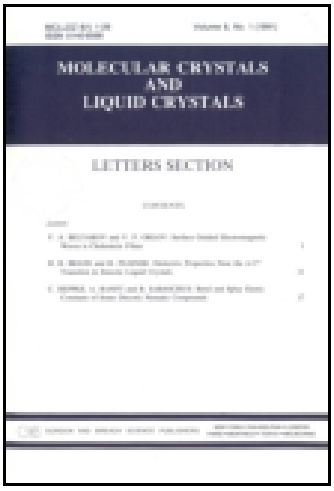

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Director Fluctuations and Ising Universality at the Paranematic-Nematic Critical Point

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A statistical mechanical calculation using renormalization group analysis is carried out which shows that the paranematic-nematic critical point (PNCP) is in the same university class as the liquid-gas critical point, namely that of the Ising model. The calculation explicitly shows how the non-critical director fluctuations play an important role in providing features in the phase diagram, not present in mean-field theories, such as a non-analytic order parameter diameter (two-phase average dielectric (or magnetic) anisotropy on the coexistence curve), and confirms the predictions of the scaling theory of the PNCP.

Keywords phase transition; critical point; paranemantic; director fluctuations; Ising model

The theoretical study of uniaxially anisotropic liquid crystals has typically been presented in terms of mean-field model systems that neglect fluctuations. The reason for this is two-fold. One is that fluctuation effects appear to be experimentally small in the vicinity of the phase change from the isotropic to anisotropic liquid as a result of the first-order nature of the transition. The second is that the mean-field (MF) approximation, which neglects fluctuations, apparently gives a qualitative description of the observed liquid crystal systems.

On the other hand, if anisotropic liquids consisting of uniaxial nematic molecules are place in an external electric (or magnetic) field, the possibility of multicritical points has been shown in models solved in the MF approximation [1, 2, 3]. In particular, for systems with positive dielectric (or magnetic) anisotropy, it has been shown that the coexistence of nematic and paranematic phases terminates at a critical point, the paranematic-nematic critical point (PNCP). Since critical points signal the appearance of large-scale fluctuations in the system, a theoretical analysis that entirely neglects fluctuations is unsatisfactory. We present in this paper, a discussion of the statistical mechanical analysis of the PNCP which includes fluctuations.

The statistical mechanical problem involves evaluating the partition function

$$Z = \left[\prod_{\vec{x},ij} \int dQ_{ij}(\vec{x})\right] exp\left(-H[Q_{ij}(\vec{x})]/k_B T\right), \tag{1}$$

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where the functional integral is over all values of the uniaxial order parameter field, written in a general d-dimensional space

$$Q_{ij}(\vec{x}) = S(\vec{x})\left[dn_i(\vec{x})n_j(\vec{x}) - \delta_{ij}\right]/(d-1). \tag{2}$$

In (1) and (2), $\vec{x}$ is the position vector in d-dimensional space, and the second-rank tensor indices, (i, j), each take on the values, 1, 2, 3, 4, ..., d. The reason for considering a d-dimensional space is to make the connection with the renormalization group analysis in $d = 4 - \varepsilon$, where $0 < \varepsilon << 1$ (see, for example, [4]). The quantity, $n_i(\vec{x})$, is the ith component of the local (spatially varying) unit vector that specifies the macroscopic direction of the local anisotropy, the director, and $S(\vec{x})$ is the magnitude of the local anisotropy relative to perfect director alignment, the statistically averaged value, $0 \leq \langle S(\vec{x})\rangle \leq 1$.

The functional, $H\left[Q_{ij}(\vec{x})\right]$, is the effective Hamiltonian of the uniaxial nematic liquid crystal. It is obtained by integrating over the molecular orientational degrees of freedom for a given $Q_{ij}(\vec{x})$. The spatial variation of the order parameter has an implicit length scale cut-off ("ultraviolet" cut-off in $\vec{k}$-space) which results in slow variations over a macroscopic scale. Near the isotropic-nematic (IN) transition, the order parameter and its spatial variations are small, and the effective Hamiltonian has a Landau expansion [5]

$$H_0\left[Q_{ij}\right]/k_BT = \int d^dx \left\{(1/2)r_0\left(Q_{ij}\right)^2 + (1/2)c_0\left(\vec{\nabla}Q_{ij}\right)^2 - v_0 Q_{ij}Q_{jk}Q_{ki} + u_0\left[\left(Q_{ij}\right)^4 + Q_{ij}Q_{jk}Q_{k\ell}Q_{\ell i}\right]\right\} \tag{3}$$

In (3), the sum over repeated indices is implied. The coefficients in the expansion, (3), are analytic functions of the temperature, and thermodynamic stability requires that both c_0, u_0 are positive throughout the phase transition region, and $v_0 > 0$ for positive anisotropy. The coefficient, $r_0 > 0$, in the isotropic region, and decreases as the temperature decreases. It changes sign at a temperature below the IN transition. In the MF analysis, the order parameter is taken to be spatially uniform and its thermal equilibrium value is that which minimizes (3).

The imposition of an external, uniform electric field, $\vec{E}$, in the isotropic phase breaks the isotropic invariance and provides a preferred direction in space. The free energy, $F = -k_BT\ell nZ$, of the paraelectric nematic system is invariant under inversion symmetry, $\vec{E} \to -\vec{E}$. In the macroscopic linear response limit, the following field-dependent term is added to (3)

$$H_0'\left[Q_{ij};\vec{E}\right]\Big/k_BT = -\chi_0 E_i E_j \int d^dx Q_{ij}, \tag{4}$$

where $\chi_0 = (1/2k_BT)\,\Delta\alpha$, with $\Delta\alpha$ the strength of the anisotropic part of the polarization tensor [6].

The effective nematic Hamiltonian in an external field, $H = H_0 + H_0'$, (3) and (4), gives the free energy cost of the local interactions of the uniaxial anisotropic strength, $S(\vec{x})$, with the director, the direction of the local uniaxial anisotropy, $\vec{n}(\vec{x})$. In the presence of an applied external field, the local director fluctuates in a plane perpendicular to the direction of the applied field. These fluctuations in-turn interact with the local fluctuations of the uniaxial anisotropic strength. As the PNCP is approached, the anisotropy fluctuations become critical (exhibit macroscopic long-range correlations) while the director fluctuations remain non-critical. However, the coupling of the critical and noncritical degrees of freedom have a profound influence on the critical phenomena at the PNCP. Such is the case found in other

systems such as in the formation of the so-called closed-loop miscibility phase diagrams in binary fluid mixtures. In this system, the noncritical molecular orientational fluctuations drive the fluid mixture into formation of a lower critical solution point [7, 8].

The uniform electric field may be taken in the "z-direction" without loss of generality. In d-dimensions, this is taken to be the "dth" direction, $\vec{E} = (0, 0, 0, ..., 0, E_0)$, $E_0 > 0$. Since the director is a unit vector, the "z-component" (dth-component) is

$$n_d = \sqrt{1 - \left|\vec{m}\right|^2} = 1 - (1/2)\left|\vec{m}\right|^2 + ..., \tag{5}$$

where the vector $\vec{m} = (m_1, m_2, ..., m_{d-1})$ is the component of the director perpendicular to the "z-direction" (or in the plane perpendicular to the "z-direction"), the "co-director".

Upon substitution of (2) in (3) and (4), the effective Hamiltonian is written in terms of the fields, $S(\vec{x})$, $\vec{m}(\vec{x})$, and the partition function "sum" is the functional integral over both $S(\vec{x})$ and $m(\vec{x})$. At the PNCP, the statistical average of the anisotropy order parameter has a nonzero value, $\langle S(\vec{x})\rangle_c = S_c$. Therefore, one needs to separate this value from the fluctuations

$$S(\vec{x}) = S_c + \psi(\vec{x}). \tag{6}$$

Thus, $\psi(\vec{x})$ is the order parameter that undergoes critical fluctuations at the PNCP, with $\langle\psi(\vec{x})\rangle_c = 0$. When the above is carried out mathematically, the result is an effective Hamiltonian that consists of three parts: a Landau-like expansion part that only depends on $\psi(\vec{x})$, a part that only depends on $\vec{m}(\vec{x})$, which is to lowest order

$$H_1\left[\vec{m}\right]/k_BT = \left(1/2\right)\int d^dx\left\{r_m\left|\vec{m}\right|^2 + c_m\left|\nabla_i\vec{m}\right|^2\right\}, \tag{7}$$

with

$$r_m = (2d/(d-1))\,\chi_0 S_c E_0^2, \tag{8}$$

$$c_m = 2\,(d/(d-1))^2\,c_0 S_c^2, \tag{9}$$

and an "interaction" part that couples $\psi(\vec{x})$ and $\vec{m}(\vec{x})$, which is to lowest order in $\vec{m}(\vec{x})$

$$H_{INT}\left[\psi, \vec{m}\right]/k_BT = (1/2)\,w_1\int d^dx\,\psi\left|\vec{m}\right|^2, \tag{10}$$

with

$$w_1 = (2d/(d-1))\,\chi_0 E_0^2. \tag{11}$$

Note that (7) indicates that the co-director has a correlation length

$$\xi_m = (c_m/r_m)^{1/2} = (dc_0S_c/(d-1)\chi_0)^{1/2}\,(1/|E_0|)\,, \tag{12}$$

which is finite (and nonzero) at the PNCP, since the critical value of the electric field is finite and nonzero. Hence, the co-director fluctuations are non-critical and the quadratic (Gaussian) form (7) is adequate.

The interaction term, (10), is now treated as a perturbation to (7) using standard graphical field theoretic methods [9, 10]. The result is that renormalizations to the coefficients of the Landau-like $\psi(\vec{x})$ part occurs, leading to the effective Hamiltonian of the paraelectric

nematic (PN) system near the PNCP

$$H_{PN}[\psi]/k_BT = \int d^dx \left\{ -h\psi + (1/2)\, r\psi^2 + (1/2)\, c \left(\vec{\nabla}\psi\right)^2 + u\psi^4 \right\}, \qquad (13)$$

where the coefficients are

$$\begin{aligned} h &= h_1 - r_1 S_c + 3v_1 S_c^2 - 4u_1 S_c^3 + \delta h \\ r &= r_1 - 6v_1 S_c + 12u_1 S_c^2 + \delta r \\ c &= c_1 + \delta c \\ v &= v_1 - 4u_1 S_c + \delta v \equiv 0 \\ u &= u_1 + \delta u \end{aligned} \qquad (14)$$

with

$$\begin{aligned} h_1 &= \chi_0 E_0^2 \\ r_1 &= (d/(d-1))\, r_0 \\ c_1 &= (d/(d-1))\, c_0 \\ v_1 &= \left(d(d-2)/(d-1)^2\right) v_0 \\ u_1 &= \left\{ \left[\left(d/(d-1)\right)^2 \right] + \left[d(d^3 - 4d^2 + 6d - 4)/(d-1)^4 \right] \right\} u_0 \end{aligned}$$

and the perturbation contributions of the co-director fluctuation renormalizations

$$\begin{aligned} \delta h &= -(1/2)\,(d-1) w_1 \int d^dk G_0(\vec{k}) \\ \delta r &= -(1/4)\,(d-1) w_1^2 \int d^dk G_0(\vec{k})^2 \\ \delta c &= +(1/4)\,(d-1) c_m w_1^2 \int d^dk G_0(\vec{k})^2 \\ \delta v &= -(1/6)\,(d-1) w_1^3 \int d^dk G_0(\vec{k})^3 \\ \delta u &= -(1/8)\,(d-1) w_1^4 \int d^dk G_0(\vec{k})^4 \end{aligned}$$

where $G_0(\vec{k}) = 1/(r_m + c_m|\vec{k}|^2)$ is the co-director fluctuation correlator in wavevector $\vec{k}$-space. All the integrals converge due to the "ultraviolet" cut-off.

Hence, we reach the conclusion that the effective Hamiltonian (13) is the scalar field theoretical representation of the Ising model and, therefore, its critical point in the same universality class [9, 10, 11]. The condition $v \equiv 0$ in (14) insures that $\langle\psi\rangle_c = 0$ at the PNCP, which amounts to determining the critical value, S_c. Since all the coefficients in (13) depend on both the electric field, E_0, and the temperature, T, the scaling fields found in a renormalization group analysis in $d = 4 - \varepsilon$ also do so [4, 9, 10]. Thus, the scaling hypothesis regarding the PNNCP is verified from statistical mechanics [12]. Among the main conclusions found in [12] was that the average of the order parameter, ψ, on the coexistence curve (the "diameter") is asymmetrical and develops a singularity; its slope

diverges as the critical point is approached with the specific heat exponent of the Ising model. This in in contrast with MF theory which predicts that the diameter vanishes along the coexistence curve. As has been shown, this feature is due to the coupling of non-critical director fluctuations with the critical anisotropy field in the vicinity of the PNCP.

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