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Molecular theory of cholesteric liquid crystals and cholesteric mixtures*

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A molecular theory of cholesteric liquid crystals is presented. By means of symmetry considerations we obtain a general form of the intermolecular potential containing chiral contributions, which are then shown to be responsible for forming the cholesteric phase. The temperature dependence of the cholesteric pitch is calculated. It is found that the pitch depends on temperature through a ratio of orientational order parameters in the form $[\sigma_4(T)/\sigma_2(T)]^2$. A general mean-field theory for binary cholesteric mixtures is also presented, along with a formula showing how the pitch depends on temperature and concentration. Under certain conditions, the formula reduces at fixed $T-T_c$ to a simple quadratic rational fraction in the concentration. This is consistent with experimental observation.

I. INTRODUCTION

The cholesteric mesophase is generally regarded as a distorted form of the nematic mesophase: one which is characterized by a macroscopic twist.[1] Besides this helical structure, there is no long-range order in the spatial distribution of molecules. The optical response of a cholesteric is usually uniaxial, or at most very weakly biaxial.[2] For this reason, the steric or packing model, which assumes molecules of planar shape (slab-like) piling up on top of one another to form twisted layers, had to be abandoned.

The description of cholesterics as twisted nematics is consistent with experimental observation. It provides at the least a very good approximation to physical reality. Thus the existence of a finite pitch is a common feature of all materials found in the cholesteric mesophase. This phenomenon results from the microscopic structure of the molecules and the nature of the intermolecular interactions. From the point of view of global symmetry, one can argue that cholesterics are made up of chiral molecules. The few potential models in existence[3-5] all agree that chirality is the major cause for the macroscopic twist. Unfortunately they also share the common conclusion that the pitch is insensitive to temperature variations.

In actual experimental situations it is found that the pitch of a cholesteric invariably depends on the temperature. An interesting explanation was offered by Keating.[6] He assumed the forces opposing the twist to be anharmonic, so that a macroscopic twist results automatically from the ensemble-averaging process. Also, he found the pitch decreasing with rising temperature, in qualitative agreement with experimental observation on most cholesterics. There do indeed exist certain exceptional cases[7] in which the pitch *increases* with rising temperature. Such cases are hard to understand in terms of Keating's model.

In a previous paper,[8] hereafter referred to as I, we proposed a planar model for cholesteric liquid crystals which in some sense is a synthesis of Goossen's potential model[3] and Keating's kinetic model. By means of a mean-field analysis, we were able to show that the cholesteric phase is a natural product of an orientation-dependent potential which contains chiral contributions, and that even though a decreasing pitch at rising temperature is preferred, other kinds of temperature dependence are also possible under proper conditions. The mechanism proposed for forming cholesterics yields a simple yet coherent picture. On the other hand, there are certain inherent deficiencies in a planar model. The long axis of each molecule is unrealistically restricted to lie in a plane normal to the twist axis. As we know, the molecules should in principle be permitted to rotate freely in space, and at least occasionally swing out of these nematic planes. The removal of this degree of freedom is artificial, in the sense that even if the molecular axes prefer to stay on the nematic planes, the phenomenon should be a *consequence* of theoretical calculations rather than an input to the model. Moreover, the isotropic-cholesteric transition that results from the mean-field analysis on a planar model turns out to be second order, contrary to what is well known experimentally.

In this paper, we present as a continuation of our previous effort an analysis on a three-dimensional model. The theory is a natural generalization of our work on the planar model, but the difficulties mentioned above are completely eliminated.

II. UNIAXIAL MODEL

We shall characterize the configuration of a constituent molecule by its position vector $\vec{r}$ and its

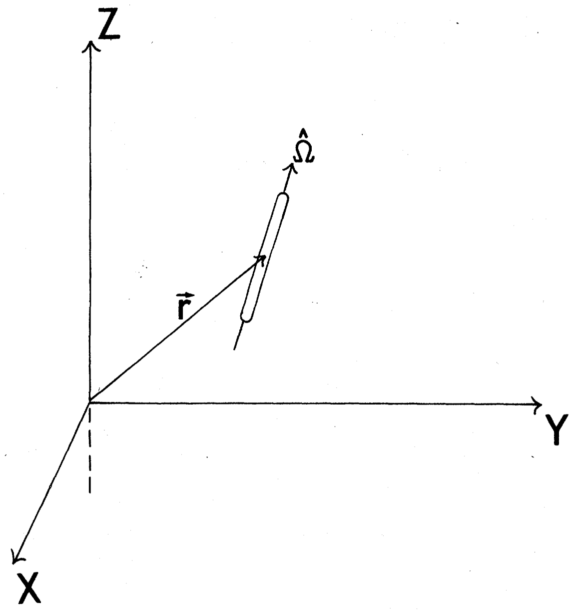

FIG. 1. The geometry. A constituent molecule is at $\vec{r}$, with orientation vector $\hat{\Omega}$.

orientation vector $\hat{\Omega}$. $\hat{\Omega}$ will have two angular components: θ and φ in some fixed coordinate frame as shown in Fig. 1. Thus the molecule possesses cylindrical symmetry. Molecular biaxiality, and therefore phase biaxiality, cannot exist in this model.

We assume the interactions between the molecules to be pairwise:

$$V(1,2)=V(\vec{r}_1,\hat{\Omega}_1;\vec{r}_2,\hat{\Omega}_2)=V(2,1). \tag{1}$$

It is generally believed that permanent dipoles play no essential role in the formation of the nematic phase. We assume that this is equally true for the cholesteric phase. Thus the interaction is symmetric with respect to inversion of molecules about their own centers:

$$\begin{aligned} V(\vec{r}_1,\hat{\Omega}_1;\vec{r}_2,\hat{\Omega}_2) &= V(\vec{r}_1,-\hat{\Omega}_1;\vec{r}_2,\hat{\Omega}_2)\\ &= V(\vec{r}_1,\hat{\Omega}_1;\vec{r}_2,-\hat{\Omega}_2)\\ &= V(\vec{r}_1,-\hat{\Omega}_1;\vec{r}_2,-\hat{\Omega}_2). \end{aligned} \tag{2}$$

Following the consideration of translational and rotational symmetries,[9] V reduces to a function of five variables:

$$V(1,2)=V(r_{12},\hat{\Omega}_1\cdot\hat{r}_{12},\hat{\Omega}_2\cdot\hat{r}_{12},\hat{\Omega}_1\cdot\hat{\Omega}_2,\hat{\Omega}_1\times\hat{\Omega}_2\cdot\hat{r}_{12}), \tag{3}$$

where $r_{12}\equiv|\vec{r}_1-\vec{r}_2|$. Since $|\hat{\Omega}_1\times\hat{\Omega}_2\cdot\hat{r}_{12}|^2$ can be expressed in terms of $\hat{\Omega}_1\cdot\hat{\Omega}_2$, $\hat{\Omega}_2\cdot\hat{r}_{12}$, and $\hat{\Omega}_2\cdot\hat{r}_{12}$, the potential can be decomposed into two parts with no loss of generality:

$$\begin{aligned} V(1,2) &= V_N(r_{12},\hat{\Omega}_1\cdot\hat{r}_{12},\hat{\Omega}_2\cdot\hat{r}_{12},\hat{\Omega}_1\cdot\hat{\Omega}_2)\\ &\quad+(\hat{\Omega}_1\times\hat{\Omega}_2\cdot\hat{r}_{12})V_\chi(r_{12},\hat{\Omega}_1\cdot\hat{r}_{12},\hat{\Omega}_2\cdot\hat{r}_{12},\hat{\Omega}_1\cdot\hat{\Omega}_2). \end{aligned} \tag{4}$$

The lack of symmetry between a molecule and its mirror image defines a chiral molecule. While the appearance of the V_χ term in Eq. (4) manifests what is known as chirality, it is not quite the same thing as calling our molecules chiral. This point was discussed in much detail in I, and will not be dealt with here, suffice it to say that in all except the rarest cases the two usages of "chirality" are equivalent. The V_χ term is crucial in our theory. It vanishes for nonchiral molecules.

A completely general form of $V(1,2)$, with appropriate symmetries, is thus obtained. $\hat{\Omega}_1\cdot\hat{r}_{12}$, $\hat{\Omega}_2\cdot\hat{r}_{12}$, as well as $\hat{\Omega}_1\times\hat{\Omega}_2\cdot\hat{r}_{12}$ represent scalars coupling orientational and spatial variables. At the present stage of development, it is safer and more instructive to work with a model which is more manageable though less general. By dropping the dependence of V_N and V_χ on $\hat{\Omega}_1\cdot\hat{r}_{12}$ and $\hat{\Omega}_2\cdot\hat{r}_{12}$, we take

$$V(1,2)=V_N(r_{12},\hat{\Omega}_1\cdot\hat{\Omega}_2)+(\hat{\Omega}_1\times\hat{\Omega}_2\cdot\hat{r}_{12})V_\chi(r_{12},\hat{\Omega}_1\cdot\hat{\Omega}_2). \tag{5}$$

Up to this point, other than making sure that the spatial nature of the rotation does not affect the arguments employed in I for planar rotations, we have not done anything new. The mathematics that follows will now become more complicated, though still straightforward. Equation (2) requires that V_N be even in $\hat{\Omega}_1\cdot\hat{\Omega}_2$, and V_χ be odd. Expanding both in their arguments, we find

$$V_N(r_{12},\hat{\Omega}_1\cdot\hat{\Omega}_2)=V_0(r_{12})+\sum_{l=1}^{\infty}V_{2l}(r_{12})P_{2l}(\hat{\Omega}_1\cdot\hat{\Omega}_2), \tag{6}$$

and

$$V_\chi(r_{12},\hat{\Omega}_1\cdot\hat{\Omega}_2)=\sum_{l=0}^{\infty}V'_{2l+1}(r_{12})P_{2l+1}(\hat{\Omega}_1\cdot\hat{\Omega}_2). \tag{7}$$

In particular, the truncated forms

$$\begin{aligned} V_N(r_{12},\hat{\Omega}_1\cdot\hat{\Omega}_2) &= V_0(r_{12})+V_2(r_{12})P_2(\hat{\Omega}_1\cdot\hat{\Omega}_2)\\ &\quad+V_4(r_{12})P_4(\hat{\Omega}_1\cdot\hat{\Omega}_2), \end{aligned} \tag{8}$$

and

$$\begin{aligned} V_\chi(r_{12},\hat{\Omega}_1\cdot\hat{\Omega}_2) &= V'_1(r_{12})P_1(\hat{\Omega}_1\cdot\hat{\Omega}_2)\\ &\quad+V'_3(r_{12})P_3(\hat{\Omega}_1\cdot\hat{\Omega}_2) \end{aligned} \tag{9}$$

are rather familiar. V_N, an intermolecular potential that accounts for the formation of the nematic phase, in the form of Eq. (8), was used by Maier and Saupe[10] and other authors[11] offering generalizations of the Maier-Saupe theory. The appearance of V_χ will be shown to distinguish cholesterics from nematics. The V_3' term represents a more natural way to bring in anharmonicity: our extension of an idea due originally to Keating.

III. THEORY

In the statistical mechanics of a classical system, the central quantity is the Helmholtz free energy functional $\mathfrak{F}$. For liquid crystals in the mean-field approximation,[12]

$$\mathfrak{F} = \mathfrak{F}\{f(\vec{r},\hat{\Omega})|T,\rho\} = \mathfrak{F}_0(T,\rho) + \rho kT \int f(\vec{r}_1,\hat{\Omega}_1)\ln 4\pi f(\vec{r}_1,\hat{\Omega}_1)\,d\vec{r}_1\,d\hat{\Omega}_1 + \tfrac{1}{2}\rho^2 \int f(\vec{r}_1,\hat{\Omega}_1) f(\vec{r}_2,\hat{\Omega}_2) V(\vec{r}_1,\hat{\Omega}_1;\vec{r}_2,\hat{\Omega}_2)\,d\vec{r}_1\,d\hat{\Omega}_1\,d\vec{r}_2\,d\hat{\Omega}_2\,, \tag{10}$$

where ρ is the average number density, $\mathfrak{F}_0$ the ideal-gas free energy, and $\rho f(\vec{r},\hat{\Omega})$ the one-particle distribution function (or density function) normalized as follows:

$$\int \rho f(\vec{r},\hat{\Omega})\,d\vec{r}\,d\hat{\Omega} = N\,, \tag{11}$$

N being the total number of particles in the system. The minimization of $\mathfrak{F}$ with respect to $f(\vec{r},\hat{\Omega})$ under the constraint Eq. (11) gives rise to the usual self-consistency equation.[13] The mean field, V_{mf}, is given by the optimum $f(\vec{r},\hat{\Omega})$ through the following Eqs. (12)–(14):

$$\rho f(\vec{r},\hat{\Omega}) = \frac{N}{Z}\exp\left(-\frac{1}{kT}V_{\text{mf}}(\vec{r},\hat{\Omega})\right), \tag{12}$$

$$Z = \int \exp\left(-\frac{1}{kT}V_{\text{mf}}(\vec{r},\hat{\Omega})\right)d\vec{r}\,d\hat{\Omega}\,, \tag{13}$$

$$V_{\text{mf}}(\vec{r}_1,\hat{\Omega}_1) = \rho\int f(\vec{r}_2,\hat{\Omega}_2)V(\vec{r}_1,\hat{\Omega}_1;\vec{r}_2,\hat{\Omega}_2)\,d\vec{r}_2\,d\hat{\Omega}_2\,. \tag{14}$$

In considering cholesterics, we assume that the local molecular arrangement can be described by a distribution function $f(\hat{\Omega}|\vec{r})$, or, to be more specific: $f(\hat{\Omega}|\hat{n}(\vec{r}))$, where $\hat{n}(\vec{r})$ is the local director (direction of the local nematic axis). Based on the concept of a local nematic, we expect that f will possess the following properties.

(i) The local molecular alignment has complete cylindrical symmetry about $\hat{n}(\vec{r})$. In other words,

$$f = f(\hat{n}(\vec{r})\cdot\hat{\Omega})\,. \tag{15}$$

(ii) $\hat{n}$ and $-\hat{n}$ are equivalent, i.e.,

$$f(\hat{n}(\vec{r})\cdot\hat{\Omega}) = f(-\hat{n}(\vec{r})\cdot\hat{\Omega})\,. \tag{16}$$

(iii) The molecular centers of mass are randomly distributed, i.e.,

$$\int \rho f(\hat{n}(\vec{r})\cdot\hat{\Omega})\,d\hat{\Omega} = \rho$$

or

$$\int f(\hat{n}(\vec{r})\cdot\hat{\Omega})\,d\hat{\Omega} = 1\,. \tag{17}$$

(iv) By defining orientational order parameters in the usual way,

$$\sigma_{2l} = \int f(\hat{n}(\vec{r})\cdot\hat{\Omega})P_{2l}(\hat{n}(\vec{r})\cdot\hat{\Omega})\,d\hat{\Omega}\,, \tag{18}$$

f can be expanded in Legendre polynomials; thus

$$f(\hat{n}(\vec{r})\cdot\hat{\Omega}) = \frac{1}{4\pi}\left(1 + \sum_{\substack{l\geq 2\\ \text{even}}}(2l+1)\sigma_l P_l(\hat{n}(\vec{r}),\hat{\Omega})\right). \tag{19}$$

Note that the order parameters do not depend on $\vec{r}$.

In terms of σ_{2l} and $\hat{n}(\vec{r})$, the free energy functional can be expressed as follows:

$$\mathfrak{F}\{f(\vec{r},\hat{\Omega})|T,\rho\} = \mathfrak{F}_0(T,\rho) + 4\pi NkT\int_{-1}^{1}\tfrac{1}{2}f(\cos\psi)\ln 4\pi f(\cos\psi)\,d\cos\psi + U_0 + U_2 + U_4 + U_1' + U_3'\,, \tag{20}$$

where

$$\cos\psi = \hat{n}(\vec{r})\cdot\hat{\Omega}\,, \tag{21}$$

$$U_0 = \tfrac{1}{2}\rho^2\int f(\hat{n}(\vec{r}_1)\cdot\hat{\Omega}_1)f(\hat{n}(\vec{r}_2)\cdot\hat{\Omega}_2)\,V_0(r_{12})\,d\vec{r}_1\,d\hat{\Omega}_1\,d\vec{r}_2\,d\hat{\Omega}_2 = \tfrac{1}{2}\rho^2\int V_0(r_{12})\,d\vec{r}_1\,d\vec{r}_2 = \tfrac{1}{2}N\rho\gamma_0\,, \tag{22}$$

$$\begin{aligned} U_l &= \tfrac{1}{2}\rho^2\int f(\hat{n}(\vec{r}_1)\cdot\hat{\Omega}_1)f(\hat{n}(\vec{r}_2)\cdot\hat{\Omega}_2)\,V_l(r_{12})\,P_l(\hat{\Omega}_1\cdot\hat{\Omega}_2)\,d\vec{r}_1\,d\hat{\Omega}_1\,d\vec{r}_2\,d\hat{\Omega}_2 \\ &= \tfrac{1}{2}\rho^2\sigma_l^2\int V_l(r_{12})P_l(\hat{n}(\vec{r}_1)\cdot\hat{n}(\vec{r}_2))\,d\vec{r}_1\,d\vec{r}_2 = \tfrac{1}{2}N\rho\gamma_l\sigma_l^2 + \tfrac{1}{2}\rho^2\sigma_l^2\int V_l(r_{12})[P_l(\hat{n}(\vec{r}_1)\cdot\hat{n}(\vec{r}_2)) - 1]\,d\vec{r}_1\,d\vec{r}_2\,, \quad l = 2, 4\,, \end{aligned} \tag{23}$$

$$U_l' = \tfrac{1}{2}\rho^2 \int f(\hat{n}(\vec{r}_1)\cdot\hat{\Omega}_1) f(\hat{n}(\vec{r}_2)\cdot\hat{\Omega}_2) V_l'(r_{12})\,(\hat{\Omega}_1\times\hat{\Omega}_2\cdot\hat{r}_{12}) P_l(\hat{\Omega}_1\cdot\hat{\Omega}_2)\, d\vec{r}_1\, d\hat{\Omega}_1\, d\vec{r}_2\, d\hat{\Omega}_2 , \quad l=1,3 .$$

After some lengthy but straightforward algebra, we find

$$U_1' = \tfrac{1}{2}\rho^2\sigma_2^2 \int V_1'(r_{12})[\hat{n}(\vec{r}_1)\times\hat{n}(\vec{r}_2)\cdot\hat{r}_{12}] P_1(\hat{n}(\vec{r}_1)\cdot\hat{n}(\vec{r}_2))\, d\vec{r}_1\, d\vec{r}_2 \tag{24}$$

and

$$\begin{aligned} U_3' = {} & \tfrac{1}{2}\rho^2\sigma_4^2 \int V_3'(r_{12})[\hat{n}(\vec{r}_1)\times\hat{n}(\vec{r}_2)\cdot\hat{r}_{12}]\, P_3(\hat{n}(\vec{r}_1)\cdot\hat{n}(\vec{r}_2))\, d\vec{r}_1\, d\vec{r}_2 \\ & + \tfrac{3}{14}\rho^2(\sigma_4^2-\sigma_2^2) \int V_3'(r_{12})[\hat{n}(\vec{r}_1)\times\hat{n}(\vec{r}_2)\cdot\hat{r}_{12}]\, P_1(\hat{n}(\vec{r}_1)\cdot\hat{n}(\vec{r}_2))\, d\vec{r}_1\, d\vec{r}_2 . \end{aligned} \tag{25}$$

If $\hat{n}(r)$ is a constant unit vector throughout the whole space, then $U_1'=0$, $U_3'=0$, and the free-energy functional reduces to

$$\mathfrak{F} = \mathfrak{F}_1 + \mathfrak{F}_N ,$$

where

$$\mathfrak{F}_1 = \mathfrak{F}_0 + \tfrac{1}{2}N\rho\gamma_0 , \tag{26}$$

$$\begin{aligned} \mathfrak{F}_N = {} & 4\pi NkT \int_{-1}^{1} \tfrac{1}{2} f(\cos\psi) \ln 4\pi f(\cos\psi)\, d\cos\psi \\ & + \tfrac{1}{2}N\rho\gamma_2\sigma_2^2 + \tfrac{1}{2}N\rho\gamma_4\sigma_4^2 . \end{aligned} \tag{27}$$

$$\gamma_l = \int V_l(r)\, d\vec{r} , \quad l=0,2,4 . \tag{28}$$

In this case, the state of the system is either isotropic or nematic. For this reason we separated the total free-energy functional into

$$\mathfrak{F} = \mathfrak{F}_1 + \mathfrak{F}_N + \mathfrak{F}_T ,$$

where $\mathfrak{F}_T$ denotes the distortion energy due to spatial variation of the directors.

In order to carry out the variational program, we proceed with the usual ansatz[14]:

$$\hat{n}(\vec{r}) = (\cos qz, \sin qz, 0) . \tag{29}$$

Such a representation assumes that the director is uniformly twisted along the z axis with a pitch $p=2\pi/q$. Here q will be treated as a variational parameter. Since there is no external field, both the z axis and the origin of the coordinate frame can be chosen at will. If a nontrivial solution, i.e., $q\neq 0$, exists there will of course be an infinite number of degenerate configurations. Equation (29) merely defines a most convenient choice.

Combining Eqs. (23)–(25) we obtain after some algebraic manipulations

$$U_2 = \tfrac{1}{2}N\rho\gamma_2\sigma_2^2 + \tfrac{1}{2}N\rho\sigma_2^2 \int d\vec{r}\, V_2(r)[\tfrac{3}{4}(\cos 2qz - 1)] , \tag{30}$$

$$\begin{aligned} U_4 = {} & \tfrac{1}{2}N\rho\gamma_4\sigma_4^2 \\ & + \tfrac{1}{2}N\rho\sigma_4^2 \int d\vec{r}\, V_4(r)[\tfrac{35}{64}\cos 4qz + \tfrac{20}{64}\cos 2qz - \tfrac{55}{64}] , \end{aligned} \tag{31}$$

$$U_1' = \tfrac{1}{2}N\rho\sigma_2^2 \int d\vec{r}\, V_1'(r)\left(-\frac{1}{2}\,\frac{z}{r}\,\sin 2qz\right) , \tag{32}$$

and

$$\begin{aligned} U_3' = {} & \tfrac{1}{2}N\rho\sigma_4^2 \int d\vec{r}\, V_3'(r)\left(\frac{1}{8}\,\frac{z}{r}\,\sin 2qz - \frac{5}{16}\,\frac{z}{r}\,\sin 4qz\right) \\ & + \tfrac{1}{2}N\rho(\sigma_4^2-\sigma_2^2) \int d\vec{r}\, V_3'(r)\left(-\frac{3}{14}\,\frac{z}{r}\,\sin 2qz\right) . \end{aligned} \tag{33}$$

All these quantities can be written in terms of transforms of the intermolecular potential. It is most convenient to use the following definitions:

$$\lambda_l(Q) \equiv d^3 \int d\vec{\eta}\, V_l(\eta)(\cos Q\zeta - 1) , \quad l=2,4 , \tag{34}$$

$$\mu_m(Q) \equiv d^3 \int d\vec{\eta}\, V_m'(\eta)\frac{\zeta}{\eta}\sin Q\zeta , \quad m=1,3 , \tag{35}$$

where $Q=qd$, $\vec{\eta}=\vec{r}/d$, and $\zeta=z/d$, with d measuring the range of the interaction. Thus, from Eqs. (27) and (30)–(35),

$$\mathfrak{F}_T(Q) = \tfrac{1}{2}N\rho\sigma_2^2 G_2(Q) + \tfrac{1}{2}N\rho\sigma_4^2 G_4(Q) , \tag{36}$$

where

$$G_2(Q) = \tfrac{3}{4}\lambda_2(2Q) - \tfrac{1}{2}\mu_1(2Q) + \tfrac{3}{14}\mu_3(2Q) \tag{37}$$

and

$$G_4(Q) = \tfrac{20}{64}\lambda_4(2Q) + \tfrac{35}{64}\lambda_4(4Q) - \tfrac{5}{56}\mu_3(2Q) - \tfrac{5}{16}\mu_3(4Q) . \tag{38}$$

Or,

$$\begin{aligned} \mathfrak{F} = {} & \mathfrak{F}_1(T,\rho) + 4\pi NkT \int_{-1}^{1} \tfrac{1}{2} f(\cos\psi) \ln 4\pi f(\cos\psi)\, d\cos\psi \\ & + \tfrac{1}{2}N\rho\tilde{\gamma}_2\sigma_2^2 + \tfrac{1}{2}N\rho\tilde{\gamma}_4\sigma_4^2 , \end{aligned} \tag{39}$$

with

$$\tilde{\gamma}_l(Q)=\gamma_l+G_l(Q), \quad l=2,4. \tag{40}$$

This is a form identical to the free-energy functional used for analyzing the nematic phase in the (generalized) Maier-Saupe theory,[10,11] except that the average interaction strengths $\tilde{\gamma}_l$ and the angular variable ψ depend on Q.

As soon as the intermolecular potential is specified, $G_2(Q)$ and $G_4(Q)$ can be evaluated for all values of Q. One can then employ the usual variational procedure[15] to determine the optimum solution(s) by solving a set of self-consistency equations for each Q. The result is

$$f(\cos\psi)=(1/4\pi A)\exp[B_2P_2(\cos\psi)+B_4P_4(\cos\psi)], \tag{41}$$

with A a normalization constant,

$$B_l=-\rho\tilde{\gamma}_l\sigma_l/kT, \quad l=2,4, \tag{42}$$

and σ_l given by Eqs. (18) and (21). Finally, one determines which configuration is thermodynamically stable by comparing the free energies at varying Q. It is interesting to know, for example, how Q (or therefore the cholesteric pitch p) depends on the details of the intermolecular potential.

We learn from experiments that the cholesteric pitch is of macroscopic scale, while the range of the interaction d, is microscopic. For $p=2\pi/q \sim 10^4$ Å, $Q=qd\ll 1$. It is then meaningful to consider a small-Q expansion of Eq. (39). First of all,

$$\lambda_l(Q)=\tfrac{1}{2}\lambda_l''(0)Q^2+O(Q^4), \tag{43}$$

$$\mu_m(Q)=\mu_m'(0)Q+O(Q^3), \tag{44}$$

where

$$\lambda_l''(0)=-d^3\int \zeta^2V_l(\eta)\,d\vec{\eta}, \quad l=2,4, \tag{45}$$

$$\mu_m'(0)=d^3\int\frac{\zeta^2}{\eta}V_m'(\eta)\,d\vec{\eta}, \quad m=1,3. \tag{46}$$

Next, Eqs. (36)–(38) yield

$$\mathfrak{F}_T(Q)=\tfrac{1}{2}N\rho[\tfrac{3}{2}\lambda_2''(0)\sigma_2^2+5\lambda_4''(0)\sigma_4^2][(Q-Q_0)^2-Q_0^2], \tag{47}$$

where

$$Q_0=\frac{\frac{1}{2}\mu_1'(0)\sigma_2^2-\frac{3}{14}\mu_3'(0)\sigma_2^2+\frac{10}{7}\mu_3'(0)\sigma_4^2}{\frac{3}{2}\lambda_2''(0)\sigma_2^2+5\lambda_4''(0)\sigma_4^2}, \tag{48}$$

as resulting from completing squares.

For numerical work, the problem can be solved in two successive steps. As far as the orientational order is concerned, it is totally safe to ignore the Q-dependent distortion energy in our present small-Q regime. Thus the first step is identical to solving the Maier-Saupe equation. After the order parameters σ_l are obtained in this manner, we turn toward the determination of the equilibrium Q by means of Eqs. (47) and (48). This is the second step.

The main conclusions of our analysis are: (i) The isotropic-cholesteric transition is like the isotropic-nematic transition, hence first order. To see this, we note that as far as the orientational order is concerned our treatment is identical to that for the nematic phase. (ii) Since $Q=Q_0$ always minimizes the total free energy when σ_2 and σ_4 do not both vanish, the cholesteric phase is always more stable than the nematic phase. There is no nematic-cholesteric transition. (iii) The cholesteric pitch can be expressed in terms of the order parameters and moments of the chiral contributions in the intermolecular potential.

IV. TEMPERATURE DEPENDENCE OF PITCH

Experiments indicate that there are different types of temperature dependence of the pitch in cholesterics. By means of a simple anharmonic model, we illustrated in I how these different types could emerge from a coherent picture. In addition, we suggested a yet-unobserved kind of temperature dependence—one in which the helical structure would first untwist and then reverse helicity after passing through a divergence in pitch at some definite temperature. In this section, we shall present the results of a more quantitative

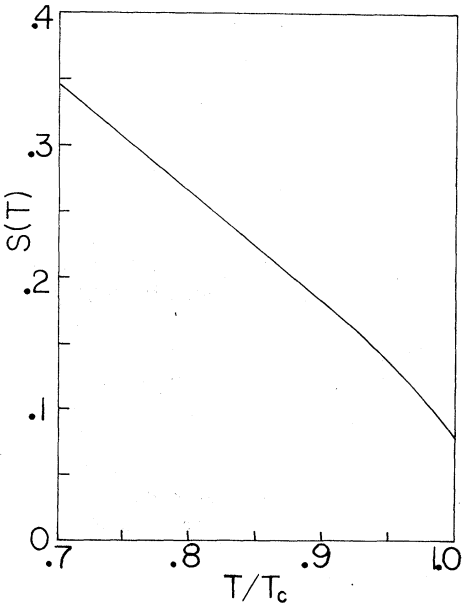

FIG. 2. $S(T)\equiv[\sigma_4(T)/\sigma_2(T)]^2$ as a function of T/T_c. See Eq. (49).

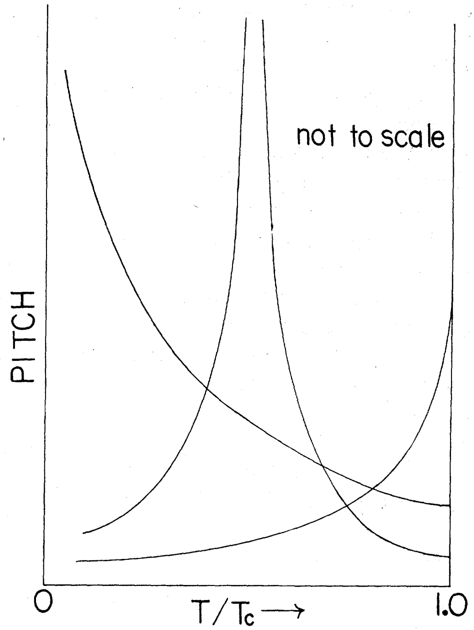

FIG. 3. Representative curves showing various types of temperature dependence of the cholesteric pitch in pure substances.

study using the model described in previous sections.

For simplicity, we ignore higher-order terms in the nematic part of the interaction; i.e., we assume that $\lambda_4''(0) \ll \lambda_2''(0)$. Equation (48) then reads

$$Q_0 = \alpha + \beta S(T), \tag{49}$$

where

$$\alpha = [\tfrac{1}{3}\mu_1'(0) - \tfrac{1}{7}\mu_3'(0)]/\lambda_2''(0), \tag{50}$$

$$\beta = \tfrac{20}{21}\mu_3'(0)/\lambda_2''(0), \tag{51}$$

$$S(T) = [\sigma_4(T)/\sigma_2(T)]^2. \tag{52}$$

According to this picture, then, the temperature dependence of the pitch comes through the temperature dependence of the orientational order parameters. This is most convenient since the function $S(T)$ can be calculated using just the (generalized) Maier-Saupe theory. The results are given in Fig. 2.

Figure 3 shows the different kinds of temperature dependence of the cholesteric pitch. The essential parameter that governs these temperature dependences is the ratio

$$R \equiv \mu_3'(0)/\mu_1'(0). \tag{53}$$

By varying the value of R, cholesterics can be classified into the following categories.

$R \leqslant 0$

(i) $-0.412 < R \leqslant 0$. In this range, the pitch increases with decreasing temperature, and remains finite at all temperatures.

(ii) $-\infty < R \leqslant -0.412$. The pitch increases with decreasing temperature. At certain temperature T_d between 0 and $0.935T_c$, however, the pitch diverges; after which the helicity reverses and the pitch decreases as temperature is lowered further.

$R > 0$

(iii) $0 < R \leqslant 4.861$. The pitch decreases with decreasing temperature, and remains finite at all temperatures.

(iv) $4.861 < R < \infty$. The same phenomenon as in (ii) occurs, except that the pitch diverges at a higher temperature T_d between $0.935T_c$ and T_c.

Case (i) is of course the most familiar in cholesterics. Case (iii) is unusual. It has recently been observed in, e.g., CEEC.[7] We find it possible to fit the experimental data on CEEC rather satisfactorily to our theory. See Fig. 4.

Cases (ii) and (iv) have not been observed[16] in pure cholesterics. We see no fundamental reason why they should not occur in nature. One may argue that the relatively narrow temperature range spanned by the cholesteric phase prevents the phenomenon from taking place. Or nature does not care for large moments in the higher-order parts of the chiral potential. We feel that for reasons of both theoretical understanding and technical applications, such behavior by cholesteric materials is well worth searching for.

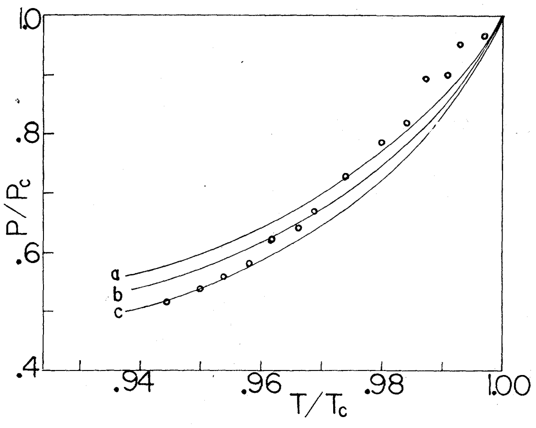

FIG. 4. Temperature dependence of the cholesteric pitch for CEEC. The points denoted by ○ were taken from Ref. 7. The solid lines are theoretical curves with R equal to (a) 2.19, (b) 2.33, (c) 2.50.

V. BINARY CHOLESTERIC MIXTURES

In this section, we generalize the theory presented for a pure cholesteric substance to binary cholesteric mixtures. The generalization is quite straightforward, but the notations are clumsy. The reader will please bear with us until the final lines for a bit of physical insight.

We consider molecular species A and B, a total of N molecules at number density ρ, such that

$$N=N_A+N_B, \quad \text{and} \quad \rho=\rho_A+\rho_B .$$

There are three kinds of intermolecular potentials:

$$V^{\alpha}(1,2)=V_N^{\alpha}(r_{12},\hat{\Omega}_1\cdot\hat{\Omega}_2)+(\hat{\Omega}_1\times\hat{\Omega}_2\cdot\hat{r}_{12})V_{\chi}^{\alpha}(r_{12},\hat{\Omega}_1\cdot\hat{\Omega}_2), \tag{54}$$

where the single index α stands for the paired label (A,A), (B,B), (A,B), or (B,A). Note that $V^{(A,B)}(1,2)=V^{(B,A)}(2,1)$. Expending these potentials in Legendre polynomials as before, and truncating at leading terms, we obtain

$$V_N^{\alpha}(r_{12},\hat{\Omega}_1\cdot\hat{\Omega}_2)=V_0^{\alpha}(r_{12})+V_2^{\alpha}(r_{12})P_2(\hat{\Omega}_1\cdot\hat{\Omega}_2)+V_4^{\alpha}(r_{12})P_4(\hat{\Omega}_1\cdot\hat{\Omega}_2), \tag{55}$$

$$V_{\chi}^{\alpha}(r_{12},\hat{\Omega}_1\cdot\hat{\Omega}_2)=V_1'^{\alpha}(r_{12})P_1(\hat{\Omega}_1\cdot\hat{\Omega}_2)+V_3'^{\alpha}(r_{12})P_2(\hat{\Omega}_1\cdot\hat{\Omega}_2). \tag{56}$$

The calculation begins with the distribution functions

$$f_i=f_i(\hat{n}(\vec{r})\cdot\hat{\Omega}), \tag{57}$$

the normalization conditions

$$\int f_i(\hat{n}(\vec{r})\cdot\hat{\Omega})\,d\hat{\Omega}=1, \tag{58}$$

and the order parameters

$$\sigma_{2l,i}\equiv\int f_i(\hat{n}(\vec{r})\cdot\hat{\Omega})P_{2l}(\hat{n}(\vec{r})\cdot\hat{\Omega})\,d\hat{\Omega}, \tag{59}$$

where i stands for the species label A or B. Note that the order parameters refer to species A and B *in the mixed medium.*

The free-energy functional now takes the form

$$\mathfrak{F}=\mathfrak{F}^{(A)}+\mathfrak{F}^{(B)}+\mathfrak{F}^{(A,B)}, \tag{60}$$

where

$$\mathfrak{F}^{(i)}=\mathfrak{F}_1^{(i)}+\mathfrak{F}_N^{(i)}+\mathfrak{F}_T^{(i)}, \quad i=A \text{ or } B, \tag{61}$$

with $\mathfrak{F}_1^{(i)}$, $\mathfrak{F}_N^{(i)}$, and $\mathfrak{F}_T^{(i)}$ given by Eqs. (26), (27), and (36), except that everywhere in the notations $(\mathfrak{F}_0, N, \rho, \gamma_0, \gamma_2, \gamma_4, f, \sigma_2, \sigma_4, G_2, G_4)$ a label i must now be attached. The defining equations of γ_l, G_2, G_4, λ_l, and μ_m: (28), (37), (38), (34), and (35) are generalized in the same way, with (A,A) or (B,B) placed in the index whenever i calls for A or B, and (A,B) placed in the index for a third class of such functions to be used immediately below:

$$\mathfrak{F}^{(A,B)}=\mathfrak{F}_1^{(A,B)}+\mathfrak{F}_N^{(A,B)}+\mathfrak{F}_T^{(A,B)}, \tag{62}$$

where

$$\mathfrak{F}_1^{(A,B)}=\mathfrak{F}_0^{(A,B)}(T,\rho_A,\rho_B)+\tfrac{1}{2}(N_A\rho_B+N_B\rho_A)\gamma_0^{(A,B)}, \tag{63}$$

$$\mathfrak{F}_N^{(A,B)}=\tfrac{1}{2}(N_A\rho_B+N_B\rho_A)(\gamma_2^{(A,B)}\sigma_{2,A}\sigma_{2,B}+\gamma_4^{(A,B)}\sigma_{4,A}\sigma_{4,B}), \tag{64}$$

$$\mathfrak{F}_T^{(A,B)}=\tfrac{1}{2}(N_A\rho_B+N_B\rho_A)[G_2^{(A,B)}(Q)\sigma_{2,A}\sigma_{2,B}+G_4^{(A,B)}(Q)\sigma_{4,A}\sigma_{4,B}]. \tag{65}$$

The total twist energy is then

$$\begin{aligned}\mathfrak{F}_T&=\mathfrak{F}_T^{(A)}+\mathfrak{F}_T^{(B)}+\mathfrak{F}_T^{(A,B)}\\&=\tfrac{1}{2}N_A\rho_A[\sigma_{2,A}^2G_2^{(A,A)}(Q)+\sigma_{4,A}^2G_4^{(A,A)}(Q)]\\&\quad+\tfrac{1}{2}N_B\rho_B[\sigma_{2,B}^2G_2^{(B,B)}(Q)+\sigma_{4,B}^2G_4^{(B,B)}(Q)]\\&\quad+\tfrac{1}{2}(N_A\rho_B+N_B\rho_A)[\sigma_{2,A}\sigma_{2,B}G_2^{(A,B)}(Q)+\sigma_{4,A}\sigma_{4,B}G_4^{(A,B)}(Q)].\end{aligned} \tag{66}$$

Once again, by carrying out a small-Q expansion and completing the square, we find

$$\mathfrak{F}_T=\tfrac{1}{2}(C_1Q+C_2Q^2)=\tfrac{1}{2}C_2[(Q-Q_0)^2-Q_0^2], \tag{67}$$

with

$$Q_0=-C_1/2C_2, \tag{68}$$

where

$$\begin{aligned}C_1&=N_A\rho_A\{\sigma_{2,A}^2[-\mu_1^{(A,A)\prime}(0)+\tfrac{3}{7}\mu_3^{(A,A)\prime}(0)]-\tfrac{20}{7}\sigma_{4,A}^2\mu_3^{(A,A)\prime}(0)\}\\&\quad+N_B\rho_B\{\sigma_{2,B}^2[-\mu_1^{(B,B)\prime}(0)+\tfrac{3}{7}\mu_3^{(B,B)\prime}(0)]-\tfrac{20}{7}\sigma_{4,B}^2\mu_3^{(B,B)\prime}(0)\}\\&\quad+(N_A\rho_B+N_B\rho_A)\{\sigma_{2,A}\sigma_{2,B}[-\mu_1^{(A,B)\prime}(0)+\tfrac{3}{7}\mu_3^{(A,B)\prime}(0)]-\tfrac{20}{7}\sigma_{4,A}\sigma_{4,B}\mu_3^{(A,B)\prime}(0)\},\end{aligned} \tag{69}$$

and

$$\begin{aligned}C_2&=N_A\rho_A[\tfrac{3}{2}\sigma_{2,A}^2\lambda_2^{(A,A)\prime\prime}(0)+5\sigma_{4,A}^2\lambda_4^{(A,A)\prime\prime}(0)]+N_B\rho_B[\tfrac{3}{2}\sigma_{2,B}^2\lambda_2^{(B,B)\prime\prime}(0)+5\sigma_{4,B}^2\lambda_4^{(B,B)\prime\prime}(0)]\\&\quad+(N_A\rho_B+N_B\rho_A)[\tfrac{3}{2}\sigma_{2,A}\sigma_{2,B}\lambda_2^{(A,B)\prime\prime}(0)+5\sigma_{4,A}\sigma_{4,B}\lambda_4^{(A,B)\prime\prime}(0)].\end{aligned} \tag{70}$$

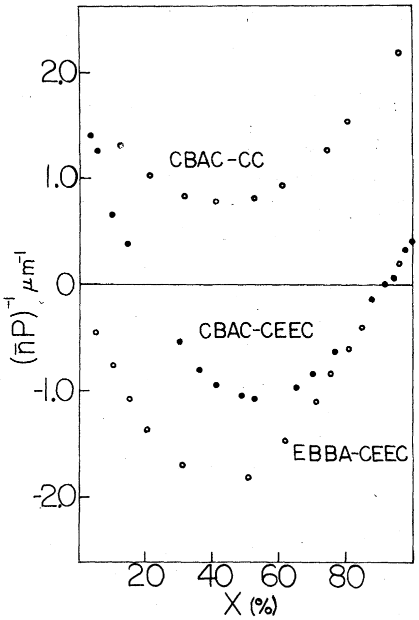

FIG. 5. Typical concentration dependence of the cholesteric pitch in binary cholesteric mixtures, plotted at constant $T - T_c$. $\bar{n}$ is the mean refractive index; P is the cholesteric pitch.

Finally, by defining

$$x \equiv N_B/N, \quad 1 - x \equiv N_A/N, \tag{71}$$

we can rewrite Q_0 as

$$Q_0 = \frac{A_0 + A_1 x + A_2 x^2}{B_0 + B_1 x + B_2 x^2}, \tag{72}$$

with coefficients A's and B's given by complicated expressions extracted from Eqs. (68)-(70).

Equation (72) appears as a quadratic rational fraction in x, but it is not, since the A's and B's depend on the order parameters, which in turn depend on x. However, there are some special circumstances under which the latter dependence can be neglected. We would like to conclude by constructing such a set of conditions.

Let us plot Q_0 versus x. At some concentration x_1, the mixture has a transition temperature $T_c(x_1)$. Let us select a temperature T_1, and enter into the graph a point $Q_0(T_1, x_1)$. Take next another concentration x_2 and its corresponding transition temperature $T_c(x_2)$. Instead of selecting the same temperature T_1, let us select a temperature T_2 such that

$$T_2 - T_c(x_2) = T_1 - T_c(x_1), \tag{73}$$

and enter $Q_0(T_2, x_2)$ into the plot. In this manner we continue to plot $Q_0(T_n, x_n)$ until a curve is obtained for x covering the whole range 0 to 1. Every point on this curve has the same $T - T_c$. Since

$$T/T_c = 1 + (1/T_c)(T - T_c), \tag{74}$$

and $1/T_c$ changes relatively little throughout the range $0 \leq x \leq 1$, our Q_0 curve is essentially done at fixed T/T_c. In the mean-field theory, this corresponds to fixed order parameters, that is, order parameters which are independent of x. Under these conditions, the coefficients A's and B's in Eq. (72) become independent of x_1 and we arrive at a quadratic rational fraction. This is then the molecular basis for the plot in Fig. 5, we obtained by experimenters.[17-19]

Quantitative results for binary mixtures will be reported elsewhere.

Note added in proof. We have recently learned that B. W. Van der Meer, G. Vertogen, A. J. Dekker, and J. G. J. Ypma have independently arrived at some similar conclusions by a different approach [J. Chem. Phys. 65, 3935 (1976)].

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