Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 22 Feb 2010

To cite this article: Takahiro Yamada*, Masashi Torikai & Mamoru Yamashita (2010): Uniaxial Order of Lattice Maier-Saupe Model in an External Field - Phase Diagram in Bethe Approximation, Molecular Crystals and Liquid Crystals, 516:1, 64-73

To link to this article: http://dx.doi.org/10.1080/15421400903400654

Mol. Cryst. Liq. Cryst., Vol. 516: pp. 64–73, 2010
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903400654

Uniaxial Order of Lattice Maier-Saupe Model in an External Field – Phase Diagram in Bethe Approximation

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Phase transition of nematic phase exposed to a uniaxial field is studied in the Behte approximation. The transition is of first order, and a jump at the transition decreases as the field is increased. At length a critical point appears at a critical field, beyond which no transition occurs. The critical point is especially of interest, where an estimated value of the critical field derived here is smaller than a half of an approximate value of mean field theory. Calculus of a free energy, which is inevitable for an analysis of first order phase transition, is discussed. The specific heat diverges with an index 2/3 at the critical field as temperature changes, which is elucidated to be a general character of the critical point without symmetry change at every classical theory.

Keywords Bethe approximation; calculus of free energy; critical point without symmetry change; external field; Lebwohl-Lasher model; nematic phase

1. Introduction

Nematic-isotropic phase transition is of the first order, and in the framework of Maier-Saupe model, a mean field theory describes well the phase transition qualitatively [1–3]. However, a high approximate approach taking account of correlation is required for quantitative and deep understanding. In practice, various methods have been developed, i.e., high temperature series expansion method [4], Bethe approximation [5,6], cluster variation method [7], and Monte Carlo simulation [8,9]. On the other hand, in an external field with positive anisotropy, a jump of an order parameter decreases with increasing field strength, and a critical point appears at a critical field, over which the system undergoes only continuous change [10–13]. Near the critical point, an effect due to fluctuation becomes large, and it is important for global understanding of the nematic-isotropic phase transition to improve an analysis beyond the mean field theory. We report here a study of nematic phase

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transition exposed to the positive uniaxial field by using the Bethe approximation in a framework of a lattice Maier-Saupe model (called a Lebwohl-Lasher model) [1,2,8].

In an analysis exceeding the mean field theory, couplings between positional degrees of freedom of molecules and orientational ones appear, while in the mean field theory these degrees of freedom decouple to each other. For simplicity and concreteness, we adopt the lattice Maier-Saupe model to avoid complexity arising from the coupling of both degrees of freedom, as an essential part of the nematic-isotropic phase transition is an orientational ordering. In practice, the studies above-mentioned are based on the lattice model [4–9].

In the next section, a system and formalism are introduced for the Bethe approximation. Following to this, main results of analyses are shown, in which a present estimate of the critical field is noted to be smaller than a half of an approximate value by mean field theory. At the critical field, a specific heat diverges with an index 2/3 as a temperature crosses the critical point, which is proved to be a general property of a critical point accompanying no symmetry change at any classical theory. Finally, summary is given.

2. System and Formalism of Bethe Approximation

Hamiltonian of the Lebwohl-Lasher model is given with an interaction parameter V by

$$\mathcal{H} = -V \sum_{(m,n)} P_2(\cos\theta_{mn}), \tag{1}$$

where θ_{mn} denotes an angle between long axes of the m-th and n-th molecules, $P_2(x)$ the second Legendre polynomial and the summation is taken over all nearest neighbouring pairs. Let's consider a cluster composed of one central molecule and ν neighbouring molecules, embedded in a bulk system of nematic molecules. In the Bethe approximation, the interaction is taken only between the central molecule and molecules neighbouring to this in the cluster. Interactions between the neighbouring molecules and molecules surrounding the cluster are replaced by a molecular field. Then, a Hamiltonian for the cluster, i.e., Bethe Hamiltonian, in the external field is expressed as

$$\mathcal{H}_B = -h_e P_2(\cos\theta_0) - \sum_{n=1}^{\nu}[VP_2(\cos\theta_{0n}) + (h_e + h)P_2(\cos\theta_n)], \tag{2}$$

where θ_0 and θ_n denote polar angles of long axes of central and n-th molecules taken from a principal axis, say, z-axis, respectively, h the molecular field and h_e ($=\varepsilon_a E^2/3$) the external field applied in z-axis with E an electric field and ε_a dielectric anisotropy. In case of positive anisotropy, $\varepsilon_a > 0$, an order remains uniaxial in the field, and following order parameters, s_i ($i=0$ and 1), are utilized

$$s_i = < P_2(\cos\theta_i) >, \tag{3}$$

in which the bracket <...>denotes a thermal average. Here, the addition theorem is noticed,

$$P_2(\cos\theta_{0n}) = P_2(\cos\theta_0)P_2(\cos\theta_n) + \frac{3}{4}\sin 2\theta_0 \sin 2\theta_n \cos(\varphi_0 - \varphi_n) + \frac{3}{4}\sin^2\theta_0 \sin^2\theta_n \cos 2(\varphi_0 - \varphi_n), \tag{4}$$

for φ_0 and φ_n, azimuthal angles of long axes of central and n-th molecules, respectively. Even in the uniaxial order, the second and third terms in Eq. (4) should never be neglected except for the case of the mean field theory.

The partition function with symmetry breaking field ζ applied to the central molecule is given with a solid angle element $d\omega_j$ by

$$\begin{aligned} Z(\beta) &= \prod_{j=0}^{\nu}\left[\int d\omega_j\right] \exp\{\zeta P_2(\cos\theta_0) - \beta\mathcal{H}_B\} \\ &= \int_0^{\pi} d\theta_0 \sin\theta_0 \int_0^{2\pi} d\varphi_0\, exp[(\zeta + \beta h_e)P_2(\cos\theta_0)]\, z_1^{\nu}(\theta_0, \varphi_0), \end{aligned} \tag{5}$$

where β denotes an inverse temperature $1/kT$ with Boltzmann constant k, and $z_1(\theta_0, \varphi_0)$ is defined by

$$z_1(\theta_0, \varphi_0) = \int_0^{\pi} d\theta_1 \sin\theta_1 \int_0^{2\pi} d\varphi_1 \exp[\beta\{VP_2(\cos\theta_{01}) + (h_e + h)P_2(\cos\theta_1)\}]. \tag{6}$$

Then, the order parameters are given by

$$s_0 = \frac{\partial \ln Z(\beta)}{\partial\zeta}, \tag{7}$$

$$s_1 = \frac{1}{\nu\beta}\frac{\partial \ln Z(\beta)}{\partial h}. \tag{8}$$

The central molecule and the neighbouring ones are equivalent intrinsically to each other, because the central molecule is chosen arbitrarily from the bulk. So the following self-consistency equation is imposed

$$s_0 = s_1 (= s), \tag{9}$$

from which the molecular field h, and eventually s, are determined, i.e., h and s are given as functions of ζ, $h(\zeta)$, and $s(\zeta)$. Inversely, from $s = s(\zeta)$, ζ is obtained as a function of s, $\zeta(s)$. Then, Landau free energy $\Phi(s)$, a variation function for free energy, is calculated as [13,14]

$$\Phi(s) = \Phi(0) + kT\int_0^{s} \zeta(s')ds'. \tag{10}$$

Minimized value of $\Phi(s)$ with respect to s is a thermal equilibrium value of the free energy with only extensive variables, T and h_e. The minimum condition of $\Phi(s)$ leads to $\zeta = 0$ for thermal equilibrium. We calculate $\Phi(s)$ numerically, because it is difficult to derive $s(\zeta)$ analytically and also to carry out the integration in Eq. (10).

3. Numerical Analysis

Equation (9) is rewritten in a concrete form as

$$\begin{aligned}\int_0^{\pi} \mathrm{d}\theta_0 \, \sin\theta_0 \int_0^{2\pi} \mathrm{d}\varphi_0 P_2(\cos\theta_0) \exp[(\zeta + \beta h_\mathrm{e}) P_2(\cos\theta_0)] \, z_1^{\nu}(\theta_0, \varphi_0) \\ = \int_0^{\pi} \mathrm{d}\theta_0 \, \sin\theta_0 \int_0^{2\pi} \mathrm{d}\varphi_0 \exp[(\zeta + \beta h_\mathrm{e}) P_2(\cos\theta_0)] \, z_1^{\nu-1}(\theta_0, \ \varphi_0) \\ \times \int_0^{\pi} \mathrm{d}\theta_1 \, \sin\theta_1 \int_0^{2\pi} \mathrm{d}\varphi_1 P_2(\cos\theta_1) \exp[\beta\{ V P_2(\cos\theta_{01}) \\ + (h_\mathrm{e} + h) P_2(\cos\theta_1)\}] \qquad (11)\end{aligned}$$

We solve Eq. (11) numerically for given value of ζ, and derive $h(\zeta)$ and $s(\zeta)$. The value, $\nu = 6$, is used exclusively in this article. Then, $\Phi(s)$ in Eq. (10) is calculated as shown in Figure 1 for vanishing external field, $h_\mathrm{e} = 0$, where $T = 1.1594$ (full curve), 1.1580 (broken curve) and 1.1610 (dotted curve), respectively (here and hereafter, the temperature is scaled in the unit V/k). From this result, the transition temperature T_c is obtained as $T_\mathrm{c} = 1.1594$ at $h_\mathrm{e} = 0$. This estimate for T_c agrees strictly with the result already derived by Ypma and Vertogen [6]. They used a general formula for the free energy F introduced by Krieger and James [15] given by

$$F = F(0) + kT \int_0^{\beta} U(\beta')\mathrm{d}\beta', \qquad (12)$$

where an internal energy $U(\beta)$ for vanishing external field, $h_\mathrm{e} = 0$, is calculated in the Bethe approximation using h, satisfying the self-consistency Eq. (9), as

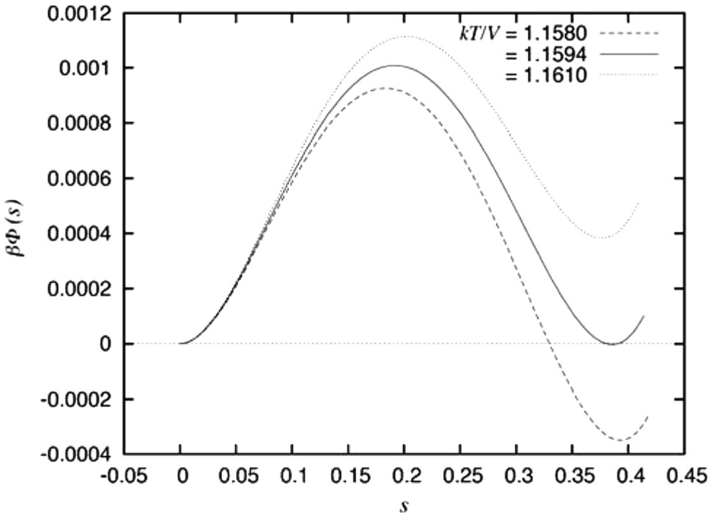

Figure 1. Temperature dependence of profile of $\Phi(s)$.

$$U(\beta) = -\frac{V\nu}{2} < P_2(\cos\theta_{01}) >$$
$$= -\frac{1}{2}\frac{\partial \ln Z}{\partial \beta} + \frac{h}{2\beta}\frac{\partial \ln Z}{\partial h}. \tag{13}$$

For the case of finite field h_e, we have only to replace the internal energy of Eq. (13) by,

$$U(\beta) = -\frac{V\nu}{2} < P_2(\cos\theta_{01}) > -h_e < P_2(\cos\theta_0) >$$
$$= -\frac{1}{2}\frac{\partial \ln Z}{\partial \beta} + \frac{\nu h + (\nu - 1)h_e}{2(\nu + 1)\beta}\frac{\partial \ln Z}{\partial h_e}. \tag{14}$$

However, in the present study, the formalism of Eq. (10) is used for the calculus of free energy, because of somewhat complicated form of Eq. (14).

For various values of h_e, numerical analyses are carried out. In Figure 2, temperature dependences of the order parameter are shown for typical cases, $h_e = 0$, 0.015 and 0.02540 ($= h_e^*$) in the unit of V. As the field is increased, a jump at the transition decreases, and at the critical field h_e^*, the curve $s(T)$ becomes continuous, while a tangent diverges at $T = T^*$ ($= 1.1932$). At the field larger than h_e^*, a continuous curve $s(T)$ with finite tangent is derived, that is, no transition occurs. For the field smaller than h_e^*, several solutions are obtained, from which the thermal equilibrium value is determined, as a matter of course, under the condition of minimum free energy. In Figure 3, a phase transition curve is shown the full line on the field versus temperature plane together with the one derived by the mean field theory shown by the broken line, where CP denotes the critical point. In the mean field theory (MFT), estimates of critical field and critical temperature are the following; $h_{e\,\mathrm{MF}}^* = 0.06272$ and $T_{\mathrm{MF}}^* = 1.3856$ [12]. It is noticed that h_e^*

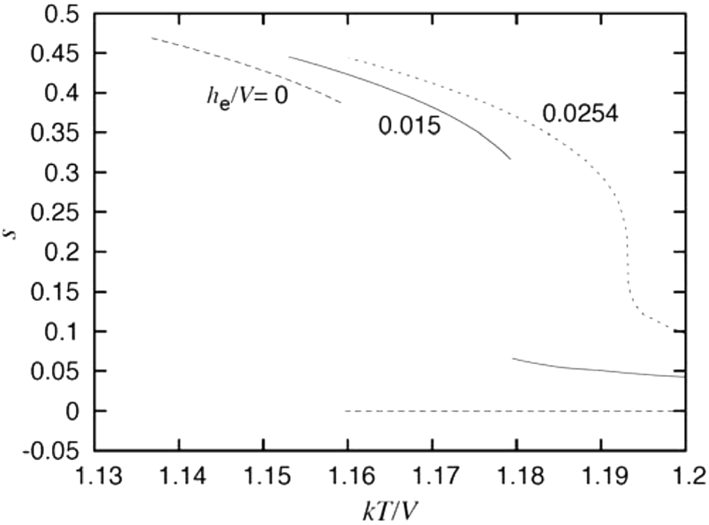

Figure 2. Temperature dependences of s for various field values.

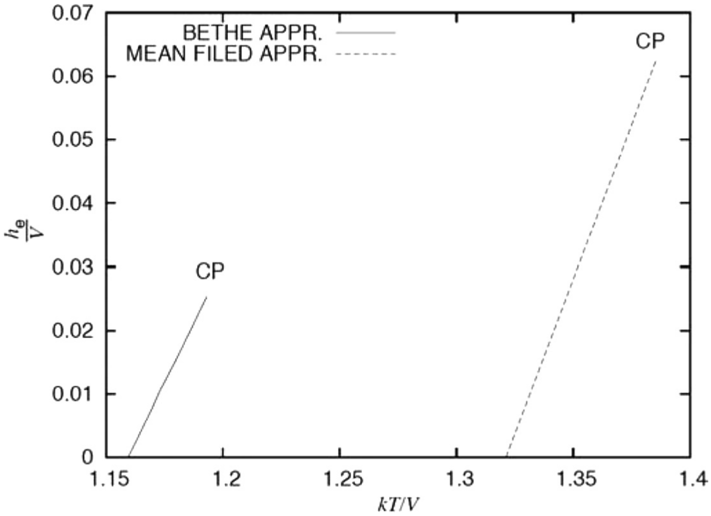

Figure 3. Phase diagram on h_e versus T plane, where CP denotes critical point.

Table 1. Critical values of T and h_e, and transition temperature T_c at $h_e = 0$

	Bethe approx.	MFT [12]
h_e^*	0.02540	0.06272
T^*	1.1932	1.3856
T_c	1.1594	1.3212

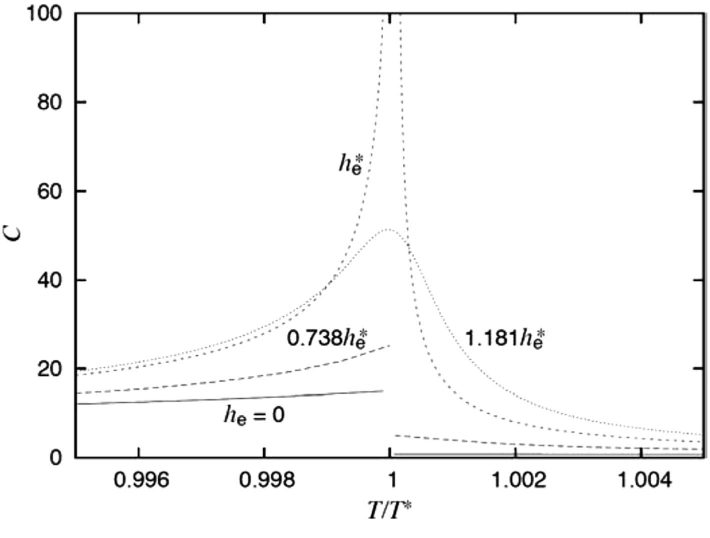

Figure 4. Specific heat versus temperature at various field values.

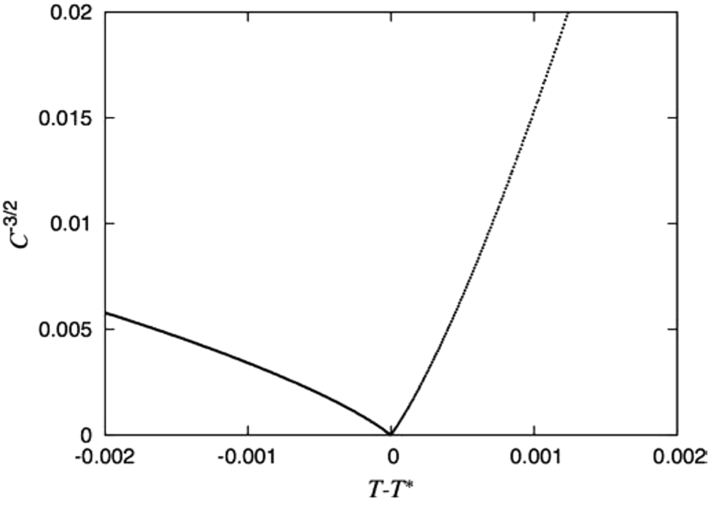

Figure 5. The $C^{-3/2}$ versus T relation.

derived here is smaller than a half of h^*_{eMF}. On the other hand, for a shift of the critical temperature, the estimated value by the Bethe approximation is about 86% of the mean field approximant, which is compared with a ratio 88% for the transition temperature T_c. These estimates are summarized in Table 1 together with a transition temperature T_c at vanishing field.

A specific heat at constant external field and constant volume, C, is given by a partial derivative of U given by Eq. (14) with respect to T. In Figure 4, C is shown for several values of field strength, in which a critical divergence is observed at $h_e = h^*_e$. By plotting data at the critical field in log-log scale, we derive an exponent, $\alpha = 2/3$, of a usual notation, $C \propto |T - T^*|^{-\alpha}$. In practice, linear dependence of $C^{-3/2}$ on the temperature near T^* is exhibited to certify the exponent as shown in Figure 5. This remarkable property is characteristic at the critical point without symmetry change, which is compared with the one at the case of a critical point with symmetry change, like magnetic system, where an order parameter remains zero at high temperature phase and discontinuous change of a specific heat is derived at the critical point. In this case a sophisticated method, such as Padé approximation, should be utilized to estimate the critical exponent. In the next section, the critical divergence of the specific heat obtained here is discussed generally on the basis of the classical theory.

4. Specific Heat at a Critical Point without Symmetry Change

In a classical theory including the Bethe approximation and so on, a thermodynamic potential $\Phi(s)$ is described in a form of Landau expansion near a transition point accompanying no symmetry change as

$$\Phi(s) = ts^2 - bs^3 + cs^4 - h_e s, \tag{15}$$

where a coefficient t stands for the temperature, and b and c are constants. Concrete forms of t, b, and c are determined depending on the theories of approximation.

Practically, in the Bethe approximation, s in Eq. (9) is expanded, using Eqs. (7) and (8) together with Eqs. (5) and (6), in the form with coefficients c_1, c_2, and c_3 given by

$$s = c_1(\zeta + \beta h_e) + c_2(\zeta + \beta h_e)^2 + c_3(\zeta + \beta h_e)^3. \tag{16}$$

Inversely, ζ is expressed from Eq. (16) as a function of s as

$$\zeta = -\beta h_e + d_1 s + d_2 s^2 + d_3 s^3, \tag{17}$$

from which $\Phi(s)$ is obtained using Eq. (10) in the form of Eq. (15).

We introduce here σ, τ, and η, deviations of s, t, and h_e from respective critical values s^*, t^*, and h_e^*, given by

$$s = s^* + \sigma, \tag{18}$$

$$t = t^* + \tau, \tag{19}$$

$$h_e = h_e^* + \eta, \tag{20}$$

where $s^* = b/4c$, $t^* = 3b^2/8c$, and $h_e^* = b^3/16c^2$, determined from $\Phi'(s^*) = 0$, $\Phi''(s^*) = 0$, $\Phi'''(s^*) = 0$. Then, Eq. (15) is reduced to

$$\Phi(\sigma) = \tau\sigma^2 + c\sigma^4 - (\eta - \frac{b}{2c}\tau)\sigma. \tag{21}$$

This free energy belongs to a general form,

$$\Phi(\sigma) = \xi\sigma^2 + c\sigma^4 - \psi\sigma, \tag{22}$$

and so long as the field h_e is fixed at h_e^*, critical behaviour at Eq. (21) is described by Eq. (22), where fields ξ and ψ are related to τ and η by

$$\xi = \frac{2c}{\sqrt{b^2 + 4c^2}}\tau, \tag{23}$$

$$\psi = \eta - \frac{b}{2c}\tau. \tag{24}$$

Relations between orthogonal coordinate systems (t, h_e), (τ, η), and (ξ, ψ) are shown in Figure 6, in which a coexisting line shown by a bold curve ends at the critical point shown by a filled circle. The axis ξ is a tangential line of the coexisting line at the critical point. In the free energy of Eq. (22), the fields, ξ and ψ, are scaled as $\lambda^{1/2}\xi$ and $\lambda^{3/4}\psi$, respectively, with scale parameter λ [16], and by taking a magnitude of order parameter into account, crossover lines are derived as

$$\psi = \pm\left(\frac{2}{c}\right)^{1/2}|\xi|^{3/2}. \tag{25}$$

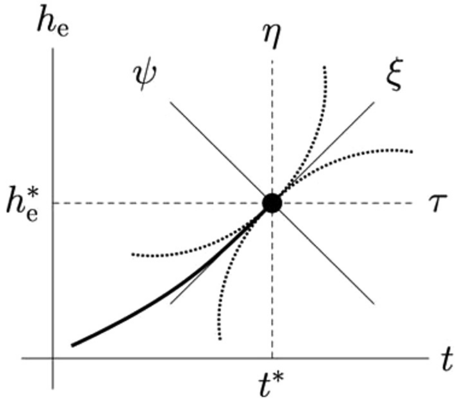

Figure 6. Critical point and coordinate systems.

In Fig. 6, the crossover lines are shown by a couple of dotted curves crossing tangentially to the coexisting line at the critical point. The line $h_e = h_e^*$, that is, τ-axis, is located in the region, where a critical behaviour is dominated by the field ψ. Accordingly, we can assume $\xi = 0$ in the free energy so long as the criticality is concerned. Then, the free energy G given by $\Phi(s_{eq})$ is obtained as $G = -3(4c)^{-1/3}\psi^{4/3}$ from Eq. (22). Under the condition $\eta = 0$, a partial derivative with respect to t is related to the one with respect to ψ as

$$\frac{\partial}{\partial t} = -\frac{b}{2c}\frac{\partial}{\partial \psi}\bigg|_{\eta=0}, \tag{26}$$

and the specific heat at constant field, $C(= -\partial^2 G/\partial T^2)$, is obtained as

$$C = \frac{1}{3\sqrt[3]{4}} b^2 c^{-7/3} \psi^{-2/3} \propto \tau^{-2/3}. \tag{27}$$

Thus, the singular behaviour of the specific heat obtained by the Bethe approximation shown in the preceding section is explained.

Generally, an order parameter is given by $-\partial G/\partial \psi$, and assumed the form $\psi^{1/\delta}$ at the critical temperature. Here we obtain $\delta = 3$ of classical exponent [16]. The present estimate $2/3$ for the specific heat is nothing but the value $-(1/\delta - 1)$.

The above theory is common to systems such as liquid-gas critical point [17] and Potts model with q-states ($q > 2$) in 3-dimension [18,19], where an invariant of the third power exists in a free energy and a phase transition is of first order. In a system such as $S = 1$ Ising model with zero-field splitting [20], where a coefficient of the forth power of order parameter can be negative while only even powers exist, a critical point also appears at finite field strength. Free energy also takes the form of Eq. (22) with positive c value near the critical point. In the above cases except for the liquid-gas transition, no symmetry breaking occurs at the critical point because the symmetry is broken by the external field, while the symmetry breaking occurs at the first order transition without field.

5. Summary

Nematic phase transition in a positive uniaxial field is studied using Bethe approximation in the framework of a lattice Maier-Saupe model, in which a phase diagram on a field versus temperature plane is obtained. An estimate of critical field is shown to be smaller than an approximate value by a mean field theory, while an estimate of critical temperature is lower only ten percent or so than that by the mean field one. A critical divergence of specific heat is obtained with a critical exponent $2/3$, which is shown to be common to the critical phenomenon appearing near a critical point accompanying no symmetry change.

In case the dielectric anisotropy is negative, the external field h_e takes negative value, and the molecular long axes tend to align in a plane perpendicular to the field direction. Eventually, the nematic phase becomes biaxial. For increasing absolute value of the field, a jump at the transition becomes small, and finally tricritical point appears, beyond which the transition is of second order [21–23]. An analysis of this situation is more interesting than the positive anisotropy studied here. However, two molecular fields, applied peripheral molecules of a cluster in the Bethe approximation, are required and numerical analysis becomes quite labourious. Yet, it is worthy to execute the calculation, which will be tried in a near future.

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