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Low-Temperature Phase of Infinite Cholesterics*

T. C. Lubensky
Physics Department, University of Pennsylvania, Philadelphia, Pennsylvania 19104
(Received 31 May 1972)

Fluctuations are shown to dephase an infinite cholesteric to a state in which the molecules are aligned preferentially in a plane perpendicular to a pitch axis, but in which all angles in that plane are probed with equal probability. Correlation functions in this state are calculated.

It has been known for some time that infinite two-dimensional systems with a continuous symmetry group cannot exhibit long-range order.[1-3] Nevertheless, high-temperature expansions indicate that there is a phase transition between the isotropic high-temperature and the strongly locally ordered low-temperature phases.[4-6] The nature of the low-temperature phase is now understood, and techniques for calculating correlation functions in this phase exist.[7,8] Recently it was discovered that cholesteric liquid crystals exhibit the same instability with respect to fluctuations in three dimensions that continuous symmetry-group systems exhibit in two dimensions.[9,10] In this Letter, we propose to investigate the properties of the low-temperature phase of an infinite cholesteric. We will rely heavily on the techniques developed by Berezinskii in Ref. 7.

The cholesteric state is characterized by a helical ordering of long barlike molecules. This order is described mathematically by a symmetric traceless tensor whose principal axis rotates in a helical pattern along a pitch axis. To keep the discussion as simple as possible, we will consider a classical spin system with a helical ground state produced by short-range forces as a model for a cholesteric liquid crystal. The spin Hamiltonian we choose is

$$H=-\tfrac{1}{2}\sum_{r,r'} J_{ij}(\vec{r}-\vec{r})n_i(\vec{r})n_j(\vec{r}'), \qquad (1)$$

where

$$J_{ij}(\vec{r}-\vec{r}')=J(|\vec{r}-\vec{r}'|)\delta_{ij}-a^{-1}J_1(|\vec{r}-\vec{r}'|)\epsilon_{ijk}(\vec{r}-\vec{r}')_k,$$

a is the distance between nearest-neighbor spins, and $n_i(\vec{r})=(\cos\varphi_2\cos\varphi, \cos\varphi_2\sin\varphi, \sin\varphi_2)$. Equation (1) is represented as a sum over spin sites which can be either at discrete lattice points or continuously distributed in space. The ground state of this Hamiltonian corresponds to a helical ordering of the classical spins,

$$n_i^0(\vec{r})=(\cos q_0 z, \sin q_0 z, 0), \qquad (2)$$

with energy

$$E_0=-\tfrac{1}{2}N[J(q_0)-a^{-1}J_1'(q_0)],$$

where

$$J(q_0)=\sum_r J(|\vec{r}|)\exp(i\vec{q}_0\cdot\vec{r})$$

and q_0 satisfies

$$J'(q_0)-a^{-1}J_1''(q_0)=0.$$

z is along an arbitrarily chosen pitch axis $\vec{p}$ ($\vec{p}$ is a unit vector). An expansion of Eq. (1) in terms of the gradients of $n_i(\vec{r})$ yields an expression equivalent to the Frank free energy with equal elastic constants.[11] Correlation functions for small deviations from this ground state have been calculated in

Refs. 9 and 10. Let small changes of $n_i(\vec{r})$ from $n_i^0(\vec{r})$ be represented by

$$\delta n_i(\vec{r}) = [-\delta\varphi_1(\vec{r})\sin q_0 z,\ \delta\varphi_1(\vec{r})\cos q_0 z,\ \delta\varphi_2(\vec{r})], \tag{3}$$

where $\varphi_1(\vec{r}) = \varphi(\vec{r}) - q_0 z$. The Hamiltonian Eq. (1) can be expressed for small $\delta\varphi_1(\vec{r})$ and $\delta\varphi_2(\vec{r})$ as

$$H - E_0 = \tfrac{1}{2}\int d^3r \int d^3r'\, \delta\varphi_\alpha(\vec{r}) K_{\alpha\alpha'}(\vec{r}, \vec{r}\,') \delta\varphi_{\alpha'}(\vec{r}\,'), \tag{4}$$

where α and α' are summed over the indices 1 and 2, and $K_{\alpha\alpha'}(\vec{r}, \vec{r}\,')$ is a 2×2 kernel which can be expressed in terms of $J_{ij}(\vec{r}, \vec{r})$ and $\vec{n}^0(\vec{r})$. $K_{\alpha\alpha'}(\vec{r}, \vec{r}\,')$ is translationally invariant for directions perpendicular to $\vec{p}$ and periodic with period $2\pi/q_0$ for directions parallel to $\vec{p}$. The two-point correlation functions for $\varphi_\alpha(\vec{r})$ are

$$\langle \delta\varphi_\alpha(\vec{r})\delta\varphi_{\alpha'}(\vec{r}\,')\rangle = k_B T \sum_n \int \frac{d^3k}{(2\pi)^3} \frac{\xi_\alpha^*(\vec{k}, n, \vec{r})\xi_{\alpha'}(\vec{k}, n, \vec{r}\,')}{E_n(\vec{k})}, \tag{5}$$

where $\xi_\alpha(\vec{k}, n, \vec{r})$ and $E_n(\vec{k})$ are, respectively, the eigenfunctions and eigenvalues of the kernel K. $\vec{k}$ is restricted to the first Brillouin zone along the z axis, and n is a zone index. The energy of the lowest branch with corresponding eigenfunctions is

$$E_0(\vec{k}) = K(k_3^{\,2} + \xi^2 k_\perp^{\,4}), \quad \xi(\vec{k}, 0, \vec{r}) = e^{i\vec{k}\cdot\vec{r}} \begin{bmatrix} 1 \\ i(\vec{k}_\perp/q_0)\cdot\vec{n}^0(\vec{r}) \end{bmatrix}, \tag{6}$$

where $\xi^2 = \frac{3}{8}q_0^{\,-2}$ and $K = \frac{1}{4}\rho a^2 |J''(0)|$, with ρ the number of spins per unit volume. K is the Frank elastic constant and is equal in order of magnitude to $k_B T_c/a$, where T_c is the transition temperature. The absence of a $k_\perp^{\,2}$ term in $E_0(k)$ leads to fluctuations in $\varphi_1(r)$ which become arbitrarily large at large separations. Letting $g(\vec{r}, \vec{r}\,') = \frac{1}{2}\langle|\varphi_1(\vec{r}\,') - \varphi_1(\vec{r}\,')|^2\rangle$, we find

$$g(\vec{r}, \vec{r}\,') = \frac{k_B T}{K}\int \frac{d^3k}{(2\pi)^3} \frac{1 - e^{i\vec{k}\cdot\vec{r}}}{k_3^{\,2} + \xi^2 k_\perp^{\,4}} \sim \alpha \ln R(|\vec{r} - \vec{r}\,'|_\perp, |z - z'|) + \gamma\left(\frac{\xi|z - z'|}{|\vec{r} - \vec{r}\,'|_\perp^{\,2}}\right), \tag{7}$$

where

$$R(\vec{r}_\perp, |z|) = |z|/\xi + r_\perp^{\,2}/\xi^2, \quad \alpha = aT/2\pi\xi T_c \sim 10^{-2}T/T_c.$$

This is the same type of logarithmic dephasing which occurs in two-dimensional systems with a continuous symmetry group. It leads to a destruction of long-range order in infinite systems.

In the above long-range order was assumed and used in the calculation of the energy spectrum. The form of the energy spectrum then implied that long-range order does not exist at finite temperature. In order to calculate correlation functions at finite temperature, we need an expression for the energy of the system which is independent of any choice of ground state. To arrive at this expression, we first argue that long-wavelength fluctuations are responsible for the destruction of long-range order; therefore, all interesting information will be contained in an expansion of the Hamiltonian in terms of gradients of φ_1 and φ_2. The lowest-order term in such an expansion is

$$\begin{aligned} H - E_0 &= \tfrac{1}{2}K\int d^3r\,(\nabla_i n_j \nabla_i n_j + 2q_0\vec{n}\cdot\nabla\times\vec{n} + q_0^{\,2}) \\ &= \tfrac{1}{2}K\int d^3r\,(\nabla_i\varphi_1\nabla_i\varphi_1 + \nabla_i\varphi_2\nabla_i\varphi_2 - 2q_0\vec{e}_2\cdot\nabla\varphi_2 + 2q_0\varphi_2\vec{e}_1\cdot\nabla\varphi_1 + q_0^{\,2}\varphi_2^{\,2}), \end{aligned} \tag{8}$$

where $\vec{e}_1$ and $\vec{e}_2$ are mutually orthogonal unit vectors which describe the molecular orientation

$$\vec{e}_1 = [\cos(q_0 z + \varphi_1), \sin(q_0 z + \varphi_1), 0], \quad \vec{e}_2 = [\sin(q_0 z + \varphi_1), -\cos(q_0 z + \varphi_1), 0]. \tag{9}$$

Remember that φ_1 depends on $\vec{r}$ in the above. At zero temperature, in the ground state, φ_1 is a constant. φ_1 and φ_2 can be varied independently. We therefore expect there to be two different types of local distortions having different energies. Furthermore, we would expect the energies of these distortions to reflect locally the energy spectrum calculated for small deviations from the ground state [Eq. (6)]. In particular, the lowest-energy distortion should have energy proportional to gradients of some variable with no term proportional to $\nabla_\perp^{\,2}$. The $\nabla_\perp^{\,2}$ disappears because of a cancelation in energy between φ_1 and φ_2 distortions. In other words, there is a particular relationship between φ_1 and φ_2 in the lowest-energy branch. We can guess at the proper relation between φ_1 and φ_2 from the eigenfunction, Eq. (6). If $\vec{n}^0(\vec{r})$ in Eq. (6) is interpreted to be the direction of local alignment $\vec{e}_1(\vec{r})$ in the plane perpendicular to $\vec{p}$, Eq. (6) says

$$\varphi_2(\vec{r}) = -q_0^{-1}\vec{e}_1(\vec{r})\cdot\nabla\varphi_1 = -q_0^{-1}\nabla\cdot\vec{e}_2(\vec{r}). \tag{10}$$

When this form of $\varphi_2(\vec{r})$ is inserted into Eq. (8), the $|\nabla_\perp\varphi_1|^2$ contribution to the energy vanishes for spatial variations slow on a scale of q_0. In order to obtain the $|\nabla_\perp{}^2\varphi_1|^2$ term, it is necessary to relate φ_2 to higher derivatives of φ_1. This is an extremely tedious but performable task. An alternative approach to finding the appropriate relation between φ_1 and φ_2 would be to minimize the local energy with respect to φ_2 for arbitrary φ_1. Armed with this information, we introduce a new variable

$$\varphi_2'(\vec{r}) = \varphi_2(\vec{r}) + q_0^{-1}\vec{e}_1\cdot\nabla\varphi_1 + O(\nabla^3\varphi_1), \tag{11}$$

where the terms proportional to $\nabla^3\varphi_1$ are those which give the correct $|\nabla_\perp{}^2\varphi_1|^2$ term to the energy. The Hamiltonian expressed in terms of $\varphi_2'(\vec{r})$ and $\varphi_1(\vec{r})$ is then

$$H - E_0 = \tfrac{1}{2}K\int d^3r\left[|\nabla_3\varphi_1|^2 + \xi^2|\nabla_\perp{}^2\varphi_1|^2 + q_0{}^2|\varphi_2'|^2 + |\vec{\nabla}\varphi_2'|^2\right]. \tag{12}$$

Terms of order $(\nabla\varphi_1)^3$ and higher have been neglected in Eq. (12). There may also be a term proportional to $\varphi_2'\nabla^3\varphi_1$, which has been neglected. (The terms proportional to $\varphi_2'\nabla\varphi_1$ vanish identically.)

The Hamiltonian is now in a form which allows a direct application of the techniques developed by Berezinskii. First note that φ_1 and φ_2' are independent and appear quadratically in the Hamiltonian. Also note that the $q_0{}^2|\varphi_2'|^2$ term serves to keep φ_2 near zero. Hence $\langle\cos\varphi_2(\vec{r})\rangle$ is nonzero. Now consider φ_1. If we interpret Eq. (12) to allow for variations of φ_1 between $+\infty$ and $-\infty$, we can calculate the generating function for periodic functions of φ_1,

$$\left\langle\exp\left[i\sum_k m_k\varphi_1(\vec{r}_k)\right]\right\rangle = \exp\left[-\tfrac{1}{2}\sum_{k,k'} m_k m_{k'} G(\vec{r}_k,\vec{r}_{k'})\right], \tag{13}$$

where m_k is an integer and

$$G(\vec{r},\vec{r}\,') = -g(\vec{r},\vec{r}\,') - \alpha\ln Aq_0L, \tag{14}$$

with A some constant and L the length of the sample. The single-point probability function is

$$P(\varphi_1,\vec{r}) = (2\pi)^{-1}\textstyle\sum_m \exp(-im\varphi_1)\exp[-m^2G(\vec{r},\vec{r})/2]. \tag{15}$$

Since $G(\vec{r},\vec{r})$ becomes infinite as $L\to\infty$, the only term that remains in the sum is $m=0$, and $P(\varphi,\vec{r})$ is isotropic. In other words, $\langle n_x(\vec{r})\rangle$ and $\langle n_y(\vec{r})\rangle$ are zero even though $\langle\cos\varphi_2\rangle$ is nonzero. The infinite cholesteric state is, therefore, one in which the molecules remain preferentially in a plane perpendicular to the pitch axis, but probe with equal probability all angles in that plane at each point in space.

The two-point probability function $P(\varphi_1,\vec{r};\varphi_1',\vec{r}\,')$ can also be calculated from Eq. (13). In the double sum over m and m' in the expression for $P(\varphi_1,\vec{r};\varphi_1',\vec{r}\,')$, there is a term proportional to $(m+m')^2\times\ln Aq_0L$ which requires m to equal $-m'$. Hence,

$$\begin{aligned}P(\varphi_1,\vec{r};\varphi_1',\vec{r}\,') &= (2\pi)^{-2}\textstyle\sum_m \exp[im(\varphi_1-\varphi_1')]\exp[-m^2g(\vec{r},\vec{r}\,')]\\ &= (2\pi)^{-2}\textstyle\sum_m \exp[im(\varphi_1-\varphi_1')]R^{-\alpha m^2};\end{aligned} \tag{16}$$

using the definition of $\varphi_1(r)$ below Eq. (3), we obtain

$$\begin{aligned}\langle n_x(\vec{r})n_x(\vec{r}\,')\rangle = \langle n_y(\vec{r})n_y(\vec{r}\,')\rangle &= \tfrac{1}{2}\langle\cos\varphi_2\rangle^2\cos q_0(z-z')R^{-\alpha},\\ \langle n_y(\vec{r})n_x(\vec{r}\,') = -\langle n_x(\vec{r})n_y(\vec{r}\,')\rangle &= \tfrac{1}{2}\langle\cos\varphi_2\rangle^2\sin q_0(z-z')R^{-\alpha}.\end{aligned} \tag{17}$$

Note that the Fourier transforms of the correlation functions are peaked at $\vec{q}=\vec{q}_0$ as is to be expected. Correlations in φ_2' die off exponentially with distance. However, because of the finite projection of φ_2 onto φ_1, correlations in φ_2 die off algebraically with distance. For example,

$$\begin{aligned}\langle\sin\varphi_2(\vec{r})\sin\varphi_2(0)\rangle \sim \langle\varphi_2(\vec{r})\varphi_2(0)\rangle &= q_0^{-2}\nabla_i\nabla_j'\langle e_{2i}(\vec{r})e_{2j}(0)\rangle\\ &= \frac{2\alpha}{\xi}\langle\cos\varphi_2\rangle^2\cos q_0(z-z')R^{-(1+\alpha)}\left[\left(1+\frac{r_\perp{}^2}{\xi|z|}\right)^{-1} - \alpha\left(1+\frac{\xi|z|}{r_\perp{}^2}\right)^{-1}\right].\end{aligned} \tag{18}$$

Experimental observation of the dephased cholesteric state will probably be extremely difficult because of the finite size of laboratory samples. The distance required for complete dephasing is astronomical, of the order of 10^{50} km.[9] It may, however, be possible to mimic an infinite sample by sandwiching a cholesteric between two fluids of greater and lesser density. This would allow the phase to fluctuate freely at the fluid interfaces rather than being pinned to some container surface. A calculation of the rotary power of the dephased state is currently under way. It is probable that the rotary power of the dephased cholesteric will be proportional to $L^{1-\alpha}$ rather than L as in a completely ordered cholesteric. This difference may be measurable.

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Experimental Test of the Linearized Boltzmann Equations for Mixtures Using Sound Dispersion*

Manuel Fuentes Losa and James D. Foch, Jr.
Department of Aerospace Engineering Sciences, University of Colorado, Boulder, Colorado 80302

(Received 12 June 1972)

Measurements of the initial frequency dependence (dispersion) of the velocity of sound in gaseous helium-argon mixtures are in good agreement with predictions based on the linearized Boltzmann equations. The dispersion shows a pronounced dependence on mole fraction, and this effect can probably be exploited to determine the interaction between different noble-gas atoms.

It has been shown elsewhere on theoretical grounds that measurements of the frequency dependence of the speed of sound in binary mixtures of noble gases should provide a sensitive test of the linearized Boltzmann equations.[1] The main purpose of this Letter is to report the results of such measurements, and to point out that the measurements can also be used to determine the potential parameters for interaction between atoms of different noble gases. Although sound-dispersion measurements have been reported for pure noble gases by other investigators,[2,3] we believe the present dispersion measurements are the first for any mixture of noble gases.

The frequency dependence of the phase velocity U in a binary mixture of noble gases can be expressed in the form

$$u_0/u = 1 - d_2(x, T)(f/p)^2 + d_4(x, T)(f/p)^4 + \cdots, \quad (1)$$

where u_0 is the low-frequency (Laplace) speed of sound, x is the mole fraction of the heavier species, T is the absolute temperature, f is the frequency, and p is the pressure. The use of a macroscopic theory (linearized Navier-Stokes equations) to calculate d_2, d_4, etc., yields quite different results than the use of a microscopic theo-