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

Generalized Rank Two Tensor Statistical Model of the Smectic A state

Richard G. Priest [a]
[a] Naval Research Laboratory, Washington, D.C., 20375

Version of record first published: 21 Mar 2007.

To cite this article: Richard G. Priest (1976): Generalized Rank Two Tensor Statistical Model of the Smectic A state, Molecular Crystals and Liquid Crystals, 37:1, 101-108

To link to this article: http://dx.doi.org/10.1080/15421407608084349

Mol. Cryst. Liq. Cryst., 1976, Vol. 37, pp. 101–108

Printed in Holland

Generalized Rank Two Tensor Statistical Model of the Smectic A State

RICHARD G. PRIEST

Naval Research Laboratory, Washington, D.C. 20375

(*Received August 23, 1976*)

A molecular statistical model for the smectic A phase based on rank two symmetry is developed. The model inter-molecular interaction does not depend critically on the magnitude of the vector joining the molecular centers of mass, as is the case in the McMillan[1]–Kobayashi[2] model, but rather on its orientation relative to the preferred orientation of the molecules. The model predicts a phase diagram similar to that calculated by McMillan.[1] It is an improvement of the McMillan–Kobayashi model because it has two additional features. It is intrinsically stable against three dimensional freezing and predicts a force which keeps the director oriented normal to the smectic layers.

I INTRODUCTION

In a previous work[3] it was found that a successful model for the smectic A–smectic C phase transition can be constructed by considering a certain class of model intermolecular interactions. For the case of uniaxial molecules, one member of this class is the familiar Maier–Saupe[4] intermolecular potential which can be written as $-AP_2(\theta_{12})$. Here A is a coupling constant and θ_{12} is the angle between the long axes of the two interacting molecules labeled 1 and 2. The function P_n is the nth order Legendre polynominal. This model interaction is also the basis of the McMillan[1]–Kobayashi[2] theory of the smectic A state. Since the other members of the class of interactions considered in Ref. 3 play an important role in the smectic A–smectic C phase transition, it is of some interest to explore the role they may have in the smectic A–nematic and smectic A–isotropic phase transitions.

In this paper we show that consideration of these other terms leads to a molecular statistical theory similar in mathematical structure to that of Ref. 1. However, certain conceptual problems associated with this latter

theory are avoided in the present development. In particular, it is found that the model affords a natural explanation of the force which keeps the director, the preferred direction of orientation of the long molecular axes, oriented normal to the layers. Further, if we view the transition to the smectic state as a one dimensional freezing, the model is stable against two and three dimensional freezing. In this sense it is an improvement of the McMillan–Kobayashi model.

II DEVELOPMENT OF THE MODEL

For the case of uniaxial molecules, the interactions discussed in Ref. 3 can be visualized fairly easily. With the aid of the spherical addition theorem, the Maier–Saupe potential can be seen to be a scalar formed by the combination of a second order spherical harmonic function of the orientation of molecule 1 with a second order spherical harmonic function of the orientation of molecule 2. In addition to this scalar, bilinear combinations of two spherical harmonics may be formed which are tensors of rank one, two, three and four. We may form scalar model interactions by contracting the tensor of rank n ($n = 1, 2, 3$ or 4) with a spherical harmonic function (of rank n) of $\hat{r}_{12}$, the orientation of the vector joining the centers of mass of molecules 1 and 2. A separate argument shows that the terms resulting from the cases $n = 1$ and $n = 3$ cannot arise for molecules which transform into themselves under the coordinate inversion operation. Therefore we do not consider these two terms. This leaves three model interactions which we denote as [2, 2, 0], [2, 2, 2] and [2, 2, 4]. However we must, for completeness, consider scalars which are formed from a second rank spherical harmonic function of the orientation of one of the molecules and a second rank spherical harmonic function of $\hat{r}_{12}$. This model interaction can be written as $-C[P_2(\theta_{13}) + P_2(\theta_{23})]$, where θ_{13} is the angle between the long axis of molecule 1 and $\hat{r}_{12}$ and θ_{23} is the angle between the long axis of molecule 2 and $\hat{r}_{12}$. We denote this interaction as [2, 0, 2] + [0, 2, 2]. For the case of uniaxial molecules the four interactions [2, 2, 0], [2, 2, 2], [2, 2, 4] and [2, 0, 2] + [0, 2, 2] exhaust the possibilities which are separately linear in second rank functions of the orientations of molecules 1 and 2.

The discussion above centers on the orientational coordinates of the molecules. To treat the position coordinates we follow Ref. 1 and assume that the density of centers of mass in the smectic state can be written as

$$\rho = \rho_0 + \Delta\rho \cos(qz) \tag{1}$$

Here $q = 2\pi/d$ where d is the layer spacing. The z axis has been chosen normal to the layers hence the factor of qz. Note that all but the lowest

Fourier coefficient of the density has been neglected. There are several ways to arrive at the final equations of the model. Instead of using the method of Ref. 1, we employ a derivation more suited to the general class of interactions considered here.

We consider each molecule to reside at the center of a sphere of radius r_0 on the surface of which are distributed the molecules with which it interacts (its "nearest neighbors"). The probability P, neglecting two body correlations, that a molecule is located at a point X on the surface of the sphere is proportional, with some proportionality coefficient λ, to ρ.

$$P = \lambda[\rho_0 + \Delta\rho \cos[q(z' + r_0 \cos(\alpha))]] \tag{2}$$

Here z' is the distance from the center of the layer to the center of the sphere ($z' \leq d/2$) and α is the angle between the z axis and the line defined by the center of the sphere and the point X. We note that $\Delta\rho = \frac{1}{2}\langle\cos(qz')\rangle$, where the angle brackets indicate an average over all positions in the layer weighted by the single partial distribution function.

Under the assumption that $qr_0 \ll 1$, Eq. (2) can be expanded to give a simple form. This assumption is not necessary but does simplify the analysis. Its adoption precludes discussion of the smectic C state[3] and of contributions from higher order Fourier components of the density. The expanded form can be written in the suggestive form:

$$\begin{aligned} P(z', \alpha)/\lambda = {} & \rho_0 + \Delta\rho \cos(qz')(1 - \tfrac{1}{6}(qr_0)^2)P_0(\alpha) \\ & + \Delta\rho \sin(qz')(qr_0)P_1(\alpha) \\ & - \tfrac{1}{3}\Delta\rho \cos(qz')(qr_0)^2 P_2(\alpha) + \mathcal{O}(qr_0)^3 \end{aligned} \tag{3}$$

Equation 3 is in the form of a Legrundre series in α. The term proportional to P_0 simply reflects the fact that a molecule near the center of the layer has more neighbors than does one far from the center. The other terms describe the distribution of neighbors as a function of α.

The effective mean field in which molecule 1 finds itself can be written as

$$H = \int \langle u(\Omega_1, \Omega_2, \hat{r}_{12})\rangle P(z', \alpha)\sin\alpha d\alpha \tag{4}$$

The angle brackets here indicate a weighted average over the coordinates of molecule 2. The quantities Ω_1 and Ω_2 are the orientations of molecules 1 and 2. The integration represents a sum over nearest neighbors. To carry it our $\hat{r}_{12}$ must be referred to a coordinate system with $\hat{z}$ axis normal to the layers so that $\hat{r}_{12} \cdot \hat{z} = \cos\alpha$.

By combining Eq. (4) and Eq. (3) with the explicit forms of the interactions[3] [2, 2, 0], [2, 2, 2], [2, 2, 4] and [2, 0, 2] + [0, 2, 2] the explicit form of the

effective mean field can be calculated. However the essential features can be easily deduced without using the explicit forms. There is no contribution from the [2, 2, 4] term because it involves a fourth order dependence on α and there is no P_4 term in Eq. (3). The [2, 2, 2] and [2, 0, 2] + [0, 2, 2] interactions contribute exclusively through the term proportional to P_2 in Eq. (3). The [2, 2, 0] interaction contributes exclusively through the terms proportional to P_0 in Eq. (3). This latter term is the essence of the model of Ref. 1. The corresponding contribution to H can be written as

$$H_1 = -A\langle P_2(\theta)\rangle P_2(\theta) - B\langle\cos(qz')P_2(\theta)\rangle\cos(qz')P_2(\theta). \tag{5}$$

In this equation θ is the angle between the long axis of molecule 1 and the director. The quantities A and B are interaction strengths. The angle bracket indicates an average with respect to the single particle distribution function which depends on both position and orientation. In the mean field approximation this distribution function is determined self-consistently as discussed below and in Ref. 1. It is important to note that Eq. (5) does not depend on the orientation of the director, $\hat{n}$, with respect to the z axis which is the direction normal to the layers. If the smectic state is thermodynamically stable with respect to the nematic and isotropic states, then a state with density periodic in three dimensions will be stable with respect to the isotropic, nematic and smectic states. That is to say, the model is unstable against freezing. This can be easily seen in the context of Eq. (5). A periodicity in the density along the y direction would add to Eq. (5) the contribution $-B\langle\cos(qy')P_2(\theta)\rangle\cos(qy')P_2(\theta)$. It can be argued that the approximation of neglecting two body correlations in deriving Eq. (5) is much less valid if there is three dimensional periodicity than if there is only one dimensional periodicity. However, even if isotropic two body correlations were considered, the three dimensional freezing instability would remain. The source of the problem is that the interaction [2, 2, 0] does not depend on α.

If the director is parallel to the z axis, the interaction [2, 2, 2] contributes a term to H of exactly the same form as the term in Eq. (5) which is proportional to B. If the director is not parallel to the z axis, a much more complicated form depending explicitly on $\hat{n}\cdot\hat{z}$, results. If this term is averaged over the orientations of molecule 1, the result is proportional to $-((\hat{n}\cdot\hat{z})^2 - \frac{1}{3})$. This implies that there is a force which keeps the director normal to the layers. A periodicity in the density along the y direction would give rise to a term proportional to $-((\hat{n}\cdot\hat{y})^2 - \frac{1}{3})$. Since the director can point only in one direction, only one dimensional periodicity in the density is energetically favorable. Therefore the model is stable against freezing in two or three dimensions.

The contribution from the [2, 0, 2] + [0, 2, 2] interaction is similar in that it favors one dimensional periodicity. However, the form of its con-

tribution to H is different. It can be written as:

$$H_2 = -C[\langle\cos(qz')\rangle P_2(\theta)\cos(qz') + \langle\cos(qz')P_2(\theta)\rangle\cos(qz')] \tag{6}$$

Here again θ is the angle between the long molecular axis and the z axis.

The full effective mean field is the sum of H_1 and H_2 where A, B, and C are viewed as arbitrary coupling coefficients. The solution for the case $C = 0$ is calculated in Ref. 1. We extend the analysis by considering the case $B = 0$. We obtain the solution in two limiting cases and deduce the general features of the phase diagram. Since the phase diagram does not differ essentially from that calculated in Ref. 1 for $B = 0$, we conclude that the solution for $B \neq 0$, $C \neq 0$ is similar as well.

III NATURE OF THE PHASE DIAGRAM

We define three order parameters η, S_1 and S_2 by the following equations

$$\eta = \langle P_2(\theta)\rangle \tag{7a}$$

$$S_1 = \langle P_2(\theta)\cos(qz')\rangle \tag{7b}$$

$$S_2 = \langle\cos(qz')\rangle \tag{7c}$$

with

$$\langle f\rangle \equiv \frac{\int_{-\pi}^{\pi} d(qz') \int_0^{\pi} d\theta \sin\theta f e^{-\beta H}}{\int_{-\pi}^{\pi} d(qz') \int_0^{\pi} d\theta \sin\theta e^{-\beta H}}$$

$$-H = A\eta P_2(\theta) + BS_1\cos(qz')P_2(\theta) + C[S_1\cos(qz') + S_2\cos(qz')P_2(\hat{v})] \tag{8}$$

Here β is equal to the reciprocal of the product of Boltzmann's constant and the temperature. It is evident that the order parameter S_2 does not enter the calculation if $C = 0$. However, for the case we consider here, $B = 0$, all three order parameters must be considered.

For $B = 0$ the free energy, F, can be written as:

$$\beta F = \tfrac{1}{2}\beta A\eta^2 + \beta CS_1S_2 - \ln\left[\frac{1}{2\pi^2}\int_{-\pi}^{\pi} d(qz') \int_0^{\pi} d\theta e^{\beta H}\sin\theta\right] \tag{9}$$

We note that $\partial F/\partial \eta = 0, \partial F/\partial S_2 = 0, \partial F/\partial S_1 = 0$ generate Eq. (7a), (7b) and (7c) respectively. Therefore Eq. (9) gives the free energy only when it is an extrema with respect to η, S_1 and S_2. In general the physically significant extrema are saddle pourts.

To map out the phase diagrams in the C, A plane it is necessary to solve the coupled set of self-consistent Eq. (7) for the three order parameters. If there is more than one solution for given values of C and A, Eq. (9) must be used to determine the most stable one. The phase diagram is composed of three regions (i) the isotropic region, $S_1 = S_2 = \eta = 0$; (ii) the nematic region, $S_1 = S_2 = 0, \eta \neq 0$; (iii) the smectic region where all the order parameters are non zero.

The determination of the phase boundaries and order parameters as functions of A and B is a numerical problem if of considerable difficulty. We limit the discussion here to a few easily determined features. The boundary between the isotropic and nematic regions is characterized by the condition $S_1 = S_2 = 0$. Therefore the phase boundary is given by the Maier–Saupe values $\beta A = 4.542$ and $\eta = 0.429$. Two limiting cases can also be solved. If $C \gg A$, A can be neglected in Eq. (7). We proceed by substituting Eq. (8) into (7a) and (7b) and expanding the exponentials to first order in $S_n, n = 1, 2$. The resulting pair of equations have a solution only if $\beta C = \sqrt{20}$. Since there are no terms in Eq. (7) quadratic in S_n, this result gives the temperature at which a second order isotropic–smectic transition takes place. The other limiting case is $A \gg C$. We again expand the exponentials in Eq. (7a) and (7b) to first order in S_n. The θ integrals are completed under the assumption that averages of $[P_2(\theta)]^m$ can be calculated from Eq. (8) neglecting contributions from C. The procedure results in the relation

$$\beta C = 2/[\langle P_2^2 \rangle_{C=0}^{1/2} + \langle P_2 \rangle_{C=0}] \tag{10}$$

Since the η and S_n equations are effectively decoupled in this limit, Eq. (10) gives the temperature at which a second order smectic–nematic phase transition takes place. Note that the unweighted average of P_2^2 is 1/5 so Eq. (10) actually gives the result in the limit $C \gg A$ as well. If it were not for the coupling between the η and S_n equations, Eq. (10) would describe a line of critical points and a phase boundary. We may conclude from this that Eq. (10) represents the approximate boundary of the smectic phase for all values of C/A.

Figure 1 schematically represents the phase diagram. Equation (10) is shown schematically as the dot dashed line. For $C \sim A$ the coupling between η and S_n causes the transition to the smectic phase to be first order in the general case. If Eq. (7) is expanded for small values of all the order parameters, quadraic terms of the form ηS_n are found. Equations of this type have been discussed in other contexts.[5] It is known that they predict tricritical

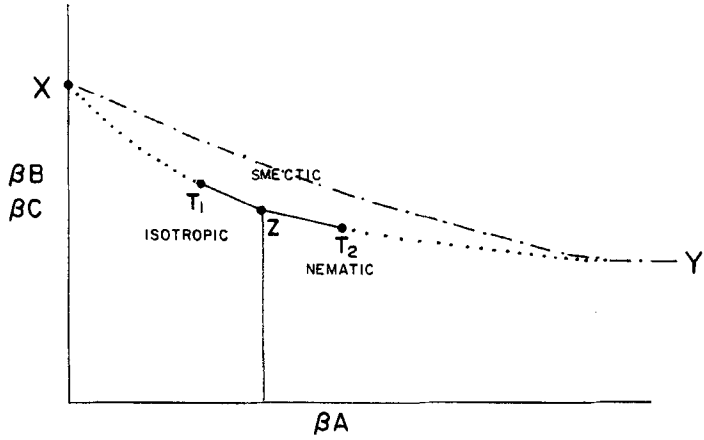

FIGURE 1 Schematic phase diagram. Solid lines are lines of first order transition points. Dotted lines are lines of second order transition points. Dot-dash line is discussed in the text. See Table I for numerical values of the labeled points.

points at which a line of first transition points ends and a line of critical points begins. This observation allows the schematic diagram of Figure 1 to be completed. The tricritical points are designated T_1 and T_2. The dotted line segments XT_1 and YT_2 are lines of critical points. The point Z is a triple point. The solid lines are lines of first order transition points. Note that the locus of points for a given ratio of C/A is a straight line passing through the origin.

It can be concluded from this diagram that the smectic–isotropic phase boundary is not an extension of the nematic isotropic phase boundary. In fact it is more nearly an extension of the nematic–smectic phase boundary. This conclusion follows mainly from the relation given in Eq. (10) .This feature is in disagreement with experiment.[7] It may be the case that higher order Fourier coefficients of the density must be considered in order to get agreement with experiment on this point.

An analysis similar to the one above can be made for the model in the case $C = 0$. In this case Eq. (10) is replaced by $\beta B = 2/\langle P_2^2(\theta)\rangle_{B=0}$. The other features remain the same with the role of C assumed by B. In Ref. 1 numerical values for some of the points in Figure 1 are calculated. Table I summarizes the values known.

Since the phase diagrams in these two cases are quite similar its clear that the phase diagram corresponding to any fixed value of C/B is also similar. The diagram can thus serve as a guide to understanding the behavior of a series of homologous compounds where B/A and C/A are considered to be smoothly varying functions of molecular structure.[7]

TABLE I

	$B = 0$	$C = 0$[a]
X	$\beta A = 0$	$\beta A = 0$
	$\beta C = \sqrt{20}$	$\beta B = 10$
Y	$\beta A \to \infty$	$\beta A \to \infty$
	$\beta C = 1$	$\beta B = 2$
Z	$\beta A = 4.54$	$\beta A = 4.54$
		$\beta B = 4.45$
T_2		$\beta A = 5.24$
		$\beta B = 3.67$

[a] Numerical values taken from Ref. 1.

IV CONCLUSION

Consideration of a class of second rank tensor model interactions including the Maier–Saupe interaction leads to an improved version of the McMillan–Kobayashi model of the smectic A state. The phase diagram of the model is similar to that given in Ref. 1. However it is shown that in contrast to the original model this model is stable against freezing in more than one dimension. It includes a force which keeps the director normal to the smectic layers. This force is missing in the original model. Unfortunately it does not reproduce the observed phase diagram in that the isotropic–smectic phase boundary is not an extension of the nematic–smectic phase boundary.

References

1. W. L. McMillan, *Phys. Rev.*, **A4**, 1238 (1971).
2. K. K. Kobayashi, *J. Phys. Soc. Jpn.*, **29**, 101 (1970).
3. R. G. Priest, *J. Chem. Phys.*, **65**, 408 (1976); *J. Phys. Paris*, **36**, 437 (1975).
4. W. Maier and A. Saupe, *Z. Naturforsch*, **13A**, 564 (1958); **14A**, 882 (1959); **15A**, 287 (1960).
5. C. Fan and M. J. Stephen, *Phys. Rev. Lett.*, **25**, 500 (1970); M. Blume, V. J. Emery, and R. B. Griffiths, *Phys. Rev.*, **A4**, 1071 (1971).
6. Experimental evidence for the tricritical point T_2 is given in: P. H. Keyes, H. T. Weston, and W. B. Daniels, *Phys. Rev. Lett.*, **31**, 628 (1973).
7. H. Arnold, *Z. Physik Chem. (Leipzig)*, **239**, 283 (1968); **240**, 185 (1969).