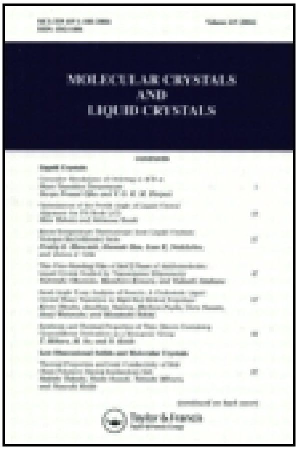

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Generalized Mean-Field Equations with Application to Nematic-Isotropic Transitions

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Generalized Mean-Field Equations with Application to Nematic-Isotropic Transitions

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The mean-field equations are derived for a system whose energy depends arbitrarily on any number of continuous order-parameters. The results are applied to a non-linear one-order-parameter model of nematic liquid crystals, exhibiting an improvement over the Maier-Saupe model similar to that previously obtained using a two-order-parameter model.

I INTRODUCTION

The crucial step towards the formulation of a successful mean-field theory for liquid crystals was the realization that the main order parameter is associated with the second Legendre polynomial $P_2(\cos\theta)$.[1] A very reasonable, though not compelling argument results in the expression.

$$E(\eta, \theta) = -\gamma \cdot \eta \, P_2(\cos\theta)$$

for the energy of a typical molecule in the mean-field of its neighbors, where γ is a positive parameter independent of the temperature and $\eta = \langle P_2(\cos\theta)\rangle$ is the order-parameter. This expression is the basis of the Maier-Saupe theory.[1]

The main result of this treatment is a universal behavior of the order parameter as a function of T/T_{NI}, where T_{NI} is a first-order transition temperature. The current version of mean-field theory for liquid crystals consisting of cylindrically symmetric molecules involves the introduction of an additional order-parameter, $\langle P_4(\cos\theta)\rangle$, which improves the agreement with the experimental results.[2] Similar improvements in the agreement between theory and experiment are also obtained by allowing for deviations from molecular cylindrical symmetry.[3]

In the present note we derive the mean-field equations for a very general situation involving an arbitrary dependence of the energy on any number of order parameters. The distribution function obtained differs from the commonly assumed Boltzmann type exponential of the one particle energy. A one-order-parameter modification of the Maier-Saupe model is discussed as an application of the general formalism. It exhibits the same qualitative improvement over the Maier-Saupe results previously obtained using the two-parameter mean-field theory. Actually, the energy expression proposed had already been examined by Humphries, James and Luckhurst,[2] but they obtained disappointing results because of the difference in the form of the distribution function used.

II GENERAL MEAN-FIELD EQUATIONS

In a nematic liquid crystal, symmetry restricts the order parameters to be associated with even Legendre polynomials. In the present section we relax this restriction to consider the most general form

$$E(\theta) = \sum_{l=1}^{L} v_l(\eta_1, \eta_2 \ldots \eta_L)\, P_l(\cos\theta) \tag{1}$$

where

$$\eta_l \equiv \langle P_l(\cos\theta)\rangle,\ l = 1,2, \ldots L.$$

The variational procedure with respect to $f(\theta)$ in the free energy expression

$$A = \int E(\theta) f(\theta) \sin\theta d\theta + kT \int f(\theta) \log[f(\theta)]\cdot \sin\theta d\theta \tag{2}$$

leads to

$$\delta A = \int \delta f \{E(\theta) + kT \log[e\cdot f(\theta)] - \lambda\} \sin\theta d\theta$$

$$+ \int f(\theta)\cdot \sin\theta\cdot d\theta \sum_{l,l'} P_l(\cos\theta)\cdot \frac{\partial v_l}{\partial \eta_{l'}} \int \delta f\cdot P_{l'},\ (\cos\theta') \sin\theta' d\theta'$$

$$= \int \delta f \left\{E(\theta) + kT \log[e\cdot f(\theta)] - \lambda + \sum_{l,l'} P_{l'}(\cos\theta)\eta_l \frac{\partial v_l}{\partial \eta_{l'}}\right\} \sin\theta d\theta = 0$$

and

$$f(\theta) = N\cdot e^{-(1/kT)[E(\theta) + \sum_{ll'} \eta_l (\partial v_l/\partial \eta_{l'}) P_{l'}(\cos\theta)]}$$

$$= N\cdot\exp\left\{-\frac{1}{kT}\sum_l\left[v_l+\sum_{l'}\eta_{l'}\frac{\partial v_{l'}}{\partial\eta_l}\right]P_l(\cos\theta)\right\}$$

$$= N\cdot\exp\left\{-\frac{1}{kT}\sum_l\frac{\partial}{\partial\eta_l}\left(\sum_{l'}\eta_{l'}v_{l'}\right)P_l(\cos\theta)\right\}. \qquad (3)$$

The mean-field equations for the order parameters $\eta_i\equiv\int f(\theta)P_i(\cos\theta)\cdot\sin\theta d\theta$ are finally obtained in the form

$$\eta_i=-\frac{\partial}{\partial\alpha_i}\log\left[\int e^{-\sum_l\alpha_lP_l(\cos\theta)}\sin\theta d\theta\right]\equiv W_i(\{\alpha_l\})\quad i=1,2,\ldots L \qquad (4)$$

where

$$\alpha_l=\frac{1}{kT}\frac{\partial}{\partial\eta_l}\left(\sum_{l'}\eta_{l'}v_{l'}\right).$$

Noting that

$$\bar{E}=\int E(\theta)f(\theta)\sin\theta d\theta=\sum_l v_l\cdot\eta_l$$

we can write

$$\alpha_l=\frac{1}{kT}\cdot\frac{\partial\bar{E}}{\partial\eta_l}.$$

Equation (4) is a set of L-coupled equations for the L order-parameters η_1, $\eta_2\ldots\eta_L$. If the interaction depends on a single order parameter η_l, i.e., $E(\theta)=v_l(\eta_l)$. $P_l(\cos\theta)$ than

$$\eta_l=-\frac{\partial}{\partial\alpha_l}\log\int e^{-\alpha_lP_l(\cos\theta)}\sin\theta d\theta\bigg|_{\alpha_l=(1/kT)(\partial\bar{E}/\partial\eta_l)} \qquad (5)$$

For $l=1$,

$$\eta_1=-\mathrm{cth}(\alpha_1)+\frac{1}{\alpha_1}\equiv B_\infty\left[-\frac{1}{kT}\frac{\partial\bar{E}}{\partial\eta_1}\right],$$

corresponding to the $\sigma=\infty$ limit of the magnetization equation for a general infinite-range spin Hamiltonian.[4] For $l=2$

$$\eta_2=W_2(\alpha)\Big|_{\alpha=(1/kT)(\partial\bar{E}/\partial\eta_2)}$$

where

$$W_2(\alpha) = \frac{1}{2\alpha} - \frac{1}{2} - \frac{\sqrt{\dfrac{3}{2\pi\alpha}} \cdot e^{-(3\alpha/2)}}{erf\sqrt{\dfrac{3\alpha}{2}}} \tag{6}$$

which, for $\nu_2(\eta_2) = \gamma \cdot \eta_2/2$, reduces to the Maier-Saupe equation.[5]

An interesting aspect of the structure of the general mean-field equations, Eq. (4), is the fact that they involve functions, W_l, whose forms depend on the degeneracy (number of states) dictated by the symmetries of the relevant order-parameters, but not on the specific form of the interaction, which enters through the arguments α_l. A similar separation has been noted in the form of the general mean-field equations for spin-Hamiltonians.[4]

III APPLICATION

The expression

$$E(\eta_2, \eta_4 \ldots; \theta) = \sum_{l=1} \gamma_{2l} \cdot \eta_{2l} \cdot P_{2l}(\cos\theta) \tag{7}$$

which has been used in attempts to generalize and improve the Maier-Saupe theory, follows from a treatment of the bimolecular interaction potential involving several approximations.[2,6] Humphries, James, and Luckhurst[2] have pointed out that avoiding certain aspects of these approximations, the expression for the effective one-particle potential can involve a non-linear dependence on the order parameters. A rather extensive comparative discussion of various forms of this dependence has been presented by Horn and Faber.[7] The simplest such dependence, beyond the linear Maier-Saupe form, is:

$$E(\eta_2; \theta) = \nu_2(\eta) \cdot P_2(\cos\theta) \tag{8}$$

where

$$\nu_2 = -\frac{\gamma}{2} \cdot \eta + \frac{\delta}{3}\eta^2 \text{ and } \eta \equiv \eta_2.$$

This dependence corresponds to $E = -(\gamma/2)\eta^2 + (\delta/3)\eta^3$ or $\alpha = (1/kT) \cdot (-\gamma \cdot \eta + \delta\eta^2)$ in Eq. (6). To determine the order of the transition we expand Eq. (6) near $\eta_2 = 0$. The temperature at which $\eta_2 = 0$ is $k \cdot T_c = (\gamma/5)$. Near this temperature we obtain

$$\eta_2 \simeq \left(1 - \frac{T_c}{T}\right) \Big/ \left(\frac{5}{7} - \frac{\delta}{\gamma}\right).$$

To obtain a first order transition the slope of η_2 *vs.* T should be positive near T_c, i.e., $\delta < \frac{5}{7}\gamma$. For $\delta > \frac{5}{7}\gamma$ we obtain either a second order transition with a critical exponent $\beta = 1$ into a nematic phase, or, if negative values of the order parameter make sense physically, a first order transition into a different type of ordered phase. Only this last case is described by the Landau theory, which is the basis of the common statement that only first order transitions are possible in liquid crystals.[5]

In order that the ordered phase be the more stable one at low temperatures we have to require that $\alpha(\eta_2 = 1) < 0$, i.e., $\delta < \gamma$. This condition on δ is actually too severe because the nematic phase ceases to exist at temperatures higher than $T = 0°\mathrm{K}$, i.e., with an order-parameter less than unity. Hence the range of values for which a second order transition from an isotropic phase at $T > T_c$ to a nematic phase at $T < T_c$ is at least $\frac{5}{7}\gamma < \delta < \gamma$.

To investigate the behavior of the order parameter for the whole range of temperatures, we solve the mean field equation, Eq. (6), numerically. To satisfy the two equations

$$\eta = W_2(\alpha)$$

and

$$\alpha = \frac{1}{\tau}(-\eta + \Delta\cdot\eta^2) \tag{9}$$

where $\Delta = \delta/\gamma$ and $\tau = kT/\gamma$ we plot $-(\eta/\alpha)$ *vs.* α from both, i.e., $-(W_2(\alpha)/\alpha)$ and $(\sqrt{1 + 4\tau\cdot\Delta\cdot\alpha} - 1)/(2\Delta\cdot\alpha)$ *vs.* α (Figure 1). Note that the first function is universal and the second one, containing the dependence on the parameters, is of very simple form. In particular, when $\Delta = 0$ (Maier-Saupe case) the second curve is simply the horizontal line $-(\eta/\alpha) = \tau$.

In Figure 2 we present the solutions of the self consistency equations, Eq. (9), for several values of Δ. To obtain the first order transition temperature we evaluate the free energy, Eq. (2), which for values of η satisfying Eq. (9) takes the form

$$\frac{A(\eta) - A(0)}{\gamma} = \left(\frac{1}{2} + \Delta\right)\eta^2 - \eta - \frac{2\Delta}{3}\eta^3 + \tau\cdot\log\left[1 + (1 + 2\eta)\frac{\eta - \Delta\cdot\eta^2}{\tau}\right]. \tag{10}$$

The transition temperature corresponds to $A(\eta) - A(0) = 0$. For $\Delta = 0$ we obtain the Maier-Saupe values of the transition temperature and the order parameter at that temperature. Some results are presented in Table I. Comparison with Figure 3 suggests that the experimental results for 4,4′-dimethoxy- and 4,4′-diethoxy-azoxybenzene[2] can be roughly accounted for in terms of this

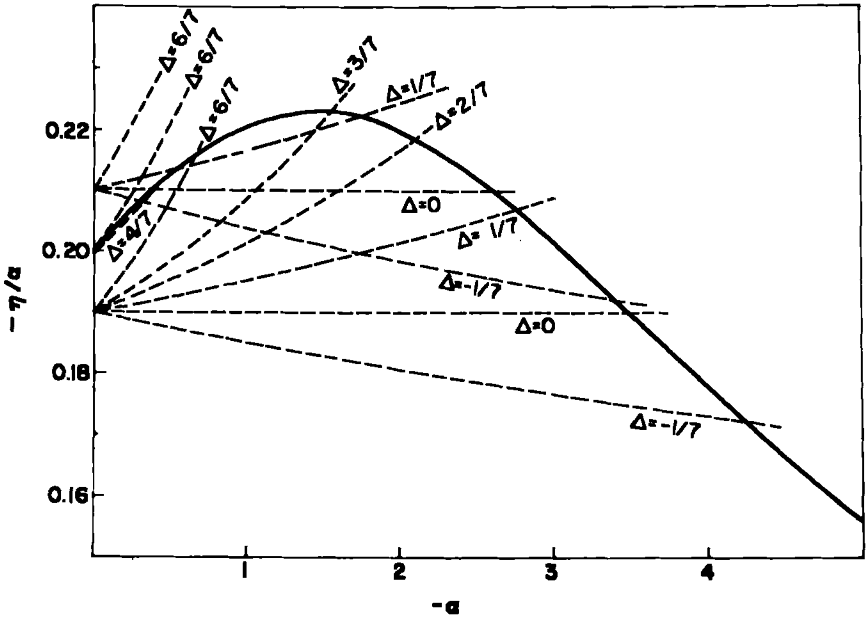

FIGURE 1 Graphical solution of the mean-field equation. The continuous line denotes the universal degeneracy function $-W_1(\alpha)/\alpha$. The broken lines correspond to $(\sqrt{1+4\tau\cdot\Delta\cdot\alpha}-1)/(2\Delta\alpha)$ for the values of Δ marked and the values of τ corresponding to the intersection with the ordinate.

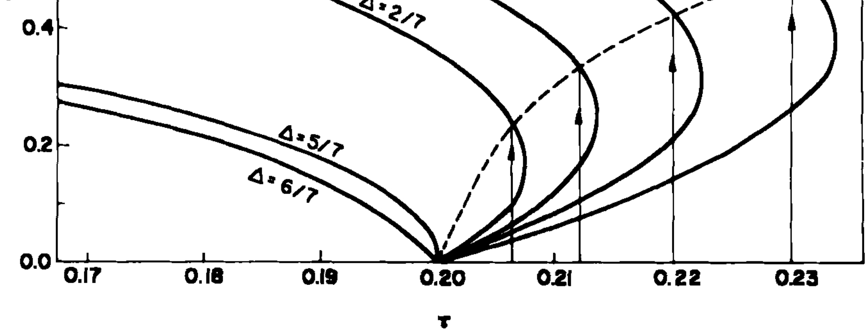

FIGURE 2 Solutions of the mean-field equations. The vertical arrows denote the first order transitions.

TABLE I

Parameters of the first-order transition (temperature, order-parameter, entropy change).

Δ	kT_{NI}/γ	$\langle P_2 \rangle$	$\Delta S/k$
−1/7	0.2304	0.500	−0.569
0	0.2202	0.425	−0.410
1/7	0.2122	0.335	−0.256
2/7	0.2065	0.235	−0.128

model with $\Delta \sim 0.07$ and $\Delta \sim -0.07$, respectively. However, the difference in ordering observed for these two nematogens stems, almost certainly, from the different chain lengths as suggested by Marcelja.[8]

Our results differ significantly from those presented for the same form of one particle potential by Humphries *et al.*[2] In particular, at temperatures close to the transition, the order parameter η they obtain is independent of Δ. On the basis of their results they rejected this model in favor of the one involving the two order-parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$. The origin of this discrepancy in the results was discussed by Horn and Faber[7] who stressed that the form of the angular distribution function $f(\theta)$ obtained from the variational treatment within the mean-field context differs from the straight-forward Boltzmann-type expression. It should, of course, be admitted that as far as the number of adjustable parameters, the present model is equivalent to the two-order parameter model of Humphries *et al.*,[2] both introducing one more parameter than in the Maier-Saupe theory. This could indicate that the way in which the

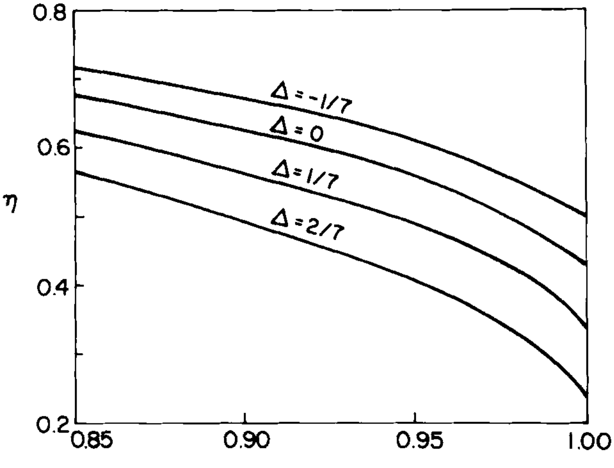

FIGURE 3 The order parameter $\eta = \langle P_2 \rangle$ *vs.* T/T_{NI}.

additional parameter enters the theory is unimportant, or that a choice between these two models should ultimately be made on the basis of an understanding of their microscopic significance, which had been discussed by Humphries *et al.*[2]

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