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The nematic critical point in the molecular field approximation

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Résumé. — On traite un système de spins classiques avec interaction d'échange biquadratique et anisotropie à un spin dans l'approximation du champ moyen. La variation thermique des quantités thermodynamiques est étudiée en fonction de l'anisotropie et l'effet de crossover du point critique ordinaire au point critique nématique est discuté. La variation avec la température est décrite au voisinage de la transition de phase par une loi de puissance. On détermine numériquement les exposants dans le domaine de température d'intérêt expérimental

$$10^{-4} \leq |\varepsilon = (T - T_i)/T_i| \leq 10^{-2}$$

au-dessus et au-dessous du point de transition T_i . Les valeurs des exposants critiques estimées au point critique nématique sont : $\nu^+ = 0,321 \pm 0,001$, $\nu^- = 0,357 \pm 0,004$ et $\Delta^+ = 1,32 \pm 0,005$, $\Delta^- = 1,29 \pm 0,01$.

Abstract. — The classical spin system with biquadratic exchange interaction and single spin anisotropy is analysed in the molecular field approximation. The temperature dependence of important thermodynamic quantities versus anisotropy strength is studied and the crossover from ordinary critical point behaviour to nematic point behaviour is discussed. The power-law parameters describing the temperature dependence are numerically estimated in the experimentally available temperature region of $10^{-4} \leq |\varepsilon = (T - T_i)/T_i| \leq 10^{-2}$ both below and above the transition point T_i . The estimated values of the gap and the correlation exponents at the nematic critical point are : $\Delta^+ = 1.32 \pm 0.005$, $\Delta^- = 1.29 \pm 0.01$ and $\nu^+ = 0.321 \pm 0.001$, $\nu^- = 0.357 \pm 0.004$ respectively.

In recent years the problem of the values of critical exponents for the isotropic-nematic phase transition has become a subject of growing interest [1, 2]. The suggestion [1] that these exponents take values characteristic of a tricritical point now seems to be confirmed experimentally [2]. In this letter a simple model exhibiting a nematic critical point is analysed in the molecular field approximation. It has been found that the estimated values of the power-law exponents for this model agree approximately with those determined experimentally.

1. The model Hamiltonian and the molecular field approximation. — A classical spin system with a biquadratic exchange interaction is the simplest theoretical model exhibiting nematic ordering. A unit vector $\mathbf{S}$ — classical spin — is assigned to each nematogenic molecule showing the direction of its main axis. We assume the Hamiltonian of the N particle system is of the form

$$\mathcal{H} = - \sum_{i,j} 3 J(ij) (\mathbf{S}(i) \cdot \mathbf{S}(j))^2 - D \sum_i (S^z(i))^2 - g \sum_i (\mathbf{H}(i) \cdot \mathbf{S}(i))^2 \quad (1)$$

consisting of three terms namely the particle-particle interaction energy, the single-particle anisotropy energy and the energy of interaction with an external field. $J(ij)$ is the positive particle-particle (spin-spin) interaction constant, and we assume that $J_0 = \sum_j J(ij)$ is finite. $D = aJ_0$ represents the anisotropy field and $a > 0$ is the anisotropy parameter. $\mathbf{H}(i)$ is the external magnetic field at the site of the i -th particle with spin $\mathbf{S}(i)$. g is the coupling constant between field and the spin.

The behaviour of the system will be discussed in the molecular field approximation obtained by means of the cluster expansion method of Strieb, Callen and Horwitz [3].

In order to separate out that part of the Hamiltonian suitable for the MFA (1) the Ypma, Vertogen and Koster [4] transformations are used here, leading to the Ising type Hamiltonian $\mathcal{H}'$, after rejecting small terms containing products of the spin x and y components

$$\mathcal{H}' = - \sum_{i,j} 2 J(ij) P_2(i) P_2(j) - \sum_i [D_1 + g_1 H^2(i)] P_2(i) \quad (2)$$

where

$$P_2(i) = \frac{1}{2}[3(S^2(i))^2 - 1] \quad (3)$$

and $g_1 = 2g/3$, $D_1 = 2D/3$. The external field $\mathbf{H}$ has been chosen to be parallel to the anisotropy axis.

The next step consists of splitting the Legendre polynomials $P_2(i)$ into two terms

$$P_2(i) = \bar{P}_2(i) + \Delta(i) \quad (4)$$

where $\bar{P}_2(i)$ is the parameter which will be chosen so as to minimize the Gibbs potential, while $\Delta(i)$ is the deviation variable. By means of rejection of terms proportional to $\Delta(i)$ from the Hamiltonian $\mathcal{H}$ a molecular field Hamiltonian $\mathcal{H}_{\text{MF}}$ is obtained in the following form

$$\mathcal{H}_{\text{MF}} = \sum_{i,j} 2 J(ij) \bar{P}_2(i) \bar{P}_2(j) - \sum_i A(i) P_2(i) \quad (5)$$

where

$$A(i) = \sum_j 4 J(ij) \bar{P}_2(j) + \frac{2}{3} J_0 \hat{a} + g_1 H^2(i). \quad (6)$$

The Gibbs potential for the system described by the Hamiltonian (5) is given by

$$G_{\text{MF}} = \sum_{i,j} 2 J(ij) \bar{P}_2(i) \bar{P}_2(j) - k_B T \sum_i \ln \int_0^1 du \exp[\beta A(i) P_2(u)] \quad (7)$$

where $\beta = 1/k_B T$. The minimization of the Gibbs potential (7) with respect to $\bar{P}_2(i)$ leads to the following set of self-consistency equations

$$P_2(i) = F(\beta A(i)) \quad (8)$$

where $F(x)$ is the Maier-Saupe function given by the formula

$$F(x) = \frac{d}{dx} \ln \int_0^1 du \exp[x P_2(u)]. \quad (9)$$

In the case of a homogeneous system without an external field, when $\bar{P}_2(i) = \bar{P}_2^0$, the minimization procedure leads to a self-consistency equation equivalent to that discussed by Sheng and Wojtowicz [5] because the influence of anisotropy can be treated as equivalent to that of the external field. The resulting phase diagram in the $a - T$ plane consists of a single line corresponding to quasi-first order phase transitions (in which the order parameter exhibits high-temperature tails) described by a linear law

$$t_c(a) = 0.880\,774 + 0.685\,0\,a \quad (10)$$

where $t = k_B T/J_0$. In terms of the classical theory of phase transitions the end point of this line described by the coordinates

$$a_c = 0.062\,725, \quad t_c = 0.923\,741$$

is the critical point (the nematic critical point). Phase diagrams for similar models have been discussed in the case of the quadrupolar ordering [8] and lattice-gas problems [9]. The successive derivatives of the Gibbs potential (7) with respect to $H^2(i) = H^2 \equiv h$ yield the quadrupolar susceptibility χ_2 and its field derivative χ_3

$$\chi_2 = - \left(\frac{\partial^2 G_{\text{MF}}}{\partial h^2} \right)_{T,h=0} = \frac{Ng_1^2 \beta F_0^{(1)}}{1 - 4 \beta J_0 F_0^{(1)}} \quad (11)$$

$$\chi_3 = - \left(\frac{\partial^3 G_{\text{MF}}}{\partial h^3} \right)_{T,h=0} = \frac{Ng_1^3 \beta^3 F_0^{(2)}}{(1 - 4 \beta J_0 F_0^{(1)})^3} \quad (12)$$

where the derivatives of the Maier-Saupe function

$$F_0^{(n)} = \left(\frac{d^n F(x)}{dx^n} \right)_{\bar{P}_2 = \langle P_2 \rangle} \quad (13)$$

are evaluated for the stable solution $\bar{P}_2 = \langle P_2 \rangle$ of the self-consistency equation (8) for the homogeneous system (when $\bar{P}_2(i) \equiv \bar{P}_2$ and $A(i) \equiv A$).

The temperature dependence of the inverse of χ_2 is presented in figure 1a (see Eq. (15)). One can clearly see the nonlinearity of this dependence when the value of the anisotropy parameter a approaches a_c .

Fig. 1a. — Temperature dependence of the correlation parameter κ^2 and the inverse of the quadrupolar susceptibility $\chi_2^{-1} \sim \kappa^2 w$ for different values of the anisotropy parameter a .

Recently it has been pointed out [2] that the temperature dependence of the ratio

$$f = \chi_3/\chi_2 \quad (14)$$

is important in determining the character of the isotropic-nematic phase transition. Since the critical exponent of f is the gap exponent Δ [2, 14] we call f the gap parameter.

Fig. 1b. — Variations of the power-law (16) parameters as functions of the anisotropy parameter a for the correlation parameter κ^2 . The broken curve represents the $2\nu^-$ dependence on a below the transition point. The difference between κ_0^{2+} and κ_0^{2-} is too small to be distinguished in this plot.

A plot of $f_1 = (3J_0/g)f$ versus normalized temperature for several values of the anisotropy parameter is presented in figure 2a. Using equation (8) one can easily find an expression for the correlation

Fig. 2a. — Dependence of the gap parameter f_1 on temperature for some values of the anisotropy parameter a .

Fig. 2b. — Variations of the power-law (16) parameters as functions of the anisotropy parameter a for the inverse of the gap parameter f_1^{-1} . f_{ON}^{-1} and f_{OP}^{-1} are the values of f_1^{-1} at the transition points for the low- and high-temperature phases respectively.

parameter κ (the inverse of the longitudinal correlation length)

$$\kappa^2 = \frac{Ng_1^2}{2wJ_0\chi_2} \quad (15)$$

where

$$w = J_2^{\parallel}/J_0, \quad \text{with} \quad J_2^{\parallel} = \int d^3\mathbf{r} J(\mathbf{r}) z^2.$$

2. The power-law parameters. — We have analysed numerically the temperature dependence of several thermodynamic parameters of the system above and below the transition point for different values of the anisotropy parameter a .

It is assumed that each quantity x follows the generalized power law

$$x = x_0^{\pm} + c_0^{\pm} |\varepsilon|^{y^{\pm}}, \quad \varepsilon = (T - T_t)/T_t \quad (16)$$

where x_0^+ and x_0^- are the limits $x_0^{\pm} = \lim_{T \rightarrow T_t \pm 0} x(T)$ of x at the transition point $T_t(a)$. Since the analysis is most appropriate in the limit $x_0 = 0$, the inverse of

the quantities which diverge at the critical point are analysed. The exponents $y^{\pm}$ and constants $c_0^{\pm}$ were determined by means of least square fits over the experimentally available interval,

$$10^{-4} \leq |\varepsilon| \leq 10^{-2}.$$

For the correlation parameter $x = \kappa^2$ the dependence of $x_0 = \kappa_0^2$ and $y = 2\nu$ on the anisotropy parameter a is presented in figure 1b. Analogous plots of f_0^{-1} and Δ for the inverse of the gap parameter f_1^{-1} are given in figure 2b.

The estimated values of exponents α , β , ν and Δ for the nematic critical point ($a = a_c$ and $t_t = t_c$) are

given in table I and are compared with those obtained from the appropriate Landau expansion of free energy. The values of the Landau exponents are the same as those for the ferroelectric critical point induced by an electric field [10, 11] and the spin-one anisotropic Ising system [12]. The estimated values of ν and β agree quite well with those given by the Landau theory. The small differences stem from the finite interval in the numerical procedure used in the estimation of the critical indices. This method models the fitting of the law (16) to the experimental data. The value of α has been significantly affected by this procedure although the values of Δ are most altered. In this respect the present theory seems to represent a special case $\Delta = 2\gamma$ (as one can see from equations (11) and (12)) of the equation of state approach [13] discussed by Keyes and Shane [2].

Table I. — Values of the critical indices.

Quantity	Landau theory	Estimated values	
		$T > T_c$	$T < T_c$
Order parameter	1/3	0.29 ± 0.01	0.365 ± 0.005
Correlation length	1/3	0.321 ± 0.001	0.357 ± 0.004
Gap parameter	1	1.320 ± 0.005	1.29 ± 0.01
Specific heat	2/3	0.89 ± 0.03	0.52 ± 0.02

Conversely the Landau expansion near the nematic critical point provides an example of $\Delta = \gamma + \beta$. A qualitative picture of the temperature dependence of the analysed quantities is demonstrated clearly by the example of κ^2 . The plot of $\kappa^{2+} - \kappa_0^{2+}$ versus ε for different values of a is presented in figure 3. It is evident that for $a < a_c$ there is a region where ν^+ is approximately 1/2 i.e. the classical value for the ordinary critical point. The width of this region decreases to zero as a approaches a_c . This diminishing region gives way to the region with ν^+ approximately equal 1/3 i.e. the classical value for the nematic critical point.

In order to estimate the anisotropy parameter we have analysed the experimental data for light scattering [6] and the Cotton-Mouton effect [2] in the MBBA. We find that the exponents in the power law (16) take the values : $2\nu^+ = 0.9 \pm 0.05$ and

$$\Delta^+ = 1.15 \pm 0.1.$$

Fig. 3. — Log-log plots of the correlation parameter $\kappa^{2+} - \kappa_0^{2+}$ against reduced temperature $\varepsilon = (T - T_t)/T_t$ for different values of the anisotropy parameter a .

These data give the following crude estimates of a ; 0.05 for the sample used in the light scattering experiment of Gulari and Chu [6] and 0.055 for that used by Keyes and Shane [2] in their Cotton-Mouton effect study. In terms of the present theory this agreement can be explained as the effect of longitudinal fluctuations occurring in strongly aligned nematic clusters. This might suggest that the nematic critical point is induced by the strong anisotropy field [5] which need not be attributed to any external factor. We think that the presence of this anisotropy can be regarded as a measure of the strong orientational clustering tendency observed in nematogens. This conjecture has been quite successful recently in explaining certain experimental results [7].

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References

[1] KEYES, P. H., *Phys. Lett.* **67A** (1978) 132.
[2] KEYES, P. H. and SHANE, J. R., *Phys. Rev. Lett.* **42** (1979) 722.
[3] STRIEB, B., CALLEN, H. B. and HORWITZ, G., *Phys. Rev.* **130** (1963) 1798.
[4] YPMA, J. G. J., VERTOGEN, G. and KOSTER, H. T., *Mol. Cryst. Liq. Cryst.* **37** (1976) 57.
[5] WOJTOWICZ, P. J. and SHENG, P., *Phys. Lett.* **48A** (1974) 235.
[6] GULARI, E. and CHU, B., *J. Chem. Phys.* **62** (1975) 798.
[7] OGORODNIK, K. Z., *Acta Phys. Pol. A* **56** (1979) 879.
[8] SIVARDIÈRE, J., BERKER, A. N., WORTIS, M., *Phys. Rev. B* **7** (1973) 343.
[9] LAJZEROWICZ, J. and SIVARDIÈRE, J., *Phys. Rev. A* **11** (1975) 2079.
[10] FALK, G., in *Critical Phenomena in Alloys, Magnets and Superconductors*, edited by R. E. Mills, E. Ascher, R. I. Jaffer (Mc Graw Hill) 1971, p. 135.
[11] GRINDLAY, J., *An Introduction to the Phenomenological Theory of Ferroelectricity* (Pergamon Press, Oxford) 1970, Ch. 5.
[12] GRIFFITHS, R. B., *Physica* **33** (1967) 689.
[13] PRIEST, R. G. and LUBENSKY, T. C., *Phys. Rev. B* **13** (1976) 4159.
[14] STANLEY, H. E., *Introduction to Phase Transitions and Critical Phenomena* (Clarendon Press, Oxford) 1971.