Fluctuations in the Low-Temperature Phase of a Model Cholesteric Liquid Crystal

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(Received 25 May 1973)

The fluctuations in a generalized version of Lubensky's spin model for cholesterics are shown to still diverge (for an infinite system). The generalization consists in allowing the skew term of the interaction Hamiltonian to include a dependence on the directions of the "short" molecular axes. Some such dependence is expected in molecules of real cholesterics.

INTRODUCTION

It has been found by Lubensky[1-3] that both the usual Frank free energy[4] and a simple spin model for cholesteric liquid crystals imply the absence of long-range *helical* order in an infinite sample. Besides the purely theoretical interest of this question it seems likely that this dephasing of a "cholesteric" has a measurable effect on its optical rotatory power.[1] In this paper the low-temperature phase of a generalization of the spin model introduced by Lubensky is considered. In our model the part of the intermolecular interaction responsible for the twisting of the cholesteric is allowed to depend also on the directions of the "short" molecular axes. It seems clear that some dependence of the interaction potential on the directions of the short molecular axes is to be expected in real cholesterics (e.g., molecules of cholesterics tend to be flatter than molecules of nematics). The question we ask is whether the introduction of this new degree of freedom may help to stabilize the helical structure. The answer, judging from our result, is no. Thus, the present calculation lends additional support to the assumption that the Frank free energy correctly describes fluctuations in a cholesteric.[3]

MODEL

We assume for simplicity that the molecules are at fixed lattice points $\vec{r}$. The directions of the long and short molecular axes are given by unit vectors $\vec{n}(\vec{r})$ and $\vec{n}_s(\vec{r})$, respectively. Two angles specify $\vec{n}$ and an additional angle ν is required for $\vec{n}_s$ ($\vec{n}_s$ is perpendicular to $\vec{n}$). The way ν is defined is indicated in Fig. 1. Either $+\vec{n}_s$ or $-\vec{n}_s$ is above the XY plane; ν is the angle between $\pm\vec{n}_s$ and $0z$ such that $-\frac{1}{2}\pi<\nu<\frac{1}{2}\pi$. An index with two values (one value for $\vec{n}_s$ above and one for $\vec{n}_s$ below the XY plane) completes the specification of a molecule's orientation. However, this index plays no role here because we assume that the system is unchanged under $\vec{n}_s \to -\vec{n}_s$.

The Hamiltonian is taken to be

$$H=-\frac{1}{2}\sum_{r,r'}\vec{n}\cdot[\vec{n}'J(|\vec{r}-\vec{r}'|)+\vec{n}'\times(\vec{r}'-\vec{r})W(n)J_1(|\vec{r}-\vec{r}'|)/a], \tag{1}$$

where

$$W(n)=1-G(n)[(\vec{n}\times\vec{n}')^2-\tfrac{1}{2}(\vec{n}_s\cdot\vec{n}\times\vec{n}')^2-\tfrac{1}{2}(\vec{n}_s'\cdot\vec{n}\times\vec{n}')^2] \tag{2}$$

and $G(n)$ is any well-behaved non-negative function of $\vec{n}\times\vec{n}'$, $\vec{n}\cdot\vec{n}'$, $\vec{n}_s\cdot\vec{n}\times\vec{n}'$, $\vec{n}_s'\cdot\vec{n}\times\vec{n}'$, and $\vec{n}_s\cdot\vec{n}_s'$, symmetric under $\vec{r}\rightleftarrows\vec{r}'$; for example, one can have $G(n)=[(\vec{n}\times\vec{n}')^2+b^2]^{-1}$, $b>0$. Of course, $\vec{n}=\vec{n}(r)$, $\vec{n}'=\vec{n}(r')$, etc. The functions J are positive and have range a. When $G(n)\equiv 0$, H is identical to the interaction Hamiltonian chosen by Lubensky and has the helically ordered ground state[1,2]

$$\vec{n}^0(r)=\cos q_0 z\,\vec{\epsilon}_1+\sin q_0 z\,\vec{\epsilon}_2, \tag{3}$$

where q_0 satisfies

$$J'(q_0)-a^{-1}J_1''(q_0)=0, \tag{4}$$

with $J(q_0)=\sum_r J(r)e^{-i\vec{q}_0\cdot\vec{r}}$ and $\vec{q}_0=q_0\vec{\epsilon}_3$. (No confusion should arise from using the same notation for a function and its Fourier transform.) For $\vec{n}_s$ and $\vec{n}_s'$ in the direction of $\vec{n}\times\vec{n}'$, $W(n)=1$. It will be verified now that the ground state of Eq. (1) is still given by Eq. (3), combined with $\nu(\vec{r})\equiv 0$.

Small deviations of $\vec{n}(r)$ from $\vec{n}^0(r)$ can be written

$$\delta\vec{n}(r)=\vec{n}_\perp^0(r)\,\delta\phi_1(r)+\vec{\epsilon}_3\delta\phi_2(r), \tag{5}$$

where $\vec{n}_\perp^0(r)=\vec{\epsilon}_3\times\vec{n}^0(r)$. It is straightforward to decompose $\pm\vec{n}_s$ along $\vec{\epsilon}_3$, $\vec{n}^0$, $\vec{n}_\perp^0$:

$$\vec{n}_s=\cos\nu\cos\delta\phi_2\,\vec{\epsilon}_3-(\cos\nu\sin\delta\phi_2\sin\delta\phi_1+\sin\nu\cos\delta\phi_1)\vec{n}_\perp^0-(\cos\nu\sin\delta\phi_2\cos\delta\phi_1-\sin\nu\sin\delta\phi_1)\vec{n}^0 \tag{6}$$

(assuming for definiteness that $+\vec{n}_s$ is above the XY plane). Now the function $W(n)$, Eq. (2), is calculated to second order in $\delta\phi_1$, $\delta\phi_2$, and ν:

$$\begin{aligned}\vec{n}\times\vec{n}' &\simeq [\vec{n}^0(1-\tfrac{1}{2}\delta\vec{n}^2)+\delta\vec{n}]\times[\vec{n}^{0\prime}(1-\tfrac{1}{2}\delta\vec{n}'^2)+\delta\vec{n}'] \\ &= \vec{\epsilon}_3[\sin q_0(z'-z)(1+Q_0)+\cos q_0(z'-z)L] \\ &\quad +\vec{\epsilon}_1(\sin q_0 z,\delta\phi_2')_- +\vec{\epsilon}_2(-\cos q_0 z,\delta\phi_2')_-; \\ Q_0 &= \delta\phi_1\delta\phi_1' - \tfrac{1}{2}(\delta\phi_1^2+\delta\phi_1'^2+\delta\phi_2^2+\delta\phi_2'^2), \\ L &= \delta\phi_1' - \delta\phi_1, \\ (f(r),g(r'))_- &\equiv f(r)g(r') - f(r')g(r).\end{aligned} \tag{7}$$

[We only need $(\vec{n}\times\vec{n}')_{1,2}$ up to first order because $(\vec{n}_s)_{1,2}$ already are first order.] Equations (6) and (7) give

$$\begin{aligned}\vec{n}_s\cdot\vec{n}\times\vec{n}' &\simeq \cos\nu\cos\delta\phi_2[\sin q_0(z'-z)(1+Q_0) \\ &\quad +\cos q_0(z'-z)L]+Q_1+Q_2; \\ Q_1 &= (\nu\sin q_0 z - \delta\phi_2\cos q_0 z)(\sin q_0 z,\delta\phi_2')_-, \\ Q_2 &= (-\nu\cos q_0 z - \delta\phi_2\sin q_0 z)(-\cos q_0 z,\delta\phi_2')_-.\end{aligned} \tag{8}$$

Combining Eqs. (7) and (8) we get

$$\begin{aligned}(\vec{n}\times\vec{n}')^2 - (\vec{n}_s\cdot\vec{n}\times\vec{n}')^2 &\simeq (\nu^2+\delta\phi_2^2)\sin^2 q_0(z'-z)+\delta\phi_2^2+\delta\phi_2'^2 \\ &\quad -2\cos q_0(z'-z)\delta\phi_2\delta\phi_2' \\ &\quad -2\sin q_0(z'-z)(Q_1+Q_2).\end{aligned} \tag{9}$$

Using Eq. (9) and

$$Q_1+Q_2 = \nu\delta\phi_2' - \nu\delta\phi_2\cos q_0(z'-z)+\delta\phi_2^2\sin q_0(z'-z),$$

we obtain, to second order,

$$W(n)\simeq 1-G(n^0)F(n), \tag{10}$$

where

$$\begin{aligned}F(n) &= [\tfrac{1}{2}(\nu^2+\nu'^2)\sin^2 x+\tfrac{1}{2}(\delta\phi_2^2+\delta\phi_2'^2)(1+\cos^2 x) \\ &\quad -2\cos x\delta\phi_2\delta\phi_2' - \sin x(\nu\delta\phi_2' - \delta\phi_2\nu') \\ &\quad +\sin x\cos x(\nu\delta\phi_2 - \nu'\delta\phi_2')];\end{aligned} \tag{11}$$

$x = q_0(z'-z)$ and $G(n^0)$ means G evaluated with $\vec{n}=\vec{n}^0$, $\nu=0$, etc. Thus, $G(n^0)$ is a function of $z'-z$. Note that

$$\begin{aligned}F(n) &= \tfrac{1}{2}[\nu\sin x+(\delta\phi_2\cos x-\delta\phi_2')]^2 \\ &\quad +\tfrac{1}{2}[\nu'\sin(-x)+(\delta\phi_2'\cos x-\delta\phi_2)]^2\geq 0.\end{aligned} \tag{12}$$

The Hamiltonian has the expansion, up to second order in $\delta\phi_i$, $i=1,2,3(\delta\phi_3\equiv\nu)$,

$$H\simeq H^0+H',$$

where

$$H' = -\frac{1}{2a}\sum_{r,r'} G(n^0)F(n)J_1(|r-r'|)(\vec{r}-\vec{r}')\cdot\vec{n}^0\times\vec{n}^{0\prime}. \tag{13}$$

$H'\geq 0$ because $(\vec{r}-\vec{r}')\cdot\vec{n}^0\times\vec{n}^{0\prime} = (z-z')\sin x$ and $q_0 a \ll 1$. H^0 does not depend on ν and is simply the expansion of Lubensky's Hamiltonian. Because $F(n)$ contains only quadratic terms in the deviations $\delta\phi_i$, the minimum condition $\delta H=0$ is equivalent to $\delta H^0=0$; therefore, the ground state has $\vec{n}(r)$ given by (3) and $\nu(r)\equiv 0$.

It may be noted that the last term of (11) does not contribute to the double sum of Eq. (13).

ENERGY OF LONG-WAVELENGTH FLUCTUATIONS

The energy necessary to make a small deformation $\delta\phi_i(r)$ away from the ground state can be written

$$H-E_0 = \frac{1}{2}\sum_{r,r'}\delta\phi_\alpha(\vec{r})K_{\alpha\alpha'}(\vec{r},\vec{r}')\delta\phi_{\alpha'}(\vec{r}'), \tag{14}$$

where

$$K(\vec{r},\vec{r}') = K^0(\vec{r},\vec{r}')+K'(\vec{r}-\vec{r}'). \tag{15}$$

The matrix K^0 has $K^0_{\alpha\alpha'}(r,r')=0$, for α or $\alpha'=3$, and carries the contribution from H^0. Its nonvanishing elements are proportional to Eq. (30) of Ref. 2. (Put $\rho^2\langle S\rangle^2=1$ in Ref. 2 to get our K^0.) The matrix K' carries the contribution from H'. We do not bother to give its matrix elements explicitly but only note some properties which are used below: (i) K' is translationally invariant, i.e., $K'=K'(r-r')$; (ii) $K'_{\alpha\alpha'}=0$ for α or $\alpha'=1$; (iii) $K'_{23}(\vec{r})=-K'_{32}(\vec{r})=K'_{32}(-\vec{r})$; $K'_{\alpha\alpha}(\vec{r})=K'_{\alpha\alpha}(-\vec{r})$; (iv) $K'_{33}(\vec{r})\propto\delta_{\vec{r},0}$; (v) $\det K'(0,q_0)=\det K'(0,-q_0)=0$.

To establish relation (v) for the Fourier transform, $K'(k_\perp,k_3)=\sum_{\vec{r}}K'(\vec{r})e^{-i\vec{k}_\perp\cdot\vec{r}_\perp-ik_3 z}$ (the subscript $\perp$ denotes here the component perpendicular to the pitch axis), observe, first of all, that H' can be written in terms of the matrix K' for $\vec{r}$

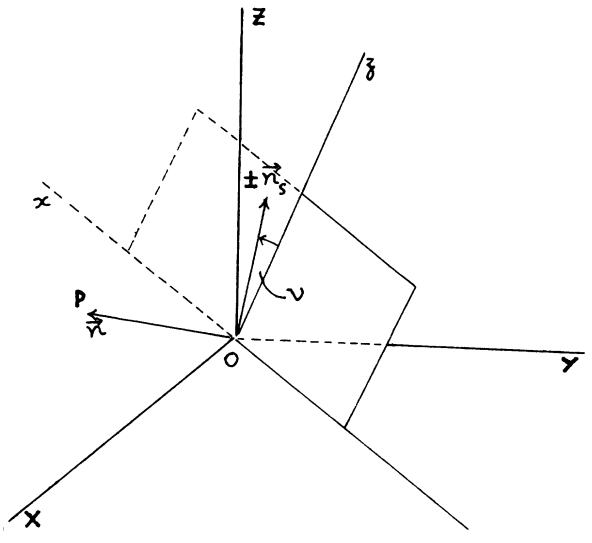

FIG. 1. The plane $x0z$ is perpendicular to $\vec{n}$; $\vec{n}_s$ lies in $x0z$. $0x$ is in the XY plane and $0z$ is in the plane $P0Z$.

and $\vec{r}'$ summed over an arbitrary volume V, provided $V \gg a^3$ (neglecting surface contributions in limit $V \to \infty$). From Eq. (12) it follows that $F(n)=0$ for deformations satisfying

$$\delta\phi_2(\vec{r}') = \mathrm{Re}\, Z\, e^{iq_0 z'},$$
$$\nu(\vec{r}') = \mathrm{Re}\, i\, Z\, e^{iq_0 z'}, \tag{16}$$
$$Z = \delta\phi_2(0) - i\nu(0).$$

Therefore, for deformation (16),

$$0 = \sum_V \sum \delta\phi_\alpha K'_{\alpha\alpha}\, \delta\phi'_{\alpha'}$$
$$= \sum_V \sum \theta_{\alpha s}\, e^{isq_0 z} K'_{\alpha\alpha'}(\vec{r}-\vec{r}')\, \theta_{\alpha' s'}\, e^{is'q_0 z'}$$
$$= \sum_{\vec{r}\ \mathrm{in}\ V} \theta_{\alpha s}\, \theta_{\alpha' s'}\, K'_{\alpha\alpha'}(0, s'q_0)\, e^{iq_0(s+s')z},$$

where $s=+1$, -1 and $\theta_{2+}=\frac{1}{2}Z$, $\theta_{3+}=\frac{1}{2}iZ$, $\theta_{\alpha-}=\theta^*_{\alpha+}$. Because V is arbitrary the coefficients of the three different exponentials $e^{2iq_0 z}$, $e^{-2iq_0 z}$, and 1, must vanish separately

$$\theta_{\alpha+}\theta_{\alpha'+}K'_{\alpha\alpha'}(0,q_0)=0, \tag{17a}$$
$$\theta_{\alpha-}\theta_{\alpha'-}K'_{\alpha\alpha'}(0,-q_0)=0, \tag{17b}$$
$$\theta_{\alpha+}\theta_{\alpha'-}K'_{\alpha\alpha'}(0,-q_0)+\theta_{\alpha-}\theta_{\alpha'+}K'_{\alpha\alpha'}(0,q_0)=0. \tag{17c}$$

Equation (17a) [combined with (iii)] implies (vi), $K'_{22}(0,q_0)=K'_{33}(0,q_0)$. Equation (17c) gives (vii), $K'_{22}(0,q_0)+K'_{33}(0,q_0)+2iK'_{23}(0,q_0)=0$. From (vi) and (vii) one obtains immediately $\det K'(0,q_0)=0$. A similar argument, starting from Eq. (17b), shows $\det K'(0,-q_0)=0$. Relations (vi) and (vii) can easily be checked using explicit expressions for $K'_{\alpha\alpha'}(\vec{r}-\vec{r}')$.

Thermal averages at low temperatures can be evaluated with the help of the Hamiltonian expression (14). It can be shown that

$$\beta\langle\delta\phi_\alpha(\vec{r})\,\delta\phi_{\alpha'}(\vec{r}')\rangle = K^{-1}_{\alpha\alpha'}(\vec{r},\vec{r}') \quad (\beta = 1/k_B T),$$

where K^{-1} is the inverse of the operator K and has the expansion

$$K^{-1}_{\alpha\alpha'}(\vec{r},\vec{r}') = \sum f^*_\alpha(\vec{r};u) f_{\alpha'}(\vec{r}';u)/E_u \tag{18}$$

in terms of the eigenfunctions $f_\alpha(\vec{r};u)$ of K.

$K^0(\vec{r},\vec{r}')$ is translationally invariant in directions perpendicular to the z-axis[1,2] and, therefore, so is $K(\vec{r},\vec{r}')$. Accordingly, the substitution $f(\vec{r}) = e^{i\vec{k}_\perp\cdot\vec{r}_\perp} f(z)$ reduces the problem of finding the eigenfunctions and eigenvalues of K to solving the eigenvalue equation

$$\sum_{z'} K_{\alpha\alpha'}(k_\perp; z, z') f_{\alpha'}(z'; k_\perp, u) = E(k_\perp, u) f_\alpha(z; k_\perp, u), \tag{19}$$

where

$$K(k_\perp; z, z') = \sum_{\vec{r}_\perp} K(\vec{r}_\perp; z, z')\, e^{-i\vec{k}_\perp\cdot\vec{r}_\perp}. \tag{20}$$

The structure of $K(k_\perp)$ is

$$\begin{pmatrix} K_{11}(k_\perp; z-z') & -\frac{1}{2}i(k_+ e^{-iq_0 z} + k_- e^{iq_0 z})\mu(k_\perp; z-z') & 0 \\ \frac{1}{2}i(k_+ e^{-iq_0 z'} + k_- e^{iq_0 z'})\mu(k_\perp; z-z') & K_{22}(k_\perp; z-z') & K'_{23}(k_\perp; z-z') \\ 0 & K'_{32}(k_\perp; z-z') & K'_{33}(k_\perp; z-z') \end{pmatrix}$$

[cf. Eq. (35) of Ref. 2]. As in the Lubensky model this matrix is "almost" translationally invariant. The symmetry operator commuting with $K(k_\perp)$ is in this case $\tilde{\sigma}_3 T_0$, where T_0 is the translation by π/q_0 and

$$\tilde{\sigma}_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

The required functions $f_\alpha(z)$ may be chosen to be eigenfunctions of $\tilde{\sigma}_3 T_0$, i.e. of the form

$$f(z) = e^{ik_3 z} \begin{pmatrix} \sum A_m e^{i2mq_0 z} \\ \sum B_m e^{i(2m+1)q_0 z} \\ \sum C_m e^{i(2m+1)q_0 z} \end{pmatrix} \tag{21}$$

(note that $\tilde{\sigma}_3 T_0$ is norm preserving so that all its eigenvalues have modulus 1; k_3 is real).

Substitution of (21) in (19) yields the following set of equations for the coefficients A, B, and C:

$$[E - K_{11}(2m)]A_m + \tfrac{1}{2}ik_-\mu(2m-1)B_{m-1} + \tfrac{1}{2}ik_+\mu(2m+1)B_m = 0, \tag{22a}$$
$$-\tfrac{1}{2}ik_-\mu(2m+1)A_m - \tfrac{1}{2}ik_+\mu(2m+1)A_{m+1} - K'_{23}(2m+1)C_m + [E - K_{22}(2m+1)]B_m = 0, \tag{22b}$$
$$-K'_{32}(2m+1)B_m + [E - K'_{33}(2m+1)]C_m = 0. \tag{22c}$$

The abbreviations $K(2m) = K(k_\perp, 2mq_0 + k_3)$, etc., have been used. From property (iv) above see that $K'_{33}[k_\perp, (2m+1)q_0 + k_3]$ is independent of $\vec{k}, m$.

Also, as will soon be seen, $E \to 0$ as $k \to 0$. Therefore, $E - K'_{33}(2m+1) \neq 0$ for small k, and (22c) can be used to eliminate C_m from (22b). Eliminating the coefficients B from the remaining two equations gives

$$\{E - K_{11}(2m) - \tfrac{1}{4}k_\perp^2[W(2m-1) + W(2m+1)]\}A_m - \tfrac{1}{4}k_-^2 W(2m-1)A_{m-1} - \tfrac{1}{4}k_+^2 W(2m+1)A_{m+1} = 0, \tag{23}$$

where

$$W(2m+1) = [\mu(2m+1)]^2 / [(E - K_{22}^T(2m+1)], \tag{24}$$

and

$$K_{22}^T(2m+1) = K_{22}(2m+1) - \frac{[K'_{23}(2m+1)]^2}{E - K'_{33}(2m+1)}. \tag{25}$$

The recursion relation (23) has the same form as Eq. (40) of Ref. 2 and can be handled by the technique explained in Morse and Feshbach.[5] One finds that the series in Eq. (21) converge and that $A_{m+1}/A_m = O(k_\perp^2)$, for $m \geq 0$, and $A_{m-1}/A_m = O(k_\perp^2)$ for $m \leq 0$. Taking $m = 0$ in Eq. (23) and dividing by A_0 it follows that

$$E = K_{11}^0(k_\perp, k_3) + \tfrac{1}{4}k_\perp^2[W(0, -q_0) + W(0, q_0)] \tag{26}$$

to $O(k^2)$. From Ref. 2 we get $K_{11}^0(\vec{k}) = \text{const} \times k_3^2 + [\mu(q_0)/2q_0]k_\perp^2$; therefore, Eq. (26) shows that $E \to 0$ as $k \to 0$, as expected. The remaining thing to observe is that $K_{22}^T(0, \pm q_0) = K_{22}^0(0, \pm q_0)$. This holds because, owing to properties (iii) and (v),

$$K'_{22}(0, q_0) + [K'_{23}(0, q_0)]^2 / K'_{33}(0, q_0) = K'_{33}(0, q_0) \det K(0, q_0) = 0,$$

and similarly for $K_{22}^T(0, -q_0) - K_{22}^0(0, -q_0)$. Hence we see that, to $O(k^2)$, Eq. (26) has the same value as in the case $G(n) \equiv 0$ of Refs. 1 and 2, i.e.,

$$E = (\text{const}) \times k_3^2 + O(k_\perp^4). \tag{27}$$

[This is obtained immediately from Eqs. (24) and (26) using $K_{22}^0(0, q_0) = q_0 \mu(q_0)$ and the expression for $K_{11}^0(\vec{k})$ from Ref. 2.]

The eigenfunction corresponding to (27) is

$$f(z) = A_0 e^{ik_3 z} \begin{pmatrix} 1 \\ i\vec{k} \cdot \vec{n}^0(z)/q_0 \\ -i\vec{k} \cdot \vec{n}_\perp^0(z)/q_0 \end{pmatrix}.$$

[Use Eqs. (22) and $\pm K'_{23}(0, \pm q_0) = -iK'_{33}(0, q_0)$.] Thus, our result can be summarized as follows: For $\delta\phi_2(\vec{r}) \equiv 0$, a fluctuation $\nu(\vec{r})$ costs an energy $\propto \sum \nu(\vec{r})^2$; but, by keeping a definite relation between $\nu(\vec{r})$ and $\delta\phi_2(\vec{r})$ [cf. also Eq. (16)], the system can have deformations $\nu(\vec{r})$ which, to $O(k^2)$, do not raise its energy.

In conclusion, it has been shown that the form of the fluctuation spectrum in Lubensky's model is maintained when the interaction includes a model dependence on the short molecular axes. The form of this spectrum implies that there is no long-range order in ϕ_1, although the corresponding correlation length, for real cholesterics, is of astronomical magnitude.[3]

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