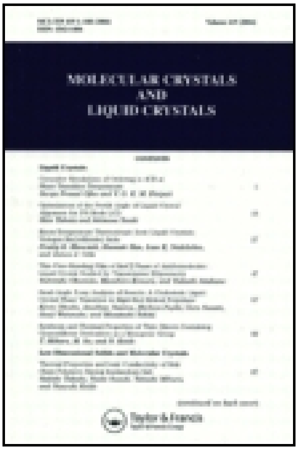

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Order Parameters and Mean Field Theory for Systems of Uniaxial Molecules

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Order Parameters and Mean Field Theory for Systems of Uniaxial Molecules†

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A general method is developed for finding the order parameters describing the various phases of a system of anisotropic molecules. The order parameters are introduced on the basis of the expansion of the one-particle distribution function in the generalized Fourier series, and the symmetry of the intermolecular potential. The free energy of the system is considered in the Landau form. This method is applied to a system of axially symmetrical molecules with the Kobayashi interaction potential. It is found that only three Fourier components of the interaction potential are responsible for the system's behaviour. The phase diagram of the system is discussed and the possibility of the existence of a biaxial nematic phase is established.

1. INTRODUCTION

The variety of ordered phases observed in the fluid systems of highly anisotropic molecules has attracted a lot of interest for the last decade. The problem of phase transitions in the liquid crystalline phases also has been a subject of numerous theoretical studies. These

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two topics: the description of the molecular order occurring in the liquid crystals, and the phase transitions between various ordered phases, are treated in the present work on the basis of the systematic theoretical description of classical fluid systems.

To describe the order occurring in a liquid crystal, a set of suitable order parameters should be introduced. Usually, the order parameters are chosen on the basis of experimentally established symmetry properties of the system. With the order parameters defined, one is able to set up a mean field[1-7] or Landau type[8] theoretical description of the system even when the details of the intermolecular interaction potential are not known.

In this paper a method is developed which allows the study of the system's phase diagrams in the mean field approximation for various intermolecular potentials. This method is based on the systematic approach of Morita and Hiroike[9] to the problem of the free energy calculations for fluid systems. A mean field approximation is considered and the Landau expansion of the free energy in terms of the order parameters is given. The order parameters are defined by an appropriate choice from the coefficients appearing in the generalized Fourier series expansion of the one-particle distribution function. As an example of the method the system of uniaxial molecules interacting via a simplified interaction potential[2] is studied.

2. THEORY

Let us consider a system of identical anisotropic rigid molecules enclosed in a volume V. The position and orientation of the i-th molecule is given by a six-dimensional variable $x_i \equiv (\mathbf{r}_i, \mathbf{\Omega}_i)$, where $\mathbf{r}_i$ is the position of the molecule's center of mass and $\mathbf{\Omega}_i$ specifies the molecule's orientation. The potential energy Φ of the system is a sum of the one-particle terms (due to the external forces) and the two-particle terms (due to intermolecular interaction)

$$\Phi = \sum_{i=1}^{N} U_1(x_i) + \sum_{i>j} U_2(x_i, x_j) \tag{2.1}$$

The grand partition function $^*gX$ of this system is

$$\begin{aligned} ^*gX = {} & \sum_{N=0}^{\infty} \frac{1}{N!} \int dx_1 dx_2 \ldots dx_N \prod_{i=1}^{N} z^*(x_i) \\ & \times \prod_{N>i>j>1} (1 + b(x_i, x_j)) \end{aligned} \tag{2.2}$$

where $b(x_i, x_j)$ is the Mayer function

$$b(x_i,x_j) = \exp\left[-\beta U_2(x_i,x_j)\right] - 1 \tag{2.3}$$

$$\beta = 1/k_B T$$

$z^*(x_i)$ is proportional to the fugacity of the system

$$z^*(x_i) = \lambda_B^{-3}\exp\left[-\beta(U_1(x_i) - \mu)\right] \tag{2.4}$$

where

$$\lambda_B = h^2/2\pi k_B T\left[I_1 I_2 I_3 m^3\right]^{1/6}$$

and μ is the given chemical potential of the system, m—the mass of a molecule, I_i (i = 1, 2, 3)—the i-th principal component of the molecule's tensor of inertia.

Using the cluster expansion method, the Helmholtz free energy of the system has been obtained, and within an accuracy up to the third order terms it reads[9]:

$$\begin{aligned} F/k_B T &= \int dx\,\rho(x)U_1(x) + \int dx\,\rho(x)\left[\ln(\lambda_B^3\rho(x)) - 1\right] \\ &- \frac{1}{2}\int dx\,dx'\,\rho(x)\rho(x')\left\{\left[1 + c(x,x')\right]\ln\frac{1 + b(x,x')}{1 + c(x,x')} + c(x,x')\right\} \\ &- \frac{1}{3!}\int dx\,dx'\,dx''\,\rho(x)\rho(x')\rho(x'')c(x,x')c(x',x'')c(x'',x) \end{aligned} \tag{2.5}$$

The free energy is written in terms of the n-particle distribution functions $\rho^{(n)}(x_1, x_2, \ldots, x_n)$

$$\rho^{(n)}(x_1,x_2,\ldots,x_n) = \sum_{N=n}\int dx_{n+1}\ldots dx_N\frac{z^N}{(N-n)!}\,\frac{\exp(-\beta\Phi)}{{}^*gX} \tag{2.6}$$

$\rho(x)$ in eq. (2.5) is the one-particle distribution function $\rho^{(1)}(x)$ normalized to the average number of particles in the system $\overline{N}$

$$\int dx\,\rho(x) = \overline{N} \tag{2.7}$$

$c(x,x')$ is given by the two-particle distribution function $\rho^{(2)}(x,x')$

$$c(x,x') = \frac{\rho^{(2)}(x,x')}{\rho(x)\rho(x')} - 1 \tag{2.8}$$

and to the lowest order in the cluster expansion[9]

$$c(x,x') = b(x,x') \tag{2.9}$$

Based on these approximations the free energy of the system is now expressed in terms of the one-particle distribution function only:

$$\begin{aligned} F/k_BT = {} & F_0/k_BT + \int dx\,\rho(x)U_1(x)/k_BT + \int dx\,\rho(x)\ln\rho(x) \\ & - \frac{1}{2}\int dx\,dx'\,\rho(x)\rho(x')b(x,x') \\ & - \frac{1}{3!}\int dx\,dx'\,dx''\,\rho(x)\rho(x')\rho(x'')b(x,x')b(x',x'')b(x,x'') \end{aligned} \tag{2.10}$$

where F_0 contains the dependence of $\bar{N}$.

The formula (2.10) furnishes the basis for the development of our approach.

3. LANDAU FREE ENERGY AND ORDER PARAMETERS

The approximate free energy of the system should now be minimized with respect to the one-particle distribution function[10]. In order to gain some insight into the mechanism of phase transitions we introduce the Landau form of the free energy. We start from the expansion of the one-particle distribution function in the generalized Fourier series

$$\rho(x) = \frac{\bar{N}}{V} \sum_{\substack{m,n,l \\ \mathbf{q}}} \left(\frac{2l+1}{8\pi^2 V} \right)^{1/2} \exp(i\mathbf{q}\cdot\mathbf{r}) D^l_{mn}(\Omega) A^{mn}_l(\mathbf{q}) \tag{3.1}$$

where $D^1_{mn}(\Omega)$ are Wigner's D-functions[11,12]. It is obvious, that $A^{00}_0(\mathbf{q} = 0) = 1$ and the case when all $A^{mn}_1(\mathbf{q}) = 0$ except $A^{00}_0(\mathbf{q} = 0)$ corresponds to the case of the isotropic fluid. All $A^{mn}_1(\mathbf{q})$ are then order parameters, since one-particle averages of the generalized Fourier base functions $(2l+1/8\pi^2V)^{1/2}e^{i\mathbf{q}\cdot\mathbf{r}}D^{l}_{mn}(\Omega)$ equal $A_l^{mn}(\mathbf{q})$. Since we are interested in order parameters which are nonzero in a certain temperature interval, we have to give the description of the set of such parameters.

For convenience we define the distribution function f as:

$$f(x)=\frac{V}{N}\rho(x) \tag{3.2}$$

The deviation $\delta f(x)$ from the isotropic fluid state, described by $f_0 \equiv 1$, is given by

$$\delta f(x)=f(x)-f_0 \tag{3.3}$$

We assume δf to be small enough so one is able to expand the eq. (2.10) in a power series of δf and calculate the free energy ΔF due to δf (for a system free of external fields):

$$\begin{aligned}
\Delta F &= F - F(f_0)\\
&= \frac{nk_BT}{4\pi}\left\{\frac{1}{2}\int dx[\delta f(x)]^2\right.\\
&\qquad\left.-\frac{1}{6}\int dx[\delta f(x)]^3+\frac{1}{12}\int dx\,[\delta f(x)]^4+\cdots\right\}\\
&\quad-\frac{n^2}{2(4\pi)^2}k_BT\int dx\,dx'\,\delta f(x)\delta f(x')b(x,x')\\
&\quad-\frac{n^3}{3!(4\pi)^3}k_BT\\
&\qquad\times\int dx\,dx'\,dx''\,\delta f(x)\delta f(x')\delta f(x'')b(x,x')b(x',x'')b(x'',x')
\end{aligned} \tag{3.4}$$

In the Landau theory of phase transitions the free energy of the system is expressed as a polynomial form in terms of the order parameters. The phase transitions occur, when the temperature change induces a change of sign of the second order coefficients. Therefore, the second order terms in δf of eq. (3.4) are crucial in this theory, although the temperature dependence of the third order terms is of importance for the discussion of tricritical points.

As can be seen from eq. (3.4), the change of sign of the second order coefficients stems from the shape of the Mayer function $b(x, x')$. This function depends only on the intermolecular interaction potential. For a given $U_2(x_i, x_j)$ the integral

$$\int d\mathbf{r}\, d\Omega\, d\mathbf{r}'\, d\Omega'\, e^{i\mathbf{q}\cdot\mathbf{r}} D^{l}_{mn}(\Omega) e^{i\mathbf{q}'\cdot\mathbf{r}'} D^{l'}_{m'n'} b(\mathbf{r}, \Omega, \mathbf{r}', \Omega')$$

will vanish for certain values of $m, n, l, \mathbf{q}$. In the Landau theory the most important are the second order terms, which can be written in the form

$$a_l^{mn}(T - T_l^{*mn}(\mathbf{q}))|A_l^{mn}(\mathbf{q})|^2 \tag{3.5}$$

where

$$T_l^{*mn}(\mathbf{q}) = -\frac{\bar{n} k_B T}{8\pi} \int dx\, dx'\, e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} D^{l}_{mn}(\Omega) D^{l*}_{mn}(\Omega') b(x, x')$$

$$(\bar{n} = \bar{N}/V) \tag{3.6}$$

and

$$a_l^{mn} = \frac{\bar{n}}{4\pi} \frac{2l+1}{8\pi^2 V}$$

From the point of view of possible phase transitions, only those $l, m, n, \mathbf{q}$ are of interest for which $T_l^{*mn}(\mathbf{q}) > 0$. In practice one should choose as the order parameters only $A_l^{mn}(\mathbf{q})$ of maximal $T_l^{*mn}(\mathbf{q})$. In that procedure the choice of order parameters depends entirely on the interaction potential. An example of the use of this approach will be provided in the next section.

4. ORDER PARAMETERS AND PHASE TRANSITIONS FOR A SYSTEM OF UNIAXIAL MOLECULES

The model of the liquid crystal system usually considered consists of a set of axially symmetrical molecules interacting via the simplified interaction potential of the form[2-5,7]

$$U_2(x_i, x_j)V(|\mathbf{r}_i - \mathbf{r}_j|) + W(|\mathbf{r}_i - \mathbf{r}_j|P_2(\cos\theta_{ij}) \tag{4.1}$$

where θ_{ij} is the angle between the long axes of the molecules i and j.

Since in this case the orientation of a molecule is described by two angles only, θ and φ and each molecule is symmetrical with respect to inversion, the generalized Fourier series for the distribution function $f(x)$ is now

$$\delta f(\mathbf{r},\theta,\varphi) = f(\mathbf{r},\theta,\varphi) - f_0 = \frac{1}{\sqrt{V}} \sum_{\mathbf{q}} \sum_{l,m} \alpha_l^m(\mathbf{q}) Y_l^m(\theta,\varphi) e^{i\mathbf{q}\cdot\mathbf{r}} \tag{4.2}$$

Let us consider the second order terms in δf on the r.h.s. of the formula (3.4) for the free energy. With the assumed form of the interaction potential, the Mayer function can be written as

$$b(\mathbf{r},\theta_{12}) = \sum_{n=1}^{\infty} \sum_{k=0}^{n} \frac{(-\beta)^n}{(n-k)!k!} V^{n-k}(\mathbf{r}) W^k(\mathbf{r}) [P_2(\cos\theta_{12})]^k \tag{4.3}$$

Now using the well known formula[13]

$$P_n(\cos\theta_{12}) = \frac{4\pi}{2n+1} \sum_{m=-n}^{n} Y_n^m(\theta_1,\varphi_1) Y_n^{m*}(\theta_2,\varphi_2) \tag{4.4}$$

and recognizing that $[P_2(x)]^n$ can be written as a linear combination of $P_{2k}(x)$, with $k = 0, 1, \dots, n$; one can see that there are no second order terms with interaction factors for parameters $\alpha_l^m(\mathbf{q})$ with odd l. On the other hand the inversion symmetry of a molecule eliminates all $\alpha_l^m(\mathbf{q})$ with odd $l + m$. Then only the terms with even l and m are coupled with the orientationally dependent part of the intermolecular potential.

Limiting further discussion to the first order term ($n = 1$) in the expansion (4.3) we obtain the crucial term in the free energy.

$$\frac{\bar{n}k_B}{8\pi} \sum_{\mathbf{q}} \left\{ \left(T + \frac{\bar{n}}{k_B} \tilde{V}(\mathbf{q}) \right) |\alpha_0^0(\mathbf{q})|^2 + \sum_{m=-2}^{2} \left(T + \frac{\bar{n}}{5k_B} \tilde{W}(\mathbf{q}) \right) |\alpha_2^m(\mathbf{q})|^2 \right\} \tag{4.5}$$

where

$$\tilde{V}(\mathbf{q}) = \int d\mathbf{r}\, V(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r})$$

$$\tilde{W}(\mathbf{q}) = \int d\mathbf{r}\, W(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r})$$

Let Q_1 be the value of the wave vector $\mathbf{q}$ for which the function $\tilde{V}(\mathbf{q})$

reaches its minimum, $\tilde{V}(Q_1) < 0$. Then at $T = T_1^* = |(n/k_B)\tilde{V}(Q_1)|$ the coefficient $T + (n/k_B)\tilde{V}(Q_1)$ changes its sign, being positive for $T > T_1^*$. In the case of the parameters $\alpha_2^m(\mathbf{q})$ such a temperature is determined from the minimum condition for the function $\tilde{W}(\mathbf{q})$. In general this minimum can be assumed at $|\mathbf{q}| = Q_2 \neq Q_1$, forcing two kinds of periodicities in the system. Note, that in most of existing theoretical treatments of the problem the proportionality $W(\mathbf{r}) = cV(\mathbf{r})$ is assumed, yielding the single period for the spatial behaviour of the particle density function in the system. The single periodicity can be also obtained if the function $\tilde{W}(\mathbf{q})$ assumes its minimum at $Q_2 = 0$. This case will now be considered.

Following the general discussion of Chap. 3 we can now define the real order parameters of the system as these $\alpha_l^m(\mathbf{q})$, which changing with the temperature can describe and define the phase transitions occuring in the system. We define then five order parameters

the uniaxial order parameter $\eta = \alpha_l^0(0)$

the translational order parameter $\tau = \alpha_0^0(Q_1) = \alpha_0^0(-Q_1)$

the biaxial order parameter $\beta = \alpha_2^2(0)$

the translational—uniaxial order parameter $\sigma = \alpha_2^0(Q_1)$

the translational—biaxial order parameter $\lambda = \alpha_2^2(Q_1)$

With these definitions introduced, we write the free energy of the system with an accuracy to fourth order terms, ignoring the third and fourth order terms containing the Mayer function. To find the explicit expressions for the coeffocients in third and fourth order terms we use the Clebsch–Gordan expansion[11]

$$Y_{l_1}^{m_1}(\Omega)_{l_2}^{m_2}(\Omega) = \sum_{LM} \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2L+1)}}\, C_{l_1 0 l_2 0}^{L0} C_{l_1 m_1 l_2 m_2}^{LM} Y_L^M(\Omega) \tag{4.7}$$

where $C_{l_1 m_1 l_2 m_2}^{LM}$ are the Clebsch–Gordan coefficients. Since each term in the free energy should be real, the sum of all $\mathbf{q}$ (coming from exponential factors $\exp(i\mathbf{q}\cdot\mathbf{r})$) in each term should be equal to zero. The free energy ΔF is now written in the form

$$\Delta F = \sum_{i=1}^{5} A_i \omega_i^2 + \sum_{i<j<k} B_{ijk}\omega_i\omega_j\omega_k + \sum_{i<j<k<l} C_{ijkl}\omega_i\omega_j\omega_k\omega_l \tag{4.8}$$

where for convenience the order parameters are denoted as $\omega_1 = \eta$,

$\omega_2 = \beta$, $\omega_3 = \tau$, $\omega_4 = \sigma$ and $\omega_5 = \lambda$. The coefficients A_i are

$$A_i = \frac{nk_B}{8\pi}(T - T_i) \tag{4.9}$$

with

$$\begin{aligned} T_1 = T_2 &= \frac{n}{5k_B}|\tilde{W}(0)| \\ T_3 &= \frac{n}{k_B}|\tilde{V}(Q_1)| \\ T_4 = T_5 &= \frac{n}{5k_B}|\tilde{W}(Q_1)| \end{aligned} \tag{4.10}$$

The third order and fourth order coefficients B_{ijk} and C_{ijkl} are expressed in terms of the Clebsch–Gordan coefficients by the use of eq. (4.7). Their explicit formulae, rather complicated, are not given here.

We have calculated the phase diagram of the system by minimization of the free energy eq. (4.8). We present this phase diagram on the $(T/T_1, T_3/T_1)$ plane, i.e. on the temperature and relative strength of $|5\tilde{V}(Q_1)/\hat{W}(0)|$ plane, Fig. 1. In the numerical calculations it was assumed that $T_4/T_1 = 0.01$. Five phases have been found in the system:

isotropic fluid (I) $\eta = \beta = \tau = \sigma = \lambda = 0$
nematic (N) with $\eta \neq 0$, $\beta = \tau = \sigma = \lambda = 0$
biaxial nematic (b) with $\eta \neq 0$, $\beta \neq 0$, $\tau = \sigma = \lambda = 0$
smectic A (S_A) with $\eta \neq 0$, $\tau \neq 0$, $\sigma \neq 0$, $\beta = \lambda = 0$

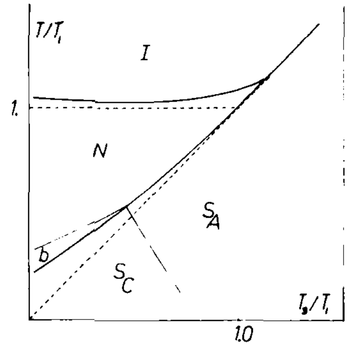

FIGURE 1 The phase diagram of the system of unaxial molecules on the temperature (T/T_1)—relative strength of the interaction potential $(T_3/T_1 = 5\tilde{V}(Q_1)/\tilde{W}(0))$ plane. The broken lines correspond to $A_1 = A_2 = 0$ and $A_3 = 0$. The full lines indicate the first order transitions.

biaxial smectic (S_C) with all order parameters different from zero. All the phase transition lines are first order.

In these calculations no tricritical point on the smectic—nematic line was detected but at least two triple points exist in the phase diagram.

5. DISCUSSION

We have outlined a simple method for studying the phase diagrams of systems of anisotropic molecules with a given intermolecular interaction potential. This method has been applied to the system of uniaxial molecules with the Kobayashi[2] interaction potential. It was shown that the three fourier components of the Kobayashi potential, $\tilde{V}(Q_1)$, $\tilde{W}(0)$ and $\tilde{W}(Q_1)$ are of importance in determinating the phase diagram. The numerical calculations were performed and the phase diagram obtained (plotted in temperature—$\tilde{V}(Q_1)/\tilde{W}(0)$ coordinates) can be compared to those obtained by McMillan, C. W. Woo and others[1,3,7]. In this respect $\tilde{V}(Q_1)/\tilde{W}(0)$ can be treated as a measure of the molecular length.

We have also calculated the quadrupolar susceptibility of the system

$$-\chi_{Quad}^{-1} = 2A_1 + \sum_{i=1}^{5} B_{11i}\omega_i + \sum_{i,j} C_{ij11}\omega_i\omega_j \tag{5.1}$$

Since there are no critical points in our model, the behaviour of χ_{Quad} shows no anomalous enhancement, except jumps occurring at the transition lines. The specific heat has also been calculated, but no anomalous temperature behaviour was found. We think that the lack of the critical and tricritical points stems from two reasons: the lack of external fields (which can induce critical end points), and the truncation of the interaction dependent third order terms in the eq. (3.4) for the free energy. The calculations considering the higher order terms in $b(x, x')$ of eq. (2.5) are now in progress and the results will be published soon.

References

1. W. L. McMillan, *Phys. Rev.* **A4**, 1238 (1971); *Phys. Rev.* **A6**, 936 (1972).
2. K. K. Kobayashi, *Phys. Lett.* **31A**, 125 (1970); *J. Phys. Soc. Japan* **29**, 101 (1970); *Mol. Cryst. Liq. Cryst.* **13**, 137 (1971).

3. F. T. Lee, H. T. Tan, Y. M. Shih and C. W. Woo, *Phys. Rev. Lett.* **31**, 1117 (73).
4. L. Shen, H. K. Sim, Y. M. Shih and C. W. Woo, *Mol. Cryst. Liq. Cryst.* **39**, 229 (1977).
5. H. T. Tan, *Phys. Rev.* **A16**, 1715 (1977).
6. M. Cotter, *Mol. Cryst. Liq. Cryst.* **39**, 173 (1977).
7. C. Shu and L. Lin, *Comm. Theor. Phys.* **1**, 107 (1982).
8. P. G. De Gennes, *Solid State Comm.* **10**, 753 (1972); *Mol. Cryst. Liq. Cryst.* **21**, 49 (1973).
9. T. Morita and K. Hiroike, *Prog. Theor. Phys.* **25**, 537 (1961).
10. M. Wadati and A. Isihara, *Mol. Cryst. Liq. Cryst.* **17**, 95 (1972).
11. D. A. Varshalovich, A. N. Moskalev and V. K. Khersonsky, "*Quantum Theory of Angular Momentum,*" (in russian), (Nauka, Leningrad, 1975).
12. D. W. Jepsen and H. L. Friedman, *J. Chem. Phys.* **38**, 846 (1963).
13. G. Arfken, "*Mathematical Methods for Physicists,*" (Academic Press, London, 1968).