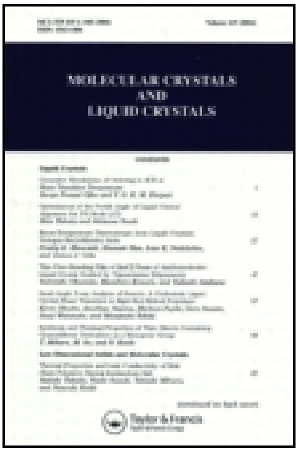

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Physical Interpretation of Polar Order Parameters in Liquid Crystals

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PHYSICAL INTERPRETATION OF POLAR ORDER PARAMETERS IN LIQUID CRYSTALS

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Abstract. The system of non-uniaxial polar molecules with the electric dipole moment directed at some arbitrary angle to the molecule long axis is considered. We present and discuss the relations between the microscopic order parameters $\alpha^l_{mn}(\mathbf{q})$ and the statistical averages of the molecular directors $<\hat{\mathbf{n}}>$ and dipole moments $<\hat{\mathbf{p}}>$.

INTRODUCTION

The liquid crystals are now widely used as active elements in many devices, from high technology to the everyday use. For those applications it is necessary to know most of the physical properties (such as optical, dielectric etc.) of liquid crystal materials. To obtain the desired features of the liquid crystal material, needed for given device, one uses the mixtures of pure compounds, whose physical properties become really important. The discussion of physical properties of compounds is possible, when the internal structure and organisation of consisting molecules is known. That is the best described by the order parameters of the system. They reflect the symmetry of consisting molecules and of the phases of the liquid crystal compounds. The theoretical models introducing calculated or phenomenologically "guessed" order parameters can be verified experimentally (by X-ray diffraction, density measurements etc.), asserting their applicability.

Thus the order parameters give us the insight into the molecular properties of the liquid crystal materials. Their proper theoretical introduction and understanding of their physical interpretation becomes obviously important.

The polarity may have a profound effect on the properties of liquid compounds. In our work we consider the system of non-uniaxial polar liquid crystal molecules with the electric dipole moment directed at some arbitrary angle to the molecule long axis. We introduce the microscopic order parameters, described as $\alpha^{l}_{mn}(\mathbf{q})$, the nontrivial set of the expansion coefficients of the one-particle, orientational and position dependent distribution function $f(\mathbf{r},\Omega)$ in the orthogonal function series $exp(i\mathbf{q}\mathbf{r})D^{l}_{mn}(\Omega)$, where $D^{l}_{mn}(\Omega)$ is the Wigner rotation function [1,2]. They are the primary results of the model theoretical calculations and they are directly related to the macroscopic measurable quantities such as $<\mathbf{n}>$ and $<\mathbf{p}>$, the mean values, or the statistical averages of the molecular directors $\mathbf{n}$ and the dipole moments $\mathbf{p}$.

The connections between those microscopic and macroscopic quantities are then essential. We present and discuss the physical meaning of $\alpha^{l}_{mn}(q)$ and $<\mathbf{n}>$, $<\mathbf{p}>$, and the relations between them. Also those arguments allow us to interpret the results of the calculations of the second order terms in the free energy performed for the model potentials such as given by Van der Meer and Vertogen and Osipov and Pikin in terms of coupling of the microscopic order parameters.

MOLECULAR MODEL AND THE STATISTICAL AVERAGES

We consider the system of identical non-uniaxial polar molecules, where the electric dipole moment is directed at some arbitrary angle to the molecule long axis (Fig.1).

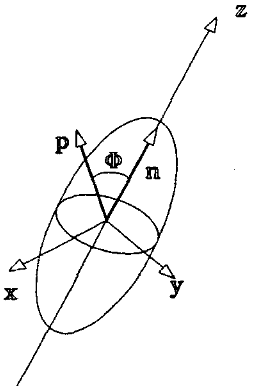

FIGURE 1 The model of the non-uniaxial molecule with permanent dipole moment non-parallel to the long axis

In our approach we assume that the molecules can be treated as rigid. That may not be exactly true, as the typical liquid crystal molecule consists of a rigid central part and the flexible hydrocarbon tails attached to the one or both ends of the rigid section. However the measurements concern presumably the position and the angular distribution of the rigid central portion of the molecule, making such assumption satisfactory. When the molecule is rigid, one can specify its orientation Ω. Then the position of the molecule is given by the vector $\mathbf{r}$ and the orientation of a particular molecule is described by the three Euler's angles$(\varphi, \theta, \chi) = \Omega$. The translational and orientational order existing in the system is described by the deviation of the one-particle distribution function $f(\mathbf{r}, \Omega)$ from the one describing the uniform isotropic liquid state f_o

$$f(\mathbf{r}, \Omega) = f_o + \delta f(\mathbf{r}, \Omega) \tag{1}$$

The structure and ordering of the system is reflected in the one-particle distribution function, containing all the microscopic information necessary to calculate one-particle properties.

The deviation of the distribution function $\delta f(\mathbf{r}, \Omega)$ can be expanded in the generalized orthogonal function series in the $(\mathbf{r}, \Omega)$ space [1-3]

$$\delta f(\mathbf{r}, \Omega) = \sum_{\substack{l,m,n \\ \mathbf{q}}} \alpha^l_{mn}(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}) D^l_{mn}(\Omega) \tag{2}$$

Here $D^l_{mn}(\Omega)$ are the Wigner rotation functions. They are of particular importance, when describing the ordering of the system.

$$D^l_{mn}(\Omega = \varphi, \theta, \chi) = e^{im\varphi} d^l_{mn}(\theta) e^{-in\chi} \tag{3}$$

where $d^l_{mn}(\theta)$ are the real functions [4].

With equations (1) and (2) we can write

$$f(\mathbf{r}, \Omega) = \sum_{\substack{l,m,n \\ \mathbf{q}}} \alpha'^l_{mn}(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}) D^l_{mn}(\Omega) \tag{4}$$

and

$$\alpha'^l_{mn}(\mathbf{q}) = \begin{cases} \alpha^l_{mn}(\mathbf{q}) & \text{for } \mathbf{q} \neq 0, \ (l, m, n) \neq 0 \\ f_o & \text{for } \mathbf{q} = 0, \ (l, m, n) = 0 \end{cases} \tag{5}$$

The statistical averages of a given molecular quantities B, bearing the physical importance and describing the macroscopic ordering occuring in the system are defined as

$$< B > = \int dx B(x) f(x) \tag{6}$$

where $x = (\mathbf{r}, \Omega)$.

If for some quantity $B(x)$ the average $< B >$ is nonzero only if the system is anisotropic, it can be regarded as the macroscopic order parameter.

We can define also the partial averages as

$$< B >_{\Omega} = \frac{\int d\Omega B(\mathbf{r},\Omega) f(\mathbf{r},\Omega)}{\int d\Omega f(\mathbf{r},\Omega)} \tag{7}$$

and

$$< B >_{\mathbf{r}} = \frac{\int d^3\mathbf{r} B(\mathbf{r},\Omega) f(\mathbf{r},\Omega)}{\int d^3\mathbf{r} f(\mathbf{r},\Omega)} \tag{8}$$

with

$$\int dx f(x) = 4\pi V \tag{10}$$

and

$$\int dx \ \delta f(x) = 0 \tag{11}$$

Consider now, that **n** is the unit vector pointing in the direction of the molecule's long axis and its orientation is given by the Eulerian angles $\Omega \boxminus (\varphi, \theta, \chi)$. If n_ξ $(\xi = x, y, z)$ are its cartesian coordinates in the laboratory frame, we have

$$\overline{n}_\xi(\mathbf{r}) \ \equiv \ < n_\xi >_\Omega = \int d\Omega P^{(1)}(\mathbf{r},\Omega) n_\xi(\Omega) \tag{12}$$

where

$$P^{(1)}(\mathbf{r},\Omega) = \frac{f(\mathbf{r},\Omega)}{\int d\Omega f(\mathbf{r},\Omega)} \tag{13}$$

We can rewrite (5.1) as

$$\overline{n}_\xi(\mathbf{r}) \ \overline{f}(\mathbf{r}) \ = \int d\Omega \ f(\mathbf{r},\Omega) \ n_\xi(\Omega) \tag{14}$$

where

$$\overline{f}(\mathbf{r}) \ = \int d\Omega \ f(\mathbf{r},\Omega) \tag{15}$$

Both $\overline{n}(\mathbf{r})$ and $\overline{f}(\mathbf{r})$ are the partial statistical averages in the orientational sense. They describe then the spatial dependence of the system ordering and so can be used for the description of the non-uniform systems. Using eq. (4) we obtain

$$\overline{n}_\xi(\mathbf{r}) \ \overline{f}(\mathbf{r}) = \sum_{\mathbf{q}} \Big[\sum_{l,m,n} \alpha'^{l}_{mn}(\mathbf{q}) A^{l}_{mn}(\xi) \Big] \exp(i\mathbf{q}\cdot\mathbf{r}) \tag{16}$$

where

$$A^l_{mn}(\xi) = \int d\Omega D^l_{mn}(\Omega) n_\xi(\Omega) \tag{17}$$

One can expand the mean values $\overline{n}_\xi(\mathbf{r})$ and $\overline{f}(\mathbf{r})$ in the Fourier series in the positional space $(\mathbf{r})$

$$\overline{n}_\xi(\mathbf{r}) = \sum_{\mathbf{k}} \tilde{n}_\xi(\mathbf{k}) \exp(i\mathbf{k}\cdot\mathbf{r}) \tag{18}$$

and

$$\overline{f}(\mathbf{r}) = \sum_{\mathbf{k}} \alpha'^{0}_{00}(\mathbf{k}) \exp(i\mathbf{k}\cdot\mathbf{r}) \tag{19}$$

After insertion of eqs. (18) and (19) into eq. (16) we obtain the equation

$$\sum_{\mathbf{q}} \alpha'^{0}_{00}\left(\frac{\mathbf{q}-\mathbf{Q}}{2}\right) \tilde{n}_\xi\left(\frac{\mathbf{q}+\mathbf{Q}}{2}\right) = \sum_{l,m,n} \alpha'^{l}_{mn}(\mathbf{Q}) A^l_{mn}(\xi) \tag{20}$$

which relates the microscopic order parameters $\alpha^l_{mn}(\mathbf{k})$ and the Fourier components of the director $\tilde{n}_\xi(\mathbf{q})$.

Similar reasoning for the orientational mean value of the dipole moment components

$$\overline{p}_\xi(\mathbf{r}) \equiv < p_\xi >_\Omega = \int d\Omega \; P^{(1)}(\mathbf{r},\Omega) \; p_\xi(\Omega) \tag{21}$$

yields the equation

$$\sum_{\mathbf{q}} \alpha'^{0}_{00}\left(\frac{\mathbf{q}-\mathbf{Q}}{2}\right) \tilde{p}_\xi\left(\frac{\mathbf{q}+\mathbf{Q}}{2}\right) = \sum_{l,m,n} \alpha'^{l}_{mn}(\mathbf{Q}) B^l_{mn}(\xi) \tag{22}$$

where

$$B^l_{mn}(\xi) = \int d\Omega \; D^l_{mn}(\Omega) \; p_\xi(\Omega) \tag{23}$$

CALCULATIONS OF PARTIAL STATISTICAL AVERAGES FOR THE MOLECULAR DIRECTOR AND THE DIPOLE MOMENT

Consider the molecule model as shown on (Fig.1), with the molecular director $\mathbf{n}$ parallel to the long axis of the molecule and the electric dipole moment $\mathbf{p}$ oriented at the arbitrary angle Φ to the molecular director. The orientation of $\mathbf{n}$ is given by its Eulerian angles $\Omega = \varphi, \theta, \chi$. The cartesian coordinates n_ξ, $\xi = x, y, z$ of the molecular director can be written as

$$\begin{aligned} n_x &= \sin\theta\cos\phi \\ n_y &= \sin\theta\sin\phi \\ n_z &= \cos\theta \end{aligned} \tag{24}$$

Using the symmetry properties of the Wigner rotation functions $D^l_{mn}(\varphi,\theta,\chi)$ we can express n_ξ as

$$\begin{aligned} n_x &= \frac{1}{\sqrt{2}}(D^1_{-10}(\Omega) - D^1_{10}(\Omega)) \\ n_y &= \frac{1}{i\sqrt{2}}(D^1_{-10}(\Omega) + D^1_{10}(\Omega)) \\ n_z &= D^1_{00}(\Omega) \end{aligned} \tag{25}$$

Considering the equations (17) and (24) we can calculate now explicitly the righthand side of the eq. (20) and we receive

$$\begin{aligned} \sum_{\mathbf{q}} \alpha'^0_{00}(\frac{\mathbf{Q}-\mathbf{q}}{2})\tilde{n}_x(\frac{\mathbf{Q}+\mathbf{q}}{2}) &= \frac{8\pi^2}{3\sqrt{2}}[\alpha^1_{10}(\mathbf{Q}) - \alpha^1_{-10}(\mathbf{Q})] \\ \sum_{\mathbf{q}} \alpha'^0_{00}(\frac{\mathbf{Q}-\mathbf{q}}{2})\tilde{n}_y(\frac{\mathbf{Q}+\mathbf{q}}{2}) &= \frac{8\pi^2}{i3\sqrt{2}}[\alpha^1_{10}(\mathbf{Q}) - \alpha^1_{-10}(\mathbf{Q})] \\ \sum_{\mathbf{q}} \alpha'^0_{00}(\frac{\mathbf{Q}-\mathbf{q}}{2})\tilde{n}_z(\frac{\mathbf{Q}+\mathbf{q}}{2}) &= \frac{8\pi^2}{3}\alpha^1_{00}(\mathbf{Q}) \end{aligned} \tag{26}$$

where α^1_{mn} are the microscopic polar ordering parameters.

The orientation of the electric dipole moment $\mathbf{p}$ is described by its Eulerian angles $(\varphi',\theta',\chi') = \Omega'$. With the abovementioned arguments used, we can have

$$\begin{aligned} p_x &= \frac{1}{\sqrt{2}}(D^1_{-10}(\Omega') - D^1_{10}(\Omega')) \\ p_y &= \frac{1}{i\sqrt{2}}(D^1_{-10}(\Omega') + D^1_{10}(\Omega')) \\ p_z &= D^1_{00}(\Omega') \end{aligned} \tag{27}$$

Using the following property of the Wigner functions [2,4]

$$D^l_{mn}(\varphi',\theta',\chi') = \sum_{m'=-l}^{l} D^l_{mm'}(\varphi,\theta,\chi)D^l_{m'n}(0,\Phi,0) \tag{28}$$

we obtain from the equation (22) the three equations for the three cartesian coordinates of $< p_\xi >$

$$
\begin{aligned}
\sum_{\mathbf{q}} \alpha'^{0}_{00}\Big(\frac{\mathbf{Q}-\mathbf{q}}{2}\Big)\tilde{p}_x\Big(\frac{\mathbf{Q}+\mathbf{q}}{2}\Big) &= \frac{8\pi^2}{3\sqrt{2}}\Big[\frac{\sin\Phi}{\sqrt{2}}\big(\alpha^1_{11}(\mathbf{Q}) - \alpha^1_{1-1}(\mathbf{Q}) + \alpha^1_{-1-1}(\mathbf{Q}) - \alpha^1_{-11}(\mathbf{Q})\big) \\
&\quad + \cos\Phi\ \big(\alpha^1_{10}(\mathbf{Q}) - \alpha^1_{-10}(\mathbf{Q})\big)\Big] \\
\sum_{\mathbf{q}} \alpha'^{0}_{00}\Big(\frac{\mathbf{Q}-\mathbf{q}}{2}\Big)\tilde{p}_y\Big(\frac{\mathbf{Q}+\mathbf{q}}{2}\Big) &= \frac{8\pi^2}{i3\sqrt{2}}\Big[\sin\Phi\big(\alpha^1_{11}(\mathbf{Q}) + \alpha^1_{1-1}(\mathbf{Q}) - \alpha^1_{-1-1}(\mathbf{Q}) + \alpha^1_{-11}(\mathbf{Q})\big) \\
&\quad + \cos\Phi\big(\alpha^1_{10}(\mathbf{Q}) - \alpha^1_{-10}(\mathbf{Q})\big)\Big] \\
\sum_{\mathbf{q}} \alpha'^{0}_{00}\Big(\frac{\mathbf{Q}-\mathbf{q}}{2}\Big)\tilde{p}_z\Big(\frac{\mathbf{Q}+\mathbf{q}}{2}\Big) &= \frac{8\pi^2}{3}\Big[\frac{\sin\Phi}{\sqrt{2}}\big(\alpha^1_{01}(\mathbf{Q}) - \alpha^1_{0-1}(\mathbf{Q})\big) + \cos\Phi\ \alpha^1_{00}(\mathbf{Q})\Big]
\end{aligned}
\tag{29}
$$

Taking into account the equations (26) we can express the $\tilde{p}_\xi$ in terms of the $\tilde{n}_\xi$

$$
\begin{aligned}
\sum_{\mathbf{q}} \alpha'^{0}_{00}\Big(\frac{\mathbf{Q}-\mathbf{q}}{2}\Big)\tilde{p}_x\Big(\frac{\mathbf{Q}+\mathbf{q}}{2}\Big) &= \frac{8\pi^2}{3\sqrt{2}}\sin\Phi\ \big(\alpha^1_{11}(\mathbf{Q}) - \alpha^1_{1-1}(\mathbf{Q}) + \alpha^1_{-1-1}(\mathbf{Q}) - \alpha^1_{-11}(\mathbf{Q})\big) \\
&\quad + \cos\Phi\ \sum_{\mathbf{q}} \alpha'^{0}_{00}\Big(\frac{\mathbf{Q}-\mathbf{q}}{2}\Big)\tilde{n}_x\Big(\frac{\mathbf{Q}+\mathbf{q}}{2}\Big) \\
\sum_{\mathbf{q}} \alpha'^{0}_{00}\Big(\frac{\mathbf{Q}-\mathbf{q}}{2}\Big)\tilde{p}_y\Big(\frac{\mathbf{Q}+\mathbf{q}}{2}\Big) &= \frac{8\pi^2}{i3\sqrt{2}}\sin\Phi\ \big(\alpha^1_{11}(\mathbf{Q}) + \alpha^1_{1-1}(\mathbf{Q}) - \alpha^1_{-1-1}(\mathbf{Q}) + \alpha^1_{-11}(\mathbf{Q})\big) \\
&\quad + \cos\Phi \sum_{\mathbf{q}} \alpha'^{0}_{00}\Big(\frac{\mathbf{Q}-\mathbf{q}}{2}\Big)\tilde{n}_y\Big(\frac{\mathbf{Q}+\mathbf{q}}{2}\Big) \\
\sum_{\mathbf{q}} \alpha'^{0}_{00}\Big(\frac{\mathbf{Q}-\mathbf{q}}{2}\Big)\tilde{p}_z\Big(\frac{\mathbf{Q}+\mathbf{q}}{2}\Big) &= \frac{8\pi^2}{3}\Big(\frac{\sin\Phi}{\sqrt{2}}\big(\alpha^1_{01}(\mathbf{Q}) - \alpha^1_{0-1}(\mathbf{Q})\big) \\
&\quad + \cos\Phi \sum_{\mathbf{q}} \alpha'^{0}_{00}\Big(\frac{\mathbf{Q}-\mathbf{q}}{2}\Big)\tilde{n}_z\Big(\frac{\mathbf{Q}+\mathbf{q}}{2}\Big)
\end{aligned}
\tag{30}
$$

DISCUSSION

We have shown, that the average molecular director and the average dipole moment in the system of polar molecules depend linearly on the microscopic order parameters $\alpha^1_{mn}(\mathbf{k})$, $(m, n = -1, 0, 1)$.

One may note that the Fourier components of the statistical average of the molecular directors depend only on the polar order parameters α^1_{00}, α^1_{-10}, α^1_{10}. However, the components of different wavevectors $\mathbf{q}$ are mixed with the pure density waves $\alpha'^{0}_{00}(\mathbf{k})$. The Fourier components of the statistical average of the dipole moments depend in turn on the polar order parameters α^1_{11}, α^1_{-11}, α^1_{1-1}, α^1_{-1-1}. They are also mixed with the pure density waves $\alpha'^{0}_{00}(\mathbf{k})$ for the whole spectrum of wavevectors $\mathbf{k}$.

It is interesting that the ξ–component of the average dipole moment depends linearly on the same ξ–component of the average molecular director. This dependence disappears for the dipole moment perpendicular to the long molecular axis.

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