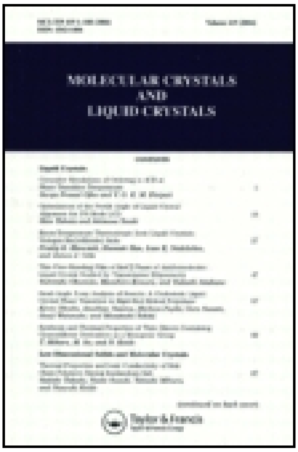

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SPATIAL DIMENSIONALITY OF A LIQUID CRYSTAL LATTICE

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Abstract The principal importance of uniaxial orientational order of anisotropic molecules in forming bulk phases with an effectively reduced spatial dimensionality of the crystal lattice is shown. The conditions under which such phases are formed in liquid crystals are determined within the framework of the Landau theory of weak crystallization. The peculiarities of the nematic molecular ordering observed in liquid crystal mesophases are explained.

Keywords: phase transitions, mesophases, crystal lattice, weak crystallization, liquid crystals, spatial dimensionality of a crystal lattice

INTRODUCTION

Liquid crystal mesophases represent a unique example of a bulk system with an effectively reduced spatial dimensionality of the crystal lattice. Along some of the spatial directions such phases display the properties of a crystal, while in other spatial directions they have the properties of a liquid.

The effective reduction of the spatial dimensionality of the crystal lattice in LC is related directly to two experimental observations: "weakness" of the transitions of the crystallization to the mesophases and the presence of rather strong orientational order of anisotropic molecules in the mesophases. The phase transitions are "weak" in the sense that the latent heats corresponding to them are, at least, an order of magnitude lower than the latent heats of an ordinary crystallization. The phenomenological theory [1], which ignores interaction of the lattice with orientational degrees of freedom of anisotropic molecules, predicts a "weak" crystallization to a three-dimensional BCC lattice. We show that predictions of the theory of a "weak" crystallization can change qualitatively when the interaction of a lattice with orientational nematic order is taken into account and that, in addition to crystallization to a BCC lattice, a crystallization to a one-dimensional (1D) lattice and two-dimensional hexagonal (Hex) lattice can take place. A crystallization of this type is possible because a BCC lattice does not interact with a uniaxial orientation order because of its symmetry, but 1D and Hex lattices are involved in such interactions. Bulk phases with effectively reduced spatial dimensionality of the crystal lattice appear at the point where the energy of this interaction is of order of (or more than) the lattice energy. For this situation to occur, the crystal lattice must be quite "weak" and the uniaxial orientational order of anisotropic molecules must be quite strong. This situation is specific to liquid crystals, which are unique in this sense.

WEAK LANDAU CRYSTALLIZATION

A crystallization gives rise to an increment $\delta\rho(\vec{r})$ to the homogeneous density of a fluid whose symmetry coincides with the symmetry of a crystal lattice. A Fourier expansion of this quantity

$$\delta\rho(\vec{r}) = \sum_{\vec{q}_i} \rho_{\vec{q}_i} \exp i\vec{q}_i\vec{r} \qquad (1)$$

is performed in reciprocal-lattice vectors $\vec{q}_i$ .In the Landau theory[1], the quantities $\rho_{\vec{q}_i}$ are order parametrs. A corresponding expansion of the free energy has the form:

$$F_{cr} = \frac{1}{2} \sum_{\vec{q}_i} \left[\Delta + \xi_o^2 (|\vec{q}_i| - q_o)^2 \right] |\rho_{\vec{q}_i}|^2 \qquad (2)$$

$$+ \frac{\gamma}{3!} \sum_{\vec{q}_i, \vec{q}_j} \rho_{\vec{q}_i} \rho_{\vec{q}_j} \rho_{-\vec{q}_i-\vec{q}_j} + \frac{\lambda}{4!} \sum_{\vec{q}_i, \vec{q}_j, \vec{q}_k} \rho_{\vec{q}_i} \rho_{\vec{q}_j} \rho_{\vec{q}_k} \rho_{-\vec{q}_i-\vec{q}_j-\vec{q}_k}$$

$$+ \ldots ,$$

where q_o is the length of one of the 2N shortest (fundamental) reciprocal-lattice vectors, ξ_0 is the direct-correlation length, and $\Delta = (T-T_c)/T_c$ is a dimensionless deviation from the bare critical temperature. A "weak" cristallization corresponds to expansion (2) where higher order terms labelled by dots are omitted.

If $q_o^2 \xi_o^2 \gg \gamma^2/\lambda$ (in LC this inequality generally holds, since $q_o \xi_o \simeq 1$ and γ^2/λ is small for weak transition: $\gamma^2/\lambda \ll 1$), the contribution of higher harmonics in the lattice energy can be neglected. Then the summation in (2) is over only the shortest wave vectors $\vec{q}_{oi}$ and the free energy of the possible structures is easily calculated [2]. An instability of the isotropic liquid with respect to a one-dimensional lattice (N = 1), a hexagonal lattice (N = 3, the vectors $\vec{q}_{oi}$ form a regular triangle) and a BCC lattice (N = 6, the vectors $\vec{q}_{oi}$ form a regular tetrahedron) occurs respectively when

$$\Delta_{1D}^{(0)} = 0 \; ; \quad \Delta_{Hex}^{(0)} = \frac{4}{45}\,\frac{\gamma^2}{\lambda} \; ; \quad \Delta_{BCC}^{(0)} = \frac{16}{135}\,\frac{\gamma^2}{\lambda} \; .$$

The inequality

$$\left[\, \Delta_{1D}^{(0)} ; \; \Delta_{Hex}^{(0)} \,\right] \le \Delta_{BCC}^{(0)} \tag{3}$$

guarantees the weak crystallization to BCC lattice, if a lattice does not interact with other degrees of freedom [2-9].

WEAK CRYSTALLIZATION IN THE CASE OF AN INTERACTION OF A LATTICE WITH ORIENTATIONAL NEMATIC ORDER

We shall show that inequality (3) may be violated if a crystal lattice interacts with the orientational nematic order of anisotropic molecules.

Nematic order is described by a traceless symmetric tensor $Q_{\alpha\beta}$. The corresponding free energy, which must be added to (2) in order to obtain the mesophase energy, is [4]:

$$\delta F = -\, h_{\alpha\beta}Q_{\alpha\beta} + \frac{\tau}{2} Q_{\alpha\beta}Q_{\alpha\beta} + \frac{r_o^2}{2} \vec{\nabla} Q_{\alpha\beta} \vec{\nabla} Q_{\alpha\beta}$$

$$+ \frac{\gamma_{Nem}}{3!} Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \frac{\lambda_{Nem}}{4!} (Q_{\alpha\beta}Q_{\alpha\beta})^2 \quad , \qquad (4)$$

where $\tau = (T-T_*)/\ T_*$ is a dimensionless deviation from the critical temperature of an isotropic liquid - nematic (IN) transition, and r_o is the direct correlation length. In the absence of a field, at $\tau = \tau_{IN} \sim \gamma_{Nem}^2 / \lambda_{Nem}$ a uniform orientational order arises described by a uniaxial mode

$$Q^o_{\alpha\beta} = \frac{1}{\sqrt{6}} Q_o(3n_\alpha n_\beta - \delta_{\alpha\beta})$$

(Q_o is amplitude of uniaxial order and $\vec{n}$ is a director).

The interaction of the lattice with orientational nematic order is described by the first term in (4). The tensor $h_{\alpha\beta}$ plays the role of the ordering field for $Q_{\alpha\beta}$. Its structure is determined completely by the lattice symmetry. A uniform component $h^o_{\alpha\beta}$ of this field is a uniaxial tensor in the 1D and Hex lattices: $h^o_{\alpha\beta} \sim c_\alpha c_\beta$ (the unit vector $\vec{c}$ defines the C_∞ and C_6 axes, respectively). A uniaxial field of this sort always gives rise to a uniform nematic order. In any cubic lattice, we have $h^o_{\alpha\beta} \sim \delta_{\alpha\beta}$. Because $Q_{\alpha\beta}$ is traceless, a cubic lattice does not interact with a uniform nematic order, so that an order of this sort in a cubic lattice can exist only when $\tau < \tau_{IN}$.

In addition to the uniform component, a crystal field $h_{\alpha\beta}$ contains components with reciprocal-lattice momenta, which cause distortions in the orientational order over a typical scale q_o^{-1}. At $\tau \ll r_o^2 q_o^2$, however, the energy of such distortions can be disregarded. This inequality always holds, since experiments have revealed that $r_o q_o \simeq 1$ in both thermotropic and lyotropic liquid crystals ($r_o \cong 7$ A in thermotropic LC and $r_o \cong 16$ A in lyotropic LC[5]).

In a general case, we have

$$h_{\alpha\beta} = -\gamma_{int} q_o^{-2} \vec{\nabla}_\alpha \delta\rho \vec{\nabla}_\beta \delta\rho . \qquad (5)$$

We assume that $(\gamma_{int}/\gamma_{Nem})\tau_{IN} \gg \Delta^{(0)}_{BCC}$ (see Appendix). The phase diagram then has a region in which the crystallization to phases with an effectively reduced dimensionality of the lattice proceeds directly from an isotropic liquid $(\tau > \tau_{IN})$. As we move away from the line $\tau = \tau_{IN}$, the field-induced value $Q_o \sim \gamma_{int}\rho_o^2/\tau$ decreases (ρ_o is the amplitude of the fundamental mass density waves), and at

$$\tau \gg [\, \gamma_{Nem} Q_o \,;\, \lambda_{Nem} Q_o^2 \,]$$

we can ignore all anharmonicities in (4). This is the so-called "weak"-field region. The presence of a uniform orientational order in 1D- and Hex-phases accounts for the fact that in this region the total free-energy of the mesophases differs from that in (2) only in the renormalization of the fourth-order constants:

$$F_{1D} = \frac{\Delta}{2}\rho_o^2 + \frac{1}{4!}\left(\frac{3\lambda}{2}\right)\left[1 - \frac{20}{3}\xi^{-1}\right]\rho_o^4 + \frac{1}{6!}\mu\rho_o^6 \qquad (6)$$

$$F_{Hex} = \frac{\Delta}{2}\rho_o^2 + \frac{1}{3!}\left(\frac{2\gamma}{\sqrt{6}}\right)\rho_o^3 + \frac{1}{4!}\left(\frac{5\lambda}{2}\right)\left[1 - \xi^{-1}\right]\rho_o^4$$

$$F_{BCC} = \frac{\Delta}{2}\rho_o^2 + \frac{1}{3!}\left(\frac{2\gamma}{\sqrt{3}}\right)\rho_o^3 + \frac{1}{4!}\left(\frac{15\lambda}{4}\right)\rho_o^4 .$$

We have also added six-order terms because of a possible change in the sign of the effective fourth-order constant and we have introduced $\xi \equiv (5\lambda/4\gamma_{int}^2)\tau$.

It follows from eqs.(6) that the temperatures of the I-1D and I-Hex transitions are renormalized markedly. In particular, $\Delta_{Hex} = \Delta^{(0)}_{Hex}(1-\xi^{-1})^{-1}$. At $\xi \leq 4$ we have $\Delta_{Hex} \geq \Delta^{(0)}_{BCC}$ and inequality (3) no longer holds. If $\Delta_{1D}(\xi=4) < \Delta^{(0)}_{BCC}$ then $\xi = 4$ specifies the triple point I-Hex-BCC (see Fig.1).

In the opposite case ($\Delta_{1D}(\xi=4) \geq \Delta^{(0)}_{BCC}$), the crystallization to the lattices with reduced spatial dimensionality begins at the triple point I-1D-BCC, at which $4 \leq \xi < 20/3$.

If $(\gamma_{int}/\gamma_{Nem})\tau_{IN} \ll \Delta^{(0)}_{BCC}$, then an effective reduction of the lattice dimensionality at crystallization does not take place even when $\tau < \tau_{IN}$. In this case, there are no phases with "underdeveloped" crystal lattice, a "weak" crystallization everywhere goes to the BCC lattice, and the line $\tau = \tau_{IN}$ is a phase transition line between the "isotropic" and birefringent BCC phases.

LIQUID CRYSTAL STRUCTURES

In liquid crystals all the phases predicted by the weak-crystallization scheme described above are known. Theory predicts that all phases in which the spatial dimensionality of the crystal lattice has been effectively reduced (1D smectics in thermotropic LC, lamellar and hexagonal phases in lyotropic LC) have a uniform orientational order. In a weak-field region this order is uniaxial because of the uniaxiality of the field $h^{o}_{\alpha\beta}$, so that $\vec{n} \parallel \vec{c}$ in this case and the sign of Q_o is determined by the sign of the field. Because the sign of the field in a 1D-phase is opposite to that in a Hex-phase ($h^{o}_{\alpha\beta} \sim \mp \gamma_{int}\rho_o^{\,2} c_\alpha c_\beta$, where the minus sign refers to a 1D-phase), a 1D-Hex transition is accompanied by a change in the sign of Q_o. In lyotropic LC this change accounts for the fact that molecules which are oriented parallel to the director in a 1D lamellar phase, are orthogonal to it in a hexagonal phase [6]. It appears [7], that this situation also applies to thermotropic LC , where only one of such transitions is known [8].

The uniaxiality of orientational ordering in 1D and Hex phases is distorted when the line $\tau = \tau_{IN}$ is approached from a weak-field region if the sign of Q_o, determi-

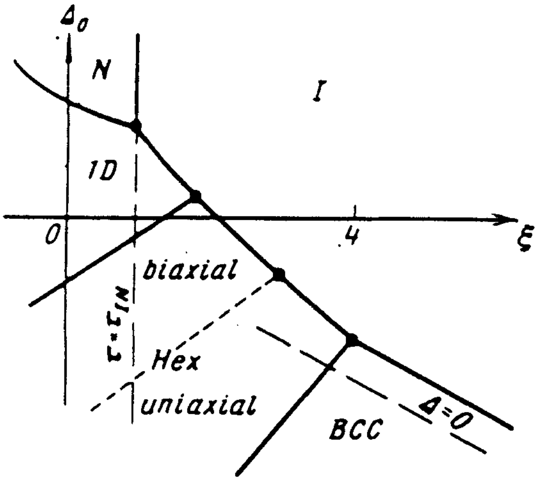

FIGURE 1 Theoretical phase diagram of a liquid crystal. The quantity $\Delta_o = \Delta - \tau$ is a dimensionless difference between the critical temperature of the IN transition and the bare critical temperature of crystallization. ($\gamma_{int}\gamma_{Nem} > 0$)

ned by the field $h^o_{\alpha\beta}$ is opposite to that determined by the nematic constant γ_{Nem}[9]. Such a situation arises in a 1D-phase if $\gamma_{int}\gamma_{Nem} < 0$ and it arises in a Hex-phase if $\gamma_{int}\gamma_{Nem} > 0$. In a Hex-phase the biaxiality of a uniform orientational ordering distorts the crystal lattice and as a result lowers its symmetry. Such optically biaxial phases with a distorted hexagonal lattice are found in lyotropic LC between the uniaxial hexagonal and lamellar phases (see Fig.1)[6].

As we show above, in the global phase diagram of a liquid crystal a BCC phase always exists in the region reasonably far removed from the IN-transition line (see Fig.1). In thermotropic LC such BCC-phases are called smectic D phases[10] and in lyotropic LC they are called "viscous isotropic" phases[7].

Thus, we argued, that because of the strong interaction of the crystal lattice with a uniform nematic order of anisotropic molecules the phases with effectively reduced spatial dimensionality of the lattice may prove to be more favorable from the energy standpoint than a three-dimensional BCC lattice. This situation also holds when in the absence of such interaction the crystallization proceeds to any other cubic lattice (FCC, SC), not only to the BCC one.

APPENDIX

The effective reduction of the spatial dimensionality of a crystal lattice does take place at $\tau \sim \tau_{IN}$, if

$$\gamma_{int}\rho_0^2\, Q_0(\tau \sim \tau_{IN}) \gg \gamma\, \rho_0^3 .$$

Taking for estimates

$$Q_0(\tau \sim \tau_{IN}) \sim \frac{\tau_{IN}}{\gamma_{Nem}}, \text{ and } \quad \gamma\, \rho_0^3 \sim \Delta_{BCC}^{(0)}\, \rho_0^2 ,$$

we obtain the inequality $(\gamma_{int}/\gamma_{Nem})\tau_{IN} \gg \Delta_{BCC}^{(0)}$ used above.

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