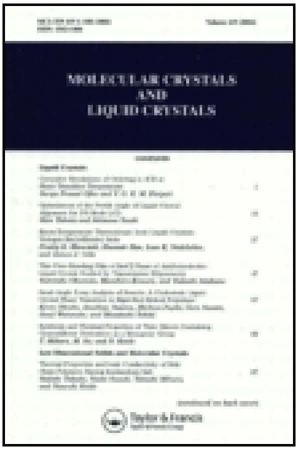

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

The Pseudocritical Concept in the Landau Theory of the Nematic—Isotropic Phase Transition

H.-J. Mögel [a]

[a] Sektion Chemie, Martin-Luther-University, Halle-Wittenberg, 4020, Halle, Mühlpforte 1, GDR

To cite this article: H.-J. Mögel (1988): The Pseudocritical Concept in the Landau Theory of the Nematic—Isotropic Phase Transition, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 159:1, 65-75

To link to this article: http://dx.doi.org/10.1080/00268948808075261

Mol. Cryst. Liq. Cryst., 1988, Vol. 159, pp. 65–75
Photocopying permitted by license only

Printed in the United States of America

The Pseudocritical Concept in the Landau Theory of the Nematic–Isotropic Phase Transition

H.-J. MÖGEL

Sektion Chemie, Martin-Luther-University, Halle-Wittenberg, 4020, Halle, Mühlpforte 1, GDR

(*Received August 1, 1985; in final form January 1, 1987*)

An extension of the scalar order parameter Landau-deGennes model for the pseudocritical theory of fluid phase transitions is used to describe pretransitional phenomena in the vicinity of the nematic–isotropic transition. The quantitatively different pretransitional behaviour of fluids near critical points and near simple spinodal points is taken into account. Using temperature, pressure and specific volume as variables, the expression for the Gibbs free energy yields the equation of state and mean-field values of pseudocritical exponents which satisfy the scaling equations. The temperature dependence of some thermodynamic quantities is obtained. The correlation length for the correlation function of scalar order parameter fluctuations is given as a function of temperature. The Ginzburg criterion is used to demonstrate two kinds of crossover behavior.

Keywords: nematic liquid crystal, phase transition, spinodal, pseudocritical theory

INTRODUCTION

Pretransitional phenomena in nematic liquid crystals near the transition to the isotropic liquid cause certain difficulties in a quantitative theoretical treatment. On one hand deviations from the linear temperature dependence of many physical properties indicate singularities of the form $(T - T_c)^x$ similar to those near a critical point. On the other hand there are jumps in the enthalpy, specific volume and entropy which obviously indicate that the transition is first order. In the framework of the Landau-deGennes theory pretransitional effects are caused by the small temperature distance from the spinodal. The jumps are related to the cubic term in the Gibbs free energy expansion. Since the latent heat and other jumps are small, the transition is often said to be close to second order and the theory of critical phenomena can be used to describe the pretransitional thermodynamics.

However, the experimental values of the critical exponents do not agree with these predicted by this theory. Several new modified theories have been proposed to give a quantitative agreement. The mean-field theories assume a critical or tricritical point[1,2] and treat the nematic–isotropic phase transition as continuous.[3] They are in conflict with results of symmetry analysis which predicts a discontinuous transition. In the framework of the renormalization group theory, special models[4,5] avoiding this conflict have been developed. However, the singularities predicted by these models do not agree with experimental data.

The aim of the present paper is to propose a solution to this problem by taking into account the quantitative difference between the singularities near a critical point and those near a simple spinodal point. The theory which deals with singularities of thermodynamic quantities in the vicinity of a spinodal is known as *pseudocritical theory*. It is based on the assumption that the isothermal compressibility becomes singular, when the spinodal is reached along a non-critical isochore.[6] At both a critical point and at simple spinodal points, the same quantities have singularities.[7] However, the critical and pseudocritical exponents which quantitatively characterize these singularities are different. This has been demonstrated for magnetic systems,[8] for binary liquid mixtures,[9] for one-component liquid–gas systems.[10] It was found experimentally for the main transition in phospholipids.[11]

The pseudocritical concept is based on a Gibbs free energy expansion with respect to a generalized order parameter: $\phi = y^* - y$ which becomes zero, when the spinodal value $y = y^*$ is reached. If the spinodal point is a critical point $y^* = y_c$, then the variable ϕ is the usual Landau order parameter.

GIBBS FREE ENERGY

To define a thermodynamic function in the vicinity of the nematic–isotropic phase transition (in the absence of external electric or magnetic fields) the temperature T, the pressure p and the specific volume V are a convenient variable set. Experimental results[12] concerning these variables give some common characteristics for the nematic–

isotropic and liquid–gas systems at a distance from the critical point: The isotherms in the p,V-diagram have similar form and the jumps of the specific volume decrease with increasing pressure. This suggests that we treat the nematic liquid crystal near the clearing point as being analogous to a simple liquid near the spinodal at temperatures much lower than the critical value.

The Gibbs free energy expansion has the form

$$G(p,T,\phi) = G_{reg}(p,T) + \frac{1}{2}A\phi^2 + \frac{1}{3}B\phi^3 + \frac{1}{4}C\phi^4 - hV^*\phi \tag{1}$$

where the generalized order parameter $\phi = (V^* - V)/V^*$ is introduced. This order parameter becomes zero at the same thermodynamic points as $Q - Q^*$. Q is defined as $Q = \langle P_2(\cos\theta)\rangle$ and θ is the angle between the molecular axis and the preferred direction in the nematic phase. Therefore one can assume a simple coupling by the relation

$$\phi = a_0(Q - Q^*)^x, \tag{2}$$

the superscript * designating the reference state at the spinodal. G_{reg} in (1) is the regular part of G,

$$A = a\tau, \qquad \tau = (T - T^*)/T^*, \tag{3}$$

a and C are constants.

In order to explain the nature of the "fluid" field h, let us consider the isomorphism between the thermodynamic environment of a liquid–gas critical point and magnetism near the Curie point. The Gibbs free energy in the mean-field variant has the form

$$G(H,T,W) = G_0(H,T) + A_0M^2 + B_0M^4 - HM, \tag{4}$$

where M and H are the magnetization and the magnetic field respectively.

$$G(p,T,V) = G_1(p,T) + A_1(V_c - V)^2 + B_1(V_c - V)^4 - [p - p_c - (\partial p/\partial T)_{V_c}(T - T_c)](V_c - V) \tag{5}$$

in the case of the liquid–gas system (p_c, T_c, V_c).[13] On the critical isochore and along the coexistence curve we have;

$$h' = p - p_c - (\partial p/\partial T)_{V_c}(T - T_c) = 0. \tag{6}$$

Thus the thermodynamic expression for H=O in magnetism and for $h^{`} = 0$ in liquid–gas systems on the coexistence curve have the same form. The generalization of the order parameter $y_c - y \rightarrow y^* - y$ corresponds to a redefinition of the fluid field

$$h^{`} \rightarrow h = \mathrm{p} - \mathrm{p}^* - (\partial \mathrm{p}/\partial \mathrm{T})_{\mathrm{V}^*}(\mathrm{T} - \mathrm{T}^*) \tag{7}$$

in the case of pseudocritical phenomena.

The coefficients B in (1) and $(\partial \mathrm{p}/\partial \mathrm{T})_{\mathrm{V}^*}$ in (7) are substance parameters which can influence the thermodynamic behaviour near the phase transition. There are two special points on the spinodal: the point (p**, T**, V**) at which B becomes zero

$$B = b\overline{\Delta \mathrm{V}}, \qquad \overline{\Delta \mathrm{V}} = (\mathrm{V}^* - \mathrm{V}^{**})/\mathrm{V}^{**}$$

and the point of intersection $(\mathrm{p}_0^*, \mathrm{T}_0^*, \mathrm{V}_0^*)$ with the line of constant zero field $h_0 = h = 0$

$$h_0 = \mathrm{p} - \mathrm{p}_0^* - \left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}_0^*}(\mathrm{T} - \mathrm{T}_0^*) \tag{8}$$

If the phase transition is of second order, then the points (p^{**}, T**, V**) and $(\mathrm{p}_0^*, \mathrm{T}_0^*, \mathrm{V}_0^*)$ coincide and the crossover from the pseudocritical to the critical behaviour takes place both for $B \rightarrow 0$ and $H \rightarrow 0$. In our case, the nematic–isotropic spinodal (p**, T**, V**) and (p_0^*, T_0^*, V_0^*) are different points. In order to ensure that the binodal and the spinodal do not have a common point, a term $\mathrm{E}\phi^6$ in (1) can be included. At thermodynamic points, where $B = 0$, the spinodal intersects the curve of constant field $h_0 = h^* \neq 0$. Where $E \neq 0$ the quantity h* may be considered as a symmetry-breaking field which prevents the realization of a second order transition. The value of h^* would be changed by applying an additional external field which couples sufficiently strongly to a molecular anisotropic quantity, *e.g.*, a large dielectric anisotropy.

THERMODYNAMICS

The thermal equation of state is obtained from the minimum condition of the thermodynamic potential (1) with respect to the order parameter

$$A\phi_0 + B\phi_0^2 + C\phi_0^3 - h\mathrm{V} = 0. \tag{9}$$

Here, and in the following discussion, ϕ_0 means the equilibrium value of the order parameter $\phi_0 = \Delta V = (V^* - V)/V^*$. From the equilibrium potential $G(p, T, \phi_0)$ the dependence of the entropy both on the volume and temperature can be found as

$$S = S_{reg} - \frac{a}{2T^*}\phi_0^2 - \left(\frac{\partial p}{\partial T}\right)_{V^*} V^*\phi_0. \tag{10}$$

From (9) and (10) the following temperature and pressure functions of thermodynamic quantities are predicted along the isobar, isochore, isotherm and adiabatic near the nematic to isotropic transition:

1. The isochore (V = V*)

$$p - p^* = T^*\left(\frac{\partial p}{\partial T}\right)_{V^*}\tau, \tag{11}$$

$$C_V = C_{V,reg} \tag{12}$$

2. The isotherm (T = T*)

$$p - p^* = (B\Delta V^2 + C\Delta V^3)/V^*, \tag{13}$$

$$-V^2\left(\frac{\partial p}{\partial V}\right)_T = V^*\beta_T^{-1} = 2B\Delta V + 3C\,\Delta T^2. \tag{14}$$

3. The isobar (p = p*)

$$\tau = -\frac{B\Delta V^2 + C\Delta V^3}{a\Delta V + V^*T^*(\partial p/\partial T)_V}, \tag{15}$$

$$\frac{C_p}{T^*} = \frac{C_p}{T^*}{,}\text{reg} - \left[\frac{a\Delta V}{T^*} + V^*\left(\frac{\partial p}{\partial T}\right)_{V^*}\right]\left(\frac{\partial V}{\partial T}\right)_p, \tag{16}$$

where ΔV and $(\partial V/\partial T)_p$ are to be calculated from (15). In order to simplify Equations (15) and (16) in the general case, where no term in the formula can be neglected, it is convenient to introduce effective coefficients and exponents, *e.g.*,

$$\Delta V = E_e\,|\tau|^{\beta_e'} \tag{17}$$

where $1/3 < \beta_e' < 1$. It is readily seen from (17) that the isobaric thermal expansion coefficient $(\partial V/\partial T)_p$ along the isobar has the same singularity as the constant pressure heat capacity

$$(\partial V/\partial T)_p/V^* \sim |\tau|^{\beta_e'-1}. \tag{18}$$

The heat capacity at constant pressure is given by

$$C_p = C_{p,reg} + \frac{a}{T^*} E_e^2\, \beta_e'|\tau|^{2\beta_e'-1} + V^*\left(\frac{\partial p}{\partial T}\right)_{V^*} E_e\beta_e'|\tau|^{\beta_e'-1}. \tag{13}$$

The effective quantities are dependent on the relation between different terms in the exact Equations (15) and (16). They are constant over small temperature ranges.

4. The adiabatic ($S = \text{const.}$)

$$\Delta V = -\frac{V^*T^*}{a}\left(\frac{\partial p}{\partial T}\right)_{V^*} + \left|\left|\frac{V^{*2}T^{*2}}{a^2}\left(\frac{\partial p}{\partial T}\right)_{V^*}^2 - (S - S_{reg})\frac{2T^*}{a}\right|\right|^{1/2}, \tag{20}$$

$$p = p^* + \frac{1}{V^*}\left[(T^*V^*\left(\frac{\partial p}{\partial T}\right)_{V^*} + a\Delta V\right] + B\Delta V^2 + C\Delta V^3 \tag{21}$$

with ΔV from (20).

PSEUDOCRITICAL EXPONENTS

All systems within one universality class have the same pseudocritical exponents. In regions removed from the above mentioned special spinodal points, the nematic–isotropic phase transition described by (1) is in the same universality class as metastable magnetic systems, superheated simple liquids and metastable binary mixtures. In order to demonstrate this, one has to investigate the temperature dependence of C_{h_0} (heat capacity at constant field h_0), of the order parameter ϕ_0, of the isothermal compressibility β_T and of the correlation length of the order parameter fluctuations in the Ornstein–Zernike approximation along the line of constant field h_0. The pseudocritical exponents are found in the limit $\phi_0 \rightarrow 0$. A connection between the fields h and h_0 can be obtained in the following way:

According to (8) for h_0 on the spinodal

$$h_0^* = p^* - p_0^* - \left(\frac{\partial p}{\partial T}\right)_{V_0^*} (T^* - T_0^*). \tag{22}$$

From (7), (8) and (22) this yields

$$h = h_0 - h_0^* + \left[\left(\frac{\partial p}{\partial T}\right)_{V_0^*} - \left(\frac{\partial p}{\partial T}\right)_{V^*}\right](T - T^*). \tag{23}$$

Therefore the condition of constant field $h_0 = \text{const.} \neq 0$ is $h_0 = h_0^*$ and can be written as

$$h = \left[\left(\frac{\partial p}{\partial T}\right)_{V_0^*} - \left(\frac{\partial p}{\partial T}\right)_{V^*}\right](T - T^*). \tag{24}$$

1. Pseudocritical exponent β

Applying the condition (24) in the equation of state (9), we obtain, for the temperature dependence of the order parameter

$$\tau = \frac{B\Delta V^2 + C\Delta V^3}{T^*V^*\left[\left(\frac{\partial p}{\partial T}\right)_{V_0^*} - \left(\frac{\partial p}{\partial T}\right)_{V^*}\right] - a\Delta V}. \tag{25}$$

At a distance from the special fields $h_0 = 0$ or $h_0 = h^*$ we obtain in the limit of $\phi_0 \rightarrow 0$

$$|\Delta V| = \left|\left|\frac{T^*V^*}{B}\left[\left(\frac{\partial p}{\partial T}\right)_{V_0^*} - \left(\frac{\partial p}{\partial T}\right)_{V^*}\right]\right|\right|^{1/2} |\tau|^{1/2} \tag{26}$$

where the exponent $\beta = 1/2$.

2. Pseudocritical exponent γ

Introducing (26) into (14) we obtain the behaviour of the isothermal compressibility on the constant field curve. In a similar way, the pseudocritical exponent is calculated from

$$\left(\frac{\partial \mathrm{p}}{\partial \mathrm{V}}\right)_{\mathrm{T}} = -\frac{2B}{\mathrm{V}^{*2}}\left|\,\left|\frac{\mathrm{V}^{*}\mathrm{T}^{*}}{B}\left[\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}_0^*} - \left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}^*}\right]\right|\,\right|^{1/2} |\tau|^{1/2} \qquad (27)$$

3. Pseudocritical exponent α

Differentiation of the caloric equation of state (10) with respect to the temperature at constant field gives:

$$\frac{C_{h_0}}{\mathrm{T}^*} = \frac{C_{h_0,\mathrm{reg}}}{\mathrm{T}^*} - \left[\frac{a}{\mathrm{T}^*}\Delta\mathrm{V} + \mathrm{V}^*\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}^*}\right]\left(\frac{\partial \Delta\mathrm{V}}{\partial \mathrm{T}}\right)_{h_0}. \qquad (28)$$

Inserting in (28) the constant field condition gives:

$$\frac{C_{h_0}}{\mathrm{T}^*} = \frac{C_{h_0,\mathrm{reg}}}{\mathrm{T}^*} + \frac{a\mathrm{V}^*}{2\mathrm{T}^*B}\left|\,\left|\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}_0^*} - \left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}^*}\right|\,\right| \qquad (29)$$

$$+ \frac{\mathrm{V}^*}{2\mathrm{T}^*}\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}^*}\left|\,\left|\frac{\mathrm{T}^*\mathrm{V}^*}{B}\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}_0^*} - \left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}^*}\right|\,\right|^{1/2} |\tau|^{-1/2}$$

with $\alpha = 1/2$ *in the case* $h_0 = \mathrm{const.} \neq h^*$.

4. Pseudocritical exponents δ and ν

As seen from (13), the exponent $\delta = 2$ on the isotherm is related to the set of exponents for constant field $h_0 = h = \text{constant}$.

In order to obtain the value for ν, a model of a free fluctuation field of the scalar order parameter is studied. The expression for the correlation length r_c has the form

$$r_c = [g/(\partial\mathrm{p}/\partial\mathrm{V})_{\mathrm{T}}]^{1/2},$$

where g is a constant. This yields the relation $\nu = \gamma/2$ which is characteristic of the mean-field approximation. Near the special spinodal points there are other pseudocritical exponents. In the case $B = 0$, which corresponds to (p^{**}, T^{**}, V^{**}) and $h_0 = h^*$ the Equations (9), (13), (17), (28) provide $\alpha = 2/3$, $\beta = 1/3$, $\gamma = 2/3$, $\delta = 3$, $\nu = 1/3$. Using (p_0^*, T_0^*, V_0^*) as spinodal reference point the condition $h_0 = h = 0$ in these equations gives $\alpha = -1$, $\beta = 1$, $\gamma = 1$, $\delta = 2$, $\nu = 1/2$.

CROSSOVER BEHAVIOUR

The crossover from one set of exponents to another can be expressed within the framework of the general crossover theory.[14] As an example, we shall briefly describe the contribution to the isothermal crossover starting with the equation

$$\mathrm{p} - \mathrm{p}^* = |\Delta \mathrm{V}|^{\delta} f_1(z) \,, \tag{30}$$

where $f_1(z)$ is the crossover function of the variable $z = \overline{\Delta \mathrm{V}}/\Delta \mathrm{V} = b/\Delta \mathrm{V}^{\delta}$. The crossover exponent is apparently $\emptyset = 1$. From (14) it follows that

$$f_1(z) = g_0 + g_1\, z. \tag{31}$$

In the limit where $z \rightarrow 0$ we have $\delta = 3$, and for $z >> z_0 = g_0/g_1$ the crossover to the pseudocritical behaviour takes place $\delta \rightarrow \delta - \emptyset = 2$.

The crossover situation between a region, where the Landau theory is valid, and the fluctuation region depends on the Ginzburg number

$$\mathrm{Gi} = \frac{\langle \Delta\phi_0^2 \rangle}{\phi_0^2} \sim \frac{\beta_\mathrm{T}}{\mathrm{V}\phi_0^2} \,. \tag{32}$$

Considering the averaged quadratic fluctuations of the order parameter $\langle \Delta\phi_0^2 \rangle \sim \beta_\mathrm{T}/\mathrm{V}$ in the volume $\mathrm{V} \sim r_c^d$ and taking into account the retaliation $\beta_T \sim r_c^2$, we estimate the Ginzburg number to be

$$\mathrm{Gi} \sim |\tau|^{d\nu - 2\beta - \gamma}. \tag{33}$$

For small values of Gi one can neglect fluctuations and our thermodynamic treatment is valid. This is the case for large enough values of $|\tau| < 1$, (*i.e.*, when we are far enough away from the spinodal), and if $d < (2\beta + \gamma)/\nu$. For $d > (2\beta + \gamma)/\nu$ Gi is small and $|\tau|$ is small and we are in the immediate vicinity of the spinodal. The fluctuations of the scalar order parameter become unimportant for dimensions $d \geq d_m = (2\beta + \gamma)/\nu$ and the mean-field theory in such hypothetical d-dimensional space is always exact.

The pseudocritical exponents and the marginal dimension d_m of all three sets are listed in Table I. In all cases the scaling equations[15]

$$\alpha + 2\beta + \gamma = 2, \qquad \beta\delta = \beta + \gamma$$

TABLE I

Pseudocritical exponents and marginal dimension for different constant fields h_0

Constant Field	α	β	γ	δ	ν	d_m
$h_0 \neq h^* \neq 0$	0.5	0.5	0.5	2	0.25	6
$h_0 = 0$	−1	1	1	2	0.5	6
$h_0 = h^*$	2/3	1/3	2/3	3	1/3	4

and the hyperscaling equalities

$$d_m \nu = 2 - \alpha, \quad \delta = \frac{d_m + 2 - \eta}{d_m - 2 + \eta}$$

with $\eta = 0$ are satisfied.

The mean-field values of the exponents can be refined by a more correct inclusion of fluctuation effects following the method of the renormalization group theory.[16] By using this method, it was shown[17] that in the given model, two crossover situations are combined. A first thermodynamic crossover depends on the material ,parameters and on the distance to special spinodal points as described in this paper. A second crossover takes place between a region, where the Landau theory is valid, and the fluctuation region depending on the proximity to the phase transition. The experimental determination of the parameters in the proposed model (1) makes it possible to separate these two kinds of crossover effects.

CONCLUSIONS

The series expansion of the Gibbs free energy proposed in this paper provides a complete thermodynamic description of pretransitional anomalies for p,V,T-data in nematic liquid crystals in the vicinity of the transition to the isotropic state. This thermodynamic treatment is valid in regions, where fluctuation effects are negligible.

Using the renormalization group method, the theory may be extended by including fluctuation effects which modify the thermodynamic relationships over the narrow temperature range close to the phase transition.

The ratio of some material constants influences the thermodynamic functions quantitatively and explains the crossover behaviour. A superposition of this thermodynamic crossover and the crossover from nonfluctuation to a fluctuation region is possible. For such crossover situations effective coefficients and exponents may be used.

The pseudocritical generalization of Landau's order parameter concept allows us to reformulate the thermodynamic formalism of critical phenomena for application to pretransitional effects near simple spinodel points.

A convenient choice of variables, especially the field definition, gives a mathematical isomorphism between the nematic–isotropic phase transition and first order phase transitions near a spinodal in other physical systems such as magnetism, binary liquid mixtures, liquid–gas, phospholipids. For all systems within one universality class this is the same set of pseudocritical exponents.

Acknowledgment

I am indebted to Prof. H. Sackmann for many useful discussions.

References

1. P. H. Keyes, *Phys. Lett.*, **67A**, 123 (1978).
2. P. H. Keyes and F. R. Shane, *Phys. Rev. Lett.*, **42**, 722 (1979).
3. J. J. Milczarek and K. Wentowska, *Mol. Cryst. Liq. Cryst.*, **101**, 267 (1983).
4. E. E. Gorodeckij and V. M. Zaprudskij, *Zh. Eksp. Teor. Fiz.*, **74**, 202 (1978).
5. A. L. Korzhenevskij and B. N. Shalaev, *Zh. Eksp. Teor. Fiz.*, **76**, 2166 (1979).
6. B. Chu, F. J. Schoenes and M. E. Fisher, *Phys. Rev.*, **185**, 219 (1969).
7. H. J. Mögel and A. V. Chalyj, *Izvest. Vusov.*, *Fizika*, **18**, 146 (1975).
8. A. Compagner, *Physica*, **72**, 115 (1974).
9. Y. Saito, *Prog. Theor. Phys.*, **59**, 375 (1978).
10. V. G. Bojko, H. J. Mögel and A. V. Chalyj, *Ukrain. Fiz. Zh.*, **31**, 127 (1986); **31**, 291 (1986).
11. I. Hatta, K. Suzuki and S. Imaizumi, *J. Phys. Soc. Japan*, **52**, 279 (1983).
12. P. H. Keyes and W. B. Daniels, *J. Phys.*, **40**, C3-380 (1979).
13. L. D. Landau and E. M. Lifshiz, *Statist. Fizika, Nauka, Moskva* (1976).
14. E. K. Riedel and F. J. Wegner, *Phys. Rev. Lett.*, **29**, 249 (1972).
15. L. P. Kadanoff, *Physics*, **2**, 268 (1966).
16. K. G. Wilson, *Physica*, **73**, 119 (1974).
17. H. J. Mögel, Conf. on Crystal Growth and Liquid Crystals, Coll. Abstr. Lodz, 1986, p. 59.