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Statistical models of mixtures with a biaxial nematic phase

E. do Carmo, D. B. Liarte, and S. R. Salinas
Instituto de Física, Universidade de São Paulo, Caixa Postal 66318, CEP 05314-970 São Paulo, SP, Brazil

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We consider a simple Maier-Saupe statistical model with the inclusion of disorder degrees of freedom to mimic the phase diagram of a mixture of rodlike and disklike molecules. A quenched distribution of shapes leads to a phase diagram with two uniaxial and a biaxial nematic structure. A thermalized distribution, however, which is more adequate to liquid mixtures, precludes the stability of this biaxial phase. We then use a two-temperature formalism, and assume a separation of relaxation times, to show that a partial degree of annealing is already sufficient to stabilize a biaxial nematic structure.

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Quenched and annealed degrees of freedom of statistical systems are known to produce phase diagrams with a number of distinct features [1]. The ferromagnetic site-diluted Ising model provides an example of a continuous transition, in the quenched case, which turns into a first-order boundary beyond a certain tricritical point, if we consider thermalized site dilution [2]. Disordered degrees of freedom in solid compounds, as random magnets and spin glasses, are examples of quenched disorder, which lead to well-known problems related to averages of sets of disordered free energies. In liquid systems, however, relaxation times are shorter, and the simpler problems of annealed disorder are more relevant from the physical perspective. In this paper, we show that distinctions between quenched and annealed degrees of freedom are particularly relevant in statistical models of mixtures, which have been used to account for the elusive biaxial nematic phase of liquid crystals [3].

Uniaxial nematic phases, with the director along a single axis, have been fully characterized in the phase diagrams of a large number of thermotropic as well as lyotropic liquid crystals [3,4]. The existence of a biaxial nematic structure, however, has been subjected to some debate [5]. A biaxial nematic phase was predicted by calculations for different lattice models [6], and has been found by Yu and Saupe [7] in the phase diagram of a ternary lyotropic mixture. In the ordered region of this mixture, in a phase diagram in terms of temperature and concentration of one of the compounds, there is a nematic biaxial structure bounded by two distinct uniaxial nematic structures, loosely associated with either prolate (cylinderlike) or oblate (disklike) molecular aggregates. Transitions between the ordered uniaxial nematic and the disordered phases are discontinuous, in agreement with the Maier-Saupe approach, and transitions between uniaxial and biaxial structures are continuous, with a critical line that is supposed to end at a Landau multicritical point. More recent experimental work has indicated the existence of nematic biaxial structures in a certain number of new thermotropic compounds, formed by anisotropic banana-shaped molecules [5].

Although earlier theoretical calculations indicated the existence of a stable biaxial nematic structure [6], which is also supported by a Landau–de Gennes expansion [8], mean-field calculations by Palffy-Muhoray and collaborators [9], using the Maier-Saupe interactions to consider a mixture of cylinders and disks, precluded the stability of an intermediate biaxial structure, except under some special circumstances. A few years ago this problem was reanalyzed, in terms of a schematic discrete version of the Maier-Saupe model, in a paper by Henriques and Henriques [10], who pointed out the existence and stability of a biaxial nematic phase, bordered by two critical lines meeting at a Landau multicritical point [8], in close contact with the experimental findings of Yu and Saupe [7]. The calculations of Henriques and Henriques, however, which can be carried out for any distribution of molecular shapes, implicitly assumed a quenched polymorphism, which may not be adequate for these liquid crystalline systems.

Given the scarcity of experimental data on these biaxial phases, the apparently conflicting theoretical results [6,11], and a few recent and not so conclusive simulations [12,13], there is still room for revisiting the statistical problem of a mixture of cylinders and disks. Along the lines of the work of Henriques and Henriques [10], we then perform standard statistical-mechanics calculations for a simple discrete version of the Maier-Saupe model, which we call the basic model, with the inclusion of a binary distribution of shapes to mimic a mixture of prolate and oblate molecules (cylinders and disks). We draw clear distinctions between quenched and annealed distributions of shapes. In the quenched case, we show the existence of a stable biaxial phase in the temperature-concentration phase diagram, in qualitative agreement with experiments, and in accordance with the work of Henriques and Henriques. In the annealed case, however, the same model system leads to an unstable biaxial phase, in connection with the earlier calculations of Palffy-Muhoray and collaborators, which provides an example of the distinctions between the effects of quenched and annealed disorder degrees of freedom.

Although the results for the quenched distribution seem to be in agreement with the experimental phase diagrams, relaxation times in both liquid and liquid crystalline systems are relatively short, and the physics of disordered couplings in these liquid systems should be better represented by thermalized variables. Even in the annealed situation, however, we should make an attempt to account for a certain degree of separation between relaxation times. We then resorted to a two-temperature formalism [14], with orientational degrees of freedom and disorder variables coupled to different heat reservoirs, at temperatures T and $T_{\lambda}=nT$. In this application of the formalism, we show that a small difference of tem-

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peratures is already enough to change the phase diagram of the fully annealed case, and to stabilize the biaxial nematic structure, which probably provides an explanation for the elusive nature of this phase behavior.

In analogy to the Curie-Weiss model of ferromagnetism, the Maier-Saupe model is given by the energy

$$\mathcal{H} = -\frac{A}{N}\sum_{1\le i<j\le N}\ \sum_{\mu,\nu=1,2,3}\lambda_i\lambda_j S_i^{\mu\nu}S_j^{\mu\nu}, \tag{1}$$

where A is a coupling constant, the orientational degrees of freedom are given by

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

where $|\vec{n}_i|=1$ for $i=1,2,\ldots,N$, and $\{\lambda_i\}$ is a set of (disordered) couplings representing either prolate ($\lambda_i=+1$) or oblate ($\lambda_i=-1$) molecular groups. This model is further simplified if we suppose that the director $\vec{n}_i$ assumes six values only, along the Cartesian axes, $\vec{n}_i=(\pm1,0,0)$, $(0,\pm1,0)$, and $(0,0,\pm1)$, according to an early suggestion of Zwanzig.

In the quenched case, $\{\lambda_i\}$ is a set of independent, identical, and identically distributed random variables, associated with a probability distribution $p(\lambda_i)$. For a given configuration $\{\lambda_i\}$, the partition function is written as

$$Z_q\{\lambda_i\} = \sum_{\{\vec{n}_i\}}\exp\left[\frac{\beta}{N}\sum_{1\le i<j\le N}\ \sum_{\mu,\nu=1,2,3}\lambda_i\lambda_j S_i^{\mu\nu}S_j^{\mu\nu}\right], \tag{3}$$

where β is the inverse of a dimensionless temperature, and we choose $A=1$. We now use standard Gaussian identities to write the partition function as an integration over the independent terms of a symmetric tensor $\mathbf{Q}$. In the thermodynamic limit, taking into account the self-averaging properties of this problem, we can write

$$Z_q = \int [d\mathbf{Q}]\exp[-\beta N f_q], \tag{4}$$

where

$$f_q = \frac{1}{2}\sum_{\mu}Q_{\mu\mu}^2 + \frac{1}{2}\langle\lambda_i\rangle\sum_{\mu}Q_{\mu\mu} - \frac{1}{\beta}\left\langle \ln\left[2\sum_{\mu}\exp\left(\frac{3}{2}\beta\lambda_i Q_{\mu\mu}\right)\right]\right\rangle. \tag{5}$$

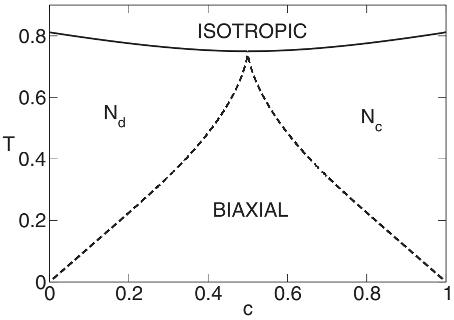

FIG. 1. Temperature-concentration phase diagram for a quenched distribution of shapes. First-order transitions between the isotropic region and the uniaxial nematic structures (N_c and N_d) are indicated by the solid line. Dashed lines indicate second-order transitions.

The equations of minima, $\partial g/\partial Q_{\mu\mu}=0$, lead to the usual traceless tensor order parameter of the Maier-Saupe approach. We then introduce the standard parametrization $Q_{xx}=-(S+\eta)/2$, $Q_{yy}=-(S-\eta)/2$, and $Q_{zz}=S$, and consider a double-delta probability distribution, $p(\lambda_i)=c\delta(\lambda_i-1)+(1-c)\delta(\lambda_i+1)$, where the parameter c represents the concentration of prolate ($\lambda=+1$) molecules. We then have

$$\begin{aligned} f_q = {} & \frac{1}{4}(3S^2+\eta^2) - \frac{1}{\beta}\ln 2 \\ & - \frac{c}{\beta}\ln\left[2\exp\left(-\frac{3}{4}\beta S\right)\cosh\left(\frac{3}{4}\beta\eta\right) + \exp\left(\frac{3}{2}\beta S\right)\right] \\ & - \frac{(1-c)}{\beta}\ln\left[2\exp\left(\frac{3}{4}\beta S\right)\cosh\left(\frac{3}{4}\beta\eta\right) + \exp\left(-\frac{3}{2}\beta S\right)\right], \end{aligned} \tag{6}$$

which leads to the phase diagram of Fig. 1, with thermodynamically stable uniaxial ($S\neq0;\eta=0$) and biaxial ($S\neq0;\eta\neq0$) nematic structures, and two critical lines meeting at the Landau multicritical point, $\beta=4/3$ and $c=1/2$.

In order to make contact with the standard Landau–de Gennes phenomenology, we expand the free energy f_q in the neighborhood of the Landau multicritical point, in terms of the quadratic and cubic, $I_2=\mathrm{Tr}\,\mathbf{Q}^2$ and $I_3=\mathrm{Tr}\,\mathbf{Q}^3$, invariants of the tensor order parameter,

$$\begin{aligned} f_q = {} & -\frac{3}{4}\ln 6 + \frac{1}{2}\left(1-\frac{3}{4}\beta\right)I_2 - \frac{1}{3}(2c-1)I_3 \\ & + \frac{1}{12}I_2^2 + \frac{1}{6}(2c-1)I_2I_3 + \frac{1}{15}I_3^2 + \cdots . \end{aligned} \tag{7}$$

According to published analyses [8] of this phenomenological expansion, a positive coefficient of I_3^2 is indeed enough to stabilize the biaxial phase.

We now turn to the annealed case, which is associated with the canonical partition function

$$Z_a = \sum_{\{\lambda_i\}}{}' \sum_{\{\vec{n}_i\}}\exp\left[\frac{\beta}{N}\sum_{1\le i<j\le N}\ \sum_{\mu,\nu=1,2,3}\lambda_i\lambda_j S_i^{\mu\nu}S_j^{\mu\nu}\right], \tag{8}$$

where the sum over $\{\lambda_i\}$ is restricted by the fixed concentrations of the molecular types. As $\lambda=+1$ corresponds to a prolate and $\lambda=-1$ to an oblate molecule, we have $N_p-N_o=\Sigma_{i=1}^{N}\lambda_i$, and $N_o=N-N_p$, where N_p (N_o) is the number of prolate (oblate) molecules, and N is the total number of molecules. We then introduce a chemical potential and change to the grand-canonical ensemble,

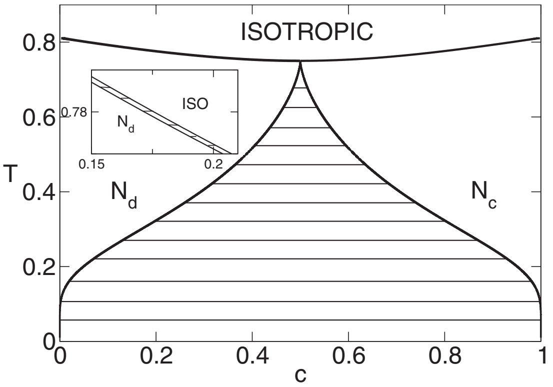

FIG. 2. Temperature-concentration phase diagram in the fully annealed case. The horizontal tie lines indicate the coexistence between two distinct uniaxial nematic phases. In the inset, we show an amplification of a section of the (narrow) coexistence region between uniaxial nematic and isotropic phases. There is no stable biaxial nematic structure.

$$\Xi_a = \sum_{N_p=0}^{N} \exp(\beta\mu N_p) Z_a = \sum_{\{\lambda_i\}}\sum_{\{\vec{n}_i\}} \exp\left[\beta\mu\frac{1}{2}\left(\sum_{i=1}^{N}\lambda_i + N\right) + \frac{\beta}{N}\sum_{1\le i<j\le N}\;\sum_{\mu,\nu=1,2,3}\lambda_i\lambda_j S_i^{\mu\nu}S_j^{\mu\nu}\right]. \tag{9}$$

For the same basic model, with six choices of the unit vectors, we have

$$\Xi_a = \int [d\mathbf{Q}]\exp[-\beta N\phi_a], \tag{10}$$

with the grand potential per particle

$$\phi_a = \frac{1}{2}\sum_{\mu} Q_{\mu\mu}^2 - \frac{1}{2}\mu - \frac{1}{\beta}\ln 2 - \frac{1}{\beta}\ln\sum_{\lambda=\pm1}\left[\exp\left(\frac{1}{2}\lambda\beta\mu - \frac{1}{2}\lambda\beta\sum_{\mu}Q_{\mu\mu}\right)\sum_{\mu}\exp\left(\frac{3}{2}\lambda\beta Q_{\mu\mu}\right)\right], \tag{11}$$

which can also be written as

$$\phi = \frac{1}{4}(3S^2+\eta^2) - \frac{1}{2}\mu - \frac{2}{\beta}\ln 2 - \frac{1}{\beta}\ln\left[2\cosh\left(\frac{3}{4}\beta\eta\right)\cosh\left(\frac{1}{2}\beta\mu - \frac{3}{4}\beta S\right) + \cosh\left(\frac{1}{2}\beta\mu + \frac{3}{4}\beta S\right)\right]. \tag{12}$$

Given the thermodynamic fields T and μ, we show that a biaxial solution exists but that it is thermodynamically unstable, in agreement with the calculations of Palffy-Muhoray and collaborators. In the $T-\mu$ phase diagram there is just a first-order boundary, at $\mu=0$, for $T=1/\beta\leq 3/4$, between two distinct uniaxial structures. In this fully annealed situation, we can also draw the corresponding temperature-concentration phase diagram, as shown in Fig. 2, in which we sketch the tie lines of coexistence of the two uniaxial nematic phases.

In order to make contact with the Landau–de Gennes phenomenology, we can also write an expansion in the neighborhood of the Landau multicritical point, $\beta=4/3$ and $\mu=0$,

$$\phi_a = -\frac{3}{4}\ln 12 + \frac{1}{2}\left[1-\frac{3}{4}\beta\right]I_2 - \frac{2}{9}\mu I_3 + \frac{1}{12}I_2^2 - \frac{1}{18}I_2I_3 - \frac{1}{135}I_3^2 + \cdots. \tag{13}$$

In contrast to Eq. (7), the coefficient of I_3^2 is negative, which now precludes the stability of a biaxial nematic structure [8].

If we use standard techniques of statistical physics, it is straightforward to show that the Helmholtz free energy f_a of the annealed version of the basic Maier-Saupe model differs from the corresponding free energy f_q of the quenched version by a term corresponding to the entropy of mixing,

$$f_a = f_q + \frac{1}{\beta}[c\ln c + (1-c)\ln(1-c)]. \tag{14}$$

This is indeed a quite general result, which we have been able to show for a class of mean-field self-averaging disorder variables, with the insertion of the appropriate form of the entropy of mixing. It is interesting to point out a resemblance with a derivation by Mazo of a quenched Helmholtz free energy that includes, in addition to the expectation of the logarithm of the partition function, a usually inaccessible term of entropy [15]. We remark that quenched situations are far from true thermodynamic equilibrium, and that in the quenched case we do not have access to the entropy of mixing. Of course, the thermodynamic analysis of the Helmholtz free energy f_a, which should be a properly convex function of the density c, leads to the same results of the analysis of the grand potential ϕ_a, written in terms of the thermodynamic fields, T and μ.

We now search for a stable biaxial phase in a situation of partial annealing, which may be represented by the introduction of two heat baths, at different temperatures, associated with the relaxation times of the orientational (quicker) and disorder (slower) degrees of freedom [14]. Given a configuration λ of the slower disorder variables, we can schematically write the probability of occurrence of a configuration σ of the orientational variables,

$$P(\sigma|\lambda) = \frac{1}{Z_\sigma}\exp[-\beta\mathcal{H}(\sigma,\lambda)], \tag{15}$$

where $T=1/\beta$ is the temperature of a heat bath, and

$$Z_\sigma = Z_\sigma(\lambda) = \sum_{\sigma}\exp[-\beta\mathcal{H}(\sigma,\lambda)]. \tag{16}$$

The time evolution of λ_i is given by a Langevin equation,

$$\Gamma\frac{\partial\lambda_i}{\partial t} = -z(t)\lambda_i - \frac{\partial\mathcal{H}}{\partial\lambda_i} + \eta_i(t), \tag{17}$$

where $z(t)$ is a multiplier associated with the chemical potential, $\langle\eta_i(t)\rangle=0$, and

$$\langle \eta_i(t)\eta_j(t')\rangle = 2\Gamma T_\lambda \delta_{ij}\delta(t'-t'), \tag{18}$$

where we have introduced the temperature T_λ of a second heat bath. With the assumption of quick and slow time scales, it is reasonable to replace $\partial\mathcal{H}/\partial\lambda_i$ by its average value,

$$\frac{\partial\mathcal{H}}{\partial\lambda_i} \Rightarrow \left\langle \frac{\partial\mathcal{H}}{\partial\lambda_i}\right\rangle_\sigma = \frac{\partial\mathcal{H}_{eff}}{\partial\lambda_i}, \tag{19}$$

where

$$\mathcal{H}_{eff} = \mathcal{H}_{eff}(\lambda) = -k_B T \ln Tr_\sigma \exp[-\beta\mathcal{H}(\sigma,\lambda)]. \tag{20}$$

We then assume that the probability of a configuration $\{\lambda_i\}$ is given by the grand-canonical expression

$$P(\lambda) = \frac{1}{\Xi(\beta_\lambda,\beta,N,\mu)}\exp[\beta_\lambda \mu N_p - \beta_\lambda \mathcal{H}_{eff}], \tag{21}$$

where

$$\Xi(\beta_\lambda,\beta,N,\mu) = \int [d\lambda]\left\{\sum_{\{\sigma\}}\exp\left[-\beta\mathcal{H}(\sigma,\lambda) + \frac{\beta\mu}{2}\left(\sum_i \lambda_i + N\right)\right]\right\}^{\mathbf{n}}, \tag{22}$$

with $n=T/T_\lambda$, which resembles the number of replicas in spin-glass problems. The application of this formalism to the basic Maier-Saupe model leads to a grand potential ϕ, with the following expansion about the Landau multicritical point, $\beta=4/3$ and $\mu=0$,

$$\phi = -\frac{3}{4}\ln 6 - \frac{3}{4n}\ln 2 + \frac{1}{2}\left[1-\frac{3}{4}\beta\right]I_2 - \frac{2}{9}n\mu I_3 + \frac{1}{12}I_2^2 + \frac{2}{27}\left[\frac{9}{10} - n\,\mathrm{sech}^2\left(\frac{2}{3}n\mu\right)\right]I_3^2 + \cdots. \tag{23}$$

For $n=1$, we regain the results for the fully annealed situation, given by Eq. (13). From the coefficient of I_3^2, we immediately see that the biaxial nematic phase is stable for $n<9/10$, which indicates that a relatively weak departure from the fully annealed situation is already enough to produce a stable biaxial structure.

In conclusion, we use a basic Maier-Saupe model of a binary mixture of cylinders and disks to investigate the stability of a biaxial nematic phase. In the quenched case, the biaxial phase is thermodynamically stable. In the fully annealed situation, it becomes unstable, but in a situation of partial annealing, represented by couplings to heat reservoirs at different temperatures, we may recover thermodynamical stability.

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[1] K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).

[2] M. Wortis, Phys. Lett. A **47**, 445 (1974).

[3] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1993).

[4] A. M. Figueiredo-Neto and S. R. A. Salinas, *The Physics of Lyotropic Liquid Crystals: Phase Transitions and Structural Properties* (Oxford University Press, New York, 2005).

[5] G. R. Luckhurst, Nature (London) **430**, 413 (2004).

[6] R. Alben, J. Chem. Phys. **59**, 4299 (1973); Z.-Y. Chen and J. M. Deutch, *ibid.* **80**, 2151 (1984).

[7] L. J. Yu and A. Saupe, Phys. Rev. Lett. **45**, 1000 (1980); Y. Galerne and J. P. Marcerou, *ibid.* **51**, 2109 (1983); A. A. de Melo-Filho, A. Laverde, and F. Y. Fujiwara, Langmuir **19**, 1127 (2003).

[8] E. F. Gramsbergen, L. Longa, and W. H. de Jeu, Phys. Rep. **135**, 195 (1986); D. Allender and L. Longa, Phys. Rev. E **78**, 011704 (2008).

[9] P. Palffy-Muhoray, J. R. de Bruyn, and D. A. Dunmur, Mol. Cryst. Liq. Cryst. **127**, 301 (1985); J. Chem. Phys. **82**, 5294 (1985); S. R. Sharma, P. Palffy-Muhoray, B. Bergersen, and D. A. Dunmur, Phys. Rev. A **32**, 3752 (1985).

[10] E. F. Henriques and V. B. Henriques, J. Chem. Phys. **107**, 8036 (1997); E. F. Henriques, C. B. Passos, V. B. Henriques, and L. Q. Amaral, Liq. Cryst. **35**, 555 (2008).

[11] Y. Rabin, W. E. McMullen, and W. M. Gelbart, Mol. Cryst. Liq. Cryst. **89**, 67 (1982); A. Stroobants and H. N. W. Lekkerkerker, J. Phys. Chem. **88**, 3669 (1984); A. Vanakaras and D. J. Photinos, Mol. Cryst. Liq. Cryst. **299**, 65 (1997).

[12] R. Berardi, L. Muccioli, S. Orlandi, M. Ricci, and C. Zannoni, J. Phys.: Condens. Matter **20**, 463101 (2008).

[13] A. Cuetos, A. Galindo, and G. Jackson, Phys. Rev. Lett. **101**, 237802 (2008).

[14] A. E. Allahverdyan and Th. M. Nieuwenhuizen, Phys. Rev. E **62**, 845 (2000); O. M. Ritter, P. C. T. DAjello, and W. Figueiredo, *ibid.* **69**, 016119 (2004); A. E. Allahverdyan and K. G. Petrosyan, Phys. Rev. Lett. **96**, 065701 (2006); R. W. Penney, T. Coolen, and D. Sherrington, J. Phys. A **26**, 3681 (1993); V. Dotsenko, S. Franz, and M. Mézard, *ibid.* **27**, 2351 (1994).

[15] R. M. Mazo, J. Chem. Phys. **39**, 1224 (1963); R. Kühn, Markov Processes Relat. Fields **10**, 523 (2004).