these isobars is the
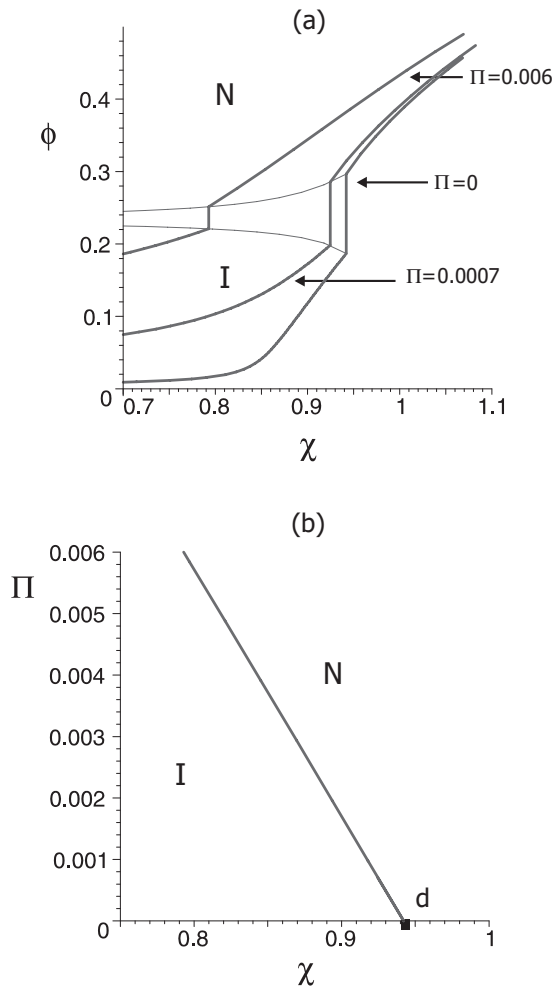
Fig. 2. Phase diagram for model 1 in the coordinates: (a) volume fraction of the network ϕ *vs.* Flory-Huggins parameter χ and (b) osmotic pressure Π *vs.* χ. Thick solid lines are isobars of constant osmotic pressure for $\Pi = 0.006$, $\Pi = 0$ and $\Pi = 0.0007$. Thin solid lines delimit the isotropic-nematic coexistence: the lower line $\phi_A(\chi)$ is the boundary of the isotropic phase (I) and the upper line $\phi_B(\chi)$ is the boundary of the nematic phase (N). The isobar $\Pi = 0$ is called the volume curve, and delimits the region of absolute stability of the gel in the absence of applied stress. The volume curve is discontinuous (collapse) at $\chi^* \simeq 0.94$, which corresponds to the point d of coordinate $(\chi^*, 0)$ in (b). The parameters are $b/a = 50$, $\beta = 0.284$, $\nu_c = 7 \cdot 10^{-6}$ and $\phi_0 = 5 \cdot 10^{-3}$.

discontinuity in volume fraction (collapse) at a particular value of χ defined as χ^*. The isobar $\Pi = 0$ is called the volume curve, and it delimits the region of absolute stability of the gel in the absence of applied stress. Collapse on the volume curve occurs at $\chi^* \simeq 0.94$. We emphasize that this collapse is fundamentally different from the collapse of an isotropic gel discussed by Tanaka [2]. In our case, the collapse is driven by the first-order nematic-isotropic transition as can be seen in Figure 3, which shows the discontinuous change of the nematic order parameter S along the volume curve. Note that $S \approx 1$ in the nematic phase, which means that the rods inside the gel are highly
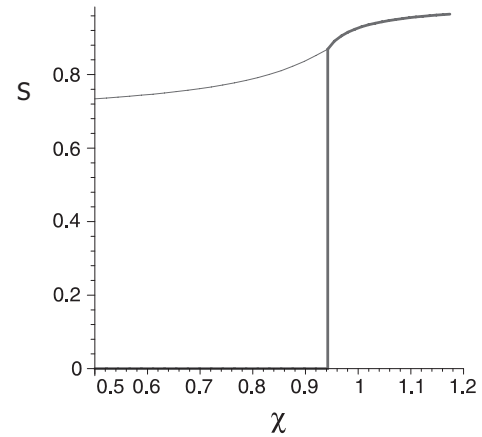

Fig. 3. Scalar nematic order parameter S as function of the Flory-Huggins parameter χ. The volume curve is the thick line and the thin curve is the nematic branch of the isotropic and nematic coexisting phases of Figure 2. All the parameters are the same as in Figure 2.

ordered. This is consistent with experimental observations on nematic elastomers [31]. As shown in Figure 4, the development of nematic order in the gel results in anisotropy in the strains.

In Figure 2a, thin solid lines delimit the isotropic-nematic coexistence: the lower line $\phi_A(\chi)$ is the boundary of the isotropic phase and the upper line $\phi_B(\chi)$ is the boundary of the nematic phase. As mentioned in Section 3, if the external condition changes rapidly and the system is quenched to a particular point within the coexistence region, macroscopic phase separation will occur. The volume fractions of the rods in the two phases are $\beta\phi_A$ and $\beta\phi_B$, respectively. They are both of the order of a/b, which is smaller than the maximum volume fraction of the rods β. Note that the coexistence region widens as χ increases. This may be attributed to the interaction between the rods becoming less repulsive as χ increases. A similar feature has been pointed out by Flory [34] and Flory and Warner [35] in a different system consisting of a solution of rods in the absence of any elastic network. Note also that a qualitatively similar behavior has been predicted theoretically [28,36] and observed experimentally [4] in solutions of rods where the interaction between rods is attractive and is induced by depletion interaction.

3.2 Nematic gels with mobile rods: model 2

In model 2, the rods are mobile but confined within the gel. Unlike model 1, the parameters in model 2 are less restricted. Using a typical value for the shear modulus of an elastomer $\sim 10^{-5}$ J/m^3 [23] and from reference [2], we estimate that $\nu_c \sim 10^{-5}$ and $\phi_0 \sim 0.001$. As can be seen in Figures 5 to 7 with different values of ν_c, β, and b/a, the phase diagrams of model 2 have two common features with model 1: the discontinuous collapse and the coexistence of isotropic-nematic phases. In addition, model 2 has two additional interesting features: the coexistence of two isotropic phases along a line terminating at a critical point

χ=0.6

χ=0.94
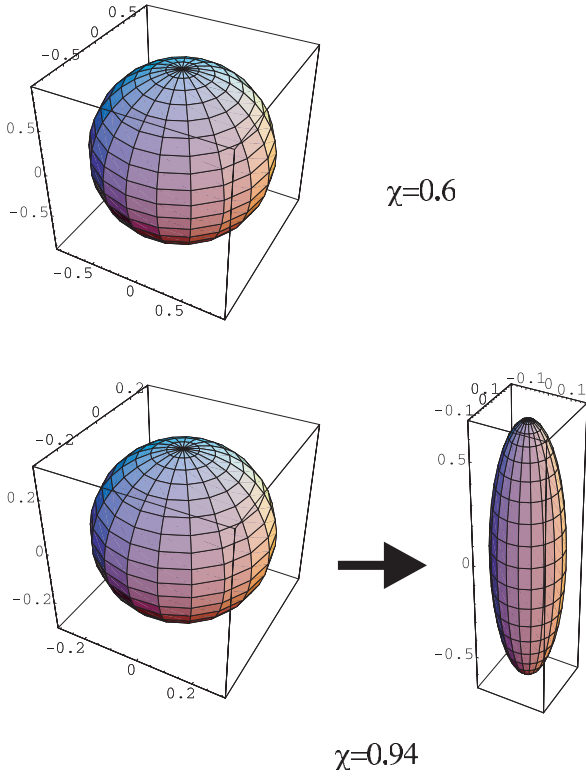
Fig. 4. Schematic picture of the extension of the chains inside the gel as characterized by the strains $\lambda_\parallel$ and $\lambda_\perp$, corresponding to the parameters of Figure 2. The upper picture corresponds to $\chi = 0.6$ in the isotropic phase, and the two lower pictures correspond to the isotropic and nematic phases which coexist when the collapse occurs at $\chi^* \simeq 0.94$. After the collapse, the resultant strains are $\lambda_\parallel \sim 0.72$ and $\lambda_\perp \sim 0.17$.

and the coexistence of two nematic phases along another line terminating at another critical point.

To see the coexistence of two isotropic phases, we expand the osmotic pressure equation (24) in the isotropic phase ($\alpha = 0$) up to fourth order in ϕ:

$$\frac{\Pi v_c}{k_B T} = \delta\phi^2 + \frac{\phi^3}{3} - \tilde{\nu}_c \phi^{1/3} + \xi\phi, \qquad (25)$$

where $\delta = \frac{1}{2} - \chi(1-\beta) + 4\beta^2/\pi$ and $\tilde{\nu}_c = \nu_c/\phi_0^{1/3}$. The last term $\xi\phi$ in equation (25), with $\xi = 4a\beta/\pi b$ comes from the translational entropy of the rods proportional to $\beta\phi\ln\phi$ in equation (15), which is specific to model 2. The coexistence of two isotropic phases ends at a critical point, the location of which is found by requiring the first and second derivative of the osmotic pressure with respect to ϕ to be zero $\Pi' = \Pi'' = 0$. This critical point located at (δ_c, ϕ_c) only exists in fact when $\Pi(\delta_c, \phi_c) \geq 0$. This last condition imposes that $\xi \geq \xi_e$, with $\xi_e = \frac{4}{9}375^{1/4}\tilde{\nu}_c^{3/4}$. Therefore as ξ varies, the critical point follows a line which ends at a critical end-point when $\xi = \xi_e$ [2]. Since $\xi_e > \xi = 0$ in model 1, the volume curve does not have a critical point in this case and the coexistence between two isotropic phases is not possible, as found indeed in the previous section.
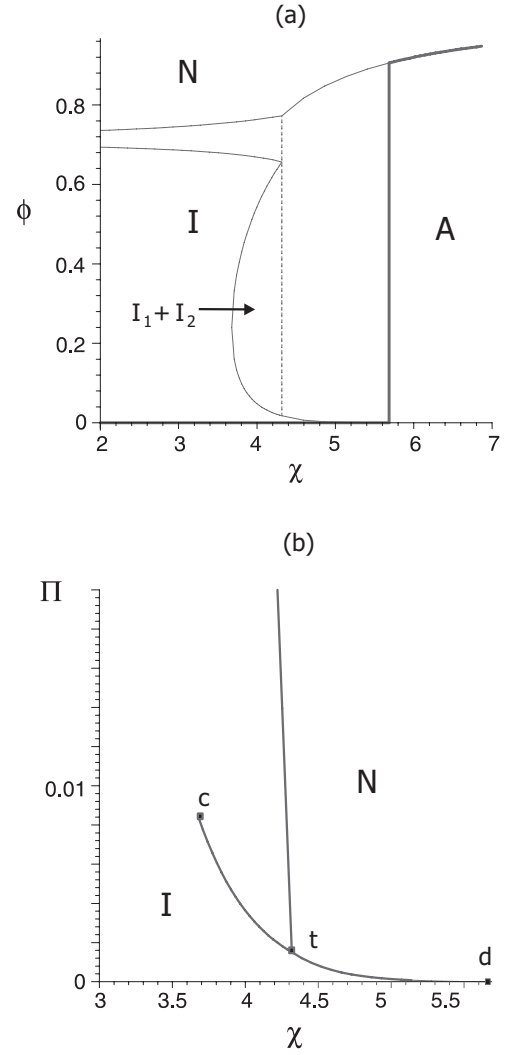
Fig. 5. Phase diagram for model 2 in the coordinates: (a) volume fraction of the network ϕ *vs.* Flory-Huggins parameter χ and (b) osmotic pressure Π *vs.* χ. The thick solid line in (a) is the volume curve and thin solid lines are coexistence lines of isotropic-nematic and isotropic-isotropic phases. In the region denoted A in (a), the osmotic pressure of the gel is negative. Solid lines in (b) represent first-order transitions. The parameters are $b/a = 8$, $\beta = 0.628$, $\nu_c = 5 \cdot 10^{-5}$ and $\phi_0 = 10^{-2}$. There is a discontinuous volume change (collapse) at $\chi^* \simeq 5.68$, between an isotropic phase (I) of volume fraction $\phi_{iso} \simeq 1.1 \cdot 10^{-4}$ and a nematic phase (N) of volume fraction $\phi_{nem} = 0.9$. The coexistence region of the two isotropic gels is denoted $I_1 + I_2$ and terminates at a critical point denoted c and located at $\chi_c \simeq 3.67$. At $\chi_t \simeq 4.31$ there is a triple point represented by the dashed line in (a) and by the point t in (b), where two isotropic gels of different volume fractions coexist with a nematic gel.

Equation (25) was derived by Tanaka for an isotropic gel with $\xi = \nu_c/2\phi_0$. As discussed in Section 2, the term proportional to ξ arises from the additional strain-dependent term $\ln\left(\lambda_\parallel^2\lambda_\perp\right)$ in the elastic free energy. Hence, the existence of the line of coexistence of two isotropic gels terminating at a critical point as observed
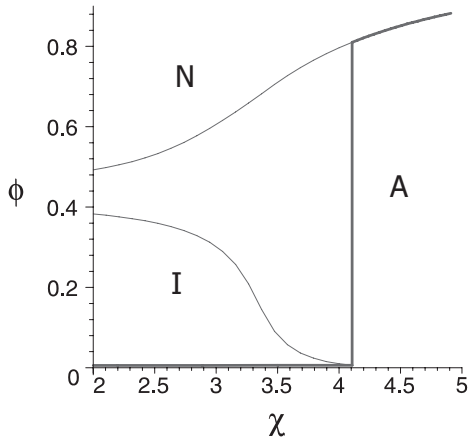
Fig. 6. For model 2, volume curve (thick line) as a function of the Flory-Huggins parameter χ, and coexistence region of isotropic-nematic (thin lines). The parameters are the same as in Figure 5 except for ν_c which has been increased to $7 \cdot 10^{-4}$. Now the collapse is at $\chi^* \simeq 4.1$.

by Tanaka is possible only if this term is included [2]. In the absence of this term, there could only be a *continuous* volume change induced by the change of quality of the solvent. In contrast, we have found in the case of nematic gels a discontinuous volume change even without including the controversial strain-dependent term. Thus, this confirms that the physical origin of the collapse for nematic gels is the isotropic-nematic transition.

Figure 5 shows the coexistence lines between two isotropic gels terminating at a critical point at χ_c, in the case where this critical point is located at $\chi_c < \chi^*$. The dashed line in Figure 5 represents a triple point, where the two isotropic gels coexist with a nematic gel. For a larger value of ν_c, we note that either $\chi_c > \chi^*$ or when there is no critical point, and the phase diagram looks very much like Figure 2, as shown in Figure 6. Thus, the isotropic-nematic coexistence region has swallowed the region of coexistence of two isotropic gels. This means that in this region phase separation into two isotropic phases is immediately followed by phase separation into a nematic phase and an isotropic phase. Note also that in this case, the collapse occurs at a smaller value of $\chi^* \simeq 4$. This is expected since the elasticity of the network favors contraction of the gel. For completeness, the phase diagram of Figure 5 is shown in the coordinates osmotic pressure Π *vs.* χ.

When the ratio of the volume fraction of the rods and that of the network defined as β is increased while keeping the other parameters fixed, the coexistence region of isotropic and nematic phases moves to lower volume fraction ϕ. This opens up the possibility of coexistence of two nematic phases at higher volume fraction with different volume fractions and different order parameters. This is indeed the case as shown in Figure 7 for $\beta = 0.78$ and $b/a = 100$. The coexistence region of the two nematic phases ends at a critical point located at $\chi_{c'} \simeq 3.1$ and $\phi_{c'} \simeq 0.14$, and at a triple point $\chi_t \simeq 3.15$, where two ne-
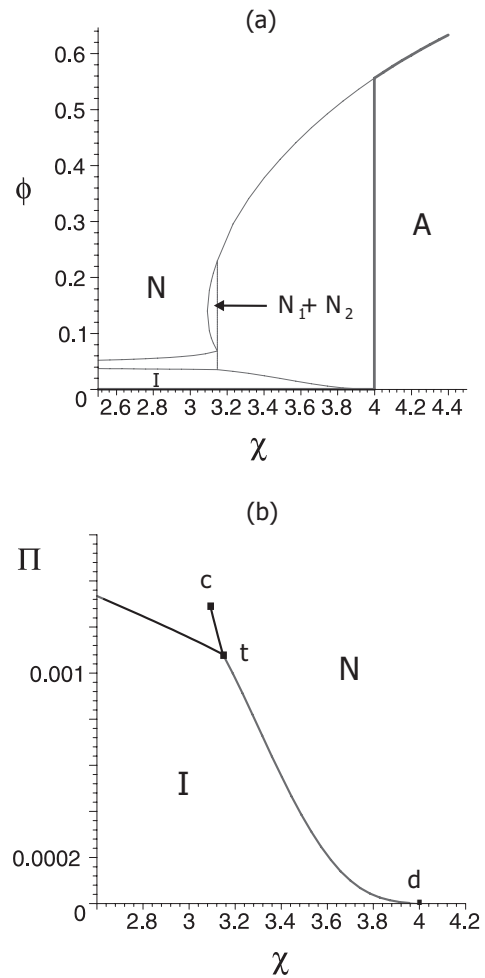
Fig. 7. Phase diagram for model 2 in the coordinates: (a) ϕ *vs.* χ and (b) Π *vs.* χ. The parameters are $b/a = 100$, $\beta = 0.78$, $\nu_c = 7 \cdot 10^{-6}$ and $\phi_0 = 3 \cdot 10^{-3}$. The collapse occurs at $\chi^* \simeq 4$. The coexistence region of two nematic gels denoted $N_1 + N_2$ terminates at a critical point located at $\chi_{c'} \simeq 3.1$ and $\phi_{c'} \simeq 0.14$. At $\chi_t \simeq 3.15$ there is a triple point represented by a vertical line segment in (a) and by the point t in (b), where two nematic gels with different volume fractions and nematic order parameters coexist with an isotropic gel.

matic gels coexist with an isotropic gel. The coexistence of two nematic phases has been predicted in the literature in systems different from the one we have considered in this paper. In a solution of rods in the absence of an elastic network, it was predicted by Flory [34,35], and more recently it was predicted in reference [21] in a system composed of a nematogenic network immersed in a nematogenic solvent. The coexistence of two nematic phases is a novel feature of our model, which is more subtle than in previous studies of nematic gels since in our case only the network has nematogenic properties. The phase diagram of Figure 7 is shown in the coordinates osmotic pressure Π *vs.* χ. As compared with Figure 5, the critical point is now on the other side of the line of coexistence of the isotropic and nematic phases.

4 Summary and conclusion

In this paper, we have studied the phase behavior and the collapse of a lyotropic nematic gel using the Onsager theory to describe the isotropic-nematic transition. Upon decreasing the quality of the solvent sufficiently, we find that a nematic gel always undergoes a discontinuous volume change, even when the rods embedded in the gel are not physically linked to the network. The discontinuous volume change is accompanied by an isotropic-nematic transition, and for this reason it is of a different nature than the one discussed by Tanaka for isotropic gels. We have discussed the possible phase diagrams that these systems should exhibit; in particular, we have shown that three distinct coexistence phases are possible, *i.e.* isotropic/isotropic (I/I), isotropic/nematic (I/N), and nematic/nematic (N/N). The I/N coexistence is always present, the I/I coexistence and N/N coexistence may be present depending on the precise value of the parameters.

Our model uses the Onsager free energy for rods in an isotropic solvent to describe rods in a polymer gel. We considered two models: model 1, in which rods are a part of the network, and model 2, in which the rods are free to move within the free space of the gel but not permitted to escape from it. In model 2, we retained the full translational entropy of the Onsager theory, whereas in model 1, we set it equal to zero since the rods formed a part of the polymer network. Thus, in both models, we overestimate the rotational entropy of the rods and we overestimate rod translational entropy in model 2. It would be interesting to consider models that provide more realistic treatments of these entropies. Our treatment also neglects completely the random torques and forces that the randomly crosslinked network exerts on the rods. These random fields are definitely present, and they may make it difficult to create an aligned lyotropic nematic gel in the laboratory.

We hope, nevertheless, that this paper will motivate experimental work on gels with rods embedded in them. These experiments are important because of the potential applications of these materials: these gels are in some sense a new type of sensors, which respond to a change in osmotic pressure by a change of volume. In particular, our work is relevant to some experiments which are now undertaken using cross-linked diblock copolymers as rigid rods embedded in a polymer network [37].

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