CHAPTER 5

RENORMALIZATION GROUP CALCULATION OF $T_c = T^*$ OF THE
NEMATIC-ISOTROPIC PHASE TRANSITION
5.1 INTRODUCTION

The low value of \((T_c - T^*)/T_c \approx 0.1\%\) for nematic-isotropic (N-I) transition is a long-standing puzzle. De Gennes [1] has pointed out how Maier-Saupe (M-S) theory implies \((T_c - T^*)/T_c \approx 8.0\%\). In order to gain insight into this, several workers showed how the inclusion of fluctuations can give considerable improvement. This was done by including spatial inhomogeneity in the order parameter in Landau-de Gennes theory. \(T^*\) is interpreted as the temperature at which the light scattering intensity will diverge in the supercooled isotropic phase. \(T^*\) and \(T_c\) are expressed in terms of several phenomenological Landau expansion parameters. It is usually seen that the experimental value of \(T_c - T^*\) = 1K [i.e. \((T_c - T^*)/T_c = 0.3\%\) in the case of p-azoxyanisole (PAA)] is consistent with the jump in entropy and jump in the order parameter at \(T_c\). These calculations include Gaussian fluctuations only and, as mentioned above, depend on several parameters to be fixed. For including higher-order fluctuations, Priest [2] did a renormalization-group calculation to show that \(T_c - T^*\) = 12.8K. The only experimental datum needed in the analysis is the jump of 0.4 in the order parameter at \(T_c\), and his method was an \(\varepsilon\) expansion about a critical point. As we have already discussed in chapter 4 that Tao, Sheng, and Lin [3] argued that fluctuation effects, being higher order effects, a remedy for the mean-field calculation, e.g., M-S theory should be considered first. They have included a density-dependent term in the pseudopotential and have shown how only one adjustable parameter can give consistent results in \((T_c - T^*)/T_c\) and also in the drop in specific
volume at $T_C$. Their further argument against fluctuation methods is that the measured critical indices do not corroborate with the model critical indices. In the previous chapter we have endeavoured to ascertain the validity of their ideas in the context of Landau theory. Although the above analysis support the molecular mean-field results of Tao et al but brings out the inadequacy in explaining the small value of $(dQ/dT)_{T=T^*}$. Furthermore we have taken $T_{NI}-T^* = 1K$ as an input in analysis.

The present work is an analysis with fluctuations as the basis. The primary reason for doing this is that in the work of Tao et al the divergence of light scattering intensity at $T^*$ is bypassed. Moreover, the discrepancy involving the model critical indices is not serious if we consider that the nematic-isotropic transition may occur near a tricritical point.

5.2 THEORY

We have followed the method adopted by Priest in our analysis. Initially, we have tried to improve this result by doing a renormalization-group calculation up to second order of $\varepsilon$. The model free energy of the Landau-de Gennes form can be written as

$$F = \int d^d x \left[ \frac{1}{4} (r_{ij}^2 + \gamma_k Q_{ij} Q_{kj}) - b Q_{ij} Q_{jk} Q_{kl} + u (Q_{ij} Q_{ij})^2 - H_{ij} Q_{ij} \right]$$

(5.2.1)

Here $d^d x$ indicates a functional integration in $d$ dimension over tensor field $Q=Q(x)$. The tensor $Q$ is $3 \times 3$, symmetric and traceless. The quadratic coefficient $r$ is linearly in temperature and $b$, $u$ and $H$ are temperature independent. If $b$ were absent, $T^*$ would be the mean-field second order
transition temperature. Since in our model $b>0$, $T^*$ is the (mean-field) absolute stability limit of the isotropic phase. In the isotropic state, $\langle Q \rangle = 0$. If $H_{ij}$ is uniaxial, then $Q_{ij}$ and $H_{ij}$ can be expressed as:

$$
Q_{ij} = S
\begin{pmatrix}
1 & 0 & 0 \\
0 & -1/2 & 0 \\
0 & 0 & -1/2
\end{pmatrix}
$$

(5.2.2a)

$$
H_{ij} = H
\begin{pmatrix}
1 & 0 & 0 \\
0 & -1/2 & 0 \\
0 & 0 & -1/2
\end{pmatrix}
$$

(5.2.2b)

Here $S = \langle P_2(\cos\theta) \rangle$ is the usual order parameter, where $\theta$ is the angle between the molecular long axis and the director. When a magnetic field or electric field is applied to the liquid crystal, if the molecules prefer to order parallel to the field the uniaxial solution (5.2.2a) is still appropriate. The initial effect of the field is to raise the transition temperature. For a strong enough field no transition at all will be observed. A more interesting situation arises if the molecules prefer to lie transverse to the field. This is more equally accomplished with an electric rather than a magnetic field. In this case the phase transition can become second order and the state is a biaxial one. The effect of an external magnetic field on the orientational order of a nematic liquid crystal was examined using both Landau-de Gennes and Maier-Saupe theories by Palffy-Muhoray et al [4-5]. We have followed the same $\xi$ and Feynman graph expansion technique [6-8] to calculate the equation of state for the uniaxial state.

5.2.1 EQUATION OF STATE

The equation of state describes the response of the
system to a constant external field $H$ at a given temperature $T$.

The Landau-de Gennes model is defined by the Hamiltonian

$$\mathcal{H} = \int d^d x \left[ \frac{1}{4} (r Q_{ij}^2 + \nabla_k Q_{ij} \nabla_l Q_{ij}) - b Q_{ij} Q_{kj} Q_{ki} + u (Q_{ij} Q_{ij})^2 - H_{ij} Q_{ij} \right]$$

(5.2.3)

Here $d$ is the dimension of space and $Q_{ij} = Q_{ij}(x)$ is traceless, symmetric and of dimension $p$.

$$Z = e^{-\mathcal{F}} = (\prod_k dQ_k) e^{-\mathcal{H}}$$

(5.2.4)

The origin of Eq. (5.2.3) is discussed in detail in the literature \cite{1,4}. In Eq.(5.2.4), $F$ is the free energy and $Z$ is the partition function. Factors of the reciprocal of the product of Boltzmann's constant and the temperature have been absorbed in $F$ and $\mathcal{H}$. The object $Q_k$ in Eq.(5.2.4) is Fourier component of a tensor field $Q$. The field $Q_{ij} = Q_{ij}(x)$ has the form of a symmetric traceless $p \times p$ matrix. The dependence of $Q$ in the position coordinates $x$ is suppressed for notational convenience. Einstein convention with respect to repeated indices is understood. This constitutes a slight generalization of the liquid crystal case for which $p=3$.

The solution of this model for general $\mathcal{H}$ is cumbersome. We will consider only the case for which $\mathcal{H}$ does not change the symmetry of the spontaneous symmetry breaking state. Here also we do not consider the other type of gradient term $\nabla_i Q_{ij} \nabla_j Q_{ij}$. This is analogous to the dipole term in the vector model. It couples to the rotational properties of the space variables to the rotational properties of $Q$.

Now an appropriate decomposition of $Q$

$$Q_{ij} = \sum_\alpha \sum_\beta A_\alpha a_{ij} \alpha + \sum_\alpha^\beta B_\alpha b_{ij} \beta$$

(5.2.5)
\[ a_{ij}^{\alpha} = \begin{cases} \delta_{ij} \left( \frac{p-\alpha}{p-\alpha+1} \right)^{1/2} & \text{if } i \leq \alpha \\ 1 & \text{if } i = \alpha \\ -1/(p-\alpha) & \text{if } i > \alpha \end{cases} \] (5.2.6)

\[ b_{ij}^{\alpha\beta} = \frac{(2)^{1/2}}{2} \left( \delta_{i\alpha} \delta_{j\beta} + \delta_{ij} \delta_{j\alpha} \right) \] (5.2.7)

There are \((p-1)\) a's and \(\frac{1}{2}p(p-1)\) b's. The a's and b's form a basis set for the traceless symmetric \(p \times p\) matrices. The normalization is chosen such that

\[ Q_{ij}Q_{ij} = \sum_{\alpha} A_{\alpha}^2 + \sum_{\alpha \beta} B_{\alpha}^2 \] (5.2.8)

Now we single out the uniaxial component of \(Q_{ij}\) from Eq.(5.2.5)

\[ Q_{ij} = M a_{ij}^{\alpha} + \sum_{\alpha \beta} b_{ij}^{\alpha\beta} + \hat{Q}_{ij} \] (5.2.9)

where \(M = A_\alpha\), \(B_{\alpha} = B_{\alpha\alpha}\) and \(\hat{Q}_{ij}\) has zeroes in the first row and column and a \((p-1)\)-dimensional traceless tensor in rows and columns 2 through \(p\).

In a uniaxial system, \(\beta_{\alpha\alpha}\) and \(\hat{Q}_{ij}\) are zero in equilibrium. We will calculate the equation of state for uniaxial states of this model to second order in \(\varepsilon\) to second order perturbation series in \(b\).

In the uniaxial state, only \(A_\alpha\) is non zero. We therefore, write \(A_\alpha\) as a constant plus a fluctuating field with zero average

\[ A_\alpha(x) = M + L(x) \] (5.2.10)

and define fluctuating nonuniaxial components \(\beta_{\alpha\alpha}\) and \(Q_{ij}\) as in Eq.(5.2.9)

\[ \langle L(x) \rangle = 0 \] (5.2.11)

Brackets denote the thermodynamic average which is defined as a functional integral

\[ \langle A \rangle = \frac{\int DQ \exp(-H/KT)A}{\int DQ \exp(-H/KT)} \] (5.2.12)

which is calculated by the Feynman graph expansion.
To do this, the Hamiltonian is then split into free part $\mathcal{H}_0$ and perturbation $\mathcal{H}_4$.

Then the Hamiltonian of Eq.(5.2.3) can be written as

$$\mathcal{H} = \int (\mathcal{H}_0 + \mathcal{H}_4) d^d x$$

(5.2.13)

The self energies $r_L$, $r_T$ and $r_R$ are expressed as

$$\int d^d x \langle L(x) L(0) \rangle = 2r_L^{-1} = 2\chi_L$$

(5.2.14)

$$\int d^d x \langle \beta_i(x) \beta_j(0) \rangle = 2r_T^{-1} \delta_{ij} = 2\chi_T \delta_{ij}$$

(5.2.15)

$$\int d^d x \langle Q_{ij}(x) Q_{ij}(0) \rangle = \left\{ \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} - [2/(p-1)] \delta_{ij} \delta_{kl} \right\} r_R^{-1}$$

$$\delta_{ij} \delta_{kl} \left[ \delta_{lk} - 1/(p-1) \right] 2r_R^{-1}$$

(5.2.16)

These definitions of the "mass" counter terms $r_L$ and $r_T$ imply that they are the inverse of longitudinal and transverse susceptibilities.

The equation of state obtained by a graphical expansion of Eq.(5.2.11). It necessarily contains the quantities $r_L$, $r_T$ and $r_R$ which appear in the propagators. These may be eliminated by $r_L = \frac{\partial H}{\partial M}$ and by obtaining an expansion for $r_T$ and $r_R$ from Eqs.(5.2.15) and (5.2.16).

An expansion upto order $\varepsilon^2$ of the relation (5.2.11) is performed. The graphs which contribute are calculated to the appropriate order in $\varepsilon^d-d$, neglecting terms which vanish with respect to the leading terms. The values of the dimensionless coupling constant $u$ of order $\varepsilon$ will ensure that the powers series in $\varepsilon$ obtained in this way will exponentiate to correct scaling behavior. Although the $u$ vertex is of order $\varepsilon$, the $uM$ vertex which appears in Eq.(5.2.13) is of order $\varepsilon^{3/2}$. The remaining vertices in $\mathcal{H}_4$ are merely counter terms which also vanish in zeroth order in $\varepsilon$. The one and two loop diagrams are considered. The procedure for the evaluation of these diagrams are given in references (4,6). Using the same procedure [4,6] we can
proceed in the standard way to calculate the equation of state.

We find
\[
\frac{H}{M} + \frac{b}{M^\alpha} = f(x)
\]
(5.2.17)

The result for \( f(x) \) can then be written as
\[
f(x) = 1 + x + \varepsilon f_1(x) + \varepsilon^2 f_2(x)
\]
(5.2.18)

with
\[
f_1(x) = \frac{1}{4(n+8)} \left[ 6(3+x)\ln(3+x) + 2(p-1)(1+x)\ln(1+x) + \right.
\]
\[
+ (p^2-p-2)(1+x)\ln(1+x) + 12x\ln(2) - 18(1+x)\ln(3) \right]
\]
(5.2.19a)

and
\[
f_2(x) = \left( \frac{1}{4(n+8)} \right)^2 \left[ 6(3+x)\ln(3+x) \right.
\]
\[
+ 2(p-1)\ln(1+x) + (p^2-p-2)\ln(1+x) \times 6(3+x)\ln(3+x) +
\]
\[
+ 2(p-1)(x+1)\ln(x+1) + (p^2-p-2)(1+x)\ln(1+x) + 12x\ln(2) -
\]
\[
18(1+x)\ln(3) \right] + (p+2)(p-1)(x+1) \times \left[ 1\ln^2(x+3) - 1\ln^2(3) \right] +
\]
\[
144\ln^2(x+3) - (x+1)\ln^2(x+1) - 216\ln(2)\ln(x+3)
\]
(5.2.19b)

where
\[
\rho = \frac{(x+3)}{4(x+1)}, \quad x = t/S^{1/\beta}
\]

\[
I_i(\rho) = \int_0^\rho \frac{du}{u} \left( \ln(u)/u(1-u) \right) \left[ (\frac{1-u/\rho}{\rho})^{1/2} - 1 \right] - \int_0^\rho \frac{du}{\rho u} \left( \ln(u)/u(1-u) \right)
\]
(5.2.20a)
and
\( \delta = 3 + \varepsilon + o(\varepsilon^2), \quad \hat{\beta} = (1/2)-(3/26)\varepsilon + o(\varepsilon^2), \quad \omega = 1 + (7/13)\varepsilon + o(\varepsilon^2), \quad t = (T - T^*)/T^*. \)

For nematic liquid crystals \( p = 3 \) and for the nematic–isotropic phase transition \( n = 5 \).

Then the equation of state in scaling form can be written as

\[
\frac{H}{\delta} + \frac{b}{\omega} = 1 + x + \frac{\varepsilon}{26} \left[ 3(x+3) \ln(x+3) + 4(x+1) \ln(x+1) \right. \\
6x \ln(2) - 9(x+1) \ln(3) + \frac{\varepsilon^2}{676} \left[ 4 + 6 \ln(2) - 9 \ln(3) + 4 \ln(x+1) \right] \times \left[ 3(x+3) \ln(x+3) + 4(x+1) \ln(x+1) + 6x \ln(2) - 9(x+1) \ln(3) \right] \right] + 36 \left[ \ln(x+3) - (x+1) \ln^2(3) + x \ln^2(2) \right] - 54 \ln(2) \\
\left[ \ln(x+3) + x \ln(2) - (x+1) \ln(3) \right] + 12 \ln(27/4) (x+1) \ln(x+1) + \frac{197}{13} \left[ (x+3) \ln(x+3) + 2x \ln(2) - 3(x+1) \ln(3) \right] + 4(x+1) \ln(x+1) \ln(x+3) - 10(x+1) \ln^2(x+1) + \frac{748}{13} (x+1) \ln(x+1) - 8 [(x+6) I_1(\rho) - 6(x+1) I_1(3/4)] - 24 [I_2(\rho) - (x+1) I_2(3/4)] + 16 [I_3(\rho) - (x+1) I_3(3/4)]
\]

(5.2.21)

From thermodynamic arguments we know that \( H = -\partial F/\partial S \). The free energy may therefore be found by integrating the equation of state with respect to \( S \). The conditions that the free energies of the isotropic and nematic states be equal and that the free energy be a local minimum with respect to \( S \) can be expressed as

\[
\int S H(S') dS' = 0 \quad (5.2.22a)
\]

\[
H(S) = 0 \quad (5.2.22b)
\]

For fixed \( b \) these equations are to be solved for \( S = S_0 \).
and \( t = t_0 \). The resulting value of \( t_0 \) is then expressed as 
\[ t_0 = \frac{(T_c - T^*)}{T^*} \]. This requires a numerical solution of 
Eq. (5.2.22) as a function of \( b \) by putting the experimental 
value \( S_0 = 0.4 \). The comparison of results are given in Table 
5.1.

5.3 TRICRITICAL CASE

In order to avoid some of the obvious drawbacks and 
also to conform with experimental values of \( \beta \) and \( \gamma \), we have 
done an analysis near a tricritical point. In general, when 
two coefficients of the same symmetry in the Landau free 
ergy expansion vanish simultaneously, such a point is 
called tricritical [9,10]. Therefore the experimental 
situation has led to the question whether the N-I transition 
is close to the tricritical point \( r = u = 0 \). This leads to an 
alternative formulation of the N-I phase transition by 
taking \( u = 0 \). In that case a positive stabilizing \( w \) term must 
be added to the free energy

\[
F = \int d^d x \left[ - \frac{1}{3} (rQ_i^2 + \nabla_k Q_i \nabla_k Q_i) - \frac{4}{9} bQ_i Q_j Q_k Q_l + \frac{4}{81} w(Q_i Q_i) - \frac{2}{3} H_i Q_i \right]
\]

(5.3.1)

When the dimensionality of the system is above its 
upper critical dimensionality, Landau's theory becomes exact 
and the renormalization-group theory reduces to the Landau 
theory. Since the marginal dimensionality in this case is 3 
we avoided \( \varepsilon \) expansion altogether.

The scaling form of the equation of state can be 
written as

\[
\frac{H}{S^\delta} + \frac{b}{S^0} = 1 + x
\]

(5.3.2)
where

\[ \delta = 5, \omega = 3, \beta = 0.25, x = t/S^{1/\beta}. \]

Applying the same procedure adopted above we get the results of \( b, S_C, t_C, \) and \( \frac{dS}{dt} \). The results are given in Table 5.1.

5.4 DISCUSSION

As it can be seen from the Table 5.1, the renormalization-group result for the second order of \( \varepsilon \) is approximately one half as small as the previous result, while still being too large in comparison with experiment. In our calculation the value of the cubic coupling is smaller than Priest’s value. The objection against taking the \( b \) term as perturbation is therefore not serious in the present case. In our renormalization-group calculation we have applied Maxwell construction. The validity of this is still an open question in renormalization-group theory. But in our second calculation this has been bypassed. It is not necessary to take a term \( -Q^5 \) into account, as it can be shown that in the presence of the cubic term it leads to only minor corrections. So all the drawbacks of Priest’s work has been bypassed in our work. Although this result is still far away from experimental result the improvement is encouraging. The justification for doing such an analysis inspite of the standard Landau de Gennes analysis considering the Gaussian fluctuations is that this method needs only one experimental data input only namely the jump in order parameter at \( T_C \).
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REFERENCES