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Phase Behaviour and Structure of Weakly Perturbed Liquid Crystals

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We study influence of a weak disorder on 1st and 2nd order phase transitions in which a continuous symmetry is broken. As illustrative cases we choose the isotropic-nematic (I-N) and nematic-smectic A (N-SmA) liquid crystal phase transitions. We yield an explanation for the established domain pattern and estimate the phase behaviour as a function of the disorder strength.

Keywords: disorder; liquid crystals; phase transitions

I. INTRODUCTION

Recently there has been an increased interest into behaviour of randomly perturbed liquid crystals [1]. The main reason behind this is a potential importance of these systems in various applications. In addition such studies are helping to resolve some open problems in basic physics. For example, they give insight into the influence of quenched disorder on translational & rotational degrees of freedom and 1st & 2nd order phase transitions, in which a continuous symmetry of the parent phase is broken [2].

Studies of quenched disorder and ordering of a condensed system had been in past mostly focused on magnetic systems. It has been shown by Imry and Wortis [3] that above critical disorder strength a first order phase transitions ceases to exist. Therefore on increasing

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a relevant control parameter (i.e., temperature), that triggers the phase transition in a pure bulk sample, the system exhibits gradual evolution of ordering. For a second order phase transition Harris [4] has found that a quenched disorder is an irrelevant perturbation if the critical exponent α for the specific heat is negative. Consequently, the disorder influences critical behaviour only if $\alpha > 0$. Latter it has been shown [5] that correlated disorder can trigger different response. Further, Imry and Ma [6] have shown that phases, reached via a continuous symmetry breaking phase transition, are particularly susceptible to disorder. The reason behind this is the existence of a Goldstone mode in such systems.

In this contribution we study theoretically a mixture $A + B$, where A stands for a liquid crystal (LC) phase and B refers to a random quenched disorder. In relevant experimental samples B mimics either aerosil spherular inclusions [7,8] or various porous matrices (e.g., aerogels [9], controlled-pore glasses [10]). We study the phase & structural behaviour across the isotropic (I), nematic (N) and smectic A (SmA) liquid crystal phase. We use Landau-Ginsburg and Landau-de Gennes type approach [2] combined with random anisotropy type model [11–13]. We show how the disorder influences phase and structural properties of these systems. The plan of paper is as follows. In Sec. II we present the free energy of the system. Results are presented in Sec. III. In the last section we summarize results.

II. FREE ENERGY

We consider a thermotropic LC crystals, in which the temperature variation triggers the I-N and N-SmA phase transition on lowering the temperature. The orientational ordering in LCs is commonly described with the tensor order parameter \underline{Q} . For simplicity we consider only uniaxial ordering, where [2] $\underline{Q} = S(\bar{n} \otimes \bar{n} - \underline{I}/3)$. Here S stands the orientational uniaxial order parameter and the nematic director field \bar{n} points along the direction of uniaxial ordering. If LC molecules are rigidly locked along the unit vector \bar{n} , then $S = 1$. On contrary $S = 0$ reveals the ordinary liquid (i.e., isotropic) ordering. In smectic phases a density wave appears. In the lowest approximation we describe the resulting translational ordering by the complex order parameter $\psi = \eta e^{i\phi}$. The translational order parameter η reveals the degree of layering (i.e., $\eta = 0$ in the nematic phase) and the phase factor ϕ defines the position of smectic layers. In the bulk SmA phase, the equilibrium phase configuration can be expressed as $\phi(\vec{r}) = q_0 \bar{n} \cdot \vec{r}$, where the layers are stacked along \bar{n} with the layer spacing $d_0 = 2\pi/q_0$.

In terms of these order parameter we express the free energy as [2,14,15]

$$F = \iiint \left(f_h^{(n)} + f_e^{(n)} + f_h^{(s)} + f_e^{(s)} + f_c \right) d^3r + \iint \left(f_s^{(n)} + f_s^{(s)} \right) d^2r. \quad (1)$$

Here $f_j^{(i)}$ stand for free energy density terms. Superscripts describe the nematic $^{(n)}$ and smectic $^{(s)}$ contributions. The first “volume” integral runs within the volume occupied by LC. The second “surface” integral runs over the A-B interface.

The “volume” density terms can be approximately expressed as

$$\begin{aligned} f_h^{(n)} &\approx a_0(T - T_*)S^2 - bS^3 + cS^4, \\ f_h^{(s)} &\approx \alpha(T - T_{NA})|\psi|^2 + \beta|\psi|^4, \\ f_c &\approx -dS|\psi|^2, \\ f_e^{(n)} &\approx L_0|\nabla S|^2 + L_1S^2 \left((\nabla \cdot \vec{n})^2 + (\nabla \times \vec{n})^2 \right), \\ f_e^{(s)} &\approx C_{\parallel} \left| (\vec{n} \cdot \nabla - iq_0)\psi \right|^2 + C_{\perp} \left| (\vec{n} \times \nabla)\psi \right|^2 + D \left| (\vec{n} \times \nabla)\psi \right|^2. \end{aligned} \quad (2)$$

The nematic and SmA homogeneous terms $f_h^{(n)}$ and $f_h^{(s)}$, as well as the coupling term f_c between the nematic orientational and smectic translational order parameter, control the I-N and N-SmA phase behaviour in the elastically non-distorted LC. The positive quantities $a_0, b, c, T_*, d, \alpha, \beta, T_{NA}$ are material constants. In this description $f_h^{(n)}$ and $f_h^{(s)}$ exhibit in bulk the 1st order I-N and the 2nd N-SmA phase transitions at temperatures $T = T_{IN}$ and $T = T_{NA}$, respectively. For most nematic phases T_{IN} takes place 1 K above the supercooling temperature T_* [2]. In some case the N-SmA phase transition can be also discontinuous [2,16]. For example, in our model it can be caused by the coupling term f_c [2,15].

The nematic ($f_e^{(n)}$) and smectic ($f_e^{(s)}$) elastic terms describe the resistance of a LC phase to long wave length distortions from equilibrium configurations. In Eq. (2) only the most representative bare (independent of temperature) nematic (L_0, L_1) and smectic ($C_{\parallel}, C_{\perp}, D$) elastic constants are introduced. The constants C_{\parallel}, D are positive for all temperatures. Note that the change in the sign of C_{\perp} triggers in a pure bulk the 2nd order SmA-SmC phase transition at T_{AC} . Close to the transition it can be expressed as $C_{\perp} \approx C_{\perp}^{(0)}(T - T_{AC})$. Below T_{AC} the term with the elastic constant D is needed to stabilize the tilt of LC molecules at a sharp angle with respect to the layer normal [17].

We henceforth restrict ourselves to the I-N-SmA phase transitions. We neglect elastic anisotropy in each ordered phase, i.e., we set $L \equiv L_1 \approx L_0$, $C \equiv C_\perp \approx C_\parallel \approx D$ and also discard the coupling term f_c .

We model the dominant nematic and smectic A interface free energy density terms as [18,19]

$$\begin{aligned} f_s^{(n)} &\approx -W_n \vec{e} \cdot \underline{\mathbf{Q}} \cdot \vec{e} = -W_n S \left((\vec{e} \cdot \vec{n})^2 - \frac{1}{3} \right), \\ f_s^{(s)} &\approx -\frac{W^* \psi + W \psi^*}{2} = -W_s \eta \cos(\phi - \phi_s). \end{aligned} \quad (3)$$

Here $W = W_s e^{i\phi_s}$, $W_s > 0$ is the positional and $W_n > 0$ the orientational anchoring constant. They tend to increase the degree of ordering and enforce orientation along the easy axis \vec{e} (W_n), and the smectic phase ϕ_s (W_s).

III. PHASE AND STRUCTURAL BEHAVIOUR

We next assume that the disorder transforms the LC structure into a domain-type pattern. Note that in pure systems domains arises temporary following a fast enough (with respect to a relevant order parameter relaxation time) continuous symmetry breaking phase transition. The domain pattern can be well explained with the so-called Kibble-Zurek (KZ) mechanism [20]. This mechanism was originally introduced in cosmology to explain coarsening dynamics of topological defects in the early universe. Because the main reasons behind this phenomenon are continuous symmetry breaking and causality, which commonly appear in nature, the KZ mechanism holds true also in several condensed matter systems [20,21]. To illustrate main features of the KZ mechanism we consider a sudden phase transition in which a continuous symmetry was broken. After the quench in causally disconnected parts of the system a different value of the symmetry breaking order parameter value is generally chosen. Consequently, a domain structure appears characterized by a single characteristic length ξ_D . Subsequent domain growth soon enters the scaling regime, and the growth obeys the power law dependence $\xi_D \propto t^\gamma$, where γ is the scaling coefficient, reflecting the dimension of the spatial space and order parameter space.

We claim that impurities in our system of interest (i.e., a perturbed LC phase) play similar role as temporal fluctuations and are even more effective, because of their persistent ordering tendency. Thus we believe that during the phase transition the domain pattern arises also in cases, where the phase transition crossing is relatively slow. After the transition the domains grow with time, until they get pinned

by impurities, attaining their equilibrium value ξ_d . Therefore this domain structure does not resemble independent crystallites. It exhibits rather smooth variations in which a characteristic length is present. This description coincides with the one given by Giamarchi and Doussal [22] for weakly perturbed magnetic systems with quasi long-range order in which, however, a typical length ξ_d nevertheless exists. Note that Feldman this description is similar to the one given by Feldman [23] for nematics. In his work he suggests quasi-long-range order with algebraically decaying correlations. But he does not predict the existence of a typical length ξ_d , marking the distance, over which a qualitative change of correlations takes place.

In the following we estimate the influence of domain pattern and impurities on the LC phase behaviour, in which either continuous or discontinuous symmetry is broken. We assume that a hydrodynamic field (HF), that has suffered a loss of continuous symmetry at the phase transition, gradually changes along ξ_d . Furthermore, we assume that an order parameter field (OPF), that reveals the degree of ordering of the phase, is relatively weakly perturbed. In the case of the nematic (SmA) phase the role of OPF is played by S (η) and of the HF by \bar{n} (ϕ). Taking this into account we restrict our attention to an effective free energy \bar{f} , that possesses the essential structure proposed by Eqs. (2) and (3). Here the over-bar indicates the averaging over the domain volume. It follows (for details see Ref. [13]) :

$$\bar{f} \approx \bar{f}_b^{(n)} + \bar{f}_b^{(s)} + \frac{L\bar{S}^2}{\xi_d^2} + \frac{C\bar{\eta}^2}{\xi_d^2} - \frac{W_n\bar{S}}{\sqrt{N_n}} - \frac{W_s\bar{\eta}}{\sqrt{N_s}}. \quad (4)$$

The third and fourth term in Eq. (4) come from the spatial variation of the HFs, and the last two interface terms are averaged over the domain volume $V_d \approx \xi_d^3$; $1/\sqrt{N_n} = \overline{(\bar{e} \cdot \bar{n})^2} - 1/3$ and $1/\sqrt{N_s} = \overline{\cos(\phi - \phi_s)}$. The averaging effectiveness is measured by the number of averaging sites $N_i \approx (\xi_d/\xi_i)^3$ in V_d . Here ξ_i measures an average distance over which the relevant hydrodynamic field (\bar{n} for $i = n$ and ϕ for $i = s$) makes an apparent random change.

In Eq. (4) the elastic term enforces $\xi_d \rightarrow \infty$ and the surface term $\xi_d \rightarrow 0$. The compromise between these terms yields a finite domain size in ordered LC phases.

Next we estimate possible phase behaviour steaming from the model. We first focus on the I-N transition. The minimization with respect to \bar{S} and ξ_d yields two coupled equations, defining the equilibrium conditions [13]. The phase diagram as a function of the dimensionless temperature $t^{(n)}$ and dimensionless surface anchoring

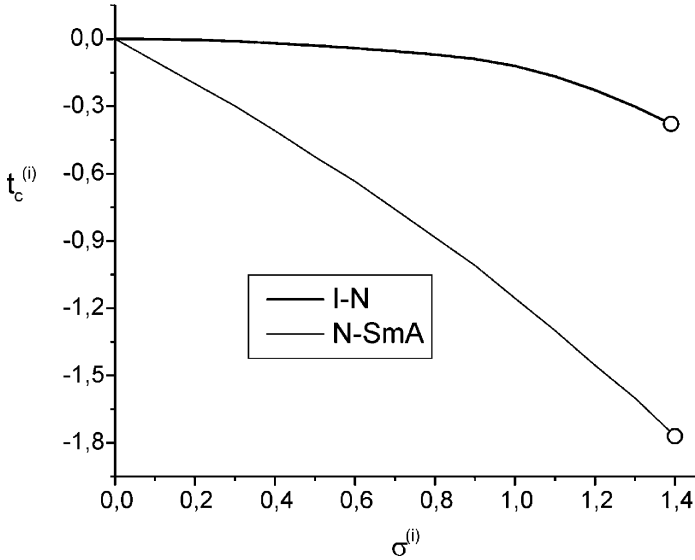


FIGURE 1 Dimensionless phase transition temperature $t_c^{(i)}$ as a function of the dimensionless anchoring strength $\sigma^{(i)}$. The superscript (i) indicates either the I-N (i.e., $t_c^{(n)}, \sigma^{(n)}$) or N-SmA (i.e., $t_c^{(s)}, \sigma^{(s)}$) phase transition case.

constant $\sigma^{(n)}$ is shown in Figure 1 and treated in detail in Ref. [13]. The jump of the order parameter at the transition is plotted in Figure 2. The dimensionless quantities $t_c^{(n)}$ and $\sigma^{(n)}$ are introduced in the Appendix. With increasing $\sigma^{(n)}$ the I-N transition temperature $t_c^{(n)}$ and the jump of the order parameter $\Delta \bar{S}$ at $t_c^{(n)}$ decrease. Note that for a finite value $\sigma^{(n)}$ a finite degree of ordering exists for all temperatures. One commonly refers to such ordering above $t_c^{(n)}$ as the paranematic phase. Above a critical value $\sigma_c^{(n)}$ the jump of order parameter at $t_c^{(n)}$ drops to zero, while the temperature derivative of \bar{S} remains discontinuous. We believe that this phenomenon is the artefact of our approach and that above $\sigma_c^{(n)}$ the transition ceases to exist. We next consider the N-SmA phase transition. Rough inspection of Eq. (4) suggests (it resembles the problem of an ferromagnet in an external field, see the Appendix), that the N-SmA transition always becomes gradual for a finite value of W_s . However the coupling between $\bar{\eta}$ and ξ_d can yield a qualitatively different response. To illustrate that we neglect nematic components in Eq. (4) and minimize the free energy with respect to ξ_d and $\bar{\eta}$. The resulting phase diagram is shown in Figure 1, where the dimensionless temperature $t_c^{(s)}$ of the N-SmA phase transition is plotted as a function of the dimensionless smectic anchoring strength

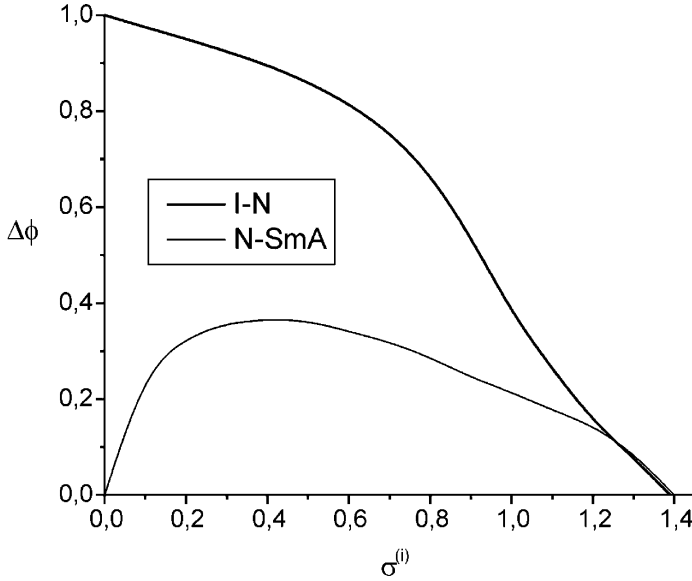


FIGURE 2 Jump of the order parameter at the phase transition. Here $\Delta\varphi$ stands for the order parameter jump at the I-N (i.e., $\Delta\varphi = \Delta\bar{S}$) and N-SmA (i.e., $\Delta\varphi = \Delta\bar{\eta}$) phase transition.

$\sigma^{(s)}$ (for definitions of $\sigma^{(s)}$ and $t_c^{(s)}$ see the Appendix). One sees that for any finite value of $\sigma^{(s)}$, below the threshold value $\sigma_c^{(s)}$, the continuous transition encountered in the pure sample becomes discontinuous, see Figure 2. Above $\sigma_c^{(s)}$ the N-SmA transition becomes gradual on decreasing $t^{(s)}$.

IV. CONCLUSIONS

We study the influence of weak quenched randomness on the I-N and N-SmA phase transition, in which continuous orientational and translational order is broken, respectively. The I-N transition is always discontinuous and we focus on continuous N-SmA transition. We claim that disorder gives rise to a domain pattern, well characterised by a single characteristic length ξ_d . The domain boundaries are not well pronounced, yielding relatively weak variations of a relevant order parameter. We assume, that such domain pattern has dynamical origin and is governed by the Kibble-Zurek mechanism and pinning of domains. We estimate the phase behaviour of weakly perturbed systems. In particular we show, that disorder can drive a

continuous phase transition into discontinuous one. We plan to carry out a more detail study of this problem. Note that this result is not in contradiction with the existing results on related systems. For example, a similar study was carried out by Aharony [24] on randomly perturbed magnets using the renormalization group. He observed that random perturbations can destabilize a fixed point describing the continuous phase transition taking place in the pure case. He claims that this instability is the signal of a smeared transition, although the first order transition might also be the reason for it.

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APPENDIX: EFFECTIVE DIMENSIONLESS FREE ENERGY DENSITIES

We express the effective dimensionless free energy of the system as

$$f^{(n)} = t^{(n)}\varphi^2 + (1 - \varphi)^2 + \frac{\kappa^{(n)}\varphi^2}{1 + \xi^2} - \frac{\sigma^{(n)}\varphi}{(1 + \xi^2)^{3/4}},$$

$$f^{(s)} = \frac{t^{(s)}\varphi^2}{2} + \frac{\varphi^4}{4} + \frac{\kappa^{(s)}\varphi^2}{1 + \xi^2} - \frac{\sigma^{(s)}\varphi}{(1 + \xi^2)^{3/4}}.$$

The quantity $f^{(i)}$ mimics the free energy density of the I-N ($i = n$) and N-SmA ($i = s$) phase transition; $\varphi \propto \bar{S}$, $\kappa^{(n)} \propto L$, $\sigma^{(n)} \propto W_n$ for $f^{(n)}$ and $\varphi \propto \bar{\eta}$, $\kappa^{(s)} \propto C$, $\sigma^{(s)} \propto W_s$ for $f^{(s)}$. ξ stands for the dimensionless average domain size. We introduced a cut off length 1 in order to avoid singularity at $\xi = 0$. The equilibrium phase behaviour in pure bulk (i.e., $\xi = \infty$) yields discontinuous and continuous phase transition for $f^{(n)}$ and $f^{(s)}$, respectively. The phase transitions take place at $t^{(n)} \equiv t_c^{(n)} = 0$, $t^{(s)} \equiv t_c^{(s)} = 0$.