# Fluctuations Dominate the Phase Diagram of Chiral Nematic Liquid Crystals

J. Englert,[1] L. Longa,[1,2] H. Stark,[1] and H.-R. Trebin[1]
[1]*Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57, D-70550 Stuttgart, Germany*
[2]*Instytut Fizyki, Uniwersytet Jagielloński, Reymonta 4, Kraków, Poland*
(Received 21 January 1998; revised manuscript received 12 March 1998)

Phase diagrams of the liquid-crystalline blue phases (BPs), as calculated by means of Landau theory, display two serious deficiencies: They contain a never-observed structure of space group $O^5$, and BP II does not disappear at very high chiralities. Here we prove by a first-order cumulant expansion that neglect of fluctuations is the cause. We also observe a smooth transition from a strongly to a weakly correlated isotropic phase, which vanishes at large chiralities. It indicates the existence of a critical point and characterizes BP III as a second isotropic phase, in agreement with recent experiments. [S0031-9007(98)06928-2]

PACS numbers: 64.70.Md, 05.40.+j, 61.30.Cz

The phase diagram and structure of the liquid-crystalline blue phases (BPs) have been a challenge to experimentalists and theoreticians since the beginning of liquid-crystal research [1]. The discovery of the body centered cubic BP I [2] and the simple cubic BP II [3] was soon followed by the observation of a third phase [4], called "blue fog" (BP III) for its amorphous appearance. Freeze-fracture electron-microscope observations of BP III supported a "spaghetti model" [5] and gave a first hint to an isotropic nature. Complete phase diagrams of the BPs were measured and showed remarkably universal features [6]. In all of them BP II disappears at high chiralities. For small chiralities and low temperatures BP I is the most stable phase. BP III always is the high chirality phase (Fig. 1). In recent measurements of specific heat, rotatory power, and light scattering [7,8] a critical point was detected at the BP III–isotropic phase transition leading to the stringent conclusion that BP III is a second isotropic phase and the critical point is of the Ising type. The correct critical exponents have been determined in a careful analysis of the experimental data [9].

Theoretically, the structure of the BPs was investigated by means of a Landau–de Gennes theory for helicity modes of the alignment tensor field [10]. With Landau–de Gennes theory Grebel, Hornreich, and Shtrikman calculated phase diagrams [11] (Fig. 2) that explain the structure of BP I ($O_c^8$) and BP II ($O^2$), but not the nature of the blue fog. Instead, another cubic phase [$O^5$(I432)] was predicted, which never has been observed experimentally. Furthermore, BP II does not vanish at high chiralities.

Despite the success of Landau theory with regard to the first two BPs, the structure of the blue fog and the artificial stability of the $O^5$ phase became a crucial test for the Landau–de Gennes theory. An icosahedral model was suggested [12] but could not be stabilized over the cubic BPs [13,14]. The "spaghetti model" gave rise to the assumption of squirming double twist tubes [15], but its stability has not been confirmed.

A "melted blue phase" [16] was suggested as a bond orientational order model for BP III [14], analogously to the hexatic phase in two dimensions [17]. It was the first model for BP III that took fluctuations into account (in a simplified way) and that was proven to be stable. After the critical point was detected it became clear that the bond order model is a secondary aspect of BP III. Isotropic models with a pseudoscalar order parameter have recently been presented [18]. It was shown how the critical point could in principle be extracted from the Landau–de Gennes Hamiltonian. A careful analysis of the physical properties around the critical point was given [19]. Full phase diagrams, however, have not been calculated.

The most natural way to include fluctuations was proposed by Brazovskiĭ and co-workers already in 1975 [20,21]. The authors predicted the existence of one or more phases between the isotropic and the cholesteric state. But their treatment of fluctuations was limited to a semiquantitative analysis of the isotropic two-point correlation function. In this Letter we follow the ideas of Brazovskiĭ and study the influence of fluctuations on the phase diagram of the BPs. However, with the cumulant expansion, which has recently been used to calculate the phase diagram of copolymers [22], we employ a different method than Brazovskiĭ. The importance of fluctuations for

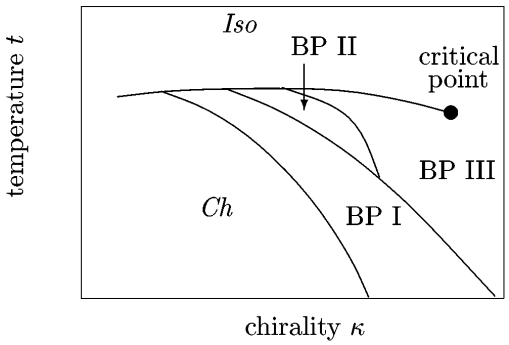


FIG. 1. Sketch of the experimental phase diagram of chiral nematic liquid crystals, $\kappa$ and $t$ in arbitrary units.

  

chiral nematic liquid crystals is undoubted, as can be seen from pretransitional effects [23]. It has been noted, that "neglecting the fluctuations ... may be a bad approximation" [24]. Even the existence of the blue fog ought to be explained by increasing fluctuations for high chiralities, which destroy the periodic structure of BP I and II.

The order of BPs can be described by a symmetric and traceless quadrupolar tensor order parameter field $\mathbf{Q}(\mathbf{r})$. Expanding it into spin tensor modes of $L = 2$ and, furthermore, into plane waves one obtains

$$\mathbf{Q}(\mathbf{r}) = \sum_{\mathbf{k}} \sum_{m} \mu_m(k) \mathbf{M}_m(\hat{\mathbf{k}}) \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}, \tag{1}$$

where $k = |\mathbf{k}|$. For practical purposes and in agreement with experiment, we restrict ourselves to the $m = 2$ mode and use a simplified notation: $\mu_2(k) = \mu_{\mathbf{k}}$ and $\mathbf{M}_2(\hat{\mathbf{k}}) = \mathbf{M}(\hat{\mathbf{k}})$.

We start from the mesoscopic Landau–Ginzburg–de Gennes Hamiltonian density

$$\mathcal{H} = \frac{1}{4} \sum_{\mathbf{q}} [\tau + (q - \kappa)^2] \mu_{\mathbf{q}} \mu_{-\mathbf{q}} - \frac{1}{2} \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3} \mu_{\mathbf{k}_1} \mu_{\mathbf{k}_2} \mu_{\mathbf{k}_3} \mathrm{Tr}[\mathbf{M}(\hat{\mathbf{k}}_1)\mathbf{M}(\hat{\mathbf{k}}_2)\mathbf{M}(\hat{\mathbf{k}}_3)] \delta_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3,\mathbf{0}}$$
$$+ \frac{\lambda}{4!} \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3 \mathbf{k}_4} \mu_{\mathbf{k}_1} \mu_{\mathbf{k}_2} \mu_{\mathbf{k}_3} \mu_{\mathbf{k}_4} \mathrm{Tr}[\mathbf{M}(\hat{\mathbf{k}}_1)\mathbf{M}(\hat{\mathbf{k}}_2)] \mathrm{Tr}[\mathbf{M}(\hat{\mathbf{k}}_3)\mathbf{M}(\hat{\mathbf{k}}_4)] \delta_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4,\mathbf{0}} . \tag{2}$$

$\kappa$ is the chirality, $\tau = t - \kappa^2$ is a rescaled temperature, $q$ is scaled by the inverse of the correlation length $\xi_{\mathrm{R}}$. The amplitudes differ by a factor of $1/\sqrt{24}$ and the Hamiltonian by a factor of 24 compared to Ref. [11]. Substituting equilibrium values of the amplitudes leads to the mean field energy, from which the results of Grebel *et al.* [11] can be derived.

The free energy density $F$ follows from the logarithm of the partition function $Z = \int \mathcal{D}\mu \exp(-\beta \mathcal{H}[\mu])$, where $\beta^{-1} = k_{\mathrm{B}} T/V$, and $V$ is the system volume. We divide $\mu = \overline{\mu} + \mu'$ into the equilibrium order parameter $\overline{\mu}$ and a fluctuating part $\mu'$ and accordingly separate $\mathcal{H}[\mu]$ into $\mathcal{H}[\mu] = \mathcal{H}_0[\overline{\mu}] + \tilde{\mathcal{H}}[\overline{\mu}, \mu']$. Thus,

$$F = -\beta^{-1} \ln Z = F^{\mathrm{MF}}[\overline{\mu}] - \beta^{-1} \ln \int \mathcal{D}\mu' \, e^{-\beta \tilde{\mathcal{H}}[\overline{\mu}, \mu']}. \tag{3}$$

$F^{\mathrm{MF}}[\overline{\mu}] = \mathcal{H}_0[\overline{\mu}]$ is the mean field free energy density.

We treat the path integral by averaging over a trial Hamiltonian density

$$\mathcal{H}'[\mu'] = \frac{1}{4} \sum_{\mathbf{q}} [\Delta + (q - \kappa)^2] \mu'_{\mathbf{q}} \mu'_{-\mathbf{q}} . \tag{4}$$

$\Delta$ is a variational parameter, sometimes also called renormalized temperature. The free energy density then reads

$$F = F^{\mathrm{MF}}[\overline{\mu}] - \beta^{-1} \ln Z' - \beta^{-1} \times \ln \langle e^{-\beta(\tilde{\mathcal{H}}[\overline{\mu}, \mu'] - \mathcal{H}'[\mu'])} \rangle_{\mathcal{H}'} , \tag{5}$$

where we introduced the partition function $Z'$ of $\mathcal{H}'$. We expand the last term into momenta of $\tilde{\mathcal{H}}[\overline{\mu}, \mu'] - \mathcal{H}'[\mu']$, also called cumulants, and keep terms of first order only [25]:

$$F \approx F^{\mathrm{MF}}[\overline{\mu}] - \beta^{-1} \ln Z' - \langle \mathcal{H}'[\mu'] - \tilde{\mathcal{H}}[\overline{\mu}, \mu'] \rangle_{\mathcal{H}'} . \tag{6}$$

Terms proportional to $\langle \mu'^3 \rangle$ and $\langle \mu'^4 \rangle$ are simplified by Wick's theorem [25]. Because of the ultraviolet divergence of the resulting integrals a cutoff $\Lambda$ is introduced as $\Lambda = n q_{\mathrm{c}}$ since the natural scale of the system is the wave number $q_{\mathrm{c}} = \kappa$. $n$ should be a small number but equal to or greater than 1. In the case $n = 1$ we completely neglect fluctuations within the unit cell as previously done [21]. For large $n$ we arrive at molecular dimensions, and the mesoscopic theory breaks down.

The two-point correlation function for the (chiral) nematic order parameter reads

$$\langle \mu'_{\mathbf{q}} \mu'_{-\mathbf{q}} \rangle_{\mathcal{H}'} = \frac{2\beta^{-1}}{\Delta + (q - \kappa)^2} = \beta^{-1} \chi(\mathbf{q}) , \tag{7}$$

where $\Delta^{-1/2}$ is the correlation length and $\chi(\mathbf{q})$ is the wave vector dependent susceptibility of $\overline{\mu}_{\mathbf{q}}$ [25].

Neglecting all constant contributions we can write the free energy as

$$F = F^{\mathrm{MF}}[\overline{\mu}] + \int_0^{\Delta} \Sigma(\tilde{\Delta}) \, d\tilde{\Delta} + \left[ \tau - \Delta + \frac{14\lambda}{15} \Sigma(\Delta) \right] \Sigma(\Delta) + \frac{7\lambda}{15} \sum_{\mathbf{k}} \overline{\mu}_{\mathbf{k}} \overline{\mu}_{-\mathbf{k}} \Sigma(\Delta) , \tag{8}$$

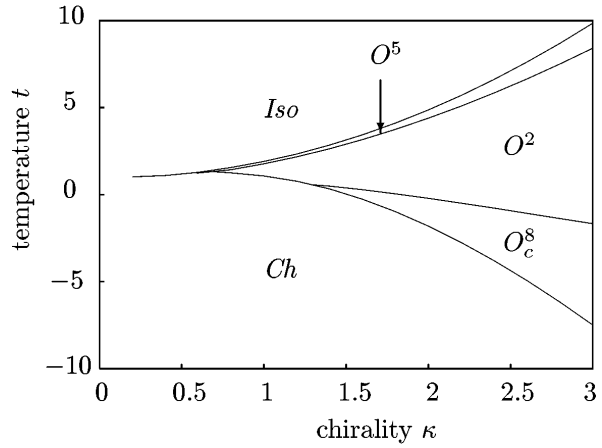


FIG. 2. Phase diagram recalculated from Landau theory cf. [11].

with a self-energy function

$$\Sigma(\Delta) = \frac{\beta^{-1}}{4\pi^2}\int_0^{n\kappa}\frac{q^2\,dq}{\Delta + (q-\kappa)^2} = \frac{\beta^{-1}}{4\pi^2}\,\kappa\left\{n - \ln\left(\frac{1+\frac{\kappa^2}{\Delta}}{1+\frac{\kappa^2}{\Delta}(n-1)^2}\right) - \frac{\sqrt{\Delta}}{\kappa}\left(1-\frac{\kappa^2}{\Delta}\right)\left[\arctan\left(\frac{\kappa}{\sqrt{\Delta}}\right) + \arctan\left(\frac{\kappa}{\sqrt{\Delta}}(n-1)\right)\right]\right\}. \quad (9)$$

Note that the cubic invariant of the Hamiltonian only contributes to the mean field free energy density $F^{\mathrm{MF}}$.

For $\Delta \ll \kappa^2/n^2$ the dominant part of the self energy is

$$\Sigma(\Delta) \sim \kappa^2/\sqrt{\Delta}\,. \quad (10)$$

This is fulfilled for sufficiently small $n$. All further calculations in this paper are carried out with $n = 1$. We have checked, however, that the qualitative results are valid up to $n = 4$, which may become important because the higher stars of the ordered structure lie outside the shell of $n = 1$.

We determine the value of the variational parameter $\Delta$ by minimizing $F$ and obtain

$$-\Delta + \tau + \frac{28\lambda}{15}\,\Sigma(\Delta) + \frac{7\lambda}{15}\sum_k \overline{\mu}_{\mathbf{k}}\overline{\mu}_{-\mathbf{k}} = 0\,. \quad (11)$$

Substituting Eq. (11) into the free energy (8) leads to the simple expression

$$\overline{F} = F^{\mathrm{MF}}[\,\overline{\mu}\,] + \int_0^{\Delta}\Sigma(\tilde{\Delta})\,d\tilde{\Delta} - \frac{14\lambda}{15}\,\Sigma^2(\Delta)\,. \quad (12)$$

The minimization procedure follows Grebel *et al.* [11], but we have to pay attention to the fact that now $\overline{\mu}$ and $\Delta$ are related via Eq. (11). We treat $\alpha := \beta^{-1}/60\pi^2$ as a free parameter fixing the energy scale of the fluctuations. The resulting effect of fluctuations on the phase diagram is seen in Fig. 3.

With increasing $\alpha$ the temperature for the phase transition from the isotropic phase into the ordered phases is lowered *destabilizing the $O^5$ structure*. For $\alpha < 0.075$, however, $O^5$ remains present. Equations (9) and (10) show that the fluctuations increase with chirality due to the growing phase volume $\int^{\kappa} q^2\,dq \propto \kappa^3$. Consequently, the transition line isotropic-ordered, which rises like $\kappa^2$ in mean field, is bent down, very similar to the experimental situation. At chirality $\kappa \approx 10$, BP II disappears from the phase diagram. Extending the mean-field results of Grebel *et al.* [11] to very high chiralities it can be shown, that the phase transition line between $O^8$ and $O^2$ goes through a minimum at $\kappa \approx 5$. Fluctuations lower the coexistence line with the isotropic phase, render BP II unstable, and, finally, also yield a direct transition between BP I and the isotropic phase. Furthermore, BP I undergoes a transition from $O_c^8$ to a different phase which we identify as the $O_b^8$ structure of Grebel *et al.* [11]. For increasing $\alpha$ the coexistence line bends down further and, consequently, $O^2$ vanishes at lower chiralities. For $\alpha \gtrsim 0.5$ it completely disappears from the phase diagram.

Additionally, we have investigated the inverse correlation length $\sqrt{\Delta}$ as a function of temperature. In Fig. 4 it is sketched on a single logarithmic scale. For low chiralities there are two regimes: one of small $\Delta$ for $t \lesssim 0$, and one of large $\Delta$ for $t \gtrsim 0$, corresponding, respectively, to a strongly correlated metastable and a weakly correlated stable isotropic phase. Near $t = 0$ there is a smooth transition between both regimes, which vanishes for increasing chirality $\kappa$. This is a hint of the occurrence of a second isotropic phase and of a critical point at high chiralities. However, within our first order cumulant expansion we do not obtain two stable isotropic phases. To test if a chiral system allows for a critical point at all

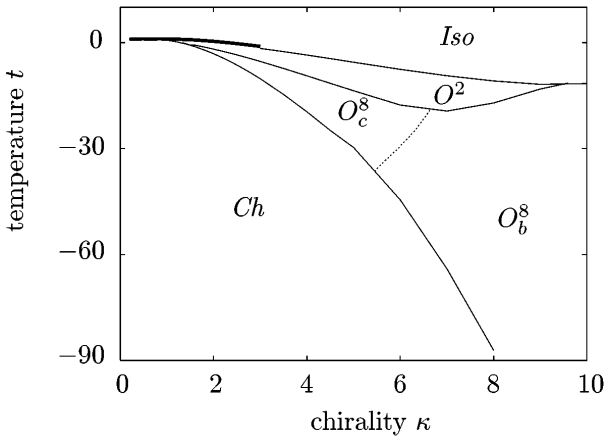


FIG. 3. Effect of fluctuations on the phase diagram of chiral nematic liquid crystals ($\alpha = 0.2, \lambda = 1, n = 1$).

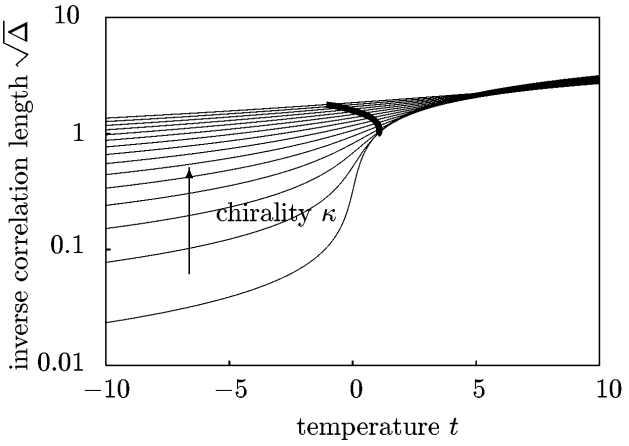


FIG. 4. Inverse correlation length $\sqrt{\Delta}$ versus temperature $t$ for chirality $\kappa$ between 0.2 and 3.0. The area on the right side of the bold line is the regime for the stable isotropic phase, the area on the left side for the metastable state. The bold line corresponds to the bold line of Fig. 3.

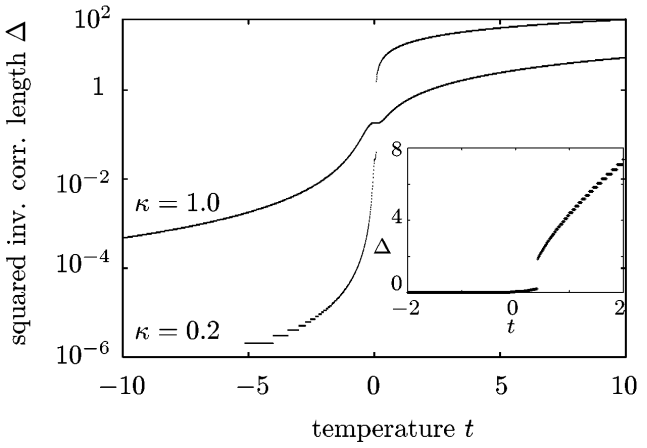


FIG. 5. Squared inverse correlation length Δ versus temperature in a logarithmic scale for a simplified Landau-Ginzburg-de Gennes Hamiltonian for one chirality below and above the critical point at $\kappa_c \approx 0.8$. As an inset Δ is plotted on a linear scale allowing for direct comparison with the experimental light scattering data at the isotropic—BP III transition [7].

and, hence, for two isotropic phases, we took a simplified version of the Hamiltonian in Eq. (2) skipping the third-order term and the traces. By extending our cumulant expansion to third order we found indeed a critical point at $\kappa_c \approx 0.8$ (see Fig. 5). The square of the inverse correlation length, Δ, is proportional to the inverse of the intensity of the scattered light. Our theoretical prediction for Δ, as shown in the inset of Fig. 5, reveals a striking agreement with experimental light scattering data of Fig. 1 in Ref. [7]. An appropriate thermodynamic quantity that can be used as an order parameter for BP III is the inverse susceptibility, which in the Ornstein-Zernicke approximation of Eq. (7) is proportional to Δ. The situation is rather unique as the new order parameter is related to the fluctuations of the original one. The new order parameter defines a second correlation length which diverges at the BP III-isotropic critical point.

In this paper we have proven that fluctuations are relevant for BPs in chiral nematic systems. Using a first order cumulant expansion we found a direct transition of BP II into the isotropic phase. The "artificial" $O^5$ structure is destabilized. Consequently, this structure is not forbidden and could be observed for systems with small transition temperatures. For very large chiralities, BP II disappears from the phase diagram according to experiment. In a simplified model we found a second isotropic phase and a critical point using higher orders of cumulants. We predict that higher orders also account for a second isotropic phase in BPs and may also yield the correct order of BP I and BP II for small chiralities.

This project is supported by the Deutsche Forschungsgemeinschaft under Grant No. Tr 154/15-1. We thank A. Rüdinger for useful discussions.

[1] F. Reinitzer, Monatsh. Chem. **9**, 421 (1888).
[2] D. Armitage and F. P. Price, J. Phys. (Paris) Colloq. **36**, C1-133 (1975).
[3] S. Meiboom and M. Sammon, Phys. Rev. Lett. **44**, 882 (1980); K. Bergmann and H. Stegemeyer, Z. Naturforsch. **34a**, 251 (1979); D. L. Johnson, J. H. Flack, and P. P. Crooker, Phys. Rev. Lett. **45**, 641 (1980).
[4] H. Stegemeyer and K. Bergmann, in *Liquid Crystals of One- and Two-Dimensional Order*, edited by W. Helfrich and G. Heppke, Springer Series in Chemical Physics, Vol. 11 (Springer-Verlag, Berlin, 1980), pp. 161–175.
[5] J. A. N. Zasadzinski *et al.*, Phys. Rev. Lett. **57**, 364 (1986).
[6] D. K. Yang and P. P. Crooker, Phys. Rev. A **35**, 4419 (1987).
[7] E. P. Koistinen and P. H. Keyes, Phys. Rev. Lett. **74**, 4460 (1995).
[8] Z. Kutnjak, C. W. Garland, J. L. Passmore, and P. J. Collings, Phys. Rev. Lett. **74**, 4859 (1995).
[9] M. A. Anisimov, V. A. Agayan, and P. J. Collings, Phys. Rev. E **57**, 582 (1998).
[10] R. M. Hornreich and S. Shtrikman, J. Phys. (France) **41**, 335 (1980).
[11] H. Grebel, R. M. Hornreich, and S. Shtrikman, Phys. Rev. A **30**, 3264 (1984).
[12] R. M. Hornreich and S. Shtrikman, Phys. Rev. Lett. **56**, 1723 (1986); V. M. Filev, Sov. Phys. JETP Lett. **43**, 677 (1986); R. M. Hornreich and S. Shtrikman, Phys. Rev. Lett. **59**, 68 (1987).
[13] D. S. Rokhsar and J. P. Sethna, Phys. Rev. Lett. **56**, 1727 (1986).
[14] L. Longa and H.-R. Trebin, Phys. Rev. Lett. **71**, 2757 (1993); J. Englert, L. Longa, and H.-R. Trebin, Liq. Cryst. **21**, 243 (1996).
[15] R. M. Hornreich, Phys. Rev. Lett. **67**, 2155 (1991); H.-S. Kitzerow, P. P. Crooker, and G. Heppke, Phys. Rev. Lett. **67**, 2151 (1991).
[16] P. H. Keyes, Phys. Rev. Lett. **65**, 436 (1990).
[17] B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. **41**, 121 (1978).
[18] L. Longa, J. Englert, and H.-R. Trebin, in *Proceedings of the LMS Symposium on Mathematical Models of Liquid Crystals and Related Polymeric Systems* (Cambridge University Press, England, 1995).
[19] T. C. Lubensky and H. Stark, Phys. Rev. E **53**, 714 (1996).
[20] S. A. Brazovskiĭ, Sov. Phys. JETP **41**, 85 (1975).
[21] S. A. Brazovskiĭ and S. G. Dmitriev, Sov. Phys. JETP, **42**, 497 (1975).
[22] A. V. Dobrynin, J. Phys. I (France) **5**, 1241 (1995).
[23] R. J. Miller and H. F. Gleeson, Liq. Cryst. **14**, 2001 (1993); P. J. Collings, Mod. Phys. Lett. B. **6**, 425 (1992).
[24] D. Bensimon, E. Domany, and S. Shtrikman, Phys. Rev. A **28**, 427 (1983).
[25] N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group*, in Frontiers in Physics Vol. 85 (Addison-Wesley, Reading, MA, 1992).