

Elastic Maier-Saupe-Zwanzig model and some properties of nematic elastomersDanilo B. Liarte,^{*} Silvio R. Salinas,[†] and Carlos S. O. Yokoi[‡]*Instituto de Física, Universidade de São Paulo, Caixa Postal 66318, CEP 05314-970 São Paulo, SP, Brazil*

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We introduce a simple mean-field lattice model to describe the behavior of nematic elastomers. This model combines the Maier-Saupe-Zwanzig approach to liquid crystals and an extension to lattice systems of the Warner-Terentjev theory of elasticity, with the addition of quenched random fields. We use standard techniques of statistical mechanics to obtain analytic solutions for the full range of parameters. Among other results, we show the existence of a stress-strain coexistence curve below a freezing temperature, analogous to the P - V diagram of a simple fluid, with the disorder strength playing the role of temperature. Below a critical value of disorder, the tie lines in this diagram resemble the experimental stress-strain plateau and may be interpreted as signatures of the characteristic polydomain-monomain transition. Also, in the monomain case, we show that random fields may soften the first-order transition between nematic and isotropic phases, provided the samples are formed in the nematic state.

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I. INTRODUCTION

Liquid-crystalline molecules imbedded in a polymer network give rise to the novel class of elastomer systems, with coupled rubber elasticity and orientational order, and rather unusual properties [1,2]. Nematic elastomers (NEs) may undergo a distortion in response to an alignment of the nematic units as the sample is cooled below the nematic-isotropic transition temperature T_{NI} . Reciprocally, the application of an external stress may give rise to nematic ordering of an initially disordered sample. There are a number of suggestions for applications of these new soft-matter materials, ranging from uses in optics (in bifocal lenses, for instance) to applications as thermomechanical devices [1].

Compared with conventional liquid crystals, NEs present a peculiar transition from the nematic to the isotropic states. In usual nematics, according to the Landau-de Gennes theory, symmetry requirements lead to a first-order transition, with a jump of the nematic-order parameter, at a transition temperature T_{NI} . A different scenario is observed in the NEs. Instead of a discontinuity there is a continuous but quick variation of the order parameter during the transition. The microscopic mechanism behind this nontrivial behavior has been discussed by many authors [3–7]. In particular, continuous three-dimensional coarse-grained theories [6] and numerical simulations of microscopic models [5] indicate that quenched random-field interactions may smooth out the characteristic first-order transition in these systems. In NEs these random fields are supposed to originate from internal stresses produced by the network cross-links [8,9]. More recently, slightly different random-field interactions have been suggested by Lu *et al.* to describe network heterogeneity in randomly cross-linked materials [10].

Random fields may also be relevant to describe the interesting transition from states of polydomain to states of monomain in NEs [11]. If the system is cooled below T_{NI} ,

NEs are known to display a stable structure, the so-called “Schlieren texture,” characterized by sets of frozen randomly oriented domains of mesogen units. This polydomain state may be turned into a monomain state by stretching the sample under uniaxial tension. For a certain range of low temperatures, experiments show an unusual stress-strain curve with three characteristic regions. In the first region, for small strain, the system is in the polydomain state, the sample is opaque, and stress increases linearly with strain, according to Hooke’s law. In the second region, the stress is constant for a range of intermediate values of strain, and there is a dramatic increase of the nematic-order parameter. This plateau is then followed by an increase of stress at larger strains, with the system in the optically transparent monomain state [12–14]. Some authors have suggested that cross-linking conditions are essential to explain the stable polydomain state [3,11]. In particular, random fields and the neoclassical theory of elasticity have been used by Fridrikh and Terentjev to obtain a good fitting of some experimental findings [11].

In this article we propose a lattice statistical model for NEs, at the mean-field level, which can be analytically solved in the presence of stress and random fields. This model has the advantage of providing a simple way to investigate a wide range of parameters; gives a unified view of the critical behavior of NEs, in general agreement with previous theoretical [6,11], numerical [5], and experimental findings [1]; and suggests the occurrence of some additional phenomena. In Sec. II, we define the basic lattice model. The global free energy is obtained in Sec. III. Some specific calculations, including stress-strain curves, comparisons with the literature, and a few new predictions are presented in Sec. IV. The main conclusions are given in the last section.

II. LATTICE MODEL FOR A NEMATIC ELASTOMER

The Maier-Saupe (MS) model, which is known to provide a good description of the isotropic-nematic transition [15,16], is the liquid-crystalline analog of the Curie-Weiss model of ferromagnetism [17]. The idea consists in the extension of the finite-range interactions of realistic systems to infinite-range interactions in order to construct a simpler model, whose exact

^{*} danilo@if.usp.br[†] ssalinas@if.usp.br[‡] cyokoi@if.usp.br

solution corresponds to the mean-field approximation of the realistic system. In the MS model, the basic elements are the molecular unit vectors \mathbf{n}_i , representing a set of N mesogens, which interact via the quadrupole energy

$$E_{\text{MS}} = -\frac{A}{N} \sum_{1 \leq i < j \leq N} \sum_{\mu, \nu = x, y, z} S_i^{\mu\nu} S_j^{\mu\nu}, \quad (1)$$

where $A > 0$ is an energy constant,

$$S_i^{\mu\nu} = \frac{1}{2}(3n_i^\mu n_i^\nu - \delta^{\mu\nu}), \quad (2)$$

and $|\mathbf{n}_i| = 1$ for $i = 1, 2, \dots, N$. The calculations may be further simplified if we adopt a suggestion of Zwanzig and restrict the number of allowed orientations of \mathbf{n}_i to the six values along the Cartesian axes,

$$\mathbf{n}_i \in \{(\pm 1, 0, 0), (0, \pm 1, 0), (0, 0, \pm 1)\}. \quad (3)$$

Generalizations of this model, which we call the Maier-Saupe-Zwanzig (MSZ) model, have been applied to the study of biaxial and uniaxial ordering in rod-plate mixtures of liquid crystals [18,19]. In agreement with predictions of the Landau-de Gennes theory [16], the isotropic-nematic transition is found to be first order, with a discontinuity in the nematic-order parameter. In the NE case, Xing *et al.* have considered similar Maier-Saupe type interactions adjunct to a microscopic model to make contact with a macroscopic Landau theory [20].

To model the mechanical and orientational character of NEs, a number of approaches have been considered [1,3,5,7,21–23]. We shall assume that elastic properties arise from an entropic contribution [1]. Thus we consider the canonical partition function

$$Z = \sum_{\{\mathbf{n}_i\}} \Omega(\{\mathbf{n}_i\}, \Lambda) \exp(-\beta E_{\text{MS}}), \quad (4)$$

where $\beta = 1/k_B T$, E_{MS} is the interaction energy of the MSZ model given by Eq. (1), and the sum is over the configurations (3) of the microscopic nematic directors \mathbf{n}_i . The entropic term Ω depends on the nematic orientations and on a global lattice distortion tensor Λ [1]. If we consider a uniform uniaxial strain along the direction of a unit vector \mathbf{m} and assume sample incompressibility, the distortion components may be written as

$$\Lambda_{\alpha\beta} = \lambda^{-1/2} \delta_{\alpha\beta} + (\lambda - \lambda^{-1/2}) m_\alpha m_\beta, \quad \alpha, \beta = x, y, z, \quad (5)$$

where λ is the distortion factor. According to an extension of the neoclassical theory of elasticity [1,2] for lattice Hamiltonian systems, proposed by Selinger and Ratna [5], we write the degeneracy as

$$\Omega = \exp(-\beta F_{\text{el}}), \quad (6)$$

with the elastic free energy

$$F_{\text{el}} = \frac{\mu}{2} \sum_i \text{Tr}(\mathbf{l}_{0,i} \cdot \Lambda^T \cdot \mathbf{l}_i^{-1} \cdot \Lambda), \quad (7)$$

where μ is the linear shear modulus, \mathbf{l}_i is a local shape tensor, and $\mathbf{l}_{0,i}$ is the local shape tensor at the time of the cross-linking. The components of the shape tensors are obtained from the equation

$$l_{i,\alpha\beta}^{-1} = l_\perp^{-1} \delta_{\alpha\beta} + (l_\parallel^{-1} - l_\perp^{-1}) n_{i,\alpha} n_{i,\beta}, \quad (8)$$

where l_\perp and l_\parallel are the effective step lengths of the nematic polymers in the perpendicular and parallel directions with respect to the nematic vectors. If the cross-linked network is formed with the sample in a totally disordered isotropic state, we assume that the shape tensor $\mathbf{l}_{0,i}^{-1}$ is given by an isotropic average of \mathbf{l}_i^{-1} ,

$$l_{0,\alpha\beta}^{-1} = \frac{1}{3}(2l_\perp^{-1} + l_\parallel^{-1}) \delta_{\alpha\beta}. \quad (9)$$

Thus we obtain

$$F_{\text{el}} = \frac{\mu}{2} \sum_{i=1}^N \left[(\lambda^2 + 2\lambda^{-1}) - \delta(\lambda^2 - \lambda^{-1}) \left(\frac{3}{2} (\mathbf{m} \cdot \mathbf{n}_i)^2 - \frac{1}{2} \right) \right] \\ = \frac{\mu N}{2} \left(\lambda^2 + \frac{2}{\lambda} \right) - \frac{\mu \delta}{3} \left(\lambda^2 - \frac{1}{\lambda} \right) \sum_{i=1}^N \sum_{\mu, \nu} M_{\mu\nu} S_i^{\mu\nu}, \quad (10)$$

where we have introduced the tensor

$$M_{\mu\nu} = \frac{1}{2}(3m^\mu m^\nu - \delta^{\mu\nu}) \quad (11)$$

and the parameter

$$\delta = \frac{2l_\perp^{-1} - 2l_\parallel^{-1}}{2l_\perp^{-1} + l_\parallel^{-1}}, \quad 0 \leq \delta \leq 1, \quad (12)$$

with $\delta = 0$ in the isotropic case and $\delta = 1$ in the limit of largest anisotropy. The first term on the right-hand side of Eq. (10) is the classical rubber free energy,

$$f_{\text{rub}} = \frac{\mu}{2} \left(\lambda^2 + \frac{2}{\lambda} \right). \quad (13)$$

Finally, the partition function may be written

$$Z = \sum_{\{\mathbf{n}_i\}} \exp(-\beta E_{\text{eff}}), \quad (14)$$

with the effective energy

$$E_{\text{eff}} = -\frac{A}{N} \sum_{1 \leq i < j \leq N} \sum_{\mu, \nu = x, y, z} S_i^{\mu\nu} S_j^{\mu\nu} \\ - \frac{4}{9} B \sum_{i=1}^N \sum_{\mu, \nu = x, y, z} M_{\mu\nu} S_i^{\mu\nu} + N f_{\text{rub}}, \quad (15)$$

where we have defined

$$B = \frac{3}{4} \mu \delta \left(\lambda^2 - \frac{1}{\lambda} \right). \quad (16)$$

Given the entropic origin of the elastic contribution to the free energy, the linear shear modulus should depend linearly on temperature,

$$\mu = n_s k_B T, \quad (17)$$

where n_s is the number of strands in the polymer chain per unit volume [1].

We further assume that the microscopic nematic directors are subjected to random fields, which originate from the distribution of local anisotropy axes generated at the time of cross-linking. These interactions may be represented by the energy term [8,9,11,21]

$$E_{\text{rf}} = -\frac{\gamma}{2} \sum_{i=1}^N \sum_{\mu, \nu = x, y, z} H_i^{\mu\nu} S_i^{\mu\nu}, \quad (18)$$

with

$$H_i^{\mu\nu} = \frac{1}{2}(3h_i^\mu h_i^\nu - \delta^{\mu\nu}), \quad (19)$$

where γ is an energy parameter and h_i^μ is the μ th component of the unit vector \mathbf{h}_i . We assume that $\{\mathbf{h}_i\}$ is a set of independent and identically distributed quenched random variables with probability distribution

$$P(\mathbf{h}) = \begin{cases} c/2, & \text{for } \mathbf{h} = (0,0,\pm 1), \\ (1-c)/4, & \text{for } \mathbf{h} = (\pm 1,0,0), (0,\pm 1,0), \end{cases} \quad (20)$$

with $0 \leq c \leq 1$. Let us choose the symmetry axis of the mesogen units along the z direction. Then the parameter c is related to the degree of anisotropy of the mesogens attached to the network cross-links, so that $c = 1/3$ for samples formed in the isotropic state and $c > 1/3$ for samples formed in the nematic state. Note that we have assumed the shape tensor $\mathbf{l}_{0,i}^{-1}$ to be fixed as an isotropic average of \mathbf{l}_i^{-1} , and we have chosen to include the network-heterogeneity history in the random-field interaction only. This choice lends itself to a simpler calculation, and is in line with previous theoretical works (see, for instance, Refs. [5] and [11]).

III. CALCULATION OF THE FREE ENERGY

Effects of a fixed external stress σ are taken into account by means of the partition function

$$Y(\{\mathbf{h}_i\}) = \int_0^\infty d\lambda e^{N\beta\sigma\lambda} \sum_{\{\mathbf{n}_i\}} \exp[-\beta(E_{\text{eff}} + E_{\text{rf}})], \quad (21)$$

for a given a configuration of random fields. The free-energy density is given by

$$f = -\frac{1}{\beta} \lim_{N \rightarrow \infty} \frac{1}{N} \ln Y = f_{\text{rub}} - \sigma\lambda - \frac{1}{\beta} \lim_{N \rightarrow \infty} \frac{1}{N} \ln \sum_{\{\mathbf{n}_i\}} \exp(-\beta E), \quad (22)$$

where f should be a minimum with respect to λ and

$$E = -\frac{A}{2N} \sum_{\mu,\nu} \left(\sum_{i=1}^N S_i^{\mu\nu} \right)^2 - \frac{4}{9} B \sum_{i=1}^N \sum_{\mu,\nu} M_{\mu\nu} S_i^{\mu\nu} - \frac{\gamma}{2} \sum_{\mu,\nu} \sum_{i=1}^N H_i^{\mu\nu} S_i^{\mu\nu}, \quad (23)$$

where we discarded terms of order smaller than N .

Using a set of standard Gaussian integral transformations [17] we decouple the interactions between different particles,

$$\sum_{\{\mathbf{n}_i\}} \exp(-\beta E) = \int [dQ] \exp\left(-\frac{N\beta A}{2} \sum_{\mu,\nu} Q_{\mu\nu}^2\right) \times \prod_i \left\{ \sum_{\{\mathbf{n}\}} \exp\left[\beta \sum_{\mu,\nu} S^{\mu\nu} \left(A Q_{\mu\nu} + \frac{4}{9} B M_{\mu\nu} + \frac{\gamma}{2} H_i^{\mu\nu} \right)\right]\right\}, \quad (24)$$

where $[dQ] = \prod_{\mu,\nu} \sqrt{\beta AN/2\pi} dQ_{\mu\nu}$. Performing the sum over the orientations \mathbf{n} of a single particle we obtain

$$f = f_{\text{rub}} + \frac{B}{3} - \sigma\lambda - \frac{1}{\beta} \ln 2 - \beta^{-1} \lim_{N \rightarrow \infty} \frac{1}{N} \times \ln \int [dQ] \exp\left[-\frac{N\beta A}{2} \left(\sum_{\mu,\nu} Q_{\mu\nu}^2 + \text{Tr} Q \right)\right] \times \exp\left\{ \sum_{i=1}^N \left[-\frac{\beta\gamma}{4} \text{Tr} \mathbb{H}_i + \ln \left(\sum_{\mu} e_{\mu}(\mathbf{h}_i) \right) \right] \right\}, \quad (25)$$

where the second-order tensor Q has components $Q_{\mu\nu}$, and

$$e_{\mu}(\mathbf{h}_i) = \exp\left[\beta \left(\frac{3A}{2} Q_{\mu\mu} + \frac{3\gamma}{4} H_i^{\mu\mu} + Bm_{\mu}^2 \right)\right]. \quad (26)$$

Invoking the law of large numbers, we have

$$\lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N \left\{ -\frac{\beta\gamma}{4} \text{Tr} \mathbb{H}_i + \ln \left(\sum_{\mu} e_{\mu}(\mathbf{h}_i) \right) \right\} = -\frac{\beta\gamma}{4} \langle \text{Tr} \mathbb{H} \rangle_h + \left\langle \ln \left(\sum_{\mu} e_{\mu}(\mathbf{h}) \right) \right\rangle_h, \quad (27)$$

where $\langle \dots \rangle_h$ denotes the expectation value with respect to the random-field variables, from which we see that the free energy is self-averaging. Carrying out the integration using Laplace's method we arrive at

$$f = f_{\text{rub}} + \frac{B}{3} - \sigma\lambda - \frac{1}{\beta} \ln 2 - \beta^{-1} \max L(Q_{\mu\nu}), \quad (28)$$

where $Q_{\mu\nu}$ maximizes the functional

$$L = -\frac{\beta A}{2} (\text{Tr} Q^2 + \text{Tr} Q) + \left\langle \ln \left(\sum_{\mu} e_{\mu} \right) \right\rangle_h. \quad (29)$$

The condition for L to be stationary with respect to $Q_{\mu\nu}$ leads to the equations of state for the order parameters

$$Q_{\mu\nu} = \frac{1}{2} \left(3 \left\langle \frac{e_{\mu}}{\sum_{\alpha} e_{\alpha}} \right\rangle_h - 1 \right) \delta_{\mu\nu}. \quad (30)$$

Notice that $\text{Tr} Q = 0$. The condition for the free energy to be stationary with respect to λ leads to the equation of state for the distortion,

$$\lambda = \frac{1}{\lambda^2} + \frac{\sigma}{\mu} + \frac{\delta}{2} \left(2\lambda + \frac{1}{\lambda^2} \right) \sum_{\mu} m_{\mu}^2 Q_{\mu\mu}, \quad (31)$$

where we have used Eq. (30). Using these equations of state we may rewrite the free-energy density as

$$f = f_{\text{rub}} + \frac{B}{3} - \sigma\lambda - \frac{1}{\beta} \ln 2 + \frac{A}{2} \text{Tr} Q^2 - \frac{1}{\beta} \left\langle \ln \left(\sum_{\mu} e_{\mu} \right) \right\rangle_h. \quad (32)$$

To make a closer contact with experiments on liquid crystals, we use the standard diagonal parametric form of the

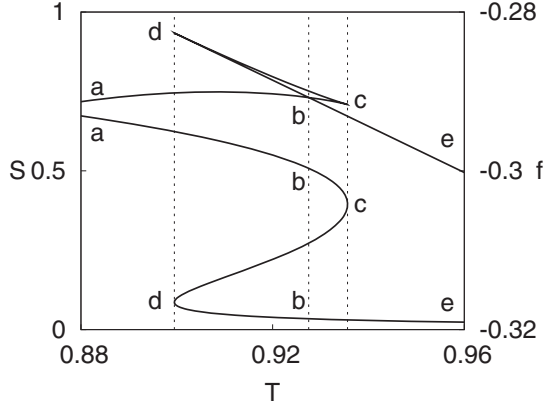


FIG. 1. Order parameter S and free-energy density f (upper curve) as a function of temperature for $\gamma = 0$ and applied stress $\sigma = 0.02$.

traceless matrix \mathbb{Q} appropriate for the nematic ordering along the z direction,

$$\mathbb{Q} = \begin{pmatrix} -\frac{S+\eta}{2} & 0 & 0 \\ 0 & -\frac{S-\eta}{2} & 0 \\ 0 & 0 & S \end{pmatrix}. \quad (33)$$

The nematic-order parameters S and η characterize the isotropic phase ($S = \eta = 0$), the uniaxial nematic phase ($S \neq 0, \eta = 0$), and the biaxial nematic phase ($S \neq 0, \eta \neq 0$). From the equation of state (30) we find

$$S = \frac{3}{2} \left\langle \frac{e_z}{\sum_{\mu} e_{\mu}} \right\rangle_h - \frac{1}{2} \quad (34)$$

and

$$\eta = \frac{3}{2} \left\langle \frac{e_y - e_x}{\sum_{\mu} e_{\mu}} \right\rangle_h. \quad (35)$$

The simplest version of the MSZ model defined by Eqs. (1)–(3) lacks the proper symmetry to describe a stable nematic biaxial phase. To check if this behavior is robust after including elasticity and random fields, we have considered the case

where the strain direction is perpendicular to the *chosen* axis of symmetry of the order parameter. In fact, there has been a lot of debate in the literature about the soft (or semisoft) response of NEs being related to the onset of biaxial behavior [1,24–26]. While the description of such phenomena is beyond the scope of this paper, we emphasize that a numerical inspection of the equations of state have led us to conclude that biaxial symmetry remains absent for a large range of parameters. Hence we shall take $\eta = 0$ and consider the strain direction parallel to the z axis, $\mathbf{m} = (0, 0, 1)$. This is a reasonable assumption since the coupling between elastic and orientational degrees of freedom provides an easy axis of symmetry for this system. Thus the free-energy density (32) becomes

$$f = f_{\text{rub}} + \frac{1}{3}B - \sigma\lambda - \frac{1}{\beta} \ln 2 + \frac{3A}{4}S^2 - \frac{1}{\beta} \left\langle \ln \left(\sum_{\mu} e_{\mu} \right) \right\rangle_h, \quad (36)$$

where

$$e_{\mu}(\mathbf{h}) = \exp \left\{ \beta \left[-\frac{3}{4}AS + \frac{3}{8}\gamma(3h_{\mu}^2 - 1) \right] \right\}, \quad \mu = x, y, \quad (37)$$

$$e_z(\mathbf{h}) = \exp \left\{ \beta \left[\frac{3}{2}AS + \frac{3}{8}\gamma(3h_z^2 - 1) + B \right] \right\}, \quad (38)$$

and the equation of state for distortion (31) takes the form

$$\lambda = \frac{1}{\lambda^2} + \frac{\sigma}{\mu} + \frac{\delta}{2} \left(2\lambda + \frac{1}{\lambda^2} \right) S. \quad (39)$$

The results obtained thus far are valid for arbitrary random-field distributions. Henceforth we limit ourselves to the discrete distribution (20). In this case the free-energy density (36) is given by

$$f = f_{\text{rub}} + \frac{1}{3}B - \sigma\lambda - \frac{1}{\beta} \ln 2 + \frac{3}{4}AS(S+1) - \frac{1}{\beta} \{ c \ln [2 + e^{\beta(9AS/4+9\gamma/8+B)}] + (1-c) \ln [1 + e^{9\beta\gamma/8} + e^{\beta(9AS/4+B)}] \}, \quad (40)$$

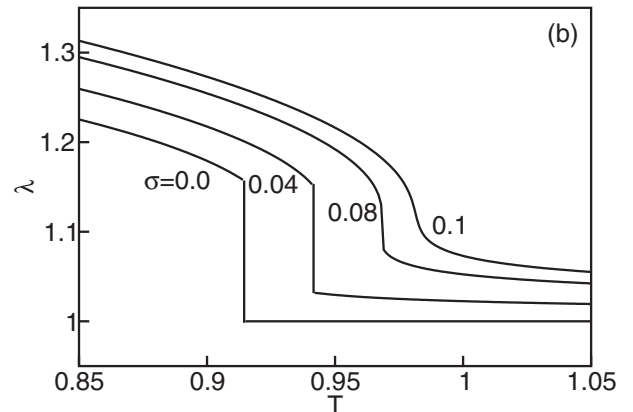
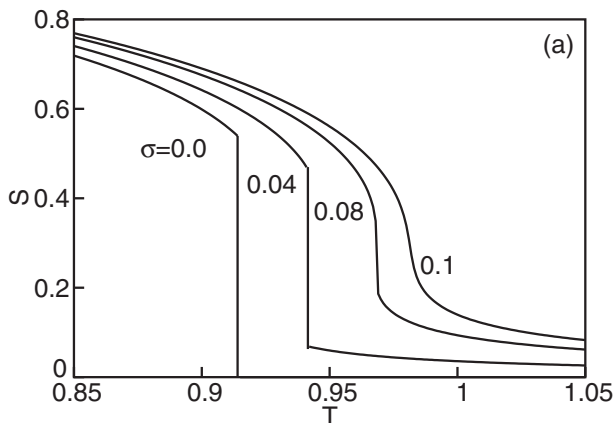


FIG. 2. Nematic order parameter (a) and distortion factor (b) as a function of temperature, for $\gamma = 0$ and various applied stresses σ .

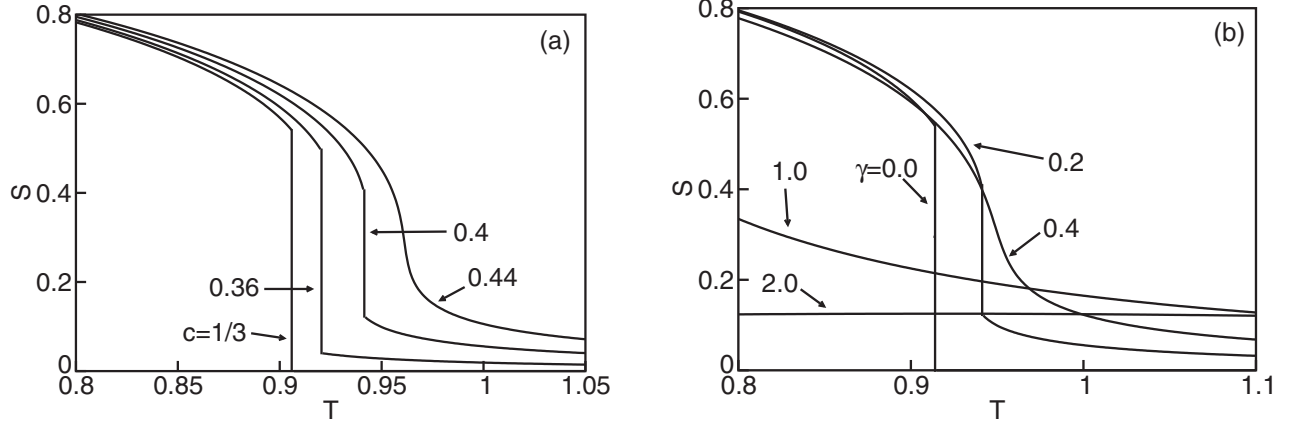


FIG. 3. Nematic-order parameter as a function of temperature for $\sigma = 0$. (a) $\gamma = 0.2$ and various values of c . (b) $c = 0.4$ and various values of γ .

where we have dropped an additive constant $3\gamma/8$. The equation of state for the order parameter (34) becomes

$$S = \frac{3}{2} \left[\frac{c e^{\beta(9AS/4+9\gamma/8+B)}}{2 + e^{\beta(9AS/4+9\gamma/8+B)}} + \frac{(1-c)e^{\beta(9AS/4+B)}}{1 + e^{9\beta\gamma/8} + e^{\beta(9AS/4+B)}} \right] - \frac{1}{2}. \quad (41)$$

IV. THERMODYNAMIC RESULTS

Without loss of generality, we assume $n_s = 1$ and $\delta = 0.5$, since other choices lead to qualitatively similar results. Let us write down the equations in terms of which we performed numerical calculations. We express the energies in units of A and the temperature in units of k_B/A . The free-energy density (40) is given explicitly as

$$f = -\sigma\lambda + \frac{3}{4}S(S+1) + T \left\{ \frac{1}{8}(5\lambda^2 + 7\lambda^{-1}) - \ln 2 - c \ln[2 + e^{9(2S+\gamma)/8T+3(\lambda^2-\lambda^{-1})/8}] - (1-c) \ln[1 + e^{9\gamma/8T} + e^{9S/4T+3(\lambda^2-\lambda^{-1})/8}] \right\}. \quad (42)$$

The equation of state for the order parameter (41) takes the form

$$S = \frac{3}{2} \left[\frac{c e^{9(2S+\gamma)/8T+3(\lambda^2-\lambda^{-1})/8}}{2 + e^{9(2S+\gamma)/8T+3(\lambda^2-\lambda^{-1})/8}} + \frac{(1-c)e^{9S/4T+3(\lambda^2-\lambda^{-1})/8}}{1 + e^{9\gamma/8T} + e^{9S/4T+3(\lambda^2-\lambda^{-1})/8}} \right] - \frac{1}{2}, \quad (43)$$

and the equation of state for the distortion (39) gives

$$\lambda = \frac{1}{\lambda^2} + \frac{\sigma}{T} + \frac{1}{4} \left(2\lambda + \frac{1}{\lambda^2} \right) S. \quad (44)$$

In the absence of applied stress ($\sigma = 0$), the equation of state (44) can easily be solved for the distortion with the result

$$\lambda = \left(\frac{1 + S/4}{1 - S/2} \right)^{\frac{1}{3}}. \quad (45)$$

The distortion increases monotonically with S , for $0 < S < 1$. In addition, $S = 0$ implies $\lambda = 1$, indicating that the strain

is driven by the orientational ordering only. For an arbitrary applied stress ($\sigma \geq 0$) the equation of state (44) is a cubic equation in λ with only one real and positive root given by the formula

$$\lambda = \frac{2\sigma}{3(2-S)T} \times \left\{ 1 + 2 \cosh \left[\frac{1}{3} \cosh^{-1} \left(1 + \frac{27(2-S)^2(4+S)T^3}{32\sigma^3} \right) \right] \right\}, \quad (46)$$

which is a monotonically increasing function of S .

In our numerical calculations we solved Eq. (43) for the order parameter S using for λ the result given by Eq. (46).

A. Results in the absence of disorder ($\gamma = 0$)

In Fig. 1 we plot the order parameter S and the free-energy density f (upper curve) as a function of temperature for applied stress $\sigma = 0.02$ in the temperature range where a first-order transition takes place. The low-temperature stable solution abc

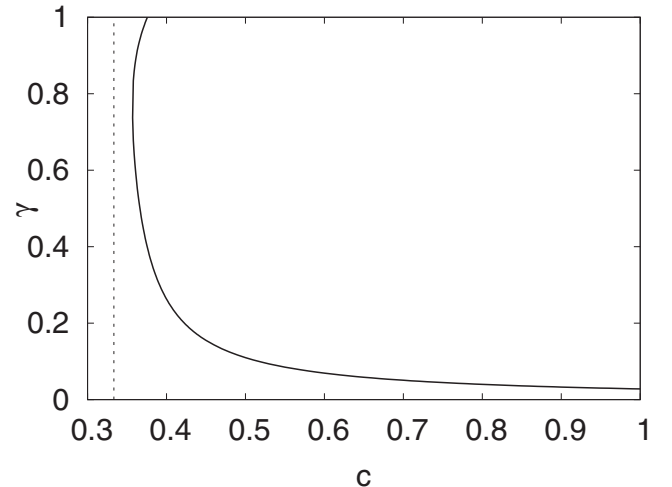


FIG. 4. The curve for $\sigma = 0$ above and to the right of which there is no first-order transition. The vertical dotted line corresponds to $c = 1/3$.

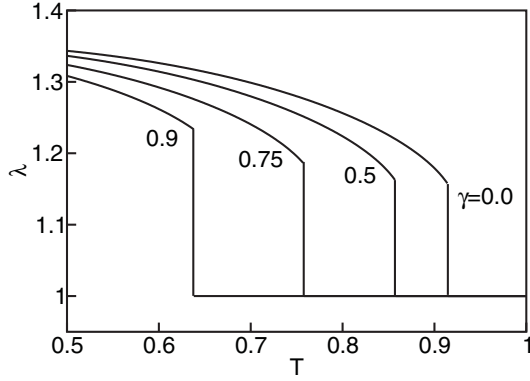


FIG. 5. Distortion factor λ as a function of temperature for $\sigma = 0$, $c = 1/3$, and γ between 0 and 1.

with larger order parameter S is called the nematic solution, whereas the high temperature solution dbe with smaller order parameter is referred to as an isotropic solution, even though S no longer vanishes as in the case of zero applied stress. The branch cd corresponds to an unstable solution. In the narrow temperature interval $T_d < T < T_c$ both the nematic and the isotropic solutions are stable, and we have to choose the one with smaller free energy. The first-order transition between nematic and isotropic phases occurs at the temperature $T_{NI} = T_b$ where the free energies become equal. We observe that, in agreement with classical elasticity theory, the free energy changes linearly with temperature in the isotropic phase [1].

In Fig. 2 we plot (a) the nematic-order parameter S and (b) the distortion factor λ as a function of temperature for several values of the applied stress σ . As expected from Eq. (46), the graph of λ follows closely that of S . For small applied stress σ the system undergoes a first-order transition with a gap between the nematic and isotropic solutions. As the aligning stress σ increases, the gap decreases until the critical point is reached, beyond which there is no phase transition. This behavior has been predicted by de Gennes in the mid-seventies [27] before NEs were proven to be chemically feasible. Experimentally, however, no first-order transition is observed down to the limit of zero applied stress. The jump in the first-order transition is smoothed out, being replaced by a continuous but quick variation of the order

parameter. This fact has been interpreted theoretically as being due to the anisotropic distribution of random fields [5,6].

B. Effects of disorder ($\gamma > 0$)

Let us examine how the random fields affect the nematic-isotropic transition. In Fig. 3(a) we show the nematic-order parameter as a function of temperature for $\sigma = 0$, $\gamma = 0.2$, and several values of c . We observe that the gap between the nematic and isotropic solutions decreases as c increases from $c = 1/3$ to $c = 0.422$, disappearing above this value of c . In Fig. 3(b) the nematic-order parameter is shown as a function of temperature for $c = 0.44$ and several values of γ . Again, the gap between the nematic and isotropic solutions decreases as γ increases from $\gamma = 0$ to $\gamma = 0.263$, and the transition disappears above this value of γ .

These results show that anisotropic ($c > 1/3$) distribution of the random fields of sufficient strength ($\gamma > 0$) is necessary to smooth out the isotropic-nematic transition, in agreement with the numerical simulations of Selinger and Ratna [5]. Figure 4 shows, for zero applied stress ($\sigma = 0$), the curve in the γ - c plane above and to the right of which there is no first-order transition.

C. Results for an isotropic disorder ($c = 1/3$, $\gamma > 0$)

We recall that an isotropic distribution of random fields $c = 1/3$ represents samples formed in the isotropic state, with the random stresses coming from the cross-linked network without preferred direction. According to Fig. 4, in this case a first-order transition occurs in zero applied stress ($\sigma = 0$) for any value of the random-field strength γ . To illustrate this fact, we plot in Fig. 5 the distortion factor λ as a function of temperature in the absence of external stress ($\sigma = 0$) for several values of the disorder parameter γ . The nematic phase decreases with increasing γ , but the first-order transition persists showing no evidence of the experimentally observed smoothed out nematic-isotropic transition in samples formed in the nematic state.

In the presence of the applied stress ($\sigma > 0$), the first-order transition is smoothed out by a sufficiently large temperature or disorder strength. This can be seen in the stress-strain curves, where the strain e is related to the distortion by

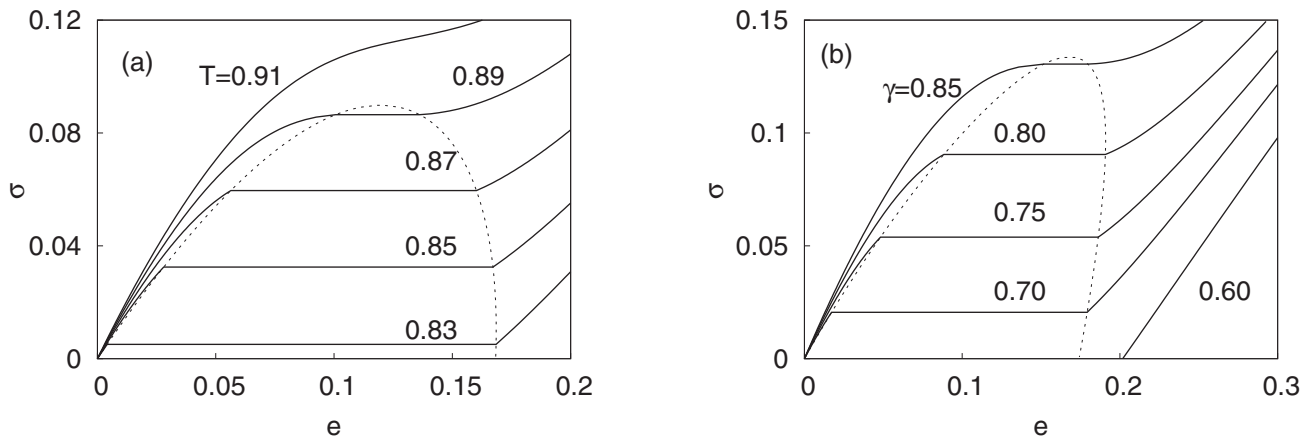


FIG. 6. Stress-strain curves for $c = 1/3$. (a) Isotherms for $\gamma = 0.6$. (b) Iso- γ curves for $T = 0.8$.

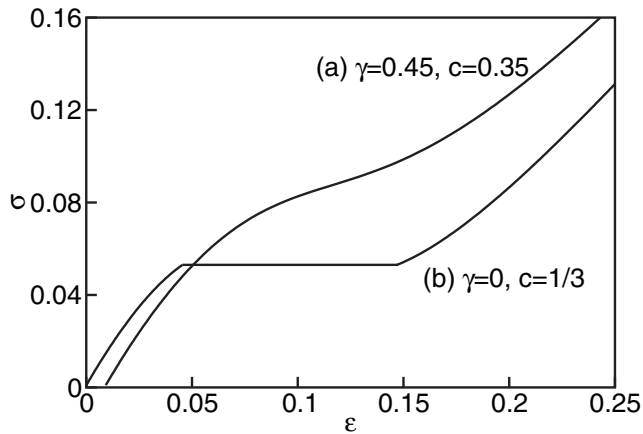


FIG. 7. Stress-strain curves for $T = 0.95$. (a) $\gamma = 0.45$ and $c = 0.35$. (b) $\gamma = 0$ and $c = 1/3$.

the equation $\lambda = 1 + e$. In Fig. 6(a) we plot isotherms for $\gamma = 0.6$ and in Fig. 6(b) we plot iso- γ curves for $T = 0.8$. It is clear from these figures that the temperature and the disorder strength have similar effects on the system. For sufficiently low temperature ($T < T_c$) or disorder strength ($\gamma < \gamma_c$), the stress grows monotonically with strain in the isotropic phase up to the first-order transition to the nematic phase. At the transition the two phases coexist and the strain is independent of stress. The stress-strain “plateau” is then followed by a stress growth at larger strains. This behavior agrees with the experimental scenario of a typical transition between polydomains and a monodomain in NEs. However, we note that our simple mean-field calculations cannot distinguish the polydomain state from the isotropic state. Although we opted for the polydomain-monodomain interpretation for the transition, the stress-induced NI transition is also a possible alternative interpretation. As the temperature or the disorder strength increases, the coexistence curve shrinks until the critical point is reached at $T = T_c$ or $\gamma = \gamma_c$. The whole phase diagram resembles a typical P - V diagram of simple fluids.

V. DISCUSSION

Recent experiments have shown that NEs cross-linked in the isotropic state display a well-defined plateau at the

stress-strain curve, for substantially lower critical stresses, in comparison with NEs cross-linked in the nematic state [28]. Optical microscopy observations suggest this behavior should be attributed to larger memory effects for NEs formed in the nematic state. We may then expect that γ is not independent, but should increase with c , according to the language of our model. Now it is not difficult to find appropriate values of γ and c satisfying this restriction, and in general agreement with the experimental results. We show in Fig. 7 two stress-strain curves for $T = 0.95$. For curve (a), we consider samples cross-linked in the isotropic state ($c = 1/3$), which implies no memory effect ($\gamma = 0$). In this case, the stress-strain curve presents a well-defined plateau for low critical stress. For curve (b), we consider samples cross-linked in the nematic state ($c = 0.35$), which should imply strong memory effects ($\gamma = 0.45$). Note that the stress-strain curve characterizes a broad polydomain-monodomain transition for higher critical stress, in good agreement with the experimental results by Urayama *et al.* [28].

In conclusion, we have introduced a simple mean-field lattice model to describe the behavior of NEs. This model combines the MSZ theory of liquid crystals [15,18,19] and the lattice version, due to Selinger and Ratna [5], of the Warner-Terentjev theory of elasticity [1]. We performed detailed calculations for a large range of parameters, with the inclusion of the effects of a quenched distribution of random fields. A stress-strain coexistence curve may be obtained for systems cooled below a freezing temperature, which is analogous to the P - V diagram of a simple fluid, with the disorder strength playing the role of temperature. Below a critical stress, the characteristic tie lines resemble the experimental stress-strain plateau and may be interpreted as signatures of a polydomain-monodomain transition. In the monodomain case, we show that random-field disorder may soften the first-order transition between nematic and isotropic phases, provided the samples are formed in the nematic state. Beyond general agreement with some previous findings, we hope our results may motivate further experimental work on the stress-strain coexistence curve of NEs.

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