Critical region of the nematic-isotropic phase transition in the epsilon expansion

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The phase transition from isotropic liquid to nematic liquid crystal is a weak first-order one. We investigate the possibility of the critical region at the first-order transition line of the nematic-isotropic phase transition in the context of epsilon (ε) expansion. We also investigate how the Landau–de Gennes theory of the nematic-isotropic phase transition may break down at a first-order transition. When the nematic-isotropic transition temperature T_{NI} is inside a critical region, we find that the critical indices of the absolute stability limit of the nematic phase are $\beta_1=\beta$ (critical index of the critical point) and $\alpha_1=\gamma_1=1-\beta$.

I. INTRODUCTION

The nematic-isotropic (*N-I*) phase transition has been a topic of active theoretical and experimental studies over the past few decades. Although the *N-I* transition is one of the most ubiquitous found in nature, it is also one of the least understood. The phase transition from isotropic liquid to nematic liquid crystal is a weak first-order one. As a rule, it is characterized by a small latent heat and by large pretransitional anomalies in a relatively wide temperature region, similar to those observed near a second-order transition. Appreciable pretransition phenomena indicate that the transition is close to being second order. It has been concluded[1] that an isolated point exists, by extrapolating the experimental dependence of the specific volume discontinuity on the temperature and pressure. There exists an appreciable region in which the fluctuations become important and Landau theory is not applicable. Below one can calculate the critical indices of the transition to the isotropic phase by the methods of expanding in $\varepsilon=4-d$ (Ref. 2) and in $1/n$.[3] The *N-I* transition is the simplest and the most studied of all phase transitions in liquid crystals. Therefore, it is surprising that until now there are no clear answers to some key questions concerning the nature of this phenomenon. First, it is not quite clear what makes this transition so weakly first order. A generally accepted description of the *N-I* transition is based on the Landau–de Gennes phenomenological theory[4,5] with the nematic order fluctuation corrections in the Gaussian approximation.[6] de Gennes was the first to put forward the question of the validity of the mean-field approach to such systems with short-range interaction.

The concept of critical phenomena at a phase transition has been used only for the case of a second-order transition. However, in several papers it was claimed that a critical behavior had been observed at the *N-I* phase transition (at a first order). The basis for this claim is the fact that one can determine a critical index β for the order parameter Q. Since the Landau theory has been applied to second-order transition[4,7] as well as to first-order transition, one can define, at a first-order transition, a critical region in which the classical theories break down. Landau theory may no longer be valid if the *N-I* transition temperature T_{NI} is near a critical point. We can look for its critical region using the Ginzburg criterion[8] and verify whether T_{NI} is or is not inside it. Hence, in the free-energy expression with the cubic coefficient of the order parameter Q, one cannot extract the critical region, unless the cubic coefficient becomes zero. The work presented here was initiated in the hope that the ε expansion might shed some light on this problem. We have studied the possibility of the critical region using epsilon (ε) expansion. We noticed that the critical region is obtained near about the first-order *N-I* phase transition line. We have also calculated the scaling equation of state in this region.

In Sec. II we give a brief review of the Landau–de Gennes model. A new calculation of the real behavior of the system of the failure of the Landau theory appears in Sec. III. In Sec. IV we determine the critical region of the *N-I* transition in the context of epsilon expansion. We calculate in Sec. V the equation of state of the *N-I* transition. Finally, Sec. VI discusses some conclusions of our results.

II. LANDAU–DE GENNES MODEL

In order to explain the critical behavior of the *N-I* transition in the neighborhood of the critical point, we resort to the ε expansion, and calculate to first order in $\varepsilon=4-d$, where d is the dimensionality of the system in space. We have followed the same method[9,10] throughout this paper. The particular form used here follows.[11,12]

For purely geometrical reasons, the *N-I* transition is first order, as was recognized by Landau. The Landau–de Gennes model[13] containing a cubic term in order parameter in the free-energy expansion was proposed and used to describe first-order transition in liquid crystals. Retaining only terms which have rotational invariance, the free-energy per unit volume, $\mathcal{F}$ is given by

$$\mathcal{F}=\mathcal{F}_0+\tfrac{3}{4}AQ_{ij}Q_{ji}-\tfrac{3}{2}BQ_iQ_{jk}Q_{ki}+\tfrac{9}{16}C(Q_{ij}Q_{ji})^2 . \qquad (1)$$

Here $\mathcal{F}_0$ is the free-energy density of the isotropic phase, Q_{ij} is the tensor order parameter which describes the degree of order in a nematic liquid crystal, and a summation over repeated indices is implied. The coefficient A is assumed to have the form $A=a(T-T^*)$, where "a" is a positive constant and T^* is the temperature of the absolute stability limit of the isotropic phase, while B and C are regarded as constants independent of the temperature. All coefficients are assumed to be independent of the volume. For a liquid crystal of uniaxial symmetry, the single preferred direction of the molecules is along the direction $\hat{n}$, and Q_{ij} takes the form

$$Q_{ij}(r)=Q(r)[\hat{n}_i(r)\hat{n}_j(r)-\tfrac{1}{3}\delta_{ij}] , \tag{2}$$

where $\hat{n}_i$'s are the components of $\hat{n}$ and $Q(r)$ denotes the fraction of molecules at r aligned parallel to $\hat{n}$.

For a uniform uniaxial crystal, substituting Eq. (2) into Eq. (1) leads to the free-energy expansion,

$$\mathcal{F}=\mathcal{F}_0+\tfrac{1}{2}AQ^2-\tfrac{1}{3}BQ^3+\tfrac{1}{4}CQ^4 . \tag{3}$$

The N-I transition temperature T_{NI} is calculated from $\mathcal{F}=0$; $\partial\mathcal{F}/\partial Q=0$ can be written as

$$T_{NI}=T^*+\frac{2B^2}{9aC} . \tag{4}$$

The value of the order parameter at the N-I transition is

$$Q_{NI}=\frac{2B}{3C} . \tag{5}$$

The minimization of Eq. (3) yield the following solutions:

$$Q=0 \quad \text{(isotropic phase)} \tag{6}$$

$$Q=\frac{B}{2C}[1+(1-4AC/B^2)^{1/2}] \quad \text{(nematic phase)} . \tag{7}$$

The temperature of the absolute stability limit of the nematic phase is determined by the disappearance of the $Q\neq 0$ solution:

$$T^{**}=T^*+\frac{B^2}{4aC} . \tag{8a}$$

Then,

$$Q^{**}=\frac{B}{2C} . \tag{8b}$$

The critical temperature T_c is determined by $\partial(\mathcal{F}-HQ)/\partial Q=0$ and $\partial^2(\mathcal{F}-HQ)/\partial Q^2=0$, that is,

$$T_c=T^*+\frac{B^2}{3aC} . \tag{9}$$

Following Corre and Benguigui[14] the order parameter Q_c and the external field H_c can be written as

$$Q_c=\frac{B}{3C} \tag{10}$$

and

$$H_c=B^3/27C^2 . \tag{11}$$

III. REAL BEHAVIOR OF THE SYSTEM

The free-energy density associated with the long-wavelength part of the order parameter fluctuation for a uniaxial nematic liquid crystal is given by

$$\mathcal{F}(x)=\mathcal{F}_0+\tfrac{1}{2}[AQ^2+(\nabla Q)^2]-\frac{B}{3}Q^3+\frac{C}{4}Q^4 , \tag{12}$$

for systems in which director fluctuations can be neglected. Since $\mathcal{F}_0$ is independent of Q, the free-energy density giving the statistical weight of a given distribution $Q(x)$ can be written in the form

$$\mathcal{H}(x)=\tfrac{1}{2}[AQ^2+(\nabla Q)^2]-\frac{B}{3}Q^3+\frac{C}{4}Q^4 . \tag{13}$$

Then the partition function averages and the correlation function are calculated with the weight

$$W\{Q\}=\exp\left[-\beta\int\mathcal{H}(x)dx\right] , \tag{14}$$

where $\beta=1/KT$.

Now consider the system described by Eq. (13) in the absence of an external field. Now write

$$Q=L+M , \tag{15}$$

where M is a constant which we choose as

$$M=\frac{B}{3C} , \tag{16}$$

in order to eliminate the cubic term. In terms of the variable L, $\mathcal{H}(x)$ reads as

$$\mathcal{H}(x)=\left[\frac{B}{3C}\right]^2\left[\frac{A}{2}-\frac{1}{12}\frac{B^2}{C}\right]+\tfrac{1}{2}(\nabla L)^2 + \left[\frac{B}{3C}\right]\left[A-\frac{2B^2}{9C}\right]L+\left[\frac{A}{2}-\frac{2B^2}{9C}\right]L^2 +\frac{C}{4}L^4 . \tag{17}$$

The problem is transformed into a usual L^4 interaction, in the presence of an effective external field, which depends on A and B,

$$h'=\left[-\frac{B}{3C}\right]\left[A-\frac{2B^2}{9C}\right]^2 . \tag{18}$$

Now the N-I phase transition will occur only if the field h' vanishes. That is, if either

$$B=0 \tag{19}$$

or

$$A=\frac{2B^2}{9C} . \tag{20}$$

The first case is the usual Ising case, since A remains free and $A=A_c<0$ is a point of second-order phase transition temperature. A_c is the temperature of the transition relative to the mean-field temperature—a depression caused by fluctuations. If $A<A_c$, one is on the coexistence curve where the N-I transition point falls, while if

$A > A_c$ all quantities are regular functions of A—there is no transition.

The second case, Eq. (20), is more interesting. The external field is still kept zero, and A from Eq. (20) is substituted into Eq. (17) to yield

$$\mathcal{H}(x)=\left[\frac{B}{3C}\right]^2\left[\frac{B^2}{36C}\right]+\tfrac{1}{2}(\nabla L)^2-\left[\frac{B^2}{9C}\right]L^2+\frac{C}{4}L^4 . \tag{21}$$

Hence we conclude that the Hamiltonian of Eq. (21) describes a regular phase if

$$\frac{B^2}{9C}<|A_c| , \tag{22}$$

a critical point if

$$\frac{B^2}{9C}=|A_c| , \tag{23}$$

and a coexistence curve if

$$\frac{B^2}{9C}>|A_c| . \tag{24}$$

With the Hamiltonian we have assumed in Eq. (13), the value of A_c depends only on C and on the cutoff Λ—the inverse of the lattice spacing. The situation is described in Fig. 1, which is a plane of zero external field h' and fixed C. For a given C and Λ, if A—the temperature—is varied at constant B then if B satisfies Eq. (22) the path will be the one denoted by X in Fig. 1, there will be regular behavior—i.e., no transition; if B satisfies Eq. (23) the system will follow path Y, on which there will be a second-order phase transition—a critical point. Finally, if Eq. (24) is satisfied by B, path Z will be followed and the first-order phase transition will show up as the line $A=2B^2/9C$ is crossed.

In fact, the above discussion establishes the result mentioned in the Sec. I for the case when no external field is applied.

If one proceeds along the parabola $h'=0$ from the origin until the point $B^2/9C=|A_c|$ is reached, the equilibrium value of L is zero. Beyond this point, further up the parabola, L has a nonzero value.[10] This, however, does

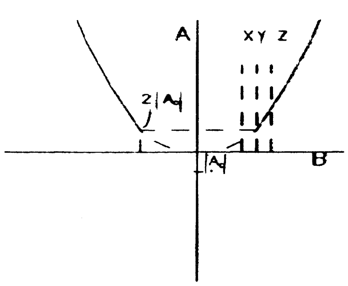

FIG. 1. The phase diagram of the system for zero external field and given c. The broken part of the zero effective field parabola is the part across which the Landau theory predicts a first-order transition, but in fact there is none.

not imply that a symmetry is broken, since from Eqs. (15) and (16) it follows that for $B=0$, the equilibrium value of Q is nonzero on both sides of the transition. In fact, when $B\neq 0$, the equilibrium value of Q is never zero. This is in contrast to the Landau theory, which predicts a symmetry breakdown, and hence cannot allow for a regular path going from one phase to the other. But the Hamiltonian, Eq. (13), possesses no symmetry to be broken.

The significance of these results is that the model (3) with BQ^3 local interaction exhibits—due to fluctuations—a first-order phase transition for $|B|>B_c>0$, a critical point at $B=B_c$, and no transition for $|B|<B_c$. $B=0$ is a special point of second-order phase transition. This is in contradiction to the Landau theory, which predicts a first-order transition for all $B>0$.

IV. THE CRITICAL REGION IN THE ε EXPANSION

The appearance of a nonzero equilibrium value of Q is taken care of by a shift

$$Q(x)=L(x)+M , \tag{25}$$

with

$$\int L(x)dx=0 , \tag{26}$$

where M is a constant and is determined by minimizing the free energy. This is equivalent to an integration over M, or to the relaxation of Eq. (26) and imposition of the constraint

$$\langle L(x)\rangle=0 . \tag{27}$$

Now,

$$F(M)=F_L(M)+\Delta F(M) , \tag{28}$$

where

$$F_L(M)=\frac{A}{2}M^2-\frac{B}{3}M^3+\frac{C}{4}M^4 \tag{29}$$

is the tree (zero-loop) or Landau approximation, and $\Delta F(M)$ can be written as

$$\Delta F(M)=-\frac{1}{V}\ln\int\mathcal{D}L\,\exp\left[-\int\mathcal{H}(L,M)dx\right] , \tag{30}$$

with

$$\mathcal{H}(L,M)=\tfrac{1}{2}(\nabla L)^2+\tfrac{1}{2}(A-2BM+3CM^2)L^2+\left[-\frac{B}{3}+MC\right]L^3+\frac{C}{4}L^4 . \tag{31}$$

The term linear in L vanishes when integrated over the volume because of Eq. (26). Now renormalize the mass and write

$$\mathcal{H}(L,M)=[\tfrac{1}{2}(\nabla L)^2+\tfrac{1}{2}r^2L^2]+H_{\rm int} , \tag{32}$$

$$H_{\rm int}=\tfrac{1}{2}\delta r^2L^2+\left[-\frac{B}{3}+MC\right]L^3+\frac{C}{4}L^4 , \tag{33}$$

$$\delta r^2 = A - 2BM + 3CM^2 - r^2 , \quad (34)$$

where r^2 is the full inverse susceptibility. Now choosing $C \sim \varepsilon$, $B \lesssim \varepsilon^{1/2}$, $M \sim \varepsilon^{-1/2}$, then the equation for $\partial F/\partial M$ to order $\varepsilon^{1/2}$ is

$$AM - BM^2 + CM^3 + (-B + 3CM)D_1(r) = 0 , \quad (35)$$

where the mass renormalization equation

$$\delta r^2 + 3CD_1(r) - 6(-B + 3CM)^2 D_2(r) = 0 \quad (36)$$

was utilized in deriving Eq. (35). D_1 and D_2 are defined as

$$D_1(r) = \frac{1}{(2\pi)^d} \int dq (q^2 + r^2)^{-1} , \quad (37)$$

$$D_2(r) = \frac{1}{(2\pi)^d} \int dq (q^2 + r^2)^{-2} . \quad (38)$$

Since $D_2(r) \to \infty$, when $r \to 0$, for $\varepsilon > 0$, if there is to be a critical point, i.e., a solution with $r = 0$, we must have

$$M = \frac{B}{3C} , \quad (39)$$

which is identical to Eq. (16). This can happen only for a special combination of the parameters, namely,

$$\left[-\frac{B}{3C} \right] \left[A - \frac{2}{9} \frac{B^2}{C} \right] = 0 , \quad (40)$$

which follows from Eq. (35) and from Eq. (36) it follows that at this point,

$$A - \tfrac{1}{3} \frac{B^2}{C} = -3CD_1(0) = A_c \quad (41)$$

to order ε. These equations reproduce Eqs. (20) and (24) to first order in ε, if $B \neq 0$. The other solution is $B = 0$ and $A = A_C$.

Away from the critical point, for general values of r, we expand about $M = B/3C$,

$$M = \frac{B}{3C} + \mu . \quad (42)$$

Equations (36) and (35) become, respectively,

$$r^2 = \left[A - \frac{1}{3} \frac{B^2}{C} \right] + 3C\mu^2 + 3CD_1(r) - 18C^2\mu^2 D_2(r) , \quad (43)$$

and

$$C\mu^3 + \left[A - \frac{1B^2}{3C} \right] + (-B/3C) \left[A - \frac{2B^2}{9C} \right] + 3C\mu D_1(r) = 0 . \quad (44)$$

The critical point is characterized by $\mu = r = 0$, and thus

$$A_c - \frac{B_c^2}{3C} = -3CD_1(0) . \quad (45)$$

Now we define

$$t = A - A_c , \quad (46)$$

$$p = \frac{4}{9C}(B^2 - B_c^2) . \quad (47)$$

Now rewrite the Eqs. (43) and (44) as

$$r^2 = t - \frac{3}{4}p + 3C\mu^2 + 3C\Delta D_1(r) - 18C^2\mu^2 D_2(r) , \quad (48)$$

$$C\mu^3 + [t - \tfrac{3}{4}p + 3C\Delta D_1(r)]\mu - \left[t - \frac{p}{2} \right] \left[-\frac{B}{3C} \right] = 0 . \quad (49)$$

To lowest order in ε,

$$\Delta D_1 = D_1(r) - D_1(0) \simeq Sr^2 \ln(r/\Lambda) , \quad (50)$$

$$D_2(r) \simeq -S[\tfrac{1}{2} + \ln(r/\Lambda)] , \quad (51)$$

where Λ is the inverse of the lattice spacing.

With the free energy we have assumed in Eq. (12), the value of A_c depends only on C and on the cutoff Λ—the inverse of the lattice spacing. The situation is described in Fig. 1 which is a plane of zero external field and fixed C. The parabola of the zero effective field in Fig. 1 can be also described by

$$p = 2t . \quad (52)$$

Along this curve Eqs. (48) and (49) take on the form

$$r^2 = -\tfrac{1}{2}t + 3C\mu^2 + 3CSr^2 \ln(r/\Lambda) + 18C^2 S\mu^2 [\tfrac{1}{2} + \ln(r/\Lambda)] , \quad (53)$$

$$C\mu^3 - [\tfrac{1}{2}t - 3CSr^2 \ln(r/\Lambda)]\mu = 0 . \quad (54)$$

The consistency of the orders in ε in the above equations is secured by the fact that, to first order in ε,

$$3CS = \tfrac{1}{3}\varepsilon , \quad (55)$$

$$\frac{C}{4}\mu^2 = 0(1) . \quad (56)$$

Equation (54) has a solution with $\mu = 0$. It then follows from Eq. (53) that we must have $t < 0$, i.e., below the critical point in Fig. 1. The behavior of r as a function of t is just as in the Ising model.[10]

Now we investigate whether there may be a solution of Eqs. (53) and (54) with $\mu \neq 0$. Substituting μ^2 from Eq. (54) in Eq. (53), one finds

$$r^2 = t - \tfrac{2}{3}\varepsilon r^2 \ln(r/\Lambda) + 2\varepsilon[\tfrac{1}{2}t - \tfrac{1}{3}\varepsilon r^2 \ln(r/\Lambda)] \times [\tfrac{1}{2} + \ln(r/\Lambda)] . \quad (57)$$

If terms of zeroth order in ε are compared one obtains

$$r^2 = t + 0(\varepsilon) , \quad (58)$$

which has no solution for $t < 0$. Thus, along the low part of the zero field parabola there is a singular regular solution, $\mu = 0$. The system is described again by the solutions of Eq. (57), and hence of Eq. (58). There are now two solutions, which to lowest order in ε are given by the two roots of Eq. (54). Along the parabola of zero field both F_L and δr^2 are even functions of μ, and thus the free energy for the two solutions is the same. This is a line of first-order transitions. Hence in this region one can easily calculate the critical exponents and also the equation of the uniaxial state.

V. EQUATION OF STATE

To calculate the equation of state let us assume that the nematic-isotropic transition temperature T_{NI} of the first-order transition is inside the critical region of the critical point, that is, the Landau theory is incorrect near T_{NI}. Furthermore, we assume that the equation of state of the critical point has the form of the scaling-law equation of state. It is known[15] that the scaling parameters are not H and T but $h_1(H,T)$ and $h_2(H,T)$. The h_2 axis is asymptotically parallel to the coexistence curve. If we are near T_c, we can adopt the linear relations, that is,

$$h_1=a_1H'+b_1T' , \tag{59}$$

$$h_2=a_2H'+b_2T' , \tag{60}$$

so that the h_1 axis is perpendicular to the coexistence curve. H' and T' are defined by $H'=H-H_c$ and $T'=T-T_c$. The scaling-law equation of state can be written as

$$h_1=Q^{\delta}f(h_2^{\beta}/Q) , \tag{61}$$

where β and δ are two of the critical indices. We assume that on the curve $Q(T)$ for $H=0$, the departure from the Landau theory can be detected by a critical exponent $\beta_1\neq\frac{1}{2}$,

$$Q-Q^{**}\propto(T^{**}-T)^{\beta_1} . \tag{62}$$

Although the experimental results suggest that $\beta=\beta_1$, there is no *a priori* theoretical reason to adopt this choice of β_1.

In the plane (H',T'), the paths defined by $H'=0$ or $T'=0$ make an angle with the coexistence curve. Following Griffiths and Wheeler,[16] the asymptotic behavior of the thermodynamic quantities are the same along these two paths. We use here a generalization of these ideas and assume that the behavior along a path $H'=$const is the same as that along a path $h_2=$const. Accordingly, we have

$$Q-Q^{**}\propto(h_1-h_1^{**})^{\beta_1} \tag{63}$$

(see Fig. 2) in the vicinity of $Q\simeq Q^{**}$ if $h_2=$const. Q^{**} and h_1^{**} are clearly functions of h_2. Since for $h_2=0$ we have $Q\propto h_1^{1/\delta}$, we adopt the following equation of state:

$$h_1-h_1^{**}(h_2)=R(h_2)[Q-Q^{**}(h_2)]^{1/\beta_1} +S[Q-Q^{**}(h_2)]^{\delta} , \tag{64}$$

with $1/\beta_1<\delta$ and $R(0)=0$, $Q^{**}(0)=0$, $h_1^{**}(0)=0$. Furthermore, we have $Q^{**}=Uh_2^{\beta}$.

We have

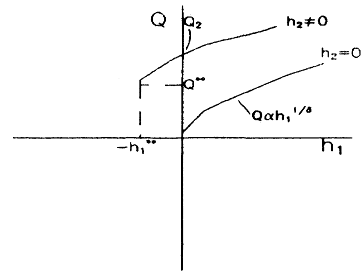

FIG. 2. Curves $Q(h_1)$ for $h_2\neq0$ and $h_2=0$.

$$\partial h_1/\partial Q=Q^{\delta-1}[\delta f(h_2^{\beta}/Q)-(h_2^{\beta}/Q)f'(h_2^{\beta}/Q)]=0 , \tag{65}$$

where f' is the first derivative of the function f. If the quantity in the square bracket is zero, it means that

$$Q^{**}\propto h_2^{\beta} , \tag{66}$$

Now we have to choose $R(h_2)$ in order that (64) may take the form of (59). For $h_1=0$, we have $Q=Q_2=Vh_2^{\beta}$ and we get for $h_1^{**}(h_2)$

$$-h_1^{**}(h_2)=R(h_2)(V-U)^{1/\beta_1}h_2^{\beta/\beta_1}+S(V-U)^{\delta}h_2^{\beta\delta} , \tag{67}$$

and we can write

$$h_1=R(h_2)Q^{1/\beta_1}[(1-Uh_2^{\beta}/Q)^{1/\beta_1} -(V-U)^{1/\beta_1}(h_2^{\beta}/Q)^{1/\beta_1}] +SQ^{\delta}[(1-Uh_2^{\beta}/Q)^{\delta}-(V-U)^{\delta}(h_2^{\beta}/Q)^{\delta}] . \tag{68}$$

We see that we must have

$$R(h_2)Q^{1/\beta_1}=Q^{\delta}m(h_2^{\beta}/Q) . \tag{69}$$

This can be satisfied if

$$m(h_2^{\beta}/Q)\equiv W'(h_2^{\beta}/Q)^{\delta-1/\beta_1} , \tag{70}$$

where W' is constant. Finally we get the function $f(x)$ of (61)

$$f(x)=Wx^{\delta-1/\beta_1}[(1-Ux)^{1/\beta_1}-(V-U)^{1/\beta_1}x^{1/\beta_1}] +S[(1-Ux)^{\delta}-(V-U)^{\delta}x^{\delta}] . \tag{71}$$

From (71), we can calculate the critical indices γ_1 and α_1 which characterize the behavior of the susceptibility $(\partial Q/\partial H)_{H=0}$ and the specific heat for $H=0$. The calculations are lengthy but straightforward, since the relation between h_1 (or h_2) and H' and T' is linear. We obtain

$$\gamma_1=\alpha_1=1-\beta \text{ and } 2\beta_1+\gamma_1=2-\alpha_1 . \tag{72}$$

VI. CONCLUSION

We have shown that a model with a tensorial order parameter, which has a BQ^3 interaction in addition to CQ^4, has a critical value $B=B_c(C,\Lambda)$ below which there is no transition. At the critical value the system undergoes a second-order transition with no symmetry break. Above the critical value of B the transition is of first order. This is contrary to the prediction of Landau's theory.

The result holds also for $d > 4$, since it depends only on the fact that $A_c = 0$. Namely, there is a finite depression of the transition temperature from its mean-field value. Since the value of A_c is not a universal quantity, one may ask about the effects of higher powers of the field in the free energy. Such effects would not invalidate the results of the present work, since these results are all stated within a specified model. The reason is that near the critical point they are irrelevant and thus the two second-order phase-transition points will survive. Their persistance will preserve the structure of the A-B phase diagram in Fig. 1. However, this question has not been investigated in detail.

We have also verified that the calculated values of the critical exponents in this region take the same values.[17] If at T_{NI} the behavior is critical, assuming that in the scaling-law equation of state the nonanalyticity appears at the critical point (fluidlike critical point) and also on the spinodal curve, the critical indices of the absolute stability limit of the nematic phase (metastable) are $\beta_1 = \beta$ and $\alpha_1 = \gamma_1 = 1 - \beta_1$. If one calculates the value of $T_{NI} - T^*$, where T_{NI} is the N-I transition temperature and T^* is the temperature at which the light scattering intensity diverges in the supercooled isotropic phase in this region, one obtains the same result.[18]

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