Self-consistent model of blue phase III to isotropic phase transition

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(Received 29 February 2004; published 21 July 2004)

In previous publications [Phys. Rev. Lett. **81**, 1457 (1998); Phys. Rev. E **61**, 2759 (2000)], a simplified model with the scalar order parameter and without the cubic term in the Hamiltonian has been used to account for the phase transition between the two isotropic chiral liquids. The present approach is a step towards full analysis of this transition using de Gennes tensor order parameter and the higher-order self-consistent approach. The importance of the cubic term for a proper description of this phase transition is indicated.

DOI: 10.1103/PhysRevE.70.012701 PACS number(s): 61.30.−v, 64.70.−p, 05.40.−a, 61.20.−p

The blue phase III (BP III) to isotropic phase transition (BP III–isotropic transition, as fits) is one of the most complex phase transitions to account for theoretically. The main reason of this complexity lies in the need of including correlation effects even at the level of mean-field-like description [1,2]. On experimental side measurements of the specific heat, the rotatory power, and the light scattering show that the BP III–isotropic transition exists only at moderate chiralities and disappears through the critical point when chirality is high enough [3].

The effective, phenomenological Hamiltonian describing this transition was proposed in Refs. [1,2]. Using the rotatory power as the scalar order parameter and assuming the existence of the critical point [2] it was shown that BP III–isotropic transition should belong to the Ising universality class, the one characterizing, e.g., the ordinary liquid-gas transition. Formulas for the light scattering intensity obtained within such phenomenological approach [2] remain in qualitative agreement with experiments.

Alternatively, there have been attempts to describe BP III–isotropic transition directly from the statistical field theory [4,5] using Landau–Ginzburg–de Gennes free energy [6] as a "mesoscopic" Hamiltonian. So far these attempts are only partly successful. For example, Englert *et al.* [4] showed a possibility of getting a stable critical point with the help of the self-consistent third order cumulant expansion calculations [7] but, owing to mathematical difficulties, we were forced to use a simplified chiral model with a scalar order parameter. Calculations with the full tensor order parameter were initialized in our recent paper [5]. Although two regimes of different correlation behavior at the mesoscopic length scale were shown to exist no direct BP III–isotropic transition was detected within the first-order self-consistent cumulant expansion. Again higher order calculations appeared extremely complex and for technical reasons they were not carried out. Here we present results obtained with the third order self-consistent cumulant expansion, where the tensorial character of the order parameter is partly taken into account. Namely, we consider only dominant fluctuating modes and, additionally, carry out summation over the momentum space using mean-spherical type of approximation. Within this simplified scheme we show that the tensorial character of the order-parameter manifests itself through the cubic term making the phase transition vanish when this term is not present.

Following the notation of the previous papers [5,6] we introduce the Landau–Ginzburg–de Gennes Hamiltonian in the Fourier space as [5]

$$\mathcal{H} = \mathcal{H}_2 + \mathcal{H}_3 + \mathcal{H}_4, \tag{1}$$

where

$$\mathcal{H}_2/v = \frac{1}{4}\sum_{\mathbf{k}}\sum_{m}\left\{t - m\kappa k + \left[1 + \frac{1}{6}\rho(4-m^2)\right]k^2\right\}|\mu_m(k)|^2,$$

$$\mathcal{H}_3/v = -\frac{1}{2}\sum_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3}\sum_{m_1,m_2,m_3}\mathrm{Tr}[\boldsymbol{M}_{m_1}(\hat{\boldsymbol{k}}_1)\boldsymbol{M}_{m_2}(\hat{\boldsymbol{k}}_2)\boldsymbol{M}_{m_3}(\hat{\boldsymbol{k}}_3)] \times \mu_{m_1}(k_1)\mu_{m_2}(k_2)\mu_{m_3}(k_3)\,\delta_{\boldsymbol{k}_1+\boldsymbol{k}_2+\boldsymbol{k}_3,0},$$

$$\mathcal{H}_4/v = \sum_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3,\boldsymbol{k}_4}\sum_{m_1,m_2,m_3,m_4}\mathrm{Tr}[\boldsymbol{M}_{m_1}(\hat{\boldsymbol{k}}_1)\boldsymbol{M}_{m_2}(\hat{\boldsymbol{k}}_2)] \times\mathrm{Tr}[\boldsymbol{M}_{m_3}(\hat{\boldsymbol{k}}_3)\boldsymbol{M}_{m_4}(\hat{\boldsymbol{k}}_4)]\mu_{m_4}(k_4)\,\delta_{\boldsymbol{k}_1+\boldsymbol{k}_2+\boldsymbol{k}_3+\boldsymbol{k}_4,0}, \tag{2}$$

and where $\boldsymbol{M}_m(\hat{\boldsymbol{k}})$ are ordinary base matrices representing different helicity modes. In order to stabilize the isotropic phase the term in curly brackets in $\mathcal{H}_2$ has to be positive, which implies that $\rho > -\frac{3}{2}$ and $\tau_m = t - \kappa^2 m^2/4[1+\frac{1}{6}\rho(4-m^2)] > 0$. The quadratic part of the Hamiltonian can be rewritten in a more convenient form as

$$\mathcal{H}_2/v = \frac{1}{4}\sum_{\boldsymbol{k},m}\{\tau_m + [f(m,k)]^2\}|\mu_m(k)|^2, \tag{3}$$

where

$$f(m,k) = \left(\frac{\kappa m}{2\sqrt{1+\frac{1}{6}\rho(4-m^2)}} - k\sqrt{1+\frac{1}{6}\rho(4-m^2)}\right). \tag{4}$$

From Eq. (3) it is immediately evident that the dominant fluctuating modes are associated with $m = \mathrm{sgn}(\kappa)2$ mode.

The quadratic Hamiltonian (3) could directly be used to introduce perturbative calculations, which is achieved by defining a trial quadratic Hamiltonian [4,5],

$$\mathcal{H}'/v = \frac{1}{4}\sum_{\boldsymbol{k},m} \{\Delta_m + [f(m,k)]^2\}|\mu_m(k)|^2. \quad (5)$$

With the definition (5) we split the Hamiltonian (1) in two parts,

$$\mathcal{H}[\mu_m(k)] = \mathcal{H}'[\mu_m(k)] + \{\mathcal{H}[\mu_m(k)] - \mathcal{H}'[\mu_m(k)]\}, \quad (6)$$

where the difference $\delta\mathcal{H}[\mu_m(k)]=\mathcal{H}[\mu_m(k)]-\mathcal{H}'[\mu_m(k)]$ will be treated as perturbation.

Our aim now is to calculate variationally the free energy of the system,

$$F = -\frac{1}{\beta}\ln Z = -\frac{1}{\beta}\ln Z' - \frac{1}{\beta}\ln\langle e^{-\beta\delta\mathcal{H}}\rangle_{\mathcal{H}'}, \quad (7)$$

where Z is defined as

$$Z = \int \prod_{\boldsymbol{k},m}\left[\sqrt{\frac{v}{2\pi}}d\mu_m(k)\right]e^{-\beta\mathcal{H}[\mu_m(k)]}. \quad (8)$$

Calculations can be performed using cumulant expansion. We need to go up to the third order,

$$\ln\langle e^{-\beta\delta\mathcal{H}}\rangle_{\mathcal{H}'} = -\beta\langle\delta\mathcal{H}\rangle_{\mathcal{H}'} + \frac{1}{2}\beta^2[\langle\delta\mathcal{H}^2\rangle_{\mathcal{H}'} - \langle\delta\mathcal{H}\rangle^2_{\mathcal{H}'}] - \frac{1}{6}\beta^3[\langle\delta\mathcal{H}^3\rangle_{\mathcal{H}'} - 3\langle\delta\mathcal{H}^2\rangle_{\mathcal{H}'}\langle\delta\mathcal{H}\rangle_{\mathcal{H}'} + 2\langle\delta\mathcal{H}\rangle^3_{\mathcal{H}'}] + O(\delta\mathcal{H}^4), \quad (9)$$

and tune Δ_m variationally by minimizing the free energy (7) to get BP III–isotropic transition. Straightforward calculations of Z' yield

$$\ln Z' = \sum_{\boldsymbol{k},m}\frac{1}{2}\ln\frac{4\pi}{\beta\{\Delta_m + [f(m,k)]^2\}}. \quad (10)$$

More work needs to be done to derive the remaining terms. The easiest one, which is also the only one in the first order calculations, has been found in Ref. [5]. It reads

$$\langle\delta\mathcal{H}\rangle_{\mathcal{H}'} = \langle\mathcal{H}_2 - \mathcal{H}' + \mathcal{H}_4\rangle_{\mathcal{H}'} = \sum_m\left\{\tau_m - \Delta_m + \frac{14}{15}\sum_{m'} S_{m'}(\Delta_{m'})\right\}S_m(\Delta_m), \quad (11)$$

where

$$S_m(\Delta_m) = \frac{1}{4}\sum_k \langle|\mu_m(k)|^2\rangle_{\mathcal{H}'} = \frac{v}{4\pi^2\beta}\int_0^\Lambda \frac{k^2dk}{\Delta_m + [f(m,k)]^2}. \quad (12)$$

The cutoff parameter Λ is introduced to eliminate unphysical, high energy modes. The reasonable values for Λ are of the order of κ [4–6].

As already mentioned before the lowest-order calculations with only the $\langle\delta\mathcal{H}\rangle_{\mathcal{H}'}$ term being present and with variational calculus following the Bogolyubov-Hellman-Feynman (BHF) theorem [7,8] do not predict a phase transition between BP III and the isotropic phase [5]. Going beyond the leading order, however, makes perturbative calculations extremely tedious. In order to make them feasible we restrict ourselves to leading terms, corresponding to the dominant $m=2$ mode. In this case the generalized BHF theorem is fulfilled [7] for calculations carried out up to the third order. Using the ordinary Wick theorem for contractions with the Gaussian trial Hamiltonian we arrive at the following contributions to the free energy:

$$\langle\delta\mathcal{H}^2\rangle_{\mathcal{H}'} = \langle(\mathcal{H}_2 - \mathcal{H}')^2 + \mathcal{H}_3^2 + \mathcal{H}_4^2 + 2(\mathcal{H}_2 - \mathcal{H}')\mathcal{H}_4^2 + \rangle_{\mathcal{H}'},$$

$$\langle\delta\mathcal{H}^3\rangle_{\mathcal{H}'} = \langle(\mathcal{H}_2 - \mathcal{H}')^3 + \mathcal{H}_4^3 + 3(\mathcal{H}_2 - \mathcal{H}')\mathcal{H}_3^2 + 3(\mathcal{H}_2 - \mathcal{H}')\mathcal{H}_4^2 + 3(\mathcal{H}_2 - \mathcal{H}')^2\mathcal{H}_4 + 3\mathcal{H}_3^2\mathcal{H}_4\rangle_{\mathcal{H}'}. \quad (13)$$

Note the existence of the cubic terms, which were not present in Eq. (11). To perform calculations further we replace

$$\delta_{\boldsymbol{k}_1+\cdots+\boldsymbol{k}_n,0}\delta_{\boldsymbol{k}_{n+1}+\cdots+\boldsymbol{k}_{n+m},0} \to \delta_{\boldsymbol{k}_1+\cdots+\boldsymbol{k}_{n+m},0}, \quad (14)$$

which is in the spirit of the mean-spherical approximation, known in statistical mechanics. Using notation $\tau\equiv\tau_2$, $\Delta\equiv\Delta_2$, and $S(\Delta)\equiv S_2(\Delta_2)$ it yields

$$\delta H^2 = (\tau-\Delta)^2S^2(\Delta) + \left[\frac{56}{25}\frac{28}{15}(\tau-\Delta)\right]S^3(\Delta) + \frac{308}{125}S^4(\Delta) \quad (15)$$

and

$$\delta H^3 = (\tau-\Delta)^3S^3(\Delta) + \frac{14}{5}\left[(\tau-\Delta) + \frac{168}{25}\right](\tau-\Delta)S^4(\Delta) + \left[\frac{924}{125}(\tau-\Delta) + \frac{16016}{625}\right]S^5(\Delta) + \frac{8008}{625}S^6(\Delta). \quad (16)$$

Consequently, the total free energy takes the form

$$F = S(\Delta)(\tau-\Delta) + \frac{14}{15}S^2(\Delta) - \frac{28}{25}\beta S^3(\Delta) - \frac{896}{1125}\beta S^4(\Delta) + \frac{2016}{625}\beta^2S^5(\Delta) + \frac{63616}{50625}\beta^2S^6(\Delta). \quad (17)$$

According to the generalized BHF inequality [7,8], which holds in this case, the variational parameter Δ that minimizes the free energy has to satisfy the following equation:

$$\frac{\partial F}{\partial\Delta} = 0 \quad \text{and} \quad \frac{\partial^2F}{\partial\Delta^2} > 0, \quad (18)$$

which gives

$$\tau - \Delta + \frac{28}{15}S(\Delta) - \frac{84}{25}\beta S^2(\Delta) - \frac{3584}{1125}\beta S^3(\Delta) + \frac{2016}{125}\beta^2S^4(\Delta) + \frac{127232}{16875}\beta^2S^5(\Delta) = 0. \quad (19)$$

Perhaps it is worthwhile to mention at this point that without the approximation (14) the parameter Δ is momentum dependent, which converts Eq. (19) into integral equations.

The approximations leading to Eq. (19) appear sufficient to explain the transition between the isotropic phase and BP III. In particular, the Δ parameter, being the inverse square of the correlation length between $m=2$ modes of orientational degrees of freedom in chiral liquids, shows characteristic discontinuous behavior in the transition region as shown in Fig. 1. In accordance with experiments the transition line ends up with the critical point when chirality is high enough. The presence of the cubic invariant is crucial to get the transition between the isotropic phase and BP III. This could be shown by carrying out the same calculations with $\mathcal{H}_3=0$. Then the terms proportional to $S^3(\Delta)$ and $S^5(\Delta)$ vanish from Eq. (17) and, correspondingly, the terms $S^2(\Delta)$ and $S^4(\Delta)$ from Eq. (19). As one can see from the inset in Fig. 1 there is no phase transition with the cubic term being absent. The same result holds for all parameters studied numerically. It seems therefore justified to postulate that the $\mathcal{H}_3$ plays an important role in proper understanding of not only the ordinary cubic blue phases but also the BP III–isotropic transition phase transition. This aspect of the theory has not been present in simplified description with the scalar order parameter [4], where the transition was present even in the absence of cubic interactions.

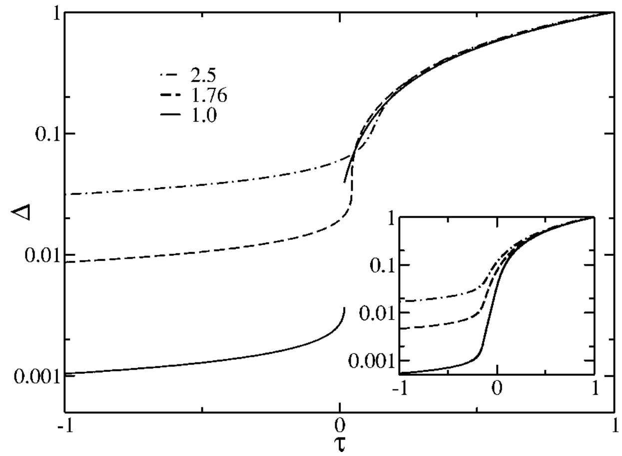

FIG. 1. Transition between isotropic chiral phases. The plot shows variational parameter Δ as function of temperature τ for different chiralities κ. The critical point corresponds to $\kappa=1.76$. Other parameters are: $\Lambda=\kappa$, $\beta=3.38$. The inset corresponds to calculations with vanishing cubic term $\mathcal{H}_3=0$. All values are dimensionless.

Summarizing, we presented calculations employing the self-consistent, third order cumulant expansion to describe the isotropic-to-BP III phase transition. Statistical field theory calculations have been carried out for the Landau–Ginzburg–de Gennes Hamiltonian expressed in terms of the alignment tensor field. The calculations not only account for the phase transition between the isotropic and BP III phases but also demonstrate the importance of the cubic invariant.

[1] L. Longa, J. Englert, and H.-R. Trebin, *LMS Symposium on Mathematical Models of Liquid Crystals and Related Polymeric Systems* (Durham, 1995, unpublished).
[2] T. C. Lubensky and H. Stark, Phys. Rev. E **53**, 714 (1996).
[3] E. P. Koistinen and P. H. Keyes, Phys. Rev. Lett. **74**, 4460 (1995); Z. Kutnjak, C. W. Garland, J. L. Passmore, and P. J. Collings, *ibid.* **74**, 4859 (1995); J. B. Becker and P. J. Collings, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **265**, 163 (1995).
[4] J. Englert, L. Longa, H. Stark, and H.-R. Trebin, Phys. Rev. Lett. **81**, 1457 (1998); J. Englert, H. Stark, L. Longa, and H.-R. Trebin, Phys. Rev. E **61**, 2759 (2000).
[5] L. Longa, M. Cieśla, and H.-R. Trebin, Phys. Rev. E **67**, 061705 (2003).
[6] H. Grebel, R. M. Hornreich, and S. Shtrikman, Phys. Rev. A **28**, 1114 (1983); **30**, 3264 (1984).
[7] C. Tsallis and L. R. da Silva, Phys. Rev. A **26**, 1095 (1982).
[8] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965); R. P. Feynman, *Statistical Mechanics* (Benjamin, Reading, MA, 1972).