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Theory of a critical point in the blue-phase-III–isotropic phase diagram

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In low to moderate chirality systems, there is a first-order phase transition between the isotropic phase and the blue phase III (BP III) in chiral liquid crystals. Recent experiments [Z. Kutnjak, C. W. Garland, J. L. Passmore, and P. J. Collings, Phys. Rev. Lett. **74**, 4859 (1995); J. B. Becker and P. J. Collings, Mol. Cryst. Liq. Cryst. **265**, 163 (1995)] on high chirality systems show no transition. This suggests that the isotropic phase and BP III have the same isotropic symmetry and that there is a liquid-gaslike critical point in the temperature-chirality plane terminating a line of coexistence. In this case the averaged alignment tensor $\langle \boldsymbol{Q}(\mathbf{x}) \rangle$ is zero in both the isotropic phase and BP III. We introduce a scalar order parameter $\langle \psi \rangle = \langle (\boldsymbol{\nabla} \times \boldsymbol{Q}) \cdot \boldsymbol{Q} \rangle$ to describe both phases and develop a Landau-Ginzburg-Wilson Hamiltonian in ψ and $\boldsymbol{Q}$, which can be motivated by a coarse-graining procedure. Our model predicts that the isotropic-to-BP-III transition is in the same universality class (Ising) as the liquid-gas transition. By looking at the fluctuations of $\boldsymbol{Q}$ around the critical point, we obtain formulas for the light scattering and the rotary power, which are in qualitative agreement with experiments [J. B. Becker and P. J. Collings, Mol. Cryst. Liq. Cryst. **265**, 163 (1995)] and need to be checked quantitatively.

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Chirality in liquid crystals produces a fascinating array of equilibrium phases with orientational structures at length scales much larger than typical molecular dimensions. These phases include the cholesteric or chiral nematic phase, blue phases [1,2], the chiral smectic-C^* phase [3,4], and the twist-grain boundary phase [5]. Three distinct blue phases (BPs) designated BP I, BP II, and BP III have been identified in calorimetric, optical, and other experiments [1]. The structures of BP I and BP II are now well understood: both are cubic crystals with unit cells characterized by a complex spatial pattern of the alignment tensor $\boldsymbol{Q}(\mathbf{x})$, but with a spatially uniform center-of-mass density. The space group symmetries of BP I and BP II are, respectively, O^8 and O^2.

There is as yet no consensus regarding the structure of the BP III, or the blue fog, as it is often called. It has been identified via calorimetric [6] and other measurements [1] in a number of compounds as a thermodynamically stable phase distinct from the other blue phases. It appears, however, to be homogeneous and isotropic like the isotropic phase: no experiments have detected evidence of icosahedral or bond orientational order suggested by various theories [7–13]. Early light scattering experiments, however, were best explained by a random, possibly isotropic distribution of double twist cylinders ("spaghetti model") [14,15]. Keyes has suggested [16,17] that the BP III and isotropic phase, such as the liquid and gas phases, have exactly the same symmetry and that there could therefore be a continuous path between them around a liquid-gaslike critical point terminating a line of coexistence [18]. Recent experiments by Kutnjak *et al.* [19] and by Becker and Collings [20] confirm the absence of any BP-III–isotropic transition in the highly chiral liquid crystal CE2. On the other hand, experiments on less chiral systems (CE6 and CE4) show a finite latent heat [21] and a jump in rotary power and scattered light intensity [20], indicating a first-order isotropic–BP-III transition. The magnitude of the latent heat and the jumps decreases in these chiral-racemic systems with increasing fraction of one of the chiral compounds, suggesting the schematic phase diagram shown in Fig. 1 with a liquid-gaslike critical point in the temperature (t) chirality (κ) plane (the analog of the pressure-temperature plane in a liquid-gas system).

If this scenario is correct, then it should be possible to establish an almost one-to-one correspondence between the liquid-gas and the BP-III–isotropic transition. To

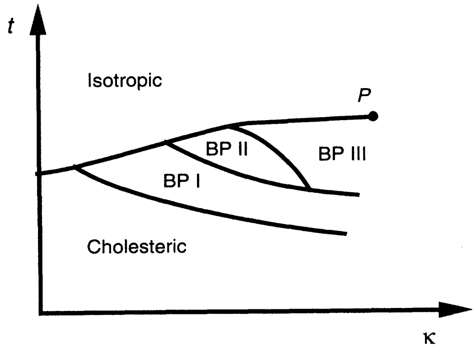

FIG. 1. Schematic phase diagram for chiral nematogens in the t-κ plane showing the liquid-gaslike critical point terminating a line of coexistence of the isotropic phase and BP III.

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do this, we need to identify an order parameter distinguishing the isotropic phase from BP III and to construct from it a Landau-Ginzburg-Wilson (LGW) Hamiltonian. As we have argued, both the isotropic and the BP III are homogeneous and isotropic. They must therefore be characterized by either scalar or pseudoscalar order parameters (the latter because the system is composed of chiral molecules that admit pseudoscalar invariants). This means that the mean value $\langle \boldsymbol{Q} \rangle$ of the thermally fluctuating alignment tensor $\boldsymbol{Q}$, which develops nonvanishing spatially modulated components in BP I and BP II, cannot be used as an order parameter: $\langle \boldsymbol{Q} \rangle$ is zero in both the isotropic phase and BP III. What then is a good order parameter? The mass density ρ is a candidate, but density changes across the BP-III–isotropic transition are extremely small. We are thus left with quadratic combinations of $\boldsymbol{Q}$ such as $\langle \mathrm{tr}\boldsymbol{Q}^2 \rangle$, $\langle \psi \rangle = \langle\, (\nabla \times \boldsymbol{Q}) \cdot \boldsymbol{Q} \rangle = \langle \varepsilon_{ijk} Q_{il} \nabla_j Q_{kl} \rangle$, and similar terms. As we shall see shortly, both $\langle \mathrm{tr}\boldsymbol{Q}^2 \rangle$ or $\langle \psi \rangle$ (or some linear combination of the two) are reasonable candidates for an order parameter. Indeed, self-consistent calculations of a BP-III–isotropic critical point reported by Keyes [17] in essence treat $\langle \mathrm{tr}\boldsymbol{Q}^2 \rangle$ as an order parameter. We feel, however, that $\langle \psi \rangle$, which exists only in a chiral system, is more fundamental because the BP-III–isotropic critical point exists only in chiral systems. The parameter $\langle \mathrm{tr}\boldsymbol{Q}^2 \rangle$ could be used to describe a liquid-gaslike critical point terminating a line of coexistence of two isotropic phases of achiral nematogens. To our knowledge no such critical point has been observed yet. We thus take $\langle \psi \rangle$ to be our order parameter, even though changes in $\langle \psi \rangle$ will necessarily be accompanied by changes in $\langle \mathrm{tr}\boldsymbol{Q}^2 \rangle$. Changes in both $\langle \psi \rangle$ and $\langle \mathrm{tr}\boldsymbol{Q}^2 \rangle$ will lead to changes in rotary power and the intensity of scattered light.

Having identified an order parameter, we next need to develop a phenomenological LGW Hamiltonian that can describe both the transition in ψ and changes in correlations of the alignment tensor $\boldsymbol{Q}$. There are several ways of arriving at this Hamiltonian, all of which will ultimately give the same result. The simplest approach is to write down the most general functional of ψ and $\boldsymbol{Q}$ consistent with the symmetry of the problem. Alternatively, one can view $\boldsymbol{Q}$ and a Hamiltonian $\mathcal{H}_\Lambda[\boldsymbol{Q}(\mathbf{x})]$ expressed in terms of $\boldsymbol{Q}$ as the providing fundamental "microscopic" description down to some length scale $a = 2\pi/\Lambda$, where Λ is a wave-number cutoff. Then an effective coarse-grained Hamiltonian as a functional of $\boldsymbol{Q}$ and ψ can be constructed by integrating out variables with wave numbers $\Lambda' < q < \Lambda$ subject to the constraint that $\psi = (\nabla \times \boldsymbol{Q}) \cdot \boldsymbol{Q}$. The Hamiltonian $\mathcal{H}_\Lambda[\boldsymbol{Q}(\mathbf{x})]$ has the scaled form of the Landau–de Gennes free energy used in most studies of blue phases [2]:

$$\mathcal{H}_\Lambda[\boldsymbol{Q}(\mathbf{x})] = \frac{1}{2}\int d^3x \left(\frac{t}{2}\,\mathrm{tr}\boldsymbol{Q}^2 + \frac{1}{2}\,(\nabla \otimes \boldsymbol{Q}) \cdot (\nabla \otimes \boldsymbol{Q}) + \frac{\varrho}{2} \nabla \boldsymbol{Q} \cdot \nabla \boldsymbol{Q} - \kappa (\nabla \times \boldsymbol{Q}) \cdot \boldsymbol{Q} \right) - \sqrt{6} \int d^3x\, \mathrm{tr}\boldsymbol{Q}^3 + \int d^3x [\mathrm{tr}\boldsymbol{Q}^2]^2 \ , \qquad (1)$$

where $(\nabla \otimes \boldsymbol{Q}) \cdot (\nabla \otimes \boldsymbol{Q}) = (\nabla_k Q_{ij})^2$ and $\nabla \boldsymbol{Q} \cdot \nabla \boldsymbol{Q} = \nabla_i Q_{ij} \nabla_k Q_{kj}$. All quantities are unitless. The distance x is measured in units of the order parameter correlation length $\xi_R = 25\,\mathrm{nm}$ at the first-order transition temperature T_N of the racemic mixture [22]. Then the chirality $\kappa = q_c \xi_R$ is the wave number q_c of the cholesteric phase relative to $1/\xi_R$. A scaling factor for the energy density is provided by $16 L \Delta T_N / T_N \approx 4 \times 10^5\,\mathrm{ergs/cm^3}$, where L is the latent heat per volume of a racemic mixture and $\Delta T_N = T_N - T_N^*$, where T_N^* is the mean-field limit of metastability of the isotropic phase [23]. The energy scale of the Hamiltonian then is $16 L \xi_R^3 \Delta T_N / T_N \approx 6 \times 10^{12}\,\mathrm{ergs}$. The reduced temperature t is defined by $t = (T - T_N^*)/\Delta T_N$ [22]. Typical values for the temperature scale are $0.5 - 1\,\mathrm{K}$. Finally, ϱ stands for the ratio c_2/c_1 of two Landau coefficients. After Stinson and Litster it is smaller than 1 for 4-methoxybenzlidene-4′-*n*-butylaniline (MBBA) [24]. We stress that higher-order terms in $\boldsymbol{Q}$ [25,26], in particular terms such as $[(\nabla \times \boldsymbol{Q}) \cdot \boldsymbol{Q}]^p, p \geq 2$, may be needed to produce a BP-III–isotropic critical point.

To implement the procedure we write the partition function as

$$Z = \int \mathcal{D}\boldsymbol{Q}\, e^{-\beta \mathcal{H}_\Lambda[\boldsymbol{Q}(\mathbf{x})]} = \int \mathcal{D}\boldsymbol{Q} \int \mathcal{D}\psi\, e^{-\beta \mathcal{H}_\Lambda[\boldsymbol{Q}(\mathbf{x})]} \Delta[\psi - (\nabla \times \boldsymbol{Q}) \cdot \boldsymbol{Q}] \ , \qquad (2)$$

where we have introduced the delta functional $\Delta[\varphi(\mathbf{x})]$ with the Fourier representation

$$\Delta[\varphi(\mathbf{x})] = \int \frac{\mathcal{D}\lambda}{2\pi} \exp\left(+i \int d^3x \lambda(\mathbf{x}) \varphi(\mathbf{x}) \right) \ , \qquad (3)$$

which can be proved by discretizing the integrals. Now we break up $\boldsymbol{Q}$ into a "slow" and a "fast" part

$$\boldsymbol{Q}(q) = \boldsymbol{Q}^<(q) + \boldsymbol{Q}^>(q) \ , \qquad (4)$$

where $\boldsymbol{Q}^<(q) = \mathbf{0}$ if $\Lambda' < q < \Lambda$ and $\boldsymbol{Q}^>(q) = \mathbf{0}$ if $q < \Lambda'$, and integrate over $\boldsymbol{Q}^>$ and λ. Then

$$Z = \int \mathcal{D}\psi \int \mathcal{D}\boldsymbol{Q}^<\, e^{-\beta \widetilde{\mathcal{H}}[\boldsymbol{Q}^<, \psi]} \qquad (5)$$

is a functional of the independent variables ψ and $\boldsymbol{Q}^<$, which we assume to have spatial variations with $q < \Lambda'$. A complete calculation of $\widetilde{\mathcal{H}}[\boldsymbol{Q}^<, \psi]$ for the initial Hamiltonian $\mathcal{H}_\Lambda[\boldsymbol{Q}]$ is tedious and not terribly illuminating. In the Appendix, we calculate this quantity for the harmonic part of $\mathcal{H}_\Lambda[\boldsymbol{Q}]$. In particular, we calculate ψ and ψ^2 terms in $\widetilde{\mathcal{H}}[\boldsymbol{Q}^<, \psi]$ and show that the dominant coupling term is proportional to $\psi (\nabla \times \boldsymbol{Q}) \cdot \boldsymbol{Q}$. The average of any function of $\boldsymbol{Q}$ or ψ with wave number q with $0 < q < \Lambda'$ can be calculated using either $\mathcal{H}_\Lambda[\boldsymbol{Q}(\mathbf{x})]$ and the partition function of Eq. (2) or $\widetilde{\mathcal{H}}[\boldsymbol{Q}^<, \psi]$ and the partition function of Eq. (5).

We are interested in properties near the critical point where $\langle\, \psi\, \rangle = \psi_c$. We therefore define φ via

$$\psi = \psi_c + \varphi \qquad (6)$$

and express our Hamiltonian in terms of φ rather than ψ omitting a constant part. Then

$$Z = \int \mathcal{D}\varphi \int \mathcal{D}\boldsymbol{Q} e^{-\beta\mathcal{H}[\boldsymbol{Q},\varphi]} \ , \tag{7}$$

where we have replaced $\boldsymbol{Q}^{<}$ by $\boldsymbol{Q}$ with the understanding that its wave vectors are restricted to $q < \Lambda'$. Our new Hamiltonian $\mathcal{H}[\boldsymbol{Q},\varphi]$ can be decomposed into parts depending, respectively, on $\boldsymbol{Q}$ and φ separately and a coupling term

$$\mathcal{H}[\boldsymbol{Q},\varphi] = \mathcal{H}_1[\boldsymbol{Q}] + \mathcal{H}_2[\varphi] + \mathcal{H}_C[\boldsymbol{Q},\varphi] \ . \tag{8}$$

To produce a critical point, $\mathcal{H}_2[\varphi]$ should have the same form as the LGW Hamiltonian describing a liquid-gas transition

$$\mathcal{H}_2[\varphi] = \int d^3x \left[\frac{1}{2}\tilde{r}\varphi^2 + \frac{1}{2}\tilde{c}(\boldsymbol{\nabla}\varphi)^2 - \tilde{w}\varphi^3 + \tilde{u}\varphi^4 - \tilde{h}\varphi\right] \tag{9}$$

in which all quantities are unitless. We restrict ourselves to the simplest forms for the other two terms

$$\begin{aligned}\mathcal{H}_1[\boldsymbol{Q}] = \frac{1}{2}\int d^3x \bigg(&\frac{t}{2}\mathrm{tr}\boldsymbol{Q}^2 + \frac{1}{2}(\boldsymbol{\nabla}\otimes\boldsymbol{Q})\cdot(\boldsymbol{\nabla}\otimes\boldsymbol{Q}) \\ &+\frac{\varrho}{2}\boldsymbol{\nabla}\boldsymbol{Q}\cdot\boldsymbol{\nabla}\boldsymbol{Q} - (\kappa + 2\lambda\psi_c)(\boldsymbol{\nabla}\times\boldsymbol{Q})\cdot\boldsymbol{Q}\bigg),\end{aligned} \tag{10}$$

$$\mathcal{H}_C[\boldsymbol{Q},\varphi] = -\lambda \int d^3x\varphi(\mathbf{x})\,(\boldsymbol{\nabla}\times\boldsymbol{Q})\cdot\boldsymbol{Q} \ . \tag{11}$$

$\mathcal{H}_1[\boldsymbol{Q}]$ has basically the same form as the harmonic part of $\mathcal{H}_\Lambda[\boldsymbol{Q}(\mathbf{x})]$ in Eq. (1), but with the chirality κ, the coefficient of the chiral term, renormalized. We now have a complete Hamiltonian allowing us to describe both the critical properties of φ and the coupling of φ to $\boldsymbol{Q}$.

The phase transition and correlations in ψ are determined by an effective Hamiltonian in which $\boldsymbol{Q}$ has been removed altogether

$$Z = \int \mathcal{D}\varphi\, e^{-\beta\mathcal{H}_{\mathrm{eff}}[\varphi]} \ , \tag{12}$$

where

$$\begin{aligned}H_{\mathrm{eff}}[\varphi] &= -\frac{1}{\beta}\ln \int \mathcal{D}\boldsymbol{Q} e^{-\beta\mathcal{H}[\boldsymbol{Q},\varphi]} \\ &= \int d^3x \left(\frac{1}{2}r\varphi^2 + \frac{1}{2}c(\boldsymbol{\nabla}\varphi)^2 - w\varphi^3 + u\varphi^4 - h\varphi\right)\end{aligned} \tag{13}$$

contains renormalized parameters r, c, w, u, and h compared to those in the Hamiltonian $\mathcal{H}_2[\varphi]$ in Eq. (9). They are all functions of the temperature t and the chirality κ. The parameters r, w, and h go linearly to zero as the critical point $(\kappa, t) = (\kappa_c, t_c)$ is approached [18]:

$$r = a_1\Delta t + b_1\Delta\kappa, \tag{14}$$

$$h = a_2\Delta t + b_2\Delta\kappa, \tag{15}$$

$$w = a_3\Delta t + b_3\Delta\kappa \ , \tag{16}$$

where we introduced $\Delta t = t - t_c$ and $\Delta\kappa = \kappa - \kappa_c$. We now have a standard description of a liquid-gas transition. Thus in the vicinity of the critical point, the order parameter $\langle\varphi\rangle$ obeys the scaling relation [18]

$$\langle\,\varphi\,\rangle = r^{\beta} Y\left(\frac{h}{r^{\Delta}}\right) \ , \tag{17}$$

where β is the order parameter and $\Delta = \beta + \gamma$ the gap exponent. In mean-field theory, $\beta = 1/2$ and $\Delta = 3/2$, whereas at a three-dimensional liquid-gas critical point $\beta \approx 0.32$ and $\Delta \approx 1.54$. To provide qualitative information about the behavior of the order parameter, which can be compared with the rotary power and light scattering data of Ref. [20], we plot in Figs. 2 and 3 the mean-field form of $-\langle\,\varphi\,\rangle$ (calculated with $w = 0$ and $u = 1$) as a function of Δt for different values of $\Delta\kappa$. In experimental phase diagrams, the coexistence curve is approximately parallel to the chirality (κ) axis [27]. We therefore take $h = -\Delta t$ [$a_2 = -1$, $b_2 = 0$ in Eq. (15)]. In Fig. 2 we take $r = \Delta\kappa$ [$a_1 = 0$, $b_1 = 1$ in Eq. (14)]. The resulting function is odd under reflections about the $\Delta t = 0$ axis: $\langle\,\varphi(\Delta t)\,\rangle = \langle\,\varphi(-\Delta t)\,\rangle$. In Fig. 3 we take $r = 2\Delta t + 0.3\Delta\kappa$. The curves $-\langle\,\varphi(\Delta t)\,\rangle$ now have no symmetry and look qualitatively like the measured rotary power and intensity curves. For $\Delta\kappa = 0$ and $|\Delta t| \to 0$ the "field" dependence of $\langle\,\varphi(\Delta t)\,\rangle$ follows $|\Delta t|^{1/\delta}$ with $\delta = \Delta/\beta = 3$ in both cases. Furthermore, the discontinuity in $\langle\,\varphi\,\rangle$ at the phase transition behaves like $\sqrt{|r|}$ or, if the coexistence line is given by $\Delta t = 0$, like $\sqrt{|\Delta\kappa|}$.

Having determined $\langle\varphi\rangle$, we can now calculate the autocorrelation function of the alignment tensor $\boldsymbol{Q}$ using $\mathcal{H}[\boldsymbol{Q},\varphi]$. We choose a mean-field approximation for φ

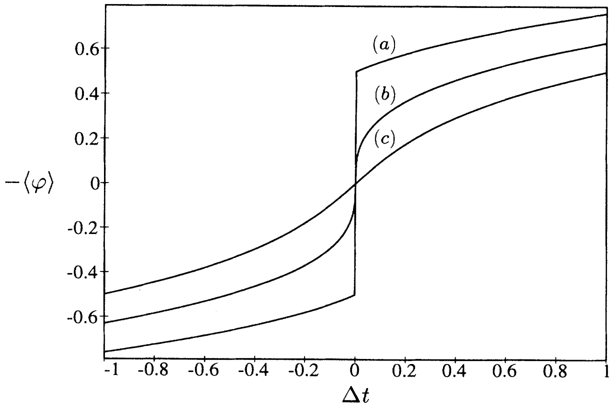

FIG. 2. Temperature behavior of $-\langle\varphi\rangle$ with $r = \Delta\kappa$, $h = -\Delta t$, and $u = 1$: (a) first-order transition at $\Delta\kappa = -1$, (b) second-order transition at the critical point ($\Delta\kappa = 0$), and (c) beyond the critical point at $\Delta\kappa = 1$. All three curves are odd under $\Delta t \to -\Delta t$.

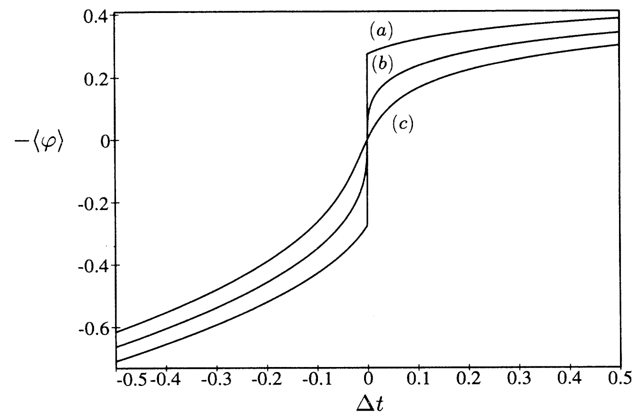

FIG. 3. Temperature behavior of $-\langle\varphi\rangle$ with $r = 2\Delta t + 0.3\Delta\kappa$, $h = -\Delta t$, and $u = 1$: (a) first-order transition at $\Delta\kappa = -1$, (b) second-order transition at the critical point ($\Delta\kappa = 0$), and (c) beyond the critical point at $\Delta\kappa = 1$. None of these curves shows any symmetry.

replacing φ by $\langle\varphi\rangle$ in $\mathcal{H}_C[\boldsymbol{Q},\varphi]$ of Eq. (10) and restrict ourselves to the harmonic part of $\mathcal{H}[\boldsymbol{Q},\varphi]$ in $\boldsymbol{Q}$. It can be diagonalized in the usual way [2] by going to a spherical basis

$$\boldsymbol{Q}(\boldsymbol{q}) = \sum_{m=-2}^{m=2} Q_m(\boldsymbol{q})\boldsymbol{M}_m(\boldsymbol{q}), \tag{18}$$

where

$$\boldsymbol{M}_0(\boldsymbol{q}) = \frac{1}{\sqrt{6}}(3\hat{\boldsymbol{q}} \otimes \hat{\boldsymbol{q}} - \boldsymbol{1}), \tag{19}$$

$$\boldsymbol{M}_1(\boldsymbol{q}) = \frac{1}{\sqrt{2}}[\hat{\boldsymbol{q}} \otimes \boldsymbol{m}(\boldsymbol{q}) + \boldsymbol{m}(\boldsymbol{q}) \otimes \hat{\boldsymbol{q}}] = \boldsymbol{M}^*_{-1}(\boldsymbol{q}), \tag{20}$$

$$\boldsymbol{M}_2(\boldsymbol{q}) = \boldsymbol{m}(\boldsymbol{q}) \otimes \boldsymbol{m}(\boldsymbol{q}) = \boldsymbol{M}^*_{-2}(\boldsymbol{q}), \tag{21}$$

with

$$\boldsymbol{m}(\boldsymbol{q}) = \frac{1}{\sqrt{2}}(\hat{\boldsymbol{\xi}} + i\hat{\boldsymbol{\eta}}) \tag{22}$$

and $\{\hat{\boldsymbol{\xi}}, \hat{\boldsymbol{\eta}}, \hat{\boldsymbol{q}}\}$ forming a right-handed system of orthonormal vectors. Then the correlation function for the amplitude $Q_m(\boldsymbol{q})$ is

$$G_m(\boldsymbol{q}) = \langle|Q_m(\boldsymbol{q})|^2\rangle = \frac{2k_BT}{t - m[\kappa + 2\lambda(\psi_c + \langle\varphi\rangle)]q + [1 + \frac{\varrho}{2}(4 - m^2)]q^2}, \tag{23}$$

with k_BT given in the energy unit we introduced above. One can check that this provides the correct description of G_m in the vicinity of the critical point even when critical fluctuations are correctly incorporated into $\langle\varphi\rangle$.

We can now discuss scattering and rotary power experiments in the vicinity of the critical point. Basically the scattering intensity at scattering vector $\boldsymbol{q}$ is

$$I(\boldsymbol{q}) = \sum_{m=-2}^{2} G_m(\boldsymbol{q})\alpha_m(\boldsymbol{q}), \tag{24}$$

where

$$\alpha_m(\boldsymbol{q}) = |\boldsymbol{e}_f^* \cdot \boldsymbol{M}_m(\boldsymbol{q})\boldsymbol{e}_i|^2 . \tag{25}$$

$\boldsymbol{e}_i$ and $\boldsymbol{e}_f$ describe, respectively, the polarization of the incident and the scattered light. In typical scattering experiments, the intensity of light scattered through 90° is monitored [19]. In this case, $q = \sqrt{2}k_0$, where k_0 is the wave number of the scattered light. The scattering intensity $I_c(\boldsymbol{q})$ at the critical point is obtained by setting $\langle\varphi\rangle = 0$ in Eqs. (23) and (24). Thus near the critical point (t_c, κ_c)

$$I(\boldsymbol{q}) = I_c(\boldsymbol{q}) + \Delta I(\boldsymbol{q}), \tag{26}$$

with

$$\Delta I(\boldsymbol{q}) = \sum_{m=-2}^{2} \Delta G_m(\boldsymbol{q})\alpha_m(\boldsymbol{q})\langle\varphi\rangle + O(\langle\varphi\rangle^2, \Delta\kappa, \Delta t), \tag{27}$$

where

$$\Delta G_m(\boldsymbol{q}) = -\frac{4k_BTm\lambda q}{\{t_c - m(\kappa_c + 2\lambda\psi_c) + [1 + \frac{\varrho}{2}(4 - m^2)]q^2\}^2} \tag{28}$$

results from the expansion of $G_m(\boldsymbol{q})$ around the critical point. Thus $I(\boldsymbol{q})$ at fixed $\boldsymbol{q}$ is linear in $\langle\varphi\rangle$ for small $\langle\varphi\rangle$. As a function of t and κ near the critical point, it should look like the curves of Figs. 2 or 3. Indeed, experiments of Becker and Collings [20] show a qualitative agreement with Fig. 3. Note, however, that the magnitude of the deviation in $I(\boldsymbol{q})$ from its value at the critical point depends on $\boldsymbol{q}$, i.e., on the wavelength and angle of scattered light. It would be interesting to investigate this effect experimentally. The quantity $\langle \mathrm{tr}\boldsymbol{Q}^2\rangle = \sum_m G_m(\boldsymbol{q})$ is also linear in $\langle\varphi\rangle$ near the critical point, indicating, as discussed earlier, that we could have used it rather than $\langle\psi\rangle$ as an order parameter.

The rotary power γ for light can be related to an integral over the correlation functions G_m. In the long-wavelength limit ($k \ll \kappa$) only the modes with helicity $m = 1$ and -1 contribute [28]. However, in the pretransitional region from the isotropic to the cholesteric or blue phases the $m = \pm 2$ modes also contribute significantly through the next higher order in the wave number of light, as was shown by Filev [29] theoretically and confirmed by Collings *et al.* [30,31] experimentally. We follow the derivation given by Bensimon *et al.* [28] and obtain, in units of ξ_R,

$$\gamma = \frac{1}{12\pi^2\epsilon_0}\int_0^\Lambda dq\,q[G_1(q) - G_{-1}(q)] - \frac{k^2}{18\pi^2\epsilon_0}\int_0^\Lambda dq\frac{1}{q}[G_1(q) - G_{-1}(q)] - \frac{2k^2}{9\pi^2\epsilon_0}\int_0^\Lambda dq\frac{1}{q}[G_2(q) - G_{-2}(q)] \ , \tag{29}$$

where ϵ_0 is the dielectric constant of the system and k the wave number of light in units of $1/\xi_R$. Here Λ should be the original upper wave number cutoff before coarse graining. Our theory provides directly an expression for $G_{\pm 1}$ and $G_{\pm 2}$ for $q < \Lambda'$. Thus, to obtain the complete expression for γ, we would have to calculate $G_{\pm 1}$ and $G_{\pm 2}$ for $q > \Lambda'$ in the presence of a nonzero $\langle\varphi\rangle$, using the original Hamiltonian $\mathcal{H}_\Lambda[\boldsymbol{Q}(\mathbf{x})]$ rather than the coarse-grained Hamiltonian $\widetilde{\mathcal{H}}[\boldsymbol{Q}^<, \psi]$. Fortunately, γ is not very sensitive to the upper cutoff and indeed in standard treatments [28] Λ is set to ∞ in Eq. (29). After integration with $\Lambda = \infty$ one finds that

$$\gamma = \frac{k_BT}{12\pi\epsilon_0}\frac{\kappa + 2\lambda(\psi_c + \langle\varphi\rangle)}{(1+\frac{g}{2})^{3/2}}\left[\frac{1 - \frac{2}{3}(1+\frac{g}{2})\frac{k^2}{t}}{(t - t_1)^{1/2}} - \frac{16}{3}\frac{(1+\frac{g}{2})^{3/2}}{(t - t_2)^{1/2}}\frac{k^2}{t}\right] \ , \quad t > [\kappa + 2\lambda(\psi_c + \langle\varphi\rangle)]^2 \ , \tag{30}$$

where

$$t_1 = \frac{[\kappa + 2\lambda(\psi_c + \langle\varphi\rangle)]^2}{4(1+\frac{g}{2})} \ , \tag{31}$$

$$t_2 = [\kappa + 2\lambda(\psi_c + \langle\varphi\rangle)]^2 \tag{32}$$

are, respectively, the critical temperatures of the $m = \pm 1$ and $m = \pm 2$ modes. They are both less than t_c since the BP-III–isotropic critical point is assumed to be far from any ordered BP structure. Finally, near the critical point

$$\gamma = \gamma_c + \Delta\gamma \tag{33}$$

with the optical activity at the critical point,

$$\gamma_c = \frac{k_BT}{12\pi\epsilon_0}\frac{\kappa_c + 2\lambda\psi_c}{(1+\frac{g}{2})^{3/2}}\left[\frac{1 - \frac{2}{3}(1+\frac{g}{2})\frac{k^2}{t_c}}{(t_c - t_{1c})^{1/2}} - \frac{16}{3}\frac{(1+\frac{g}{2})^{3/2}}{(t_c - t_{2c})^{1/2}}\frac{k^2}{t_c}\right] \ , \tag{34}$$

and the deviation

$$\Delta\gamma = \frac{k_BT}{6\pi\epsilon_0}\frac{\lambda}{(1+\frac{g}{2})^{3/2}}\langle\varphi\rangle\left[\frac{t_c - \frac{2}{3}(1+\frac{g}{2})k^2}{(t_c - t_{1c})^{3/2}} - \frac{16}{3}\frac{(1+\frac{g}{2})^{3/2}}{(t_c - t_{2c})^{3/2}}k^2\right] + O(\langle\varphi\rangle^2, \Delta\kappa, \Delta t) \ , \tag{35}$$

where

$$t_{1c} = \frac{[\kappa_c + 2\lambda\psi_c]^2}{4(1+\frac{g}{2})} \ , \quad t_{2c} = [\kappa_c + 2\lambda\psi_c]^2 \ . \tag{36}$$

In the experiments by Becker and Collings [20] the optical activity changes its sign close to the phase transition. In Eq. (34), for example, this can be achieved only when t_c is close to the critical temperature t_{2c} of the $m = \pm 2$ modes, since $k^2 \ll t_c \propto \kappa^2$. Furthermore, like ΔI, $\Delta\gamma$ should also scale as $\langle\varphi\rangle$, which is well confirmed by the measurements [20]. Note, however, that though both ΔI and $\Delta\gamma$ are linear in $\langle\varphi\rangle$ at small $\langle\varphi\rangle$, they have a different nonlinear dependence on $\langle\varphi\rangle$. Away from the critical point, the curves for ΔI and $\Delta\gamma$ may look quite different.

We have presented here a simple phenomenological model of the BP-III–isotropic critical point in which $\langle\psi\rangle = \langle(\boldsymbol{\nabla}\times\boldsymbol{Q})\cdot\boldsymbol{Q}\rangle$ is viewed as the order parameter. This model allows us to study both the critical order parameter $\langle\psi\rangle$ and its coupling to the observable alignment tensor whose fluctuations can be measured via light scattering and rotary power. It predicts that the isotropic-to-BP-III transition is in the same universality class (Ising) as the liquid-gas transition. It can easily be extended to treat a variety of problems of potential experimental interests, for example, the effect of external field on the critical point or dynamical critical properties. It can also be used to study the whole phase diagram of the BPs including the BP I and BP II provided cubic and quadratic terms in $\boldsymbol{Q}$ are added to the Hamiltonian $\mathcal{H}[\boldsymbol{Q}, \varphi]$. Such an approach was chosen by Longa and Trebin [13]. But instead of a scalar they introduced a tensor order parameter. It would be interesting to see if the inclusion of $\langle\psi\rangle$ as an order parameter eliminates the O^5 phase predicted by mean-field theories without $\langle\psi\rangle$. We should emphasize, however, that our model was constructed to describe the BP-III–isotropic transition in the vicinity of the critical point. It will not produce without further work the detailed form of light scattering intensities (such as those measured by Koistinen and Keyes [16]) and other quantities in BP III away from the critical point.

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APPENDIX

The purpose of this appendix is to show how the Hamiltonian $\widetilde{\mathcal{H}}[\boldsymbol{Q}^<,\psi]$ can be derived by coarse graining $\mathcal{H}_\Lambda[\boldsymbol{Q}]$. We want to show only the principles of our method; therefore, we restrict ourselves to the harmonic part of $\mathcal{H}_\Lambda[\boldsymbol{Q}]$, skip detailed calculations, and use a symbolic notation. We start with Eqs. (2) and (3), introduce $\boldsymbol{Q}(\mathbf{x})=\boldsymbol{Q}^<(\mathbf{x})+\boldsymbol{Q}^>(\mathbf{x})$, and get ($\beta=1$)

$$Z=\int\mathcal{D}\boldsymbol{Q}^<\int\mathcal{D}\psi\int\frac{\mathcal{D}\lambda}{2\pi}\int\mathcal{D}\boldsymbol{Q}^>\exp\left(-\frac{1}{2}\int d^3x[\boldsymbol{Q}^<(\mathbf{x})\cdot\boldsymbol{r}(\mathbf{x})\boldsymbol{Q}^<(\mathbf{x})]\right)$$
$$\times\exp\left(i\int d^3x\lambda(\mathbf{x})\{\psi(\mathbf{x})-\boldsymbol{Q}^<(\mathbf{x})\cdot[\boldsymbol{\nabla}\times\boldsymbol{Q}^<(\mathbf{x})]\}\right)$$
$$\times\exp\left(-\frac{1}{2}\int d^3xd^3y(\boldsymbol{Q}^>(\mathbf{x})\cdot\boldsymbol{B}(\mathbf{x},\mathbf{y})\boldsymbol{Q}^>(\mathbf{y})+2i\lambda(\mathbf{x})\{\boldsymbol{Q}^<(\mathbf{x})\cdot[\boldsymbol{\nabla}\times\boldsymbol{Q}^>(\mathbf{x})]+\boldsymbol{Q}^>(\mathbf{x})\cdot[\boldsymbol{\nabla}\times\boldsymbol{Q}^<(\mathbf{x})]\})\right),\tag{A1}$$

where $\boldsymbol{r}(\mathbf{x})$ is the differential operator of the harmonic part of $\mathcal{H}_\Lambda[\boldsymbol{Q}]$ and

$$\boldsymbol{B}(\mathbf{x},\mathbf{y})=[\boldsymbol{r}(\mathbf{x})+2i\lambda(\mathbf{x})\boldsymbol{\nabla}_{\mathbf{x}}\times]\delta(\mathbf{x}-\mathbf{y})\ .\tag{A2}$$

The functional integrals can be discretized; thus with the help of

$$\int_{-\infty}^{\infty}\prod_i dz_i\exp\left(-\frac{1}{2}\boldsymbol{z}\cdot\boldsymbol{V}\boldsymbol{z}+\boldsymbol{s}\cdot\boldsymbol{z}\right)\tag{A3}$$

$$=\left[\det\frac{\boldsymbol{V}}{2\pi}\right]^{-1/2}\exp\left(\frac{1}{2}\boldsymbol{s}\cdot\boldsymbol{V}^{-1}\boldsymbol{s}\right),\tag{A4}$$

the functional integral over $\boldsymbol{Q}^>$ gives

$$\left[\det\frac{\boldsymbol{B}}{2\pi}\right]^{-1/2}\exp[\cdots]\ .\tag{A5}$$

Here the determinant (det) and later the trace (tr) apply to the tensor components as well as the coordinates $\mathbf{x}$ and $\mathbf{y}$. We rewrite $\boldsymbol{B}(\mathbf{x},\mathbf{y})$ in a symbolic notation as

$$\boldsymbol{B}=\boldsymbol{G}_0^{-1}[1+i2\boldsymbol{G}_0\lambda\boldsymbol{\nabla}\times]\tag{A6}$$

and use

$$\left[\det\frac{\boldsymbol{B}}{2\pi}\right]^{-1/2}=\exp[-\tfrac{1}{2}\mathrm{tr}\ln(\boldsymbol{B}/2\pi)]\ .\tag{A7}$$

$\boldsymbol{G}_0(\boldsymbol{q})=\sum_m G_m(\boldsymbol{q})\boldsymbol{M}_m(\boldsymbol{q})\otimes\boldsymbol{M}_m(\boldsymbol{q})$ [for $G_m(\boldsymbol{q})$; see Eq. (23)] is the autocorrelation function of $\boldsymbol{Q}$ in the harmonic approximation. Since the functional integral was restricted to functions with $q>\Lambda'$, $\boldsymbol{G}_0=\langle\boldsymbol{Q}^>(\mathbf{x})\otimes\boldsymbol{Q}^>(\mathbf{y})\rangle$. After an expansion into λ and some partial integrations the first factor of (A5) now becomes

$$\left[\det\frac{\boldsymbol{B}}{2\pi}\right]^{-1/2}\approx\left[\det\frac{\boldsymbol{G}_0^{-1}}{2\pi}\right]^{-1/2}\exp\left(-\frac{1}{2}\int d^3xd^3y\lambda(\mathbf{x})\mathcal{G}^{(2)}(\mathbf{x},\mathbf{y})\lambda(\mathbf{y})-i\int d^3x\mathcal{G}^{(1)}(\mathbf{x},\mathbf{x})\lambda(\mathbf{x})+\cdots\right),\tag{A8}$$

with

$$\mathcal{G}^{(1)}(\mathbf{x},\mathbf{x})=\langle\boldsymbol{Q}^>(\mathbf{x})\cdot[\boldsymbol{\nabla}\times\boldsymbol{Q}^>(\mathbf{x})]\rangle,\tag{A9}$$
$$\mathcal{G}^{(2)}(\mathbf{x},\mathbf{y})=2\langle\boldsymbol{Q}^>(\mathbf{x})\otimes[\boldsymbol{\nabla}\times\boldsymbol{Q}^>(\mathbf{y})]\rangle\cdot\langle[\boldsymbol{\nabla}\times\boldsymbol{Q}^>(\mathbf{x})]\otimes\boldsymbol{Q}^>(\mathbf{y})\rangle\ ,\tag{A10}$$

where both $\mathcal{G}^{(1)}$ and $\mathcal{G}^{(2)}$ can be expressed in terms of $\boldsymbol{G}_0$. We neglect the second factor of (A5): It can be shown that it only contributes higher-order coupling terms between ψ and $\boldsymbol{Q}$ and that it only renormalizes the coefficients of $\mathcal{H}_\Lambda[\boldsymbol{Q}]$. Then the partition function Z is

$$Z\propto\int\mathcal{D}\boldsymbol{Q}^<\int\mathcal{D}\psi\int\frac{\mathcal{D}\lambda}{2\pi}\exp\left(-\frac{1}{2}\int d^3x[\boldsymbol{Q}^<(\mathbf{x})\cdot\boldsymbol{r}(\mathbf{x})\boldsymbol{Q}^<(\mathbf{x})]\right)$$
$$\times\exp\left(-\frac{1}{2}\int d^3xd^3y\lambda(\mathbf{x})\mathcal{G}^{(2)}(\mathbf{x},\mathbf{y})\lambda(\mathbf{y})+i\int d^3x\{\psi(\mathbf{x})-\mathcal{G}^{(1)}(\mathbf{x},\mathbf{x})-\boldsymbol{Q}^<(\mathbf{x})\cdot[\boldsymbol{\nabla}\times\boldsymbol{Q}^<(\mathbf{x})]\}\lambda(\mathbf{x})\right),\tag{A11}$$

and after an integration over λ we have the final result

$$Z \propto \int \mathcal{D}\boldsymbol{Q}^{<} \int \mathcal{D}\psi\, e^{-\beta \widetilde{\mathcal{H}}[\boldsymbol{Q}^{<},\psi]}, \tag{A12}$$

with

$$\begin{aligned}\widetilde{\mathcal{H}}[\boldsymbol{Q}^{<},\psi] = {} & \frac{1}{2}\int d^3x \boldsymbol{Q}^{<}(\mathbf{x}) \cdot \boldsymbol{r}(\mathbf{x}) \boldsymbol{Q}^{<}(\mathbf{x}) + \frac{1}{2}\int d^3x d^3y \psi(\mathbf{x}) [\mathcal{G}^{(2)}]^{-1}(\mathbf{x},\mathbf{y}) \psi(\mathbf{y}) - \int d^3x h(\mathbf{x}) \psi(\mathbf{x}) \\ & - \int d^3x d^3y \psi(\mathbf{x}) [\mathcal{G}^{(2)}]^{-1}(\mathbf{x},\mathbf{y}) \{\boldsymbol{Q}^{<}(\mathbf{y}) \cdot [\boldsymbol{\nabla} \times \boldsymbol{Q}^{<}(\mathbf{y})]\}\end{aligned} \tag{A13}$$

and

$$h(\mathbf{x}) = \int d^3y\, [\mathcal{G}^{(2)}]^{-1}(\mathbf{x},\mathbf{y})\, \mathcal{G}^{(1)}(\mathbf{y},\mathbf{y}) \ . \tag{A14}$$

A Taylor expansion of $\psi(\mathbf{x})$ around the space point $\mathbf{y}$ and an integration over $\mathbf{x}$ gives the lowest-order coupling term $\psi(\mathbf{y})\boldsymbol{Q}^{<}(\mathbf{y}) \cdot [\boldsymbol{\nabla} \times \boldsymbol{Q}^{<}(\mathbf{y})]$ and a Hamiltonian in ψ from which we constructed $\mathcal{H}[\boldsymbol{Q},\varphi]$.

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