

Spatial dimension of a liquid-crystal lattice

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The importance of orientational order in forming the phases with a reduced spatial dimension 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 and the orientational order observed in them is explained.

Liquid-crystal mesophases are a unique example of systems with a reduced spatial dimension of the crystal lattice. The reduction of the spatial dimension is linked directly to two experimental observations: “weakness” of the transitions of the crystallization of an isotropic liquid to the mesophases and the presence of rather strong orientational order in the mesophases. These transitions are “weak” in the sense that the heats corresponding to them are, at the very least, an order of magnitude lower than the heats of an ordinary crystallization. The phenomenological theory,¹ which ignores interaction with other degrees of freedom, predicts a “weak” crystallization to a three-dimensional bcc lattice. We show that theoretical predictions change when the interaction of a lattice with orientational order is taken into account and that, in addition to crystallization to a bcc lattice, a crystallization to a one-dimensional lattice and two-dimensional hexagonal lattice is possible. A crystallization of this type is possible because a bcc lattice does not interact with a homogeneous orientational order because of its symmetry, but one-dimensional and hexagonal lattices are involved in such interactions. Phases with reduced dimension appear at the point where the energy of this interaction is on the order of the lattice energy. For this situation to occur, the crystal lattice must be quite “weak” and the orientational order must be quite strong. This characteristic of liquid crystals makes them unique.

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

$$\delta\rho(\mathbf{r}) = \sum_{\mathbf{q}_i} \rho_{\mathbf{q}_i} e^{i\mathbf{q}_i \mathbf{r}} \quad (1)$$

is performed in reciprocal-lattice vectors \mathbf{q}_i . In the model of Ref. 1, the quantities $\rho_{\mathbf{q}_i}$ are order parameters. A corresponding expansion of the free energy is

$$F_{Cr} = \frac{1}{2} \sum_{\mathbf{q}_i} [\Delta + \xi_0^2 (|\mathbf{q}_i| - q_0)^2] |\rho_{\mathbf{q}_i}|^2 + \frac{\gamma}{3!} \sum_{\mathbf{q}_i + \mathbf{q}_j + \mathbf{q}_k = 0} \rho_{\mathbf{q}_i} \rho_{\mathbf{q}_j} \rho_{\mathbf{q}_k} + \frac{\lambda}{4!} \sum_{\mathbf{q}_i + \mathbf{q}_j + \mathbf{q}_k + \mathbf{q}_l = 0} \rho_{\mathbf{q}_i} \rho_{\mathbf{q}_j} \rho_{\mathbf{q}_k} \rho_{\mathbf{q}_l} + \dots, \quad (2)$$

where q_0 is the length $2N$ of the shortest reciprocal-lattice vectors, ξ_0 is the direct-

correlation radius, and $\Delta = (T - T_c)/T_c$ is a dimensionless divergence from the critical crystallization temperature. A "weak" crystallization corresponds to expansion (2) with only the terms that appear in it. If $q_0^2 \xi_0^2 \gg \gamma^2/\lambda$ (in liquid crystals this inequality generally holds, since $q_0 \xi_0 \sim 1$ and γ^2/λ , which characterizes the transitions in terms of the temperature at which they begin, is usually a small quantity, $\gamma^2/\lambda \ll 1$), the higher harmonics of the lattice energy can be disregarded. The summation in (2) is over only the shortest vectors \mathbf{q}_{0i} and the energy of the possible structures is generally² taken into account.¹⁾ An instability with respect to a one-dimensional lattice ($N = 1$), a hexagonal lattice ($N = 3$, the \mathbf{q}_{0i} vectors form a regular triangle) and a bcc lattice ($N = 6$, the \mathbf{q}_{0i} vectors form a regular tetrahedron) occurs respectively when

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

The inequality

$$\left\{ \Delta_{1D}^{(0)}; \Delta_{\text{Hex}}^{(0)} \right\} < \Delta_{\text{BCC}}^{(0)} \quad (3)$$

guarantees that crystallization to a bcc lattice is weak if there is no interaction with other degrees of freedom.^{2,3}

2. Crystallization in the case of an interaction with orientational order. We shall show that inequality (3) may be violated if a lattice interacts with the orientational nematic order.

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 (see Ref. 4)

$$\begin{aligned} \delta F = & -h_{\alpha\beta} Q_{\alpha\beta} + \frac{\tau}{2} Q_{\alpha\beta} Q_{\alpha\beta} + \frac{r_0^2}{2} \vec{\nabla} Q_{\alpha\beta} \vec{\nabla} Q_{\alpha\beta} + \frac{\gamma_{Nem}}{3!} Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} \\ & + \frac{\lambda_{Nem}}{4!} (Q_{\alpha\beta} Q_{\alpha\beta})^2, \end{aligned} \quad (4)$$

where $\tau = (T - T_{IN}^{(c)})/T_{IN}^{(c)}$ is a dimensionless divergence from the critical temperature of an isotropic liquid-nematic transition, and r_0 is the direct-correlation radius of the nematic fluctuations. At $\tau = \tau_{IN} \sim \gamma_{Nem}^2/\lambda_{Nem}$, in the absence of a field, a uniform orientational order will arise in accordance with a uniaxial mode $Q_{\alpha\beta}^{(0)} = 6^{-1/2} Q_0 (3n_\alpha n_\beta - \delta_{\alpha\beta})$; \mathbf{n} is a nematic director.

The interaction of the lattice with orientational 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 by the lattice symmetry. A uniform component $h_{\alpha\beta}^0$ of this field is a uniaxial tensor in the 1D and hexagonal lattices: $h_{\alpha\beta}^0 \sim c_\alpha c_\beta$ (the unit vector \mathbf{c} defines the C_∞ and C_6 axes, respectively). A uniaxial field of this sort always gives rise to a uniform orientational order. In any cubic lattice, we have $h_{\alpha\beta}^0 \sim \delta_{\alpha\beta}$. Because $Q_{\alpha\beta}$ is traceless, a cubic lattice does not interact with a uniform orientational order, so that an order of this sort in a cubic lattice can exist only when $\tau \leq \tau_{IN}$.

In addition to the uniform component, a crystal field contains components with reciprocal-lattice momenta, which cause distortions in the orientational order with a typical scale q_0^{-1} . At $\tau \ll r_0^2 q_0^2$, however, their energy can be disregarded. This inequality always holds, since experiments have revealed that $r_0 q_0 \sim 1$ in both thermotropic and lyotropic liquid crystals ($r_0 \sim 7 \text{ \AA}$ in thermotropic liquid crystals and $r_0 \sim 16 \text{ \AA}$ in lyotropic liquid crystals; see Ref. 5).

In general, we have

$$h_{\alpha\beta} = -\gamma_{\text{int}} q_0^{-2} \vec{\nabla}_\alpha \delta\rho \vec{\nabla}_\beta \delta\rho. \quad (5)$$

We assume that $(\gamma_{\text{int}}/\gamma_{\text{Nem}})\tau_{IN} \gg \Delta_{\text{bcc}}^{(0)}$. The phase diagram then has a region in which the crystallization to phases of reduced dimension proceeds from an isotropic liquid ($\tau > \tau_{IN}$). As we move away from the line $\tau = \tau_{IN}$, the field-induced value $Q_0 \sim \gamma_{\text{int}} \rho_0^2 / \tau$ decreases (ρ_0 is the amplitude of the density waves) and at $\tau \gg \{\gamma_{\text{Nem}} Q_0; \lambda_{\text{Nem}} Q_0^2\}$ we can ignore all anharmonicities in (4). This is the "weak"-field region. The presence of uniform orientational order in 1D and hexagonal phases accounts for the fact that in this region the total energy of the mesophases differs from that in (2) only in the renormalization of the fourfold constants:

$$F_{1D} = \frac{\Delta}{2} \rho_0^2 + \frac{1}{4!} \left(\frac{3\lambda}{2} \right) \left[1 - \frac{20}{3} \xi^{-1} \right] \rho_0^4 + \frac{1}{6!} \mu \rho_0^6,$$

$$F_{\text{Hex}} = \frac{\Delta}{2} \rho_0^2 + \frac{1}{3!} \left(\frac{2\gamma}{\sqrt{6}} \right) \rho_0^3 + \frac{1}{4!} \left(\frac{5\lambda}{2} \right) \left[1 - \xi^{-1} \right] \rho_0^4 + \dots, \quad (6)$$

$$F_{\text{BCC}} = \frac{\Delta}{2} \rho_0^2 + \frac{1}{3!} \left(\frac{2\gamma}{\sqrt{3}} \right) \rho_0^3 + \frac{1}{4!} \left(\frac{15\lambda}{4} \right) \rho_0^4.$$

We have added sixfold terms because of a possible change in the sign of the effective fourfold constant and we have introduced $\xi = (5\lambda / 4\gamma_{\text{int}}^2)\tau$.

We immediately see from (6) that the temperatures that initiate the I-1D and I-hexagonal transitions are renormalized markedly; specifically, we have $\Delta_{\text{Hex}} = \Delta_{\text{Hex}}^{(0)} (1 - \xi^{-1})^{-1}$. At $\xi \ll 4$ and $\Delta_{\text{Hex}} \gg \Delta_{\text{bcc}}^{(0)}$ inequality (3) clearly no longer holds. If $\Delta_{1D}(\xi = 4) < \Delta_{\text{bcc}}^{(0)}$, then $\xi = 4$ specifies the triple point I-Hex-bcc (see Fig. 1). In the opposite case $[\Delta_{1D}(\xi = 4) \gg \Delta_{\text{bcc}}^{(0)}]$, the crystallization to the reduced-dimension phase begins at the triple point I-1D-bcc, at which $4 \leq \xi < 20/3$.

If $(\gamma_{\text{int}}/\gamma_{\text{Nem}})\tau_{IN} \ll \Delta_{\text{bcc}}^{(0)}$, then a dimensional reduction of the lattice due to crystallization is not desirable even when $\tau < \tau_{IN}$. In this case, there are no dimensionally reduced phases, a "weak" crystallization everywhere goes to the bcc phase, and the line $\tau = \tau_{IN}$ corresponds to a phase transition between the isotropic phase and the birefringent bcc phase.

3. 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 dimension of the crystal lattice has been reduced (one-

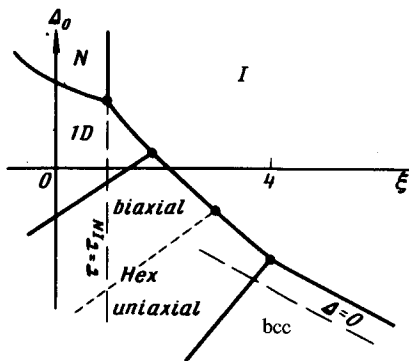


FIG. 1. Theoretical phase diagram of a liquid crystal ($\gamma_{\text{int}}\gamma_{\text{Nem}} > 0$). The quantity $\Delta_0 = \Delta - \tau$ is a dimensionless spatial separation between the critical temperature of the I-N transition and the critical temperature of crystallization. The dashed line represents the line of the phase transition between a uniaxial phase and a hexagonal biaxial phase.

dimensional smectics and hexagonal discotics in thermotropic liquid crystals, lamellar and hexagonal phases in lyotropic liquid crystals) have a uniform orientational order. In a weak field, this ordering is uniaxial because of the uniaxiality of the field $h_{\alpha\beta}^0$, so that $n \parallel c$ in this case and the sign of Q_0 is determined by the sign of the field. Because the sign of the field in a one-dimensional phase is opposite to that in a hexagonal phase ($h_{\alpha\beta}^0 \sim \mp \gamma_{\text{int}} \rho_0^2 c_\alpha c_\beta$, where the minus sign refers to a 1D phase), a 1D-hexagonal transition is accompanied by a change in the sign of Q_0 . In lyotropic liquid crystals this change accounts for the fact that molecules in a 1D lamellar phase are oriented parallel to the director, while in a hexagonal phase they are oriented orthogonal to the director (see Ref. 6). It appears (see Ref. 7) that this situation also applies to thermotropic liquid crystals in which only one such transition is known.⁸

The uniaxiality of orientational ordering in 1D and hexagonal phases is disrupted when the line $\tau = \tau_{IN}$ is approached from a weak field if the sign of Q_0 , determined by the field $h_{\alpha\beta}^0$, is opposite to that of the nematic constant γ_{Nem} (see Ref. 9). Such a situation arises in a 1D phase if $\gamma_{\text{int}}\gamma_{\text{Nem}} < 0$ and it arises in a hexagonal phase if $\gamma_{\text{int}}\gamma_{\text{Nem}} > 0$. In a hexagonal phase the biaxiality of a uniform orientational ordering distorts the crystal lattice and lowers its symmetry. Such biaxial phases with a distorted hexagonal lattice are found in lyotropic liquid crystals between the uniaxial hexagonal and lamellar phases (see Fig. 1 and Ref. 6).

In Section 2 we showed that in the phase diagram of a liquid crystal a bcc phase always exists in the region reasonably far removed from the I-N transition (see Fig. 1). In thermotropic liquid crystals such bcc phases are called smectic D phases¹⁰ and in lyotropic liquid crystals they are called "viscous isotropic" phases (see Ref. 7). The bcc phase of discotic thermotropic liquid phases has not yet been detected.

We have shown that because of the interaction of the crystal lattice with a uniform orientational order, the phases whose spatial dimension has been reduced may prove to be more desirable from the energy standpoint than a three-dimensional bcc lattice. This situation also applies when the crystallization proceeds to any cubic structure (fcc, sc) but the bcc.

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¹The authors of Ref. 2 argue that the hexagonal and bcc lattices should be chosen among all the multidimensional lattices

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