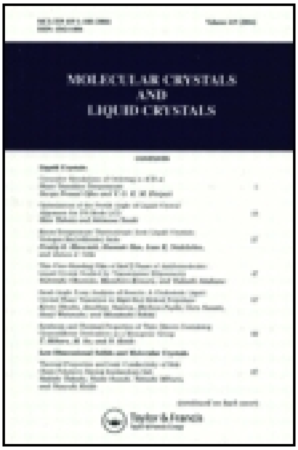

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

On the Landau Theory of the Nematic Critical Point

J. J. Milczarek [a b] & K. Wentowska [a]

[a] Institute of Physics, Warsaw Technical University, 00-662, Warsaw, Poland

[b] IEA, Swierk, 05-400, Otwock, Poland

Version of record first published: 20 Apr 2011.

To cite this article: J. J. Milczarek & K. Wentowska (1983): On the Landau Theory of the Nematic Critical Point, Molecular Crystals and Liquid Crystals, 101:3-4, 267-273

To link to this article: http://dx.doi.org/10.1080/01406568308072534

Mol. Cryst. Liq. Cryst., 1983, Vol. 101, pp. 267–273
0026-8941/83/1014–0267/$18.50/0

On the Landau Theory of the Nematic Critical Point

J. J. MILCZAREK† and K. WENTOWSKA

Institute of Physics, Warsaw Technical University
00-662 Warsaw, Poland

(*Received February 8, 1983; in final form May 24, 1983*)

The phase diagram near the nematic critical point is discussed in terms of the scalar order parameter Landau theory with some higher order terms included. The temperature behaviour of the order parameter, susceptibility and the specific heat is studied and corresponding effective critical indices are calculated. The crossover behaviour of the specific heat was found near $\epsilon \simeq 10^{-3}$.

The uniaxial quadrupolar microscopic model with single particle anisotropy has been studied recently[1] within the mean field approximation by means of numerical analysis. The temperature dependence of some thermodynamic quantities near the nematic critical point (NCP)[2] has been determined versus anisotropy parameter. In the present paper this behaviour is discussed in terms of the Landau free energy expansion in the scalar order parameter $Q = \langle P_2(\cos\vartheta)\rangle$, where ϑ is the angle between the molecular axis and the anisotropy axis of the system.

Let the order parameter Q be equal to Q_c at the NCP. Introducing the new order parameter $q = Q - Q_c$ we consider the free energy of the system in the form:[3]

$$F = F_0 + r_c(k\epsilon - \xi)q + \tfrac{1}{2}a_c\epsilon q^2 + \tfrac{1}{4}uq^4 \tag{1}$$

where ϵ and ξ are the reduced temperature and field, respectively. This form of the free energy can be obtained from the standard Landau

†Present address: IEA, Swierk, 05-400 Otwock, Poland.

expansion of the free energy in the power series of Q. Starting from

$$F = -rQ + \tfrac{1}{2}aQ^2 - Q_cQ^3 + \tfrac{1}{4}Q^4 + \tfrac{1}{5}dQ^5 + \tfrac{1}{6}eQ^6 \tag{2}$$

the expression (1) is obtained provided the fifth and sixth order terms in q are ignored and the third order term vanishes i.e. $d = -5eQ_c/3$. Here the parameter a varies continuously with temperature T changing its sign at the temperature T^*. The constant e and the anisotropy parameter (external field) r are positive.

Let us mention that the values of Q_c estimated from the experimentally determined coefficients of Landau free energy given by Poggi *et al.*[4] for MBBA and HBN, are 0.16 and 0.17, respectively.

The NCP coordinates in the (a, r) plane: a_c, r_c as well as the parameters u and k are expressed in terms of the coefficients of the expansion (2) and take the form

$$\begin{aligned} a_c &= 3Q_c^2(1 + 5x/9) \\ r_c &= Q_c^3(1 + x) \\ k &= a_cQ_c/r_c = 3(1 + 5x/9)/(1 + x) \\ u &= 1 + 10x/3 \end{aligned} \tag{3}$$

where $x = eQ_c^2$.

The reduced temperature ϵ and reduced field ξ are given by

$$\epsilon = a/a_c - 1 \qquad \xi = r/r_c - 1. \tag{4}$$

It should be noted that in the vicinity of the NCP the free energy expansion in the power series in q is more justified than that written in terms of the order parameter Q, since $q = 0$ at NCP. The condition of stability for the $q = 0$ solution of the critical point equations

$$\frac{\partial F}{\partial q} = \frac{\partial^2 F}{\partial q^2} = \frac{\partial^3 F}{\partial q^3} = 0 \tag{5}$$

is $x \geq 0$ $(5/3 < k \leq 3)$ for the free energy of the form (1).

Phase diagrams in the (ϵ, ξ) plane are presented in Figure 1 for different values of k. The phase diagram consists of the first order transition line $\xi_t = k\epsilon_t$ ending at the NCP: $\xi_c = 0$, $\epsilon_c = 0$. The metastable states region (also shown in Figure 1) is limited by semicubical parabolas

$$k^{-1}\xi = \epsilon_{\pm} (2p/3)(-\epsilon)^{3/2} \tag{6}$$

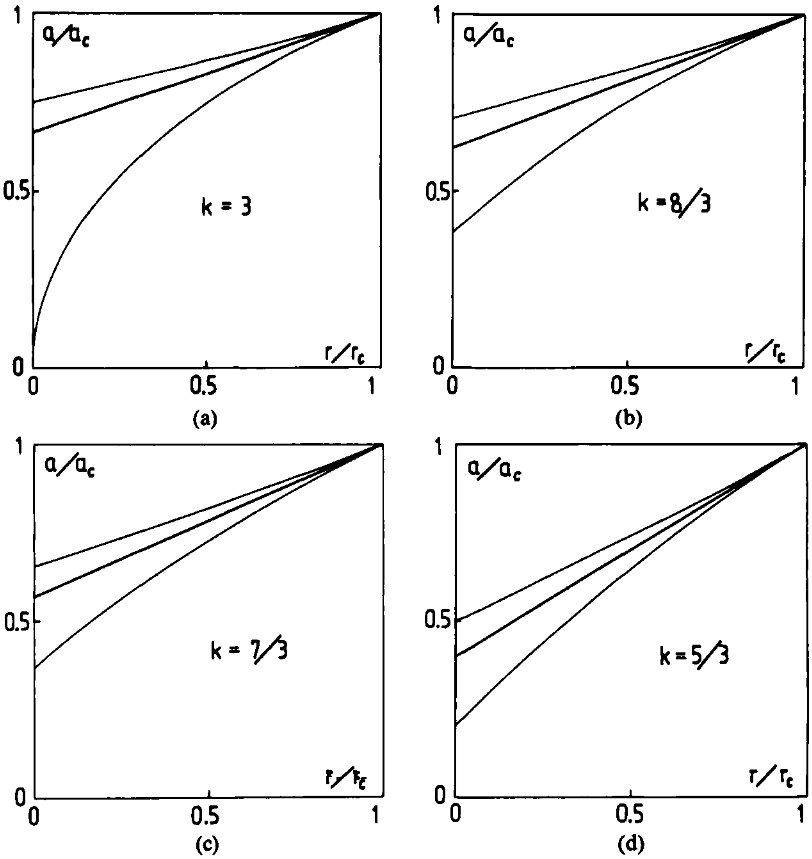

FIGURE 1 Phase diagrams in the (a, r) plane for different values of k: (a) $k = 3$, (b) $k = \frac{8}{3}$, (c) $k = \frac{7}{3}$, (d) $k = \frac{5}{3}$. The first order phase transition line $\xi_t = k\epsilon_t$ separates the metastable states regions limited by semicubical parabolas given by (6).

where $p^2 = (1 + 5x/9)/(1 + 10x/3)$. This region has been found to narrow with decreasing k (increasing x). The temperature limits of the metastable states region are denoted by ϵ_+ and ϵ_- in the high-temperature and low-temperature stable state region, respectively. The ratio τ of the temperature widths of the opposite metastable states regions

$$\tau = (\epsilon_- - \epsilon_t)/(\epsilon_t - \epsilon_+) \tag{7}$$

has been found to increase monotonically from $\frac{1}{8}$ to 1, for $k = 3$ $(x = 0)$ and from ≈ 0.5 to 1 in the case of $k = \frac{5}{3}$ $(x = \infty)$ when the anisotropy parameter r increases from zero to its critical value r_c. This behaviour is illustrated in Figure 2 where the dependence of τ on r is given also for $k = \frac{7}{3}$ $(x = 1)$ and $k = \frac{8}{3}$ $\left(x = \frac{1}{3}\right)$.

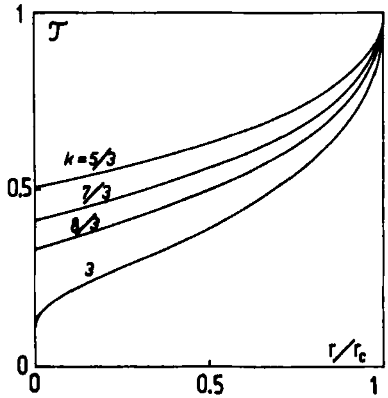

FIGURE 2 The ratio τ (Eq. (7)) of the temperature widths of the opposite metastable states regions versus the anisotropy parameter r for different values of k.

It should be mentioned that allowing k to be different from 3 introduces effectively the additional anisotropy field which causes the appearance of high-temperature tails of $Q \neq 0$ parameter even for $r = 0$.

On the other hand, we would like to point out that the estimated values of $\tau \simeq \frac{1}{2}$ and $\frac{1}{8}$ for $r = 0$ (for $k = \frac{5}{3}$ and 3, respectively) agree with the Dong and Tomchuk's[5,6] conclusion that both values of τ are reasonable from the point of view of NMR experiments on PAA.

The temperature dependence of the order parameter q, the susceptibility

$$\chi = -\frac{\partial^2 F}{\partial r^2} = \left(3uq^2 + a_c\epsilon\right)^{-1} \tag{8}$$

the gap exponent parameter f[1]

$$f = \left(\frac{\partial \chi}{\partial r}\right) \Big/ \chi = -6uq\chi^2 \tag{9}$$

and the specific heat C_r

$$C_r = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_r = a_0^2 T(q + Q_c)^2 \chi, \tag{10}$$

where we have assumed that

$$a - a_c = a_0(T - T_c),$$

has been studied in the vicinity of the NCP. The equation for q on the $\xi = 0$ isochamp

$$q^3 = -(a_c\epsilon/u)(q + Q_c) \tag{11}$$

has been solved with accuracy to $\epsilon^{5/3}$ and the analytical expression for the above quantities derived with this accuracy are given by:

$$q = Q_c(-\eta^{1/3} + 3^{-1}\eta^{2/3} - 3^{-4}\eta^{4/3} - 3^{-5}\eta^{5/3}) \tag{12}$$

$$\chi = 3^{-1}Q_c^{-2}(\eta^{2/3} - 3^{-1}\eta + 3^{-2}\eta^{4/3} + 2 \cdot 3^{-4}\eta^{5/3})^{-1} \tag{13}$$

$$f = 2Q_c^{-3}(1 - 3^{-1}\eta^{1/3} + 3^{-4}\eta + 3^{-5}\eta^{4/3})/(3\eta - 2\eta^{4/3} + \eta^{5/3}) \tag{14}$$

$$C_r = a_0^2T(1 - 2\eta^{1/3} + 5 \cdot 3^{-1}\eta^{2/3} - 2 \cdot 3^{-1}\eta + 7 \cdot 3^{-4}\eta^{4/3} + 4 \cdot 3^{-5}\eta^{5/3})/(3\eta^{2/3} - \eta + 3^{-1}\eta^{4/3} + 2 \cdot 3^{-3}\eta^{5/3}) \tag{15}$$

where $\eta = 3p^2\epsilon$. It has been established that the effective critical indices obtained from these expansions by means of the least squares fitting in the interval of $10^{-4} \leq \eta \leq 10^{-2}$ are:

$$\gamma_{ef} = 0.651 \pm 0.002$$

$$\Delta_{ef} = 0.987 \pm 0.001$$

$$\beta_{ef} = 0.315 \pm 0.002$$

They differ only slightly from the asymptotic values $\gamma = \frac{2}{3}$, $\Delta = 1$, $\beta = \frac{1}{3}$ and this difference decreases with increasing x. Although the specific heat critical exponent $\alpha = \frac{2}{3}$, the crossover behaviour from $\alpha_{ef} = 0.80 \pm 0.01$ to $\alpha_{ef} = 0.725 \pm 0.005$ has been found near $\eta = 10^{-3}$ (See Figure 3). The similar crossover behaviour near $\epsilon = 10^{-3}$ was found for correlation length in experiments on X-ray scattering in CBOOA[7] in the vicinity of S_A–N phase transition.

These exponents are of course the mean-field exponents and one can expect that the critical fluctuations near the NCP will change their values in the spirit of the renormalization group theory for the liquid-gas critical point[8,9]. However, it is worthwhile to study the Landau theory predictions at least because of some success it has achieved in describing the nematic–isotropic phase transition.[10,11] We hope that the future experiments will show how this classical behaviour is modified by the fluctuations as the NCP is approached.

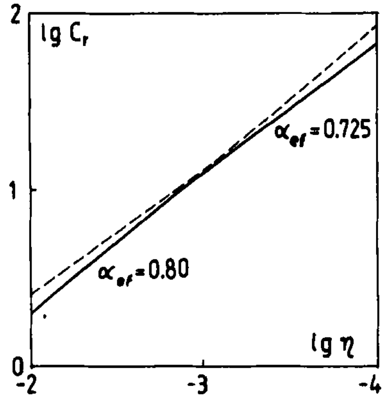

FIGURE 3 The log–log plot of the temperature dependence of the specific heat C_r (solid line). The straight line parts of the curve are extrapolated (dashed lines) to mark the crossover behaviour.

An interesting feature of the presented model is that the susceptibility χ does not change discontinuously at the first order phase transition line in contrast to similar model for ferroelectrics.[12] Along this line the reverse of the susceptibility χ_t^{-1} changes linearly with the reduced temperature ϵ_t

$$\chi_t^{-1} = 2a_c|\epsilon_t|. \tag{16}$$

This difference can be understood as stemming from the different symmetry properties of the nematic and ferroelectric ordering models. The ferroelectric model Landau free energy should not contain any odd-power terms in the order parameter,[12] whereas in the nematic ordering model any powers of the order parameter are allowed. The first order phase transition line can be obtained in the ferroelectric model with the negative quartic term and the positive sixth order term (ensuring the stability) present, whereas in the nematic ordering model with the negative third order term and positive quartic one. Rejecting of higher order terms (than sixth and fourth, respectively) in these cases yields two simplest models for the first order phase transition line ending at the critical point. Each of these models describes different physical situation and the difference in the susceptibility behaviour is of some importance.

References

1. J. J. Milczarek and K. Wentowska, *J. de Physique-Lettres*, **42** L-335 (1981).
2. P. J. Wojtowicz and P. Sheng, *Phys. Lett.*, **48A** 235 (1974).

3. L. D. Landau and E. M. Lifshitz, *Statistical Physics*, (in Russian) Moscow, 1976.
4. Y. Poggi, J. C. Filippini and R. Aleonard, *Phys. Lett.*, **57A** 53 (1976).
5. R. Y. Dong and E. Tomchuk, *Phys. Rev. A*, **17** 2062 (1978).
6. R. Y. Dong, *Phys. Rev. A*, **21** 1064 (1980).
7. J. Als-Nielsen, R. J. Birgeneau, M. Kaplan, J. D. Litster and C. R. Safinya, *Phys. Rev. Lett.*, **39** 352 (1977).
8. S. Ma, Modern Theory of Critical Phenomena, Benjamin, 1976.
9. A. Z. Patashinsky, V. L. Pokrovsky, "Fluctuation Theory of Phase Transitions," (in Russian), Moscow, 1982.
10. Y. Poggi, P. Atten and J. C. Filippini, *Mol. Cryst. Liq. Cryst.*, **37** 1 (1976).
    Y. Poggi, P. Atten and R. Aleonard, *Phys. Rev. A*, **14** 466 (1976).
11. Ch. Rosenblatt, *Phys. Rev. A*, **27** 1234 (1983).
12. J. Grindlay, "An Introduction to the Phenomenological Theory of Ferroelectricity," Pergamon Press, Oxford, 1970.