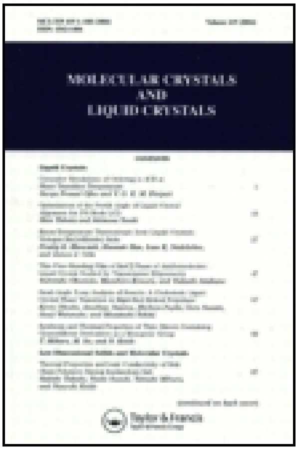

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Molecular-Field Theories of Reentrance in Liquid Crystals

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To cite this article: J. Katriel & G. F. Kventsel (1985): Molecular-Field Theories of Reentrance in Liquid Crystals, Molecular Crystals and Liquid Crystals, 124:1, 179-193

To link to this article: http://dx.doi.org/10.1080/00268948508079475

Mol. Cryst. Liq. Cryst., 1985, Vol. 124, pp. 179–193
0026-8941/85/1244-179/$20.00/0

Molecular-Field Theories of Reentrance in Liquid Crystals†

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(*Received July 19, 1984*)

Within both the Landau and microscopic mean-field theories, reentrance is shown to arise only if either the order parameter of interest is coupled to an additional degree of freedom, or the Hamiltonian is explicitly temperature dependent. Reentrant nematic and smectic phases are exhibited by a fully self-consistent treatment of a simplified McMillan's type model involving coupled nematic and smectic order parameters without any explicitly temperature dependent factors. A reentrant isotropic phase is shown to be exhibited by an explicitly temperature-dependent Hamiltonian as well as by a two-state model.

INTRODUCTION

Reentrance of a high symmetry phase at a temperature lower than a less symmetric one is a distinguished member of a class of "strange" phemonena in the field of phase transitions.[1] Several types of reentrant behaviour, involving singlet-ground-state ferromagnetism,[2] metamagnetism[3] and the competition between superconductivity and antiferromagnetism[4] have been under investigation for the last two decades.

Since the late seventies a large variety of reentrant phenomena have been discovered in liquid crystals. The first observation of a reentrant nematic phase was made by Cladis[5] and the developments until 1980 were reviewed by Prost.[1] References 6 and 7 represent some of the more recent developments. In addition, reentrant

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†Paper presented at the 10th International Liquid Crystal Conference, York, 15th–21st July 1984.

cholesteric[8] and even isotropic[9] phases have been reported. Both mixtures and pure liquid crystalline materials were studied under a variety of external conditions.

The theoretical models proposed to describe reentrant phase transitions in liquid crystals are briefly reviewed in the following section in the context of a discussion of the general requirements for reentrance.

In Section III we discuss a modification of the molecular field theory of McMillan[10]-Luckhurst-Timimi[11] which exhibits reentrance of the nematic and smectic phases in a self-consistent manner without postulating a temperature dependence of the microscopic Hamiltonian. A phenomenologically temperature dependent model and a two-state model of reentrance of the isotropic phase are presented in section IV.

SOME GENERAL PREREQUISITES FOR REENTRANCE

The counter-intuitive nature of reentrance motivated a considerable amount of effort towards the specification of the conditions for its manifestation. The thermodynamic conditions giving rise to a non-monotonic phase boundary in a pressure-temperature diagram were elucidated by Clark.[12] Within the context of the phenomenological Landau theory it is easy to formulate the prerequisites for reentrance, as follows. Writing the free-energy for a system described by means of a single order parameter in the form

$$F = a(T - T_c)S^2/2 + f(S) \tag{1}$$

where a is a constant and $f(S)$ is not explicitly temperature dependent, we obtain

$$\partial F/\partial S = 0 = a(T - T_c)S + \partial f/\partial S. \tag{2}$$

Hence,

$$T = T_c - (\partial f/dS)/(a \cdot S) \tag{3}$$

which means that T is a single valued function of S. Reentrance can therefore be manifested within the Landau theory only if either Eq. (1) contains some further explicit temperature dependence, in addition to the standard $(T - T_c)$ factor, or an additional order parameter is coupled to the one of interest. An explicit temperature dependence can be introduced either phenomenologically or via a coupling to a temperature dependent non-ordering parameter.

Imry,[13] Bruce and Aharony[14] and many subsequent authors,[15,16] have investigated the consequences of the coupling of different order parameters within the context of Landau and Landau-Ginzburg theory. Several Landau theory studies of reentrance in liquid crystals have been reported. Pershan and Prost[17] presented a free energy expression which is temperature dependent through one of its non-ordering parameters, the density.

Cladis[18] has obtained reentrance by introducing a biquadratic coupling between the nematic and the smectic order parameters, with a phenomenologically temperature dependent coefficient. Vaz and Doane[19] pointed out that the addition of a cubic term in the nematic order parameter, as is usually done to account for the fact that the isotropic to nematic transition is of first order, enables the manifestation of reentrance with a temperature independent nematic-smectic coupling constant. A Landau-Ginzburg type model, in which reentrance is induced by the fluctuations of the order parameters, was presented by Coulon and Prost.[20]

Very similar conditions to those enabling reentrance in the Landau theory can be formulated within the microscopic mean-field theory. For a system characterized by an order parameter S, mean-field theory results in the equation[21]

$$S = W_S[-\beta \partial H/\partial S] \qquad (4)$$

where $H(S)$ is the mean-field Hamiltonian and W_S is a function associated with the degeneracy of the order parameter S. It was demonstrated in reference 22 that as a consequence of the monotonically decreasing dependence of the entropy on the order parameter Eq. (4) can be inverted to express the temperature T as a function of the order parameter S,

$$kT = -(\partial H/\partial S)/\arg W_S(S). \qquad (5)$$

This result indicates that in order to obtain reentrance the Hamiltonian has either to be phenomenologically temperature dependent or to contain a coupling of the order parameter of interest to an additional order or non-ordering parameter; otherwise, the temperature is a single valued function of the order-parameter. All these possibilities can be very simply illustrated for spin models.

As an example of an explicitly temperature dependent Hamiltonian consider the spin-½ Heisenberg model

$$H = -J(T) \cdot s^2/2 \tag{6}$$

with a temperature dependent exchange integral. The magnetization corresponding to this Hamiltonian satisfies $2s = \tanh[J(T)s/T]$ and is presented in Figure 1 for $J = 1$ and for $J = -0.125 + 2.75T - T^2$, the latter exhibiting reentrance. Coupling to non-ordering parameters was considered in models of heat-magnetization[2] and magnetostriction[23] and coupling to an additional order parameter was investigated in a model of metamagnetism.[22] Both heat magnetization and metamagnetism are manifestations of reentrance.

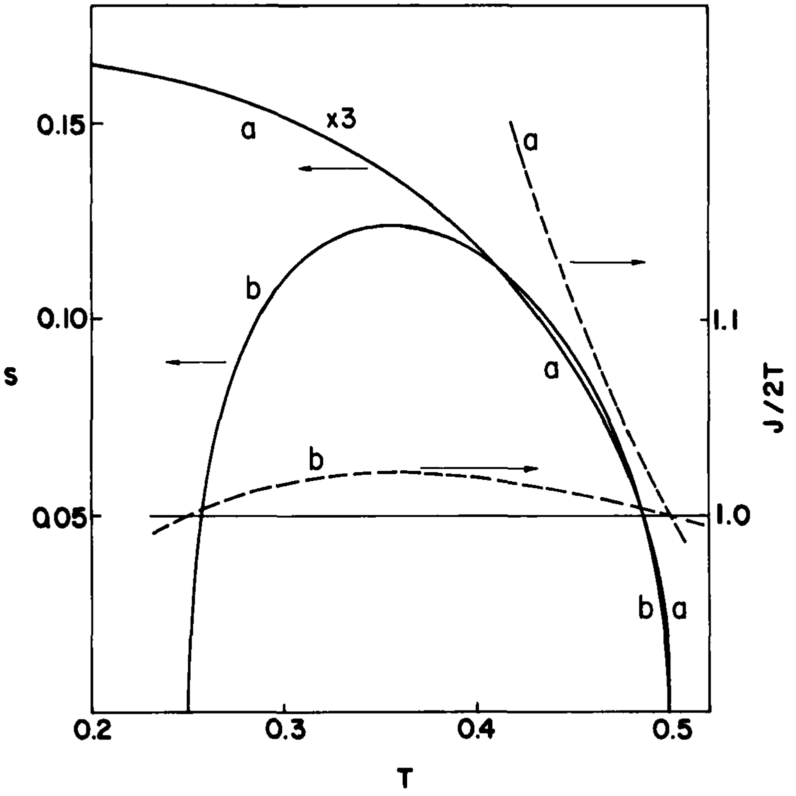

FIGURE 1 The mean-field magnetization curve for the Heisenberg model: (a) $J = 1$; (b) $J = -0.125 + 2.75T - T^2$.

Several microscopic mean-field treatments of reentrance in liquid-crystals have been recently proposed.

Longa and de Jeu[24] have obtained reentrance in a model of a nematic-smectic liquid cystal consisting of a mixture of interacting monomers and dimers with a non-self consistently determined dimer to monomer concentration ratio. The reentrance of the nematic phase is due to steric repulsive forces among the dimers at high concentration. A similar reentrance mechanism was considered by Hida[25] in the context of a mean-field treatment of a two sublattice model.

Rajan and Woo[26] considered a two state (helix-coil) model exhibiting a reentrant isotropic phase. Reentrance in this model is due to a self-consistent coupling of the nematic order parameter to a non-ordering parameter, i.e., the helix-coil concentration ratio. This model, a special case of the two states mean field approximation,[27] is analogous to a two-state model of singlet-ground state ferromagnetism.[2]

A treatment of reentrance which goes beyond mean-field theory was presented by Berker and Walker.[28]

Let us finally review the molecular theory developed by Luckhurst and Timimi,[11] which is closest to our present aims. This theory is an extension of McMillan's treatment[10] of the smectic phase. It involves three coupled equations in the order parameters $\eta = \overline{P_2(\cos\theta)}$, $\sigma = \overline{\cos z}$ and $\tau = \overline{\cos z \cdot P_2(\cos\theta)}$, with a mean-field Hamiltonian;

$$H = -u_0\{\eta^2 + \alpha \cdot \sigma^2 + \delta \cdot \alpha \cdot \tau^2\}. \tag{7}$$

In order to obtain reentrance they had to assume that the parameter α is linearly temperature dependent over the region of interest. A detailed comparison of this approach with the phenomenological Landau-type theory was presented by Dong.[6]

TWO COUPLED ORDER-PARAMETERS: REENTRANT NEMATIC AND SMECTIC PHASES

A simplification of McMillan's model[10] of nematic-smectic liquid crystals was recently proposed.[29] This simplification involves the decoupling of $\overline{P_2(\cos\theta)\cdot\cos z}$ into $\overline{P_2}\cdot\overline{\cos z}$, resulting in the Hamiltonian

$$H = -\gamma\eta^2/2 - B_0\sigma^2/2 - C\sigma^2\eta/2 - D\eta^2\sigma^2/2 \tag{8}$$

and the mean-field equations

$$\eta = W_1[\beta\cdot\partial H/\partial\eta];\, W_1(x)$$

$$= 1/(2x) - 1/2 - \sqrt{3/(2\pi x)}\cdot\exp(-3x/2)/\mathrm{erf}(\sqrt{3x/2}) \quad (9a)$$

$$\sigma = W_2[\beta\cdot\partial H/\partial\sigma];\, W_2(x) = -I_1(x)/I_0(x) \quad (9b)$$

where $I_n(x)$ ($n = 0, 1$) are the modified Bessel functions. We shall now show that this Hamiltonian can exhibit reentrance, for appropriate choices of parameters.

Writing the Hamiltonian in the form:

$$H = -\gamma\eta^2/2 - B(\eta)\sigma^2/2 \quad (8')$$

where

$$B(\eta) = B_0 + C\eta + D\eta^2$$

we note that the condition for a smectic critical temperature is

$$kT = B(\eta_0)/2; \qquad \sigma \to 0. \quad (10)$$

η_0 is the order parameter obtained for the pure nematic phase, i.e., with the Hamiltonian $H = -\gamma\eta^2/2$, resulting from (8) when $\sigma \to 0$.

In order to obtain the sequence of phases: isotropic (I) → nematic (N) → smectic (S) → reentrant nematic (rN) → reentrant smectic (rS), Eq. (10) should possess three different solutions. As a first step towards obtaining the range of parameters for which the Hamiltonian (8) exhibits the above reentrant sequence we choose as three possible solutions of Eq. (10) the temperatures T_1, T_2, T_3. This choice of temperatures determines the parameters B_0, C, D through the set of linear equations

$$B_0 + C\cdot\eta_i + D\cdot\eta_i^2 = 2T_i; \qquad i = 1,2,3 \quad (11)$$

where

$$\eta_i = \eta_0(T_i).$$

In order to ascertain that the set of parameters thus obtained results in the desired behaviour of the order parameters, we should solve the set of coupled Equations (9). Clearly, only a subspace of the space of parametes γ, B_0, C, D will correspond to Hamiltonians exhibiting these critical temperatures. Moreover, only a more limited subspace will exhibit a smectic order parameter (σ) depending on the temperature in a reentrant manner.

For other choices of parameters topologically distinct shapes of $\sigma(T)$ can arise, which may or may not be of physical interest.

As a concrete example, which exhibits the reentrant sequence of phases, we choose $\gamma = 1$, $T_1 = 0.10$, $T_2 = 0.21$ and $T_3 = 0.219$, obtaining

$$B_0 = 0.2481 \qquad C = 0.9196 \qquad D = -1.1058 \tag{12}$$

Solving Eqs. (9) for this set of parameters we obtain the results presented in Figure 2. The sequence of phases is indicated at the top of the figure, being, on decreasing the temperature

$$\mathrm{I} \xrightarrow{0.2202} \mathrm{N} \xrightarrow{0.219} \mathrm{S} \xrightarrow{0.21} \mathrm{rN} \xrightarrow{0.10} \mathrm{rS}.$$

An example, formally exhibiting three smectic critical temperatures with a different topology, is presented in Figure 3. Here, the physically relevant, minimum-free-energy curve (a) exhibits a second order transition followed by a monotonic behaviour, while the non-monotonic "reentrant" curve (b) corresponds to an unstable, maximum-free-energy, state.

We shall now investigate some further aspects of the reentrant behavior, corresponding to the choice of parameters (12). The values of the smectic order parameter obtained by solving eq. (9b) in a non-self-consistent manner, i.e., assuming the pure nematic value of the nematic order parameter (η_0), are denoted by σ_0 in Figure 2. The values of σ and σ_0 are rather close to one another and coincide at the critical temperatures. The corrsponding values of η and η_0 are even closer and can only be distinguished in the η/η_0 plot. Note that in the smectic regions $\eta < \eta_0$ and $\sigma > \sigma_0$, reflecting the repulsive nature of the nematic-smectic coupling.

The non-self-consistent procedure resulting in σ_0 is equivalent to a decoupling between the nematic and smectic order parameters such that σ_0 is determined from the effectively temperature dependent smectic Hamiltonian $H_\sigma = -B[\eta_0(T)]\sigma^2/2$.

This procedure may be viewed as a rather reasonable way of writing a phenomenologically temperature-dependent one-order-parameter

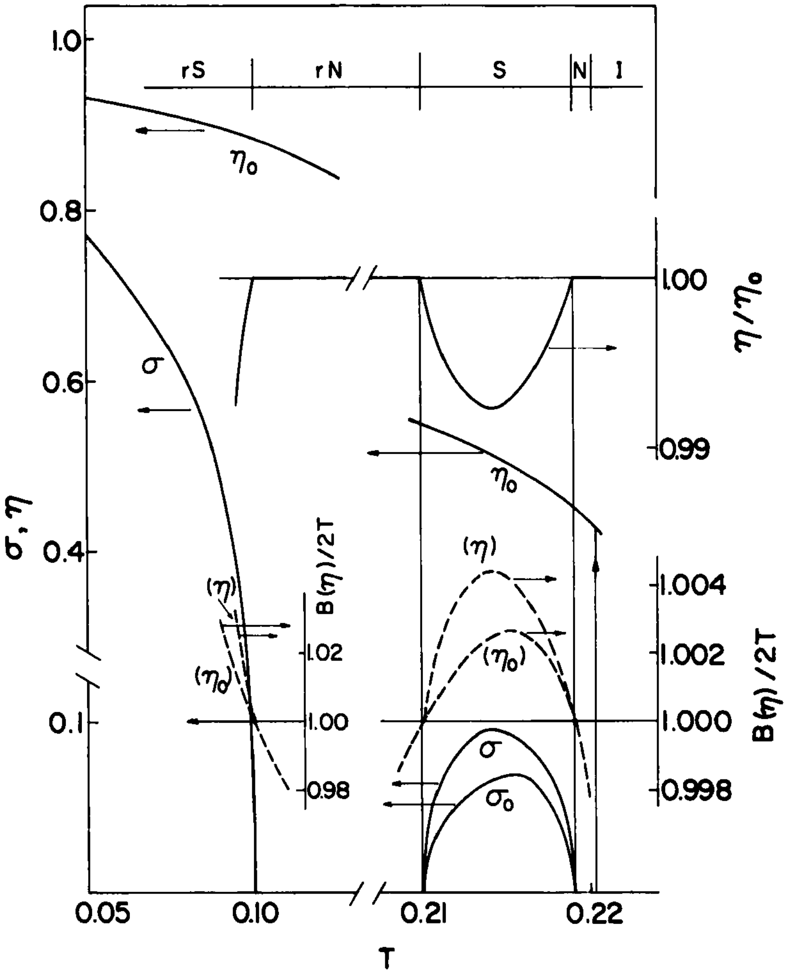

FIGURE 2 The nematic (η) and smectic (σ) order parameters for the coupled equations. η_0 is the pure nematic order parameter and σ_0 is the smectic order parameter calculated with $B(\eta_0)$ rather than $B(\eta)$.

Hamiltonian, exhibiting reentrance. As a further examination of the quality of this decoupling procedure, Figure 2 contains plots of $B(\eta)/2T$ and $B(\eta_0)/2T$, both of which are equal to 1 at each one of the three critical points.

The approach demonstrated above can be viewed as a convenient simple-minded first step in a procedure for the inversion of experimental data into a Hamiltonain.

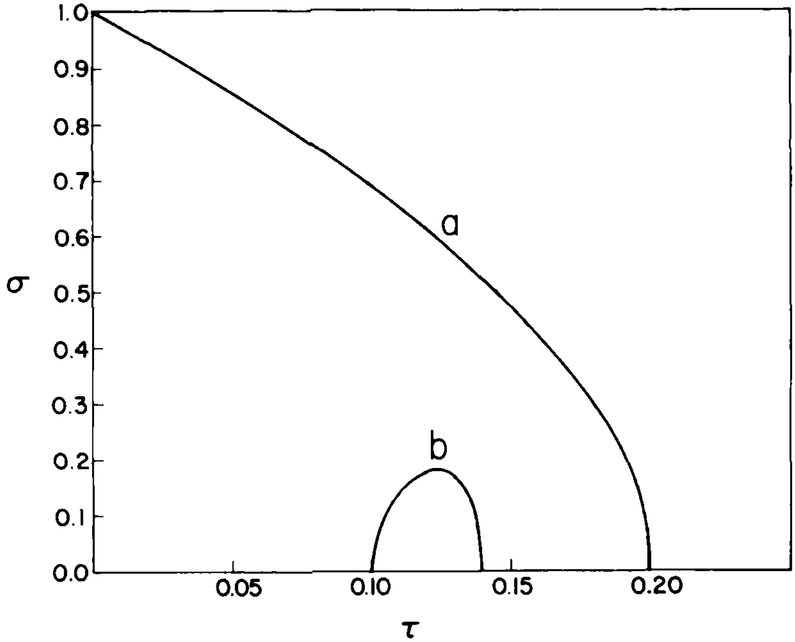

FIGURE 3 A physically non-reentrant smectic phase with three "critical temperatures." Curve *a* corresponds to the stable state, whereas curve *b* corresponds to an unstable state.

In view of the counter-intuitive nature of the formation of a less ordered phase from a more ordered one upon cooling, it is instructive to evaluate the associated entropy changes.

The entropy can be written in the form

$$S_{\text{tot}} = S_\eta + S_\sigma \tag{13}$$

where

$$S_\eta = \eta(\partial E/\partial\eta)/T + k\ln Q_\eta$$

and

$$S_\sigma = \sigma(\partial E/\partial\sigma)/T + k\ln Q_\sigma.$$

Q_η and Q_σ are the nematic and smectic partition functions, normal-

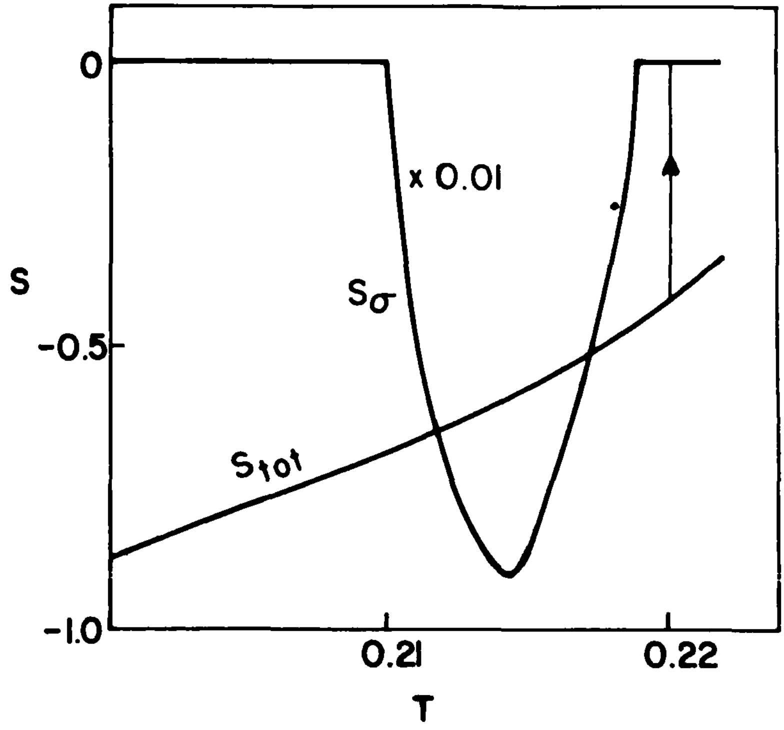

FIGURE 4 The total entropy and the smectic contribution (multiplied by 100).

ized to unity for $\eta = 0$ and $\sigma = 0$, respectively,

$$Q_\eta = \sqrt{(\pi 6\alpha_\eta)}\exp(\alpha_\eta/2)\,\mathrm{erf}(\sqrt{3\alpha_\eta/2}); \qquad \alpha_\eta = \beta(\partial H/\partial\eta) \tag{14}$$

$$Q_\sigma = I_0[\beta(\partial H/\partial\sigma)] \tag{15}$$

Figure 4 exhibits the total entropy as well as the smectic contribution. Although the latter is non monotonic, the total is a monotonically increasing function of the temperature and virtually unaffected by the creation and eventual destruction of the smectic phase.

THE REENTRANT ISOTROPIC PHASE

Reentrance of the isotropic phase seems even more peculiar than that of the nematic phase, because there is no obvious order parameter which can be assumed to be coupled to the nematic order parameter. A mean-field description of this behaviour can be achieved at two levels, one of which consists of a phenomenologically temperature-dependent nematic Hamiltonian, while at the other, this temperature dependence arises out of an explicit treatment of a coupling to an appropriate non-ordering parameter.

A phenomenological temperature dependence is easily incorporated in the Maier-Saupe model. This model is described by the Hamiltonian $H = -\gamma\eta^2/2$, resulting in the equation

$$\eta = W_1(\beta\gamma\eta) \qquad (16)$$

for the order parameter. W_1 is presented in Eq. (9a). An arbitrary form of $\eta(T)$ can be phenomenologically accounted for by assuming an appropriate temperature dependence of the parameter γ. This follows from the fact that Eq. (16) can be inverted ("solved for γ") in the form

$$\gamma = kTf(\eta)/\eta. \qquad (17)$$

In order to exhibit reentrance of the isotropic phase, γ has to satisfy the "critical point" ($\eta > 0$) condition $\gamma(T) = 5kT$ at two different temperatures. Figure 5 presents the behaviour of the nematic order parameter for the standard Maier-Saupe model, $\gamma_a = 1$, as well as for two models exhibiting reentrance, $\gamma_b = -2 + 35T - 100T^2$ and $\gamma_c = \mu(\mu-1)/[\exp(\alpha/T) + \mu(\mu-2)]$ where $\mu = \exp(5\alpha)$ and $\alpha = 0.3$. Whereas γ_b can be crudely interpreted as being due to some coupling to vibrational modes, γ_c has a structure suggestive of a two-state model. Both those possibilities were investigated for magnetic systems.(2,23) An analysis of a phenomenological $\gamma(T)$ determined by use of Eq. (17) from the experimental $\eta(T)$ may indicate features which are more reminiscent of either γ_b or γ_c, which may turn out to be a useful hint of the kind of reentrance mechanism being effective in the particular system studied.

Coupling of the nematic order parameter to vibration modes has so far not been investigated as a mechanism of reentrance. A two-state model, involving the helix-coil transition, was shown by Rajan and Woo(26) to exhibit a reentrant isotropic phase. They assumed a Maier-Saupe type nematic ordering in the upper state, with an interaction strength γ which is proportional to the upper state population. The linear dependence of γ on the upper state population is due to its proportionality to the density, as assumed by Maier and Saupe.(30) Cotter(31) has pointed out that this dependence is not ther-

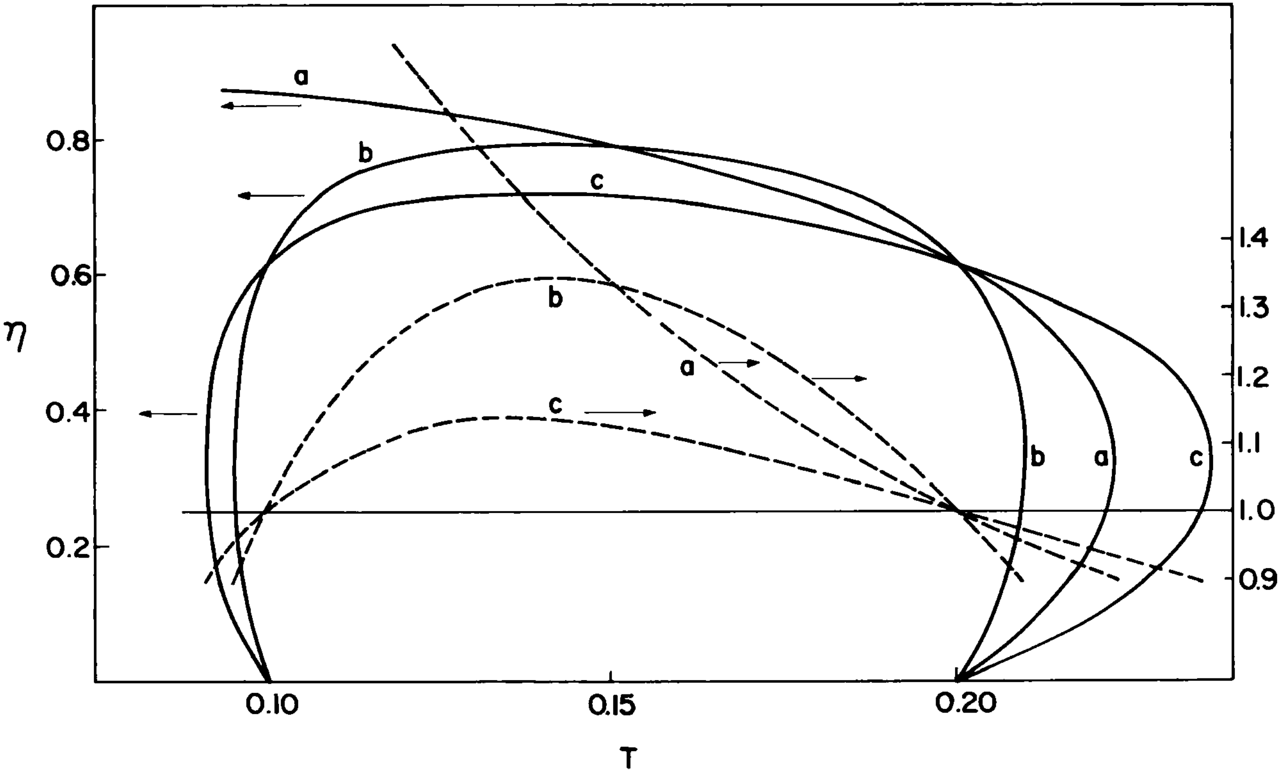

FIGURE 5 The nematic order parameter for a Maier-Saupe type Hamiltonian: (a) $\gamma = 1$; (b) $\gamma = -2 + 35T - 100T^2$; (c) $\gamma = 15.6038/[11.1222 + \exp(0.3/T)]$.

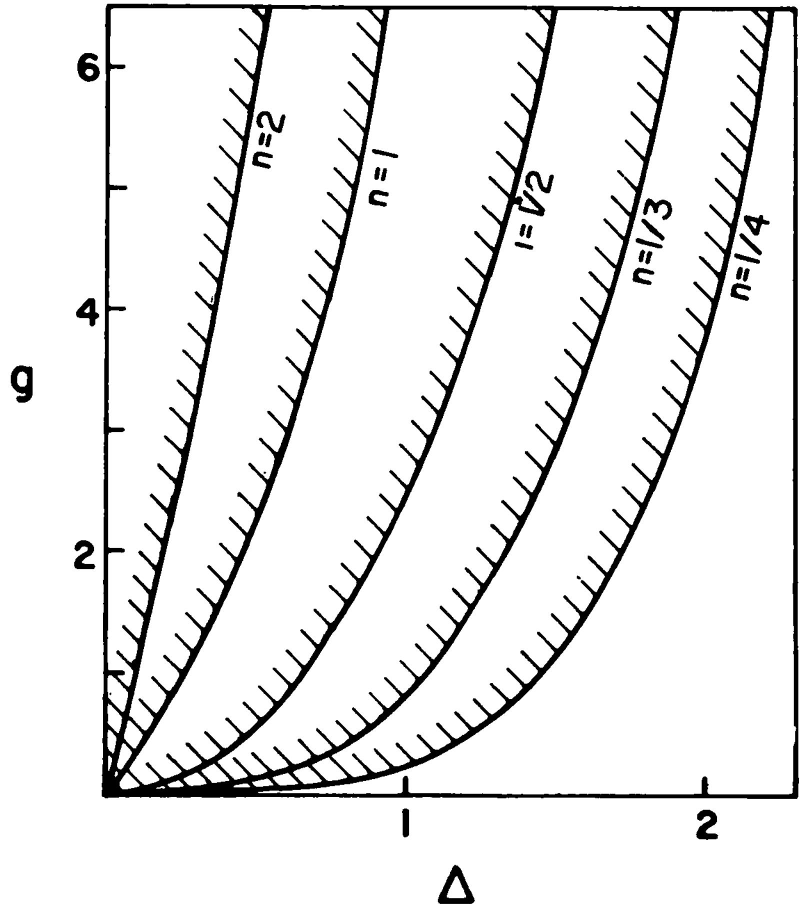

FIGURE 6 Regions of reentrance in parameter space of the two-state model. For each value of *n* the region of reentrance is above the corresponding curve. For the definition of Δ, *g* and *n* see the text.

modynamically consistent, so that the actual dependence on the upper state population need not be linear. Furthermore, the results obtained for an analogous magnetic two-state model(2) indicate that the reentrant behaviour is sensitive to the detailed dependence of the Hamiltonian on the upper state population.

To briefly examine this point, we consider a more general two-state Hamiltonian $H(\eta,x)$, where x is the upper state population. Proceeding in the standard way(23,26) we obtain the coupled equations

$$\eta = W_1\,[-\beta\partial H/\partial\eta] \tag{18}$$

$$x/(1-x) = (g_2/g_1)Z\exp(-\beta\Delta_\epsilon)\cdot\exp\{\beta[\eta(\partial H/\partial\eta) - \partial/\partial x(xH)]\} \tag{19}$$

where

$$Z = \int \exp[-\beta(\partial H/\partial\eta)P_2(\cos\theta)]d\Omega\ 4\pi \tag{20}$$

For the Hamiltonian chosen by Rajan and Woo,(26) $H(\eta,x) = -x_{\gamma\eta}^2/2$ the last exponent in Eq. (19) becomes equal to 1, and Eqs. (18–20) reduce to their set of coupled self-consistent equations.

Assuming that the Hamiltonian is homogeneous of order n in x we obtain for the "critical temperatures"

$$1 + \exp(y\Delta)/g = y^{\delta} \tag{21}$$

where
$y = T_c(0)/T_c$, $\Delta = \Delta\epsilon/kT_c(0)$, $\delta = 1/n$ and $g = g_2/g_1$. $T_c(0)$ is the Maier-Saupe "critical temperature," $\Delta\epsilon$ is the two-state energy difference and g_1,g_2 are the degeneracies of the lower and upper states, respectively.

In Figure 6 a study of the space of the Hamiltonian parameters is summarized, indicating in a quantitative manner, that the degeneracy of the higher state should be sufficiently large or its energy sufficiently low to enable reentrance. Furthermore, reentrance is easier the lower the values of n.

Acknowledgment

We are indebted to Professor A. Loewenstein for having introduced us to the fascinating problems of reentrance in liquid crystals.

This research was supported by the Technion V.P.R.-Fund.

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