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TEMPERATURE DEPENDENT PITCH IN CHOLESTERIC PHASE

H. KIMURA, M. HOSINO and H. NAKANO
Department of Applied Physics, Faculty of Engineering, Nagoya University, Nagoya 464, Japan

Résumé. — On étudie théoriquement les phases ordonnées des cristaux liquides cholestériques en considérant l'interaction moléculaire comme la somme d'un terme répulsif entre les bâtonnets chiraux rigides et de termes dispersifs attractifs de Maier-Saupe et Goossens. La méthode de symétrie brisée est appliquée pour calculer l'énergie libre en fonction du paramètre d'ordre et du pas de la structure hélicoïdale. On calcule la température de clarification et le pas dépendant des paramètres du champ intermoléculaire. On peut comprendre la relation observée entre activité optique et structure hélicoïdale.

Abstract. — Orientational ordering in the cholesteric liquid crystal is investigated theoretically by assuming the intermolecular force as the sum of a repulsion of hard-core with shape of twisted rod and of dispersion forces of Maier-Saupe and Goossens type. A method of symmetry breaking potential is applied to obtain the free energy as a function of the order parameter and the pitch in the helical structure. Thus, the clearing temperature and the pitch are calculated as functions of the parameters involved in the intermolecular force. By comparing with the results of calculation, one can understand the temperature dependence of the pitch and also the relation between the optical activity and the pitch observed in some cholesteric liquid crystals.

1. Introduction. — Such important characteristics of the cholesteric structure as the sign and temperature dependence of helical pitch have not been well explained yet on the basis of molecular theory.

Goossens [1] proposed that the cholesteric structure is caused by the attractive dispersion force due to the dipole-quadrupole as well as dipole-dipole interactions between molecules. Prior to this the dipole-dipole one was first proposed for nematics by Maier and Saupe. The Goossens model could give a proper magnitude of the pitch and succeeded to explain the fact that the cholesteric structure appears only in optical active molecules. However, the temperature dependence of the pitch remained to be unexplained.

Straley has recently extended [2] the hard-rod theory of nematic ordering, which was proposed formerly by Onsager, to discuss the cholesteric phase. According to him, the cholesteric structure can be realized as the consequence of the intermolecular repulsion of hard-core with the shape of twisted rod.

In the present paper, we assume the intermolecular force as the sum of the Maier-Saupe-Goossens type dispersion forces and the hard-core repulsion of twisted rod shape. By means of this model, we can explain the main features of cholesteric liquid crystals, including the proper temperature dependences of the helical pitch.

2. Molecular theory on cholesteric phase. — We consider a system of \( N \) molecules with a shape of twisted rod which are optically active and interact with one another by the Maier-Saupe-Goossens dispersion force. Thus, the total pair potential between the molecules \( i \) and \( j \) is expressed as

\[
\varphi_{ij} = \begin{cases} + \infty & \text{if } i \text{ and } j \text{ intersect}, \\ V_{ij} & \text{otherwise}, \end{cases}
\]

with the potential of dispersion force

\[
V_{ij} = - J(r_{ij}) P_2(\cos \theta_{ij}) - K(r_{ij}) (\hat{a}_i \cdot \hat{a}_j) (\hat{a}_i \times \hat{a}_j) \cdot \frac{r_{ij}}{r_{ij}} ,
\]

where \( \hat{a}_i \) denotes a unit vector in the direction of the principal axis of \( i \)-th molecule, \( P_2(\cos \theta_{ij}) \) the second order Legendre polynomial with the argument \( \cos \theta_{ij} \equiv \hat{a}_i \cdot \hat{a}_j \), \( J(r_{ij}) \) and \( K(r_{ij}) \) are the respective coupling strengths depending on the intermolecular distance \( r_{ij} \). The potential \( V_{ij} \) is the one first proposed by Goossens and recently simplified by van der Meer et al. [3].

We define an orientational order parameter by

\[
S = \left\langle \frac{1}{N} \sum_{i=1}^{N} P_2(\cos \theta'_i) \right\rangle ,
\]

where \( \theta'_i \) is the angle between the principal axis of
the \(i\)-th molecule and the director \(\mathbf{n}(\mathbf{r}_i)\) at the position \(\mathbf{r}_i\) of the molecule, i.e. \(\cos \theta_i = \hat{a}_i \cdot \mathbf{n}(\mathbf{r}_i)\), and \(\langle \cdots \rangle\) represents the average at thermal equilibrium. We assume the director \(\mathbf{n}(\mathbf{r})\) to follow a helix of the form

\[
\begin{align*}
    n_x &= \cos (qz), \\
    n_y &= \sin (qz), \\
    n_z &= 0,
\end{align*}
\]

where the helical axis is taken in the \(z\)-axis and use has been made of the helicity \(q\) which is related to the pitch \(p\) as \(q = 2\pi/p\).

By applying the method of symmetry breaking potential \([4]\), the free energy \(F(S, q)\) of the system as a function of the order parameter \(S\) and the helicity \(q\) is obtained in the mean field approximation as

\[
\frac{\{ F(S, q) - F(0, 0) \}}{NkT} = \eta_0 S - \ln I_0(\eta_0) - \frac{1}{2} \left[ \left\{ \frac{J_z}{kT} + \frac{5\pi nDL^2}{16} \right\} + q \left( \frac{Kz}{3kT} - cn \right) - \frac{1}{2} q^2 J_z R^2 kT \right] S^2 \]

\[
- \frac{1}{2} q^2 \frac{5\pi nDL^4}{576} S g(S),
\]

where \(S\) or \(\eta_0\) is the solution of the simultaneous equations

\[
\eta_0 = \left( \frac{J_z}{kT} + \frac{5\pi nDL^2}{16} \right) S \}
\]

\[
\text{and } S = I_1(\eta_0)/I_0(\eta_0)
\]

with the use of a function

\[
I_n(\eta_0) \equiv \int_0^1 \{ P_n(\cos \theta) \}^n \times \exp \{ \eta_0 P_n(\cos \theta) \} d(\cos \theta)
\]

\((n = 0, 1, 2, \ldots)\).

In eq. (5), \(D\) and \(L\) denote the width and the length of molecule, \(J = J(R)\), \(K = K(R)\) with the mean distance \(R\) between nearest neighbouring molecules, \(z\) the mean coordination number, and \(n\) the number density, \(g(S)\) is a function defined by

\[
g(S) \equiv 1 + 4 I_1(\eta_0)/I_0(\eta_0) - 5 I_2(\eta_0)/I_0(\eta_0).
\]

The quantity \(c\) has been defined by the relation

\[
\int r_{ij} f_{ij}^2 d r_{ij} = - c (\hat{a}_i \cdot \hat{a}_j) (\hat{a}_i \times \hat{a}_j),
\]

where \(f_{ij}^2 \equiv \exp(- g_{ij}^2/kT) - 1\) denotes the Mayer function for the twisted hard-rod potential \(g_{ij}^2\) given by the first line of eq. (1). Such a form as given by (9) has been presented by Straley \([2]\). The expressions (5) and (6) have been derived on the assumption \(|qR| \ll 1\), by making use of the similar method to that in a previous work devoted to discuss the nematic phase \([5]\).

From the condition to minimize the free energy \(F(S, q)\) with respect to the helicity \(q\), we obtain

\[
q = \frac{1}{R} J_z/k + \frac{\eta(S)}{T/S},
\]

where

\[
\begin{align*}
\kappa &\equiv nc/R, \\
\gamma &\equiv 5 \pi nDL^4/576 R^2
\end{align*}
\]

The clearing temperature \(T_c\) can be determined from the condition \(F(S, q) = F(0, 0)\), as

\[
T_c = J_z/k(4.54 - 5 \pi nDL^2/16),
\]

by neglecting the \(q\) dependence of \(F\). The order parameter at \(T_c\) is estimated \(S_c = 0.43\). This estimate and the temperature (12) are identical with those obtained in the previous paper \([5]\).

3. **Sign and temperature dependence of the cholesteric pitch.** The first term \(Kz/3 k\) of (10) represents the polar effect and the second one \(\kappa T\) does the steric effect on the cholesteric helicity \(q\). In terms of these two, the temperature dependence of the helicity or pitch of the cholesteric structure can be derived.

According to Goossens \([1]\), the quantity \(K\) is closely related to the optical activity of the molecule \((1)\).

As most of cholesterogens are actually dextro- or optical-active, we tentatively assume \(K > 0\) for those molecules.

Another constant \(\kappa\) of the steric effect is simply proportional to the deflection angle between the principal axes of a pair of molecules closely in contact. The sign and size both depend on the geometrical shape of molecule.

The denominator of eq. (10) is always positive and increases slightly with temperature due to the factor \(g(S) T/S\). In most cases, the temperature dependence of \(q\) is dominated by the numerator.

On the assumption \(K > 0\), the three types of behaviour are expected according to the value of \(\kappa\); as are shown in table 1. The temperature dependences of the pitch are shown in figure 1. It should be noted that the case where \(q < 0\) and \(\rho T > 0\) cannot exist as far as \(K > 0\).

In the case (c), the helix changes its handedness at a temperature \(T_n \equiv Kz/3 \kappa c\), although such phenomena have not been apparently observed yet in any simple cholesteric substance.

Now, we try to investigate real cholesterics on the basis of the present results.

\(1\). The relation is actually not so simple. Those components of optical tensor which are related to \(K\) do not contribute to the optical rotation in isotropic solutions but only to the rotation of light beam travelling in perpendicular to the long axis of the molecule \([6]\).
### Table I

Cases of various cholesteric structures, where \( q \) is the helicity of cholesteric phase. For the right (left)-handed structure, \( q > 0 \) (\( q < 0 \)). For the temperature dependences, we have the relation

\[
p^{-1}(dp/dT) = -q^{-1}(dq/dT) .
\]

<table>
<thead>
<tr>
<th>Case</th>
<th>( \kappa )</th>
<th>( q ) at ( T_e )</th>
<th>( \frac{1}{q}(\frac{dq}{dT})_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>( \kappa &lt; 0 )</td>
<td>0 (&lt; K_z/3kT_e )</td>
<td>+</td>
</tr>
<tr>
<td>(b)</td>
<td>0 (&lt; \kappa &lt; K_z/3kT_e )</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>(c)</td>
<td>( \kappa &gt; K_z/3kT_e )</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>

*Fig. 1.* Temperature dependences of the cholesteric pitch \( p \).

Case (a): \( \kappa < 0 \); case (b): 0 \(< \kappa < K_z/3kT_e \);

\( T_e \) : clearing temperature, \( T_e = K_z/3k\kappa \).

---

### 3.1 Cholesteryl Compounds

There exist both the right- and left-handed cholesteric structures in cholesteryl compounds. It has been recognized that the handedness depends on the sort of the attachment to the 3-\( \beta \)-carbon of cholesteryl trunk [7].

As these molecules have the same optical active (dextro-rotatory) trunk, we can expect that the values of \( K \) of those is nearly constant.

On the other hand, the magnitude of \( \kappa \) is influenced from the attachment although its sign is not. The geometrical asymmetry of those compounds is determined mainly by the cholesteryl trunk. If we assume \( \kappa > 0 \), we can expect in the cholesteryl compounds only the types (b) and (c). This expectation is consistent with the fact that the pitch in the right-handed cholesterics with \( q \) positive shows the positive temperature dependence, \( p^{-1}(dp/dT) > 0 \); on the contrary, the left-handed ones with \( q \) negative show the negative temperature dependence : \( p^{-1}(dp/dT) < 0 \). As the former case, we have cholesteryl 2-(2-ethoxyethoxy)ethyl carbonate [8], and probably cholesteryl chloride [9]; as the latter case, cholesteryl propionate, cholesteryl acetate [10], etc.

An extremely steep temperature variation of the pitch has been observed near the cholesteric-smectic transition temperature in certain cholesteryl compounds. Such a steep variation is not fitted to the present formula (10) but it is regarded to be a pre-transitional effect to the smectic phase.

### 3.2 Non-sterol Compounds

Many non-sterol cholesteric compounds have a general structure such as

\[
Y_1 \text{--} X \text{--} Y_2
\]

where the end chains \( Y_1 \) and/or \( Y_2 \) contain an asymmetric carbon. In these molecules, a remarkable relationship has been recognized between the sign of the cholesteric structure and the position of the asymmetric carbon in the constituent molecules. If the carbon is at an even-numbered position from the ring system, the cholesteric phase is always right-handed, while for the asymmetric centre located on an odd-numbered position, the structure is left-handed [11, 12].

As all these molecules have the optical activity of the same order of magnitude, we can expect the same order of magnitude of \( K \). Therefore the origin of the facts mentioned above should be attributed to the dependence of \( \kappa \) on the position of asymmetric carbon. On the assumption that for the case of even-numbered position \( \kappa < K_z/3kT_e \) (\( q > 0 \) : right-handed), while for the odd-numbered one \( \kappa > K_z/3kT_e \) (\( q < 0 \) : left-handed), the observed sign and temperature dependence of pitch can be understood, although both the sign and temperature dependence have been reported on few materials.

### 3.3 Cholesteric Order due to the H-D Asymmetry

Coats and Gray [13] have found recently that the cholesteric phase can be formed in molecules only having a hydrogen-deuterium asymmetry. As the steric effect in the helicity of these molecules are very small and so it is reasonable to assume \( \kappa = 0 \) in (10), the positive temperature dependence \( p^{-1}(dp/dT) > 0 \) can be concluded. By making use of (10), (11) and (12), we obtain

\[
p^{-1}(dp/dT) \approx 10^{-3} ^\circC
\]

for the case \( T_e = 400 \) K, \( L/D = 3 \sim 5 \). These results are consistent with the sign and the order of magnitude of the temperature dependence of pitch determined from observation.
3.4 Polypeptides. — Polypeptides form a cholesteric phase in \( \alpha \)-helix solvents, and show left- and right-handed structures depending on their own property and the kind of solvents. All of PBLG, PLGA, PELG, etc. have been reported to have positive temperature dependence, \( p^{-1}(\rho d\rho/dT) > 0 \) [14]. This fact can be well explained by an expression

\[
q \cong -\frac{\kappa S}{R_0 g(S)}, \tag{13}
\]

which is derived with the neglect of the polar effect in (10); for such molecules having large \( L/D \) ratio as polypeptides, we can assume that the hard-core repulsion is mainly responsible for the orientational ordering. The temperature dependence given by (13) agrees qualitatively with the suggestion by Straley [2].

4. Discussion. — In the present paper, we have studied cholesteric liquid crystals on the basis of molecular statistical theory. Thus, we can understand the temperature dependence and the sign of the pitch actually observed in some liquid crystals. The statistical model presented in this paper have been able to explain the respective roles of attractive and repulsive intermolecular forces in the cholesteric structure, although the quantitative analysis remains to be insufficient. Onsager’s approximation for the treatment of the hard-core repulsion has been shown to be quantitatively accurate only in cases \( L/D \gg 1 \) and to underestimate the steric effect on the orientational ordering for \( L/D = 3 \sim 5 \) which is appropriate to ordinary liquid crystals [15]. Therefore, the present expressions for the steric effect such as \( 5\pi DL^2/16 \) and \( \gamma \) are regarded as certain lower bounds. By means of the scaled particle theory, Cotter [16] has obtained an expression for the quantity which corresponds to \( 5\pi DL^2/16 \) of ours. Her expression gives the value \( 3 \sim 4 \) times larger than ours for the case that \( L/D = 3 \sim 5 \) and the packing fraction of molecules is nearly equal to 0.5. As the scaled particle theory is considered to overestimate the steric effect, we can expect that our estimate gives a correct order of magnitude for the steric effect in liquid crystals.

On the other hand, we have not tried to estimate \( \kappa \) quantitatively. Therefore \( \kappa \) is regarded as an adjustable parameter, as same as the quantities \( J \) and \( K \) which represents the polar effect.

The model will be also applicable to the cases of various mixtures by means of a small modification.

References