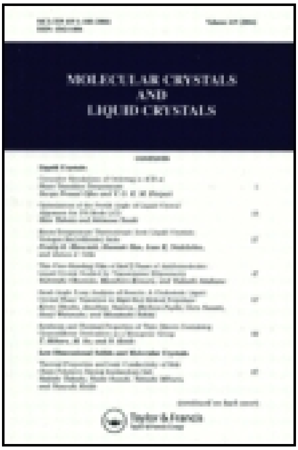

Molecular Crystals and Liquid Crystals

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Molecular Corelations in a Nematic Liquid Crystal

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Molecular Correlations in a Nematic Liquid Crystal†

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To calculate the bulk properties of a nematic liquid crystal the work of Chakravarty and Woo[1] on two-dimensional phases is generalized to three dimensions. On the basis of the Ornstein-Zernike equation the pair correlation function for the isotropic phase of a nematic liquid crystal is calculated. With the known correlations of the isotropic phase the order parameters are calculated from the first Bogoliubov-Born-Green-Kirkwood-Yvon equation. Thermodynamic properties are derived and compared with mean field results and experiments, respectively.

INTRODUCTION

Since the fundamental paper of Maier and Saupe[2] a lot of theories on nematic liquid crystals (LC) have been proposed. Until now, however, most molecular theories are mean field theories in the sense of Maier and Saupe. The LC is only described by the long-range orientational order, characterized by the order parameter $<P_2>$. Because of the substitution of the pair correlation function by unity these theories cannot explain short-range order effects.

Some years ago Chakravarty and Woo[1] published a molecular-statistical calculation of a two-dimensional LC. They used the framework of statistical mechanics of classical liquids.[3] The basic equations are those of Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) and Ornstein-Zernike (OZ).

Taking into account orientation-dependent unary and binary distribution functions we try to include short-range order effects. We apply the Percus-Yevick (PY) approximation to get a closed set of equations. For more details see Ref. 4.

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In most cases the PY theory gives better results compared to computer simulations than other theories like the hyper-netted chain (HNC) theory[3] and the Born-Green (BG) theory.[3]

Recently Lee and Woo[5] used the BG theory to deduce from the second BBGKY equation the two-particle correlation function.

Another possibility of describing short-range order phenomena is the introduction of a short-range order parameter as was done by Sheng and Wojtowicz[6] in their constant-coupling theory.

Ypma and Vertogen[7,8] have also used such a local order parameter. But their results must be interpreted in terms of microclusters.

The calculation of the two-particle correlation function gives us also an insight into the structure of the LC.

THEORY AND APPROXIMATIONS

The starting point of our theory is the following interaction potential already proposed by Kobayashi[9]

$$V_{12}(r_{12}, \vartheta_{12}) = V_0(r_{12}) + V_2(r_{12}) \cdot P_2(\cos \vartheta_{12}) \qquad (1)$$

$P_2 (\cos \vartheta_{12})$ is a Legendre polynomial of second order and ϑ_{12} is the angle between the long axes of the interacting molecules. For the distance-dependent interaction functions we choose

$$\begin{aligned} V_0(r_{12}) &= 4\epsilon\left[\left(\frac{r_0}{r_{12}}\right)^{12} - \left(\frac{r_0}{r_{12}}\right)^{6}\right] \\ V_2(r_{12}) &= \lambda 4\epsilon \cdot e^{-(r_{12}/2r_0)^2} \qquad (2) \\ r_{12} &= |\mathbf{r}_2 - \mathbf{r}_1| \end{aligned}$$

$\mathbf{r}_i$: position of the center of mass of the i-th molecule
r_{12}: intermolecular separation
λ: coupling parameter controlling the influence of the orientation-dependent interaction term
ϵ and r_0: strength and range parameter of the interaction, respectively.

The orientation dependence of the above interaction ansatz bases on the assumption of rod-like molecules. But the potential is rotationally invariant and implies a spherical molecular core in contrast to the known anisotropy of LC molecules. We must imagine the molecules as spherical particles each carrying a two-headed arrow. We suppose the interaction to be pairwise.

Because of the anisotropy of the nematic liquid crystal we have to employ generalized orientation-dependent versions of BBGKY hierarchy and the OZ equation. The first BBGKY equation reads in this case

$$kT\frac{\partial}{\partial\vartheta_1}P^{(1)}(\vartheta_1)=\iint P^{(2)}(r_{12},\omega_1,\omega_2)\frac{\partial}{\partial\vartheta_1}V_{12}(r_{12},\vartheta_{12})d\omega_2 d\overset{3}{\mathbf{r}}_2$$

$$P^{(2)}(r_{12},\omega_1,\omega_2)=P^{(1)}(\vartheta_1)\cdot P^{(1)}(\vartheta_2)\cdot g(r_{12},\vartheta_{12}) \qquad (3)$$

$$\cos\vartheta_{12}=\cos\vartheta_1\cdot\cos\vartheta_2+\sin\vartheta_1\cdot\sin\vartheta_2\cdot\cos(\varphi_1-\varphi_2)$$

$P^{(i)}(\mathbf{r}_1,\ldots,\omega_i)$ i-particle distribution function,
$g(r_{12},\vartheta_{12})$ pair correlation function,
$\omega_i=\vartheta_i,\varphi_i$ polar angles of the long axis of the i-th molecule.

The common polar axis of both molecules coincides with the preferred direction of the nematic liquid crystal. This direction follows not from the theory because of the rotational invariance of the interaction potential. We select the preferred orientation in the average process. Substituting $g(r_{12},\vartheta_{12})$ by unity and solving Eq. (3) one gets the mean field results of Maier and Saupe.

The two-particle correlation function is calculated from the OZ equation. In the case of anisotropic molecules, this equation has the following form

$$g(r_{12},\vartheta_{12})=1+C(r_{12},\vartheta_{12})+\iint P^{(1)}(\vartheta_3)C(r_{13},\vartheta_{13})[g(r_{23},\vartheta_{23})-1]d\omega_3 d\overset{3}{\mathbf{r}}_3 \qquad (4)$$

Here we have introduced the direct correlation function $C(r_{12},\vartheta_{12})$. In order to get a closed set of equations, we employ the PY approximation

$$C(r_{12},\vartheta_{12})=g(r_{12},\vartheta_{12})[1-e^{-V_{12}(r_{12},\vartheta_{12})/kT}] \qquad (5)$$

In the OZ Eq. (4) we introduce certain approximations to get manageable formulas. At first we omit the dependence on the intermolecular unity vector to avoid very involved integrations. This approximation corresponds with neglecting the intermolecular vector in Eq. (1). Further on we drop the angle dependence of the one-particle distribution function in Eq. (4). This means that we only calculate the correlations of the isotropic phase of the LC. The substitution of the real nematic correlations by the isotropic ones is the major approximation in the theory. This greatly simplifies the computation by avoiding the simultaneous calculation of the one- and two-particle distribution functions.

We expand each distribution function entering our calculation.

$$P^{(1)}(\vartheta_1)=\frac{n}{4\pi}\sum_l(2l+1)\langle P_l\rangle P_l(\cos\vartheta_1)$$

$$C(r_{12},\vartheta_{12})=\sum_k C_k(r_{12})P_k(\cos\vartheta_{12}) \qquad (6)$$

$$g(r_{12},\vartheta_{12})=\sum_m G_m(r_{12})P_m(\cos\vartheta_{12})$$

$n = (N/V)\, N$ — number of particles in the volume V. For simplification the expansions are truncated at an early stage. We retain only the first two terms. The validity of such truncated expansions depends of course on the strength of the orientation-dependent interactions.

Applying the truncated expansions of the distribution functions in Eqs. (4) and (5) we get a set of two coupled equations for the expansion coefficients $G_0(r_{12})$ and $G_2(r_{12})$

$$G_0(r_{12})I_0(r_{12}) + G_2(r_{12})I_1(r_{12}) = 1 + \int [G_0(r_{13})(1 - I_0(r_{13})) - G_2(r_{13})I_1(r_{13})][G_0(r_{23}) - 1]d\vec{r}_3$$

$$G_0(r_{12})I_1(r_{12}) + G_2(r_{12})I_2(r_{12}) = \frac{n}{25}\int [G_2(r_{13})(1 - 5\cdot I_2(r_{13})) - 5\,G_0(r_{13})I_1(r_{13})]\,G_2(r_{23})d\vec{r}_3$$

$$\begin{aligned} I_0(r) &= \int_0^1 e^{1/kT\cdot V_{12}(r,\vartheta)} d\cos\vartheta \\ I_1(r) &= \int_0^1 P_2(\cos\vartheta)e^{1/kT\cdot V_{12}(r,\vartheta)} d\cos\vartheta \\ I_2(r) &= \frac{1}{5}I_0(r) + \frac{2}{7}I_1(r) \end{aligned} \tag{7}$$

We use the correlations of the isotropic phase in the first BBGKY equation to compute the order parameters $<P_m>$

$$<P_m> = \frac{\int_0^1 P_m(x)e^{-n/kT\{\alpha_0<P_2>P_2(x)+(2/35)\alpha_2[5<P_2>P_2(x)+9<P_4>P_4(x)]\}}dx}{\int_0^1 e^{-n/kT[\alpha_0<P_2>P_2(x)+(2/35)\alpha_2[5<P_2>P_2(x)+9<P_4>P_4(x)]]}dx} \tag{8}$$

$$x = \cos\vartheta, \qquad m = 2,4,\ldots$$

$$\alpha_i = \int G_i(\mathbf{r}_{12})\,V_2(\mathbf{r}_{12})\,d\vec{r}_2, \qquad i = 0,2$$

Here the contribution of P_4 in the exponential of Eq. (8) originates from the orientation-dependent term of the correlation function and not from the interaction potential which in our model only contains the P_2 term.

RESULTS

The Eqs. (7) and (8) are solved for several parameter sets up to a density $n = 3.73\ 10^{21}\ \text{cm}^{-3}$. The interaction parameters vary in the following manner

$$1.4 \le \frac{4\epsilon}{kT} \le 1.5 \qquad 0.15 \le \lambda \le 0.5 \tag{9}$$

At first the expansion coefficients $G_0(r_{12})$ and $G_2(r_{12})$ of the pair correlation function are computed. The behavior of the expansion coefficients is qualitatively the same as in the two-dimensional case.[1] A typical result is displayed in Figure 1. The behavior of $G_0(r_{12})$ is quite similar to that of normal liquids. The local maxima and minima are much more pronounced at higher densities and lower temperatures.

As the correlation function $G_2(r_{12})$ is always positive, the probability for parallel orientation of neighboring molecules is always greater than for an orthogonal orientation, i.e. already in the isotropic phase a local nematic order has itself established. $G_2(r_{12})$ decays for large intermolecular separations because of the finite range of the orientational correlations. For $G_2(r_{12})$ only the first maximum is well pronounced. We suppose that this is due to the low value of the packing fraction (see below) and the relatively high value of the coupling constant. Figure 2 shows the behavior of the correlation function $g(r_{12}, \vartheta_{12}) = G_0(r_{12}) + G_2(r_{12}) \cdot P_2(\cos \vartheta_{12})$.

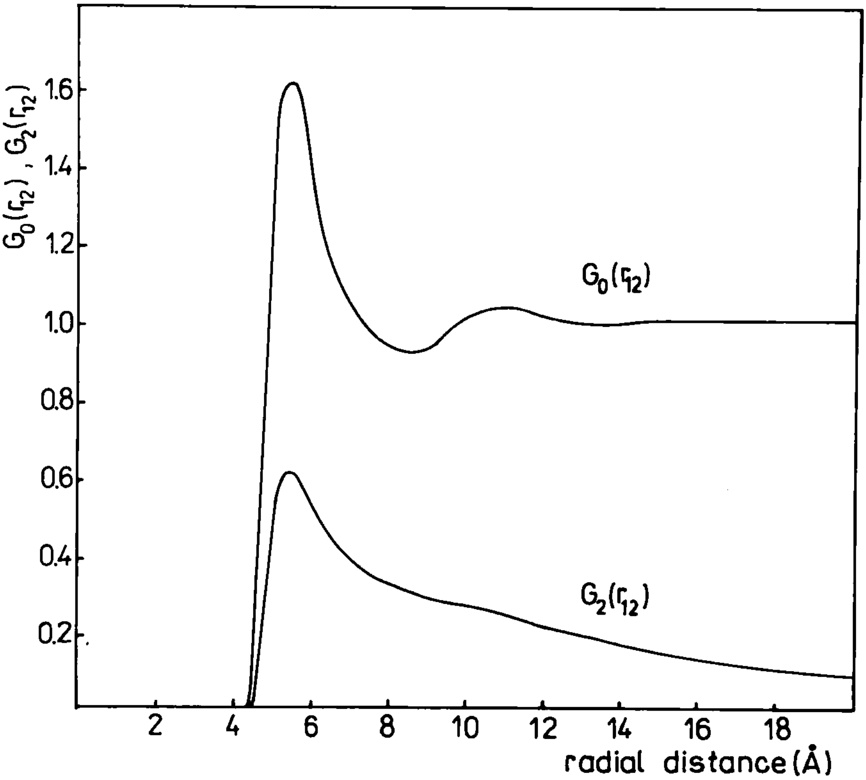

FIGURE 1 Expansion coefficients $G_0(r_{12})$ and $G_2(r_{12})$ versus intermolecular distance for $n = 3.1 \cdot 10^{21}$ cm^{-3}, $T = 300$ K, and $\lambda = 0.175$.

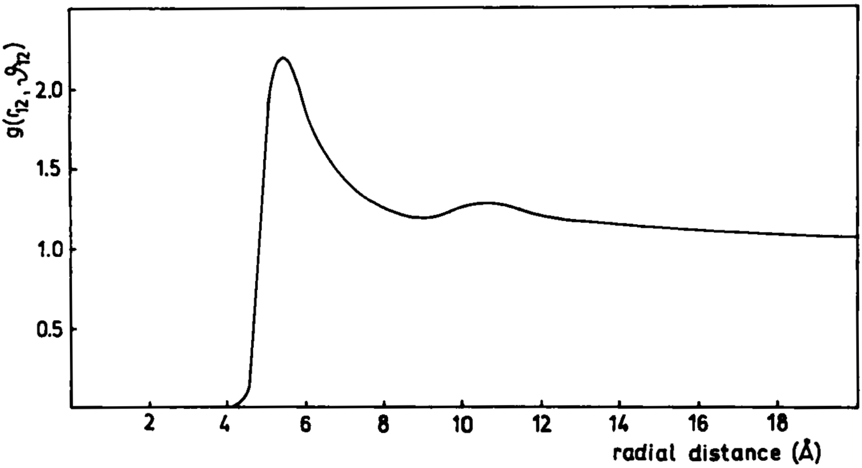

FIGURE 2 Truncated pair correlation function $g(r_{12}, \vartheta_{12}) = G_0(r_{12}) + G_2(r_{12})P_2(\cos\vartheta_{12})$ for $n = 3.1 \cdot 10^{21}$ cm^{-3}, $T = 300$ K, $\lambda = 0.175$, and $\vartheta_{12} = 0$.

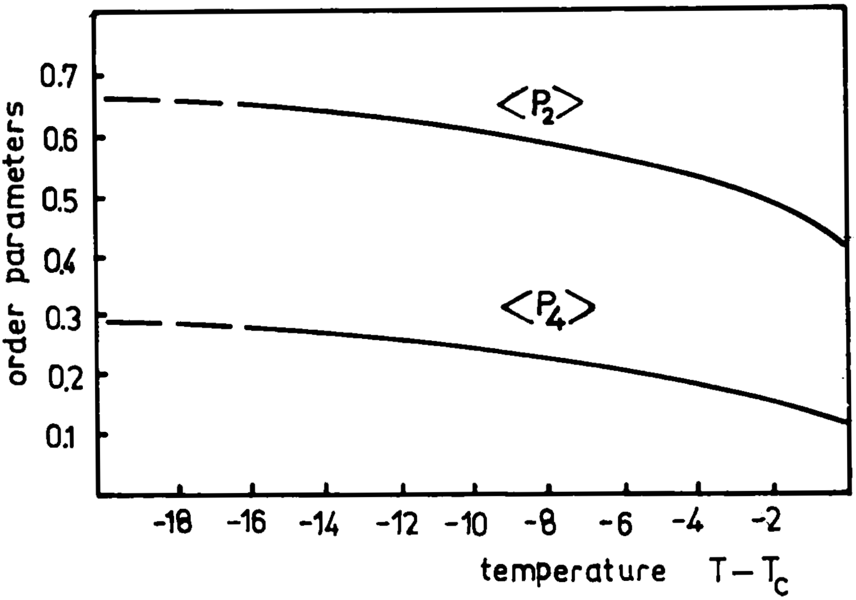

FIGURE 3 Order parameters versus temperature $T - T_c$ for $n = 2.6\,10^{21}$ cm^{-3}, and $\lambda = 0.214$.

From the known correlations we calculate the order parameters $<P_2>$ and $<P_4>$ in Eq. (8). The temperature dependence of the order parameters $<P_2>$ and $<P_4>$ is displayed in Figure 3. We remark that in the present theory the incorporation of the pair correlations has no influence on the shape of the curves. The only modification with respect to the mean field theory is a slight shift of the nematic range to higher temperatures and lower densities due to the stabilizing effect of the short-range order.

Near the clearing point the temperature and density dependence of the order parameters is different from the two-dimensional case. In the present theory both order parameters show nearly the same sensitivity to temperature and density changes. In the two-dimensional case the order parameter τ_2 is much more sensitive than τ_4.[1] This is primarily due to the choice of the order parameters associated with the underlying symmetry of the two-dimensional phase.

From the two-particle distribution function we derive a set of thermodynamic properties of our model LC. We use pressure and caloric equations of state. The kinetic part of the energy is neglected.

$$\frac{pV}{kT} = N - \frac{1}{6kT}\iiiint P^{(2)}(r_{12}, \omega_1, \omega_2) \times (\mathbf{r}_1 - \mathbf{r}_2)\nabla_1 V_{12}(r_{12}, \vartheta_{12}) d\omega_1 d\omega_2 d\overset{3}{\mathbf{r}}_1 d\overset{3}{\mathbf{r}}_2$$

$$U = \frac{1}{2}\iiiint P^{(2)}(r_{12}, \omega_1, \omega_2) V_{12}(r_{12}, \vartheta_{12}) d\omega_1 d\omega_2 d\overset{3}{\mathbf{r}}_1 d\overset{3}{\mathbf{r}}_2 \qquad (10)$$

∇_1—nabla operator acting on particle 1. In Table I the main results are summarized.

TABLE I

Predicted thermodynamic properties at the clearing point T_c for $n = 3.7\ 10^{21}\ \mathrm{cm}^{-3}$ and $\lambda = 0.15$ compared with experimental data of PAA

	Present theory	Mean field theory	PAA
$<P_2>$	0.442	0.429	~ 0.4
$<P_4>$	0.131	0.120	
$U_{\mathrm{iso}/NkT}$	−1.005		~ −30
$U_{\mathrm{aniso}/NkT}$	−0.506	−0.418	~ − 0.4
dT/dp	1.3 K/MPa	2.2 K/MPa	~ 0.5 K/MPa
$-\dfrac{n(\partial<P_2>/\partial n)_T}{T(\partial<P_2>/\partial T)_n}$	1.1	1.0	~ 4

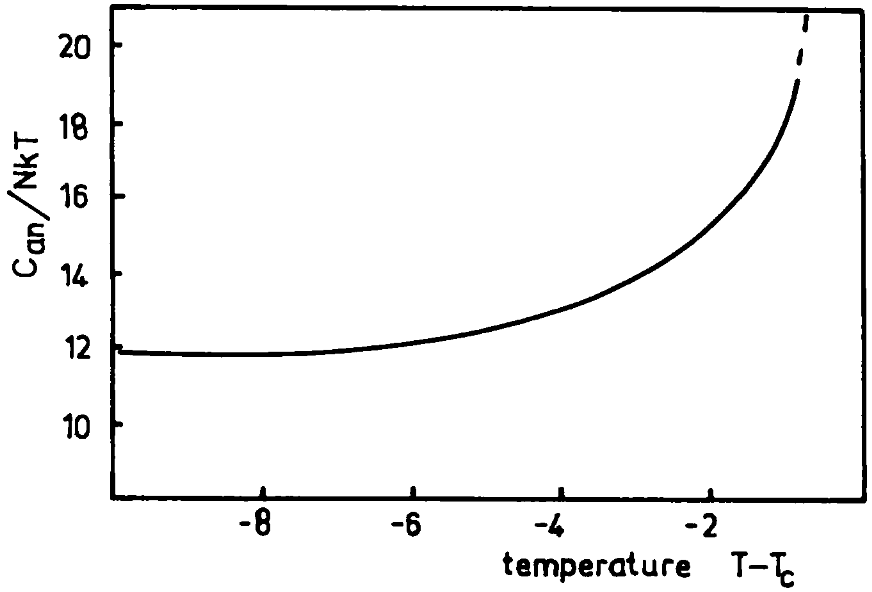

FIGURE 4 Anisotropic specific heat at constant volume versus temperature $T - T_c$ for $n = 2.6\ 10^{21}\ \mathrm{cm}^{-3}$, and $\lambda = 0.214$.

We derive the specific heat at constant volume from the anisotropic internal energy. In Figure 4 the temperature dependence below the clearing point is displayed.

DISCUSSION

In the nematic range the improvement compared to the mean field theory is moderate. The behavior of $G_0(r_{12})$ and $G_2(r_{12})$ is quite similar to that of Ref. 5. In contrast we get only one maximum in the $G_2(r_{12})$ curve as mentioned above. The temperature behavior of the order parameters is nearly unaffected by the short-range order correlations and therefore the same as in Ref. 5. Recent experimental investigations of MBBA[10] and some other compounds showed in the vicinity of the clearing point remarkably low and negative values of $<P_2>$ and $<P_4>$ respectively. In the present theory it is not possible to explain these values. We believe that this is primarily due to the interaction potential used in Eq. (1). The interaction potential shows some further deficiencies. The orientation-independent interaction yields too low values of the isotropic internal energy. But we have not optimized the strength and range parameters to get better results. The angle-dependent term suffers from the neglection of short-range repulsion. This causes an under-estimation of the thermodynamic pressure. On the other hand the pressure is always higher than in mean field theories because the pair correlations involve the molecular unpenetrability.

A second reason for the underestimated pressure is the low value of the packing fraction $n \cdot v_m$(v_m—molecular volume). Despite the number density n is in the right order of magnitude, the packing fraction is only $n \cdot v_m \sim 0.3$. To compensate this effect we have raised the density. With increasing density we get a general improvement of most thermodynamic properties.

The two-particle correlation function allows also an insight into the structure of the nematic liquid crystal. Some theories[8,11] suggest the existence of nematic microclusters even in the isotropic phase. If such clusters really exist the orientation-dependent pair correlations must vanish for distances greater than the diameter of the cluster.

Because of the non-vanishing orientational correlations even for great intermolecular separations we don't believe in the existence of nematic microclusters.

In the framework of the present theory it is also possible to describe pretransitional effects of the isotropic phase of a nematic liquid crystal.[4] Here the mean field theory fails because of the neglection of short-range correlations.

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