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A model of a liquid crystal

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A model of a liquid crystal composed of ordered "liquid columns" is considered. The character of the phase transition from the solid crystal to this mesophase (H_1) and of the further transitions to the nematic liquid crystal and the isotropic liquid is considered. A simple molecular model with a crystal—H_1—isotropic-liquid phase diagram is proposed.

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1. Very recently, Chandrasekhar *et al.*[1] have studied the phase diagrams of hexaphenyl n-alkonates. A characteristic feature of these compounds is the disk-like shape of the molecules. The thermodynamic, optical, and x-ray studies of the mesophase carried out in Ref. 1 permit us to propose the following structure for it; two-dimensional hexagonal ordering of the centers of mass of the molecules, but absence of translational order in the direction perpendicular to these layers. Schematically, such a structure can be represented in the form of "liquid" columns of disk-shaped molecules, packed in a hexagonal lattice (the ratio of the diameter of the "disk" to its thickness is ~6–7). Since, in the sense of its elastic properties, such a mesophase is similar to the anisotropic "solid" mesophase of the H type (but, possibly, does not coincide with it), henceforth we shall designate this phase as H_1.

It should be noted that the above interpretation of the x-ray patterns and optical textures[1] is not, of course, unique. Therefore, it is necessary to study other properties of this mesophase. The present paper is devoted to an analysis of the possible features of the H_1 phase. The characteristics of the H_1 mesophase in the vicinity of the transitions to the solid-crystalline, ordinary nematic, and isotropic phases are considered in the framework of the Landau theory. It is especially necessary to mention the transition to the crystalline phase. According to the Landau theory (see below), the crystallization of the H_1 phase is a rare example in which the phase transition of complete solidification can be a second-order transition.

In the three alkonates studied in Ref. 1 the nematic phase was absent; in principle, however, the situation with a nematic phase should also be investigated. In the Appendix we consider a simple molecular model with a crystal—H_1—isotropic-liquid phase diagram. It should also be emphasized that the heats of the crystal—H_1-phase and H_1-phase—isotropic-liquid transitions (~10 kcal/mole) are greater by at least an order of magnitude than the characteristic heats of transitions from a nematic liquid crystal to an isotropic liquid. Therefore, in its narrow range of existence (of the order of a few degrees), the nematic phase might not be distinguished by the calorimetric method of Ref. 1.

In Sec. 2 of the paper we study the phase transition from the solid-crystalline phase to the intermediate, H_1 phase. We use de Gennes' model[2] of the nematic–smectic-A liquid-crystal phase transition. The condition that the two-dimensional lattice be rigid requires that the Frank constant K_{11} become infinite. This condition ($K_{11}\to\infty$, and not $K_{11}\to 0$ as in the de Gennes model) removes the divergences (characteristic for the smectic phases) of the fluctuations of the order parameter (in agreement with the well known Landau-Peierls theorem[3]).

In Sec. 3 we consider certain properties of the H_1 phase—in particular, the spectrum of the low-frequency

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(hydrodynamic) normal modes.

Section 4 is devoted to a description of the possible phase transition from the H_1 state to the nematic liquid crystal. If this phase transition is almost second-order, then, in the nematic phase in the critical region, because of fluctuations of the H_1 order parameter, an increase of the Frank constant K_{11} (but not of K_{22} and K_{33} as in a transition to a smectic phase) should be observed. In the same section the transition from the H_1 phase to the isotropic liquid is briefly considered.

In conclusion (Sec. 5), some experiments that could elucidate the nature of the H_1 phase of the liquid crystal are proposed.

2. We shall consider the free energy of the H_1 phase. The density in this state is modulated in accordance with the two-dimensional hexagonal order:

$$\rho=\rho_\perp f(x,y),$$

$$f(x,y)=\sum_i \cos \mathbf{p}_i\mathbf{r}_\perp, \quad \sum_i \mathbf{p}_i=0, \quad \mathbf{r}_\perp=(x,y); \quad i=1,2,3, \tag{1}$$

where $\rho_\perp$ is a coefficient with the dimensions of density. In the perpendicular direction (z) there is no periodicity. The transition to the solid-crystalline phase implies the appearance of periodicity in this direction also. If the period along the z axis is equal to d, in place of (1) we can write

$$\rho=\rho_\perp f(x,y)+\chi, \quad \chi={}^1/_2[\psi\exp(iq_0z)+\psi^*\exp(-iq_0z)], \tag{2}$$

where $q_0=2\pi/d$.

In the H_1 phase $\chi=0$, but if the transition to the crystalline state is almost second-order, then, in the vicinity of the transition, ψ is small and (in the spirit of the Landau theory) we can expand the free energy in a series in χ:

$$F=\int d^3r\left\{a|\chi|^2+b|\chi|^4+c_\perp\left[\left|\frac{d\chi}{dx}\right|^2+\left|\frac{d\chi}{dy}\right|^2\right]+c_\parallel\left|\frac{d\chi}{dz}\right|^2\right\}, \tag{3}$$

where $a=\alpha(T-T^*)$, and b, $c_\perp$, and $c_\parallel$ are constants. Formally, (3) is equivalent to the free-energy expression used to describe the nematic-smectic-A transition. However, there is an important difference, associated with the different symmetry of the H_1 phase. To better emphasize this difference, it is convenient to introduce the orientational degrees of freedom directly into (3). As is well known, in its most general form the orientational order parameter of a liquid crystal is specified as follows:

$$Q_{\alpha\beta}=s_1(n_\alpha n_\beta-{}^1/_3\delta_{\alpha\beta})+s_2(m_\alpha m_\beta-{}^1/_3\delta_{\alpha\beta})+s_3(n_\alpha m_\beta+n_\beta m_\alpha), \tag{4}$$

where $\mathbf{n}$ and $\mathbf{m}$ are the unit vectors specifying the orientations of the long axes of the molecules ($\mathbf{n}$) and of the planes in which they are situated ($\mathbf{m}$); s_i are the corresponding order parameters.

Bearing in mind the experimental situation of Ref. 1, we put $s_1=0$ (there is no ordering of the long axes) and $s_3=0$ (the molecules are nonpolar). The unit vector $\mathbf{m}$ is analogous to the director in ordinary nematic liquid crystals. Any deformation of the field $\mathbf{m}$ gives rise to an increase of the energy. Obviously, the corresponding expression for the elastic energy coincides with the Frank energy:

$$F_y=\int d^3r\{{}^1/_2K_{11}(\operatorname{div}\mathbf{m})^2+{}^1/_2K_{22}(\mathbf{m}\operatorname{rot}\mathbf{m})^2+{}^1/_2K_{33}[\mathbf{m}\operatorname{rot}\mathbf{m}]^2\}. \tag{5}$$

The minimization of (5) corresponds to the nematic phase of the disk-shaped molecules, when the orientation of the planes in which the molecules lie is ordered. However, the symmetry of the H_1 phase imposes certain restrictions on the formula (5). The point is that the formation of a two-dimensional lattice in the planes orghogonal to $\mathbf{m}$ implies that the flux of the vector $\mathbf{m}$ through an arbitrary surface is fixed. In other words, the rigidity of the two-dimensional lattice implies the condition

$$\operatorname{div}\mathbf{m}=0. \tag{6}$$

To fulfill the requirement (6) it is necessary to put $K_{11}=\infty$ in the functional (5).

Physically, the condition $\operatorname{div}\mathbf{m}=0$ simply correspond to the fact that the rigidity of the lattice is considerably greater than the rigidity against bend and twist deformations of the "liquid" columns.

Introducing a natural system of coordinates, with one of the axes (z) along $\mathbf{m}$, we can rewrite (3) in the form

$$F=\int d^3r\{a|\chi|^2+b|\chi|^4+c_\perp([\mathbf{m}\nabla]\chi)^2+c_\parallel((\mathbf{m}\nabla)\chi)^2\}. \tag{7}$$

The fluctuations of χ are now connected with the fluctuations of $\mathbf{m}$ and are determined from (7) and (5) under the condition (6).

With allowance for what has been said above, the total free energy F_0 takes the form

$$F_0=\int d^3r\left\{\tilde{a}|\psi|^2+\frac{1}{2}\tilde{b}|\psi|^4+\frac{c_\perp}{2}[|(\nabla_\perp-iq_0\delta\mathbf{m})\psi|^2]+\frac{c_\parallel}{2}\left|\frac{d\psi}{dz}\right|^2+\frac{1}{2}K_{22}(\mathbf{m}_0\operatorname{rot}\delta\mathbf{m})^2+\frac{1}{2}K_{33}[\mathbf{m}_0\operatorname{rot}\delta\mathbf{m}]^2\right\}, \tag{8}$$

where

$$\tilde{a}={}^1/_2a+{}^1/_2c_\parallel q_0^2, \quad \tilde{b}={}^1/_2b, \quad \mathbf{m}=\mathbf{m}_0+\delta\mathbf{m}, \quad \mathbf{m}_0\delta\mathbf{m}=0,$$

and we have gone over to the complex order parameter ψ in the long-wavelength limit (i.e., it is assumed that the characteristic wave vectors of the fluctuations of the order parameter are much smaller than q_0).

The subsequent calculations are analogous to those performed in Ref. 2 for the nematic-smectic-A transition. Naturally, the conclusions about the fluctuational growth of K_{22} and K_{33}, and other consequences stemming from the analogy with superconductivity, are also the same. There is only one difference, associated with the presence of the condition (6) in the H_1 phase.

Following Ref. 2, we introduce explicitly the transverse part of $\delta\mathbf{m}$:

$$\delta\mathbf{m}-\mathbf{A}=\nabla L, \tag{9}$$

and transform the order parameter accordingly:

$$\Phi=\psi\exp(-iq_0L). \tag{10}$$

Because of the Gaussian character of the fluctuations, we have

$$\langle\psi^*(\mathbf{r})\psi(0)\rangle=\langle\Phi^*(\mathbf{r})\Phi(0)\rangle\exp\{-{}^1/_2q_0^2\langle[L(\mathbf{r})-L(0)]^2\rangle\}. \tag{11}$$

The correlator of the longitudinal part $L(\mathbf{r})$ can be found easily from the expansion (8). If we consider the nematic–smectic-A transition (i.e., we keep the term $\sim K_{11}$), we have, in the Fourier components $\mathbf{q}=(\mathbf{q}_\perp, q_z)$,

$$\langle L(\mathbf{q})L(-\mathbf{q})\rangle=\frac{T}{2c_\perp q_0^2|\Phi|^2q_z^2+K_{11}q_\perp^4}. \tag{12}$$

The logarithmic dependence of the correlator $\langle[L(\mathbf{r})-L(0)]^2\rangle$ and the power dependence of $\langle\psi^*(\mathbf{r})\psi(0)\rangle$ follow from formula (12) (in the ordered phase) in the usual way. In the H_1 phase, however, $K_{11}\to\infty$ and $\langle[L(\mathbf{r})-L(0)]^2\rangle\to 0$. Therefore, there are no divergences (in agreement with the Landau–Peierls result[3]). The divergence of (12) is associated with the longitudinal part of $\delta\mathbf{m}$ and, as was pointed out above, is absent in the H_1 phase. The correlator of the transverse part is finite:

$$\langle A_i(q)A_j(-q)\rangle=\frac{T(\delta_{ij}+q_iq_j/q^2)}{{}^1\!/_2c_\perp q_0^2|\Phi|^2q_\perp^2+K_{33}q_z^4}$$

(cf. Ref. 3).

We note that, numerically, the fluctuations of ψ depend only slightly on the size of the modulus K_{11}. The character of these dependences can be understood, e.g., in terms of the Ginzburg–Landau parameter $\varkappa$. For $K_{11}=\infty$ (the H_1 phase), we have

$$\varkappa=\frac{0.89}{q_0}\frac{(\tilde{b}K_{33})^{1/2}}{(c_\parallel c_\perp^5)^{1/6}}\left(\frac{K_{22}}{K_{33}}\right)^{1/3},$$

while for $K_{11}=0$ (the nematic–smectic-A transition),

$$\varkappa=\frac{0.89}{q_0}\frac{(\tilde{b}K_{33})^{1/2}}{(c_\parallel c_\perp^5)^{1/4}}\left(\frac{K_{33}}{K_{22}}+\frac{c_\parallel}{c_\perp}\right)^{-1/2}.$$

If the anisotropy of the "effective masses" is large ($c_\parallel/c_\perp\gg K_{33}/K_{22}$), the Ginzburg–Landau parameter for $K_{11}=0$ is substantially smaller than that for $K_{11}=\infty$. In accordance with this, the transition to the ordered state (with $K_{11}=\infty$) would be closer to a second-order phase transition. The experimental data of Ref. 1 indicate the opposite, and this implies that $K_{33}/K_{22}\sim c_\parallel/c_\perp$.

In reality, the phase transition can be classified as first-order not only on account of the above mentioned fluctuation mechanism (i.e., the interaction of ψ with the gauge field $\delta\mathbf{m}$) but also on account of striction effects of various kinds. We shall not investigate this question in more detail.

3. We shall consider certain properties of the H_1 phase. The elastic orientational energy in this state is given by the formulas (5) and (6). In addition, since there is a two-dimensional lattice in the surface perpendicular to $\mathbf{m}$, its deformations are determined by the corresponding displacement $\mathbf{u}\ (u_x, u_y, 0)$. The elastic energy of such a deformation is specified by the free energy

$$\begin{gathered}W_1={}^1\!/_2B_{11}(u_{xx}^2+u_{yy}^2)+B_{12}u_{xx}u_{yy}+(B_{11}-B_{12})u_{xy}^2,\\ u_{xx}=\frac{\partial u_x}{\partial x},\quad u_{yy}=\frac{\partial u_y}{\partial y},\quad u_{xy}=\frac{1}{2}\left(\frac{\partial u_x}{\partial y}+\frac{\partial u_y}{\partial x}\right).\end{gathered} \tag{13}$$

If we take into account the bulk compressibility of the system, we must add to (13) the term

$$W_2={}^1\!/_2A\Theta^2, \tag{14}$$

where $\Theta=-\rho(u_{xx}+u_{yy}+u_{zz})$; u_z is the displacement along $\mathbf{m}_0$. Taking into account also that the condition $\operatorname{div}\mathbf{m}=0$ leads to the relationships

$$\delta m_x=-\frac{\partial u_y}{\partial z},\quad \delta m_y=\frac{\partial u_x}{\partial z}, \tag{15}$$

we can transform (5) to the following form:

$$W_3=\frac{1}{2}K_{33}\left\{\frac{\partial^2u_x}{\partial z^2}+\frac{\partial^2u_y}{\partial z^2}\right\}^2$$

(for nonpolar media the term with K_{22} gives no contribution). Finally, we have the following expression for the total elastic energy (consistent with the requirements of the Landau–Peierls theorem[3]):

$$\begin{aligned}W_0&=\frac{1}{2}C_{11}(u_{xx}^2+u_{yy}^2)+C_{12}u_{xx}u_{yy}+(C_{11}-C_{12})u_{xy}^2\\&+\frac{1}{2}C_{33}u_{zz}^2+C_{13}u_{zz}(u_{xx}+u_{yy})+\frac{1}{2}K_{33}\left\{\frac{\partial^2u_x}{\partial z^2}+\frac{\partial^2u_y}{\partial z^2}\right\}^2,\end{aligned} \tag{16}$$

where $C_{11}=B_{11}+A\rho^2$, $C_{12}=B_{12}+A\rho^2$, and $C_{33}=C_{13}=A\rho^2$.

We note that, in an ordinary crystal with uniaxial symmetry, $C_{33}\neq C_{13}$ and, in addition, there is a modulus C_{55} (in the standard notation for the moduli, C_{55} is the coefficient of $u_{xz}^2+u_{yz}^2$).

With neglect of the dissipation, three gapless acoustic modes follow from (16). However, the velocities $v_{1,2,3}$ of the modes depend on the orientation of their wave vector with respect to the symmetry axes of the system. If we introduce a polar frame with axis $\mathbf{m}_0$, then

$$\omega_{1,2,3}=v_{1,2,3}(\theta,\varphi)q. \tag{17}$$

In the general case the expressions for $v_{1,2,3}$ are very cumbersome and we shall not give them. If, however, $C_{11}\ll C_{33}$, then, in first order in the ratio $\delta=C_{11}/C_{13}$,

$$\begin{gathered}v_1=(C_{33}/\rho)^{1/2}(1+\delta\cos^2\theta),\\ v_{2,3}=(C_{33}\delta/\rho)^{1/2}\sin\theta\cos\theta f_{2,3}(\varphi),\end{gathered} \tag{18}$$

where the function $f_{2,3}(\varphi)$ is determined by the two-dimensional symmetry of the lattice, and, in the given case (a hexagonal lattice), depends weakly on φ. The formulas (18) are fulfilled qualitatively for arbitrary values of the parameter δ. The first mode corresponds to ordinary sound in a liquid (with a weakly anisotropic velocity), and the other two (in a smectic there is only one additional mode!) correspond to deformational vibrations of the planar lattice (in which the volume is practically unchanged). The velocity of these modes depends strongly on the polar angle θ, vanishing at $q_z=0$ and $q_\perp=0$.

Thus, in the sense of the elastic properties, the H_1 phase is analogous to a "real" three-dimensional crystal (in a general direction $\mathbf{q}$) and possesses three acoustic modes. In this, the H_1 phase differs from smectic-A liquid crystals, in which, in the general case, there are only two acoustic modes.

This character of the acoustic spectrum is manifested in features of the light scattering. The cross section for scattering into unit solid angle by fluctuations $\langle u_x^2\rangle$ and $\langle u_y^2\rangle$ is determined in the usual way:

$$\frac{d\sigma}{d\Omega}=\frac{\omega^4}{16\pi^2}\langle\delta\varepsilon_{ik}\delta\varepsilon_{ml}\rangle p_ip_m'p_kp_l', \tag{19}$$

where $\mathbf{p}$ and $\mathbf{p}'$ are the polarizations of the incident and scattered beams. The fluctuations $\delta\varepsilon_{ik}$ of the dielectric permittivity are, in turn, related to fluctuations of the displacement:

$$\delta\varepsilon_{ik}=Mu_{ik}. \tag{20}$$

Thus, the scattering intensity for polarizations **p** and **p′** in the plane perpendicular to **m** is, according to (19), (20), and (16), equal to

$$I=\frac{M^2\omega^4}{16\pi^2}\frac{Tq_\perp^2}{C_{11}q_\perp^2+K_{33}q_z^4} \ . \tag{21}$$

It is interesting to note that the scattering does not have the character of critical opalescence—in fact, I is small in the entire region of existence of the H_1 phase. This is also reflected in the fact that there is no singularity in the longitudinal scattering (unlike in degenerate systems of the type of nematic and smectic liquid crystals[4]).

4. Formally, the treatment is Sec. 2 of the paper can also be generalized to the case of the phase transition to the nematic liquid crystal. The density is now given not by (2) but by the formula

$$\rho=\rho_0+\psi_1 f(x, y), \tag{22}$$

where ψ_1 is the complex order parameter of the H_1 phase (in the nematic phase, $\psi_1=0$), while $f(x,y)$ is determined by the periodicity of the two-dimensional lattice and, in hexagonal symmetry, is given by formula (1).

In analogy with the derivation of (8), in the vicinity of the transition from the nematic to the H_1 phase we can write

$$F=\int d^3r\left\{a|\psi_1|^2+\frac{1}{2}b|\psi_1|^4+c_\perp\left[\left|\frac{d\psi_1}{dx}\right|^2+\left|\frac{d\psi_1}{dy}\right|^2\right]\right.$$
$$+c_\parallel\left|\left[\frac{d}{dz}-i(\mathbf{p}_0\delta\mathbf{m})\right]\psi_1\right|^2+\left[\frac{1}{2}K_{11}(\operatorname{div}\delta\mathbf{m})^2\right.$$
$$\left.\left.+\frac{1}{2}K_{22}(\mathbf{m}_0\operatorname{rot}\delta\mathbf{m})^2+\frac{1}{2}K_{33}[\mathbf{m}_0\operatorname{rot}\delta\mathbf{m}]^2\right]\right\}\ ; \tag{23}$$

here, $\mathbf{p}_0$ is a vector in the xy plane, with components (p_0, p_0), where p_0 is the modulus of the reciprocal-lattice vector.

The free energy (23) describes the transition from the nematic to the H_1 phase. We shall discuss only one consequence of this transition—the fluctuational increase of the modulus K_{11}. Physically, this increase is entirely understandable. In fact, if the phase transition between H_1 and the nematic liquid crystal is almost second-order, fluctuational clusters of the H_1 phase already appear in the nematic region. These clusters cannot make a contribution to a deformation with div $\delta\mathbf{m}=0$, and so correspond to an effective increase of the modulus K_{11}.

The effect is easy to estimate. The energy required for a deformation in a region of H_1 phase of the order of the coherence length ξ is found from (23):

$$\delta F\sim c_\parallel|\psi_1|^2\delta m^2p_0^2\xi^3.$$

Such a fluctuation corresponds to an increase of the elastic constant K_{11}:

$$\delta K_{11}\sim c_\parallel|\psi_1|^2\xi^2p_0^2.$$

But it follows from (23) that $a|\psi_1|^2\xi^3\sim T$, from which we finally obtain

$$\delta K_{11}\sim c_\parallel p_0^2T\xi. \tag{24}$$

For a more exact calculation of δK_{11} we can use the method of response functions.[5] It is convenient to introduce a molecular field acting on $\delta\mathbf{m}$ as a result of the fluctuations of ψ_1:

$$\delta F=-\int d^3r\,\mathbf{h}\delta\mathbf{m}. \tag{25}$$

The formulas (25) and (23) define the molecular field **h**. The mean value $\langle\mathbf{h}\rangle$ is related to the small deformation $\delta\mathbf{m}$ by the response function:

$$\langle\mathbf{h}\rangle=Q\delta\mathbf{m}. \tag{26}$$

From (26) and (23) we find

$$Q(q)=c_\parallel\frac{p_0^2}{T}\int\frac{d^3\varkappa}{(2\pi)^3}\varkappa_z^2\left\langle\left|\psi_1\left(\varkappa-\frac{\mathbf{q}}{2}\right)\right|^2\right\rangle\left\langle\left|\psi_1\left(\varkappa+\frac{\mathbf{q}}{2}\right)\right|^2\right\rangle. \tag{27}$$

In formula (27) the "four-particle" fluctuations have been approximately decoupled: $\langle\psi_1^*\psi_1\psi_1^*\psi_1\rangle\to\langle|\psi_1|^2\rangle\langle|\psi_1|^2\rangle$.

On the other hand, from the Frank energy we have

$$h_x=-K_{11}q_x^2\delta m_x. \tag{28}$$

Calculating Q in (27) in the limit $q\xi\ll 1$, we obtain

$$Q=\frac{4Tp_0^2}{(2\pi)^3\xi_\perp}\int d^3\varkappa\frac{\varkappa_z^2}{[1+(\varkappa+\mathbf{q}/2)^2][1-(\varkappa-\mathbf{q}/2)^2]}. \tag{29}$$

A simple transformation in (29) gives

$$Q=-\frac{Tp_0^2}{24\pi\xi_\perp}\xi_\parallel^2q_x^2,$$

i.e.,

$$\delta K_{11}=\frac{Tp_0^2}{24\pi}\frac{\xi_\parallel^2}{\xi_\perp}. \tag{30}$$

The formula (30) agrees with the estimate (24).

If we had a second-order phase transition, it would be possible to determine the critical indices from the symmetry of the order parameter. In the given case (as for the transition from the solid crystal to the H_1 phase) there is one complex order parameter. Thus, the indices coincide with the corresponding quantities in the phase transition in helium.

5. In principle, the effects considered in the preceding sections can be used to identify the H_1 phase. The fluctuational increase of the modulus K_{11} in the transition from the nematic to the H_1 phase seems to be particularly promising in this respect. The measurement of K_{11} is easily carried out in the standard way by the Frederiks effect in the appropriate geometry.[2] Analogous measurements in the H_1 phase would make it possible to determine the fluctuational increase of the moduli K_{22} and K_{33} in the transition to the solid crystal. In this case, direct measurements of the scattered-light intensity will be more convenient, possibly, than static experiments on the Frederiks effect. As shown in Sec. 3, the acoustic properties of the H_1 phase also differ substantially from the analogous properties of nematic and smectic liquid crystals. In particular, the Brillouin scattering can give a pattern with three, two, or

one maximum, depending on the orientation of the liquid crystal.

In conclusion, we shall discuss also one of the possible reasons why the transition from the H_1 phase may occur directly to the isotropic liquid (as indicated by the experimental data of Ref. 1) and not to the nematic liquid crystal. The characteristics of the transition are determined by the expansion (23) with $K_{11}=0$. Fluctuations of **m** lead to a shift of the transition temperature (renormalization of the coefficient a):

$$a'=a+c_{\parallel}p_0^2\delta m^2, \tag{31}$$

or

$$T_c=T^*+c_{\parallel}p_0^2\delta m^2. \tag{32}$$

Thus, fluctuations of **m** lead to an increase of the temperature of the transition from the H_1 phase to the nematic phase. For sufficiently large coefficients $c_{\parallel}$ and p_0^2 (and "not very large" Frank constants K_{22} and K_{33}), T_c may be found to be already in the region of stability of the isotropic phase.

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APPENDIX

It is interesting to consider, on some simple model, what are the requirements on the interaction for a solid-crystal—H_1-phase—isotropic-liquid phase diagram to be realized. In the usual way, we assume an anisotropic pair interaction:

$$W_{12}=W_0(r_{12})+W_2(r_{12})P_2(\cos\theta_{12}), \tag{A.1}$$

where r_{12} is the distance between the centers of mass of the molecules, θ_{12} is the angle between the normals to the planes of the molecules, and P_2 is a Legendre polynomial. We shall use this kind of expansion for the two-particle correlation function g:

$$g=g_0(r_{12})+g_2(r_{12})P_2(\cos\theta_{12}). \tag{A.2}$$

If we confine ourselves to just the lowest Fourier components of the interaction, in the self-consistent field approximation we have the usual equation for the distribution function ρ_1 (Ref. 6):

$$\begin{aligned}\ln\Lambda\rho_1=&\alpha_0+2\alpha_1 f(x,y)\sigma+\beta_0P_2(\cos\theta)s\\&+2\beta_1P_2(\cos\theta)f(x,y)\eta.\end{aligned} \tag{A.3}$$

Here,

$$\alpha_0=-\frac{1}{vT}\int d^3r\left[W_0g_0+\frac{1}{5}W_2g_2\right],$$

$$\beta_0=-\frac{1}{vT}\int d^3r\left[W_2g_0+W_0g_2+\frac{2}{7}W_2g_2\right],$$

$$\alpha_1=-\frac{1}{vT}\int d^3r\left[W_0g_0+\frac{1}{5}W_2g_2\right]\exp\left(-\frac{2\pi ix}{a}\right),$$

$$\beta_1=-\frac{1}{vT}\int d^3r\left[W_2g_0+W_0g_2+\frac{2}{7}W_2g_2\right]\exp\left(-\frac{2\pi ix}{a}\right);$$

$v\sim a^3$ is the volume of the unit cell, σ is the translational order parameter (i.e., $\langle f(x,y)\rangle$), s is the orientational order parameter (i.e., $\langle P_2(\cos\theta)\rangle$), η is a mixed order parameter (i.e., $\langle f(x,y)P_2(\cos\theta)\rangle$), and Λ is the normalization constant. It is easily calculated from (A.3):

$$\Lambda=\int_0^1 du\exp(\alpha_0+s\beta_0P_2(u))I_0^2[2\sigma\alpha_1+2\eta\beta_1P_2(u)], \tag{A.4}$$

where I_0 is a modified Bessel function.

Provided that $\sigma\neq 0$, we have a solid two-dimensional crystal; when $s\neq 0$ we have a nematic liquid crystal, and $\eta\neq 0$ corresponds to the H_1 phase. Thus, for a phase diagram without a nematic region to exist it is necessary that we have $\beta_0=0$ and $\alpha_1=0$ in the interaction. After this, we have the following equation for the order parameter η:

$$\eta=\int_0^1 P_2(u)I_0\left[\frac{\eta}{2\beta_1}P_2(u)\right]I_1\left[\frac{\eta}{2\beta_1}P_2(u)\right]du\left(\int_0^1 du\,I_0^2\left[\frac{\eta}{2\beta_1}P_2(u)\right]\right)^{-1}; \tag{A.5}$$

here, β_1 plays the role of the dimensionless temperature; $I_1(z)=dI_0(z)/dz$. The equation (A.5) can be solved only numerically. There exists a critical value β_{1c} such that for $\beta_1>\beta_{1c}$ we have three solutions of (A.5): One root ($\eta_1=0$) corresponds to the isotropic liquid, and the other two ($\eta_{2,3}\neq 0$) correspond to the H_1 phase. At the lower of the two roots η_2 and η_3 the thermodynamic potential $\delta\Phi=-T\ln\Lambda$ has a maximum, while at the higher root it has a minimum. The phase transition from the H_1 phase to the isotropic liquid is a first-order transition. We shall not give more-detailed calculations. We merely point out the critical value of the parameter:

$$\beta_{1c}=0.147.$$

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