Chapter 5

Extensions of Landau-deGennes theory of liquid crystals

In the last chapter the experimental results indicated that the nematic order parameter is enhanced in a thin cell compared to a thick cell in two compounds. In this chapter we will try to account for the order parameter enhancement with reduction in cell thickness on the basis of an appropriate phenomenological Landau theory, in which the biaxiality of the molecules is taken into consideration.

5.1 Landau Theory of Phase Transitions

The Landau theory is a phenomenological theory initially developed to describe phase transitions of the second kind. Generally the more symmetrical (less ordered) phase occurs at higher temperatures and the less symmetrical (more ordered) one at lower temperatures. It is assumed that near a second order phase transition point, the free energy density F can be expanded in powers of the order parameter (S) characterising the phase with the lower symmetry [51]. The expression for F can be written as

$$F = F_o + \frac{A}{2}S^2 + \frac{B}{3}S^3 + \frac{C}{4}S^4 + \frac{D}{5}S^5 + \frac{E}{6}S^6 + ... \tag{5.1}$$

where F_o is the free energy density when $S = 0$. The dependence of the order parameter near the phase transition point is then determined by minimising F (equation 5.1) with respect to S. The term linear in S is absent to ensure the stability of the higher symmetry phase. $A > 0$ ensures that $S = 0$ corresponds to a minimum in F for the higher temperature phase and $A < 0$ corresponds to that of $S \neq 0$ for the lower temperature phase.

A can be written as $a(T - T^*)$ where T^* is the second order transition temperature and a, B, C, D and E are usually assumed to be temperature independent. For a system in which the free energy density is independent of the sign of S the cubic and higher odd powers of S are not allowed. In this case for $B = 0$, and for $C > 0$ a second order phase transition takes place between the states $S = 0$ and $S \neq 0$ at $T = T^*$.

The above argument has been extended to describe weakly first order phase transitions. For a system in which the free energy density is dependent on the sign of S i.e. $F(S) \neq F(-S)$ the cubic and higher odd power terms in S are needed. The odd power terms will in turn lead to a first order transition. A first order transition can also occur when only even powers are present in the free energy density, when the coefficient of the S^4 term becomes negative. A tricritical point is the point at which the transition changes from first order to second order. It can occur when both S^2 and S^4 terms change sign.

5.1.1 Landau-deGennes Theory for the Nematic-Isotropic Phase transition

In the nematic phase the orientational order parameter(as described in section 1.5) is a second rank tensor and for cylindrically symmetric molecules the order parameter is defined as

$$S = \frac{1}{2} < 3\cos^2\theta - 1 > . \qquad (5.2)$$

In general positive and negative S arise from different distribution functions. The distribution function peaks at θ=0 for S >0 and at $\theta=\pi/2$ for S <O. This means that the third order term in the Landau deGennes free energy density cannot be ignored. The free energy density for the nematic phase can be written as

$$F_{LdG} = \frac{a(T - T^*)}{2} S^2 + \frac{B}{3} S^3 + \frac{C}{4} S^4 \qquad (5.3)$$

where T* is the hypothetical second order transition temperature and a, B and C are assumed to be temperature independent. B is negative to get positive values of S in the nematic phase.

The predicted temperature variation of the order parameter in the nematic phase itself does not agree with extensive experimental data available [1]. Expressing the dependence in the form

$$S = S_o + \kappa(T^{**} - T)^{\beta}, \qquad (5.4)$$

where T^{**} is the highest possible superheating temperature of the nematic, the theory predicts $\beta = 0.5$, while practically all known measurements yield $\beta \lesssim 0.25$. Further S_{NI}/S_{T^*} is predicted to be 0.67 while experiments yield 0.8-0.9. This has led to the speculation that the nematic-isotropic transition may be close to a tricritical point, and also to discussions about the importance of fluctuations [1]. Recently there has been an attempt to improve upon the predictions of the original Landau theory by including the effect of density [52]. But in that paper, the relevant couplings have not been taken into account properly. We will show in the next section that by including the proper coupling terms, there is a considerable improvement in the predictions of the Landau model.

5.2 Landau deGennes model with the inclusion of order parameter-density coupling

It is well known that the orientational order parameter of a nematic depends on the density of the medium, as well as on temperature. Indeed the first successful molecular theory of the nematic proposed by Onsager [53] showed that purely packing considerations lead to a nematic order beyond some critical density of long spherocylinders. Hence it is appropriate to introduce a coupling between the density ρ and the order parameter S. The free energy density can now be written as

$$F_{LdG\rho} = \frac{a(T-T^*)}{2}S^2 + \frac{B}{3}S^3 + \frac{C}{4}S^4 - \frac{M}{2}(\delta\rho)S^2 + \frac{\lambda}{2}(\delta\rho)^2 \tag{5.5}$$

where $\delta\rho = \rho\text{-}\rho_o$ in which ρ_o would be the equilibrium density when M=0. The coupling term is negative since a nonzero value of the order parameter increases the density of the medium. λ is the inverse compressibility of the medium which resists changes in the equilibrium value of the density. By minimising the free energy with respect to $\delta\rho$ we obtain

$$\delta\rho = \frac{MS^2}{2\lambda} \tag{5.6}$$

Eliminating $\delta\rho$, equation 5.5 becomes

$$F_{LdG\rho} = a(T-T^*)\frac{S^2}{2} + B\frac{S^3}{3} + (C - \frac{M^2}{2X})\frac{S^4}{4} \tag{5.7}$$

It is seen that the coupling with $\delta\rho$ renormalises the fourth order term in S by making a negative contribution. λ is known from ultrasonic measurements [54] to be $\sim 10^{10}$ cgs units. Horn [55] has measured the order parameter of pentyl cyanobiphenyl as a function of pressure and at temperatures much lower than T_{NI}, $[\delta\rho/\delta S]_T$, $\simeq$ 0.3. Using equation 5.6 and the measured dependence of the order parameter on density at constant temperature, obtained from high pressure experiments [55] we get $M \approx 0.1\lambda$. Hence from the value of λ, M is estimated to be $\sim 10^9$ cgs units. $C \approx$

4x10^6 cgs units [50]. Using the values of λ and M, the fourth order term can indeed become negative. This means that a sixth order term is needed for stability of the system. Hence the free energy density becomes

$$F = F_o + \frac{a(T - T*)}{2} S^2 + \frac{B}{3} S^3 + \frac{C_1}{4} S^4 + \frac{E}{6} S^6 \qquad (5.8)$$

The birefringence An as a function of temperature for the compound CP7B is shown in Fig. 4.8. The Landau free energy expansion is in the bulk order parameter S. In order to calculate the bulk order parameter S we have used the birefringence data for the thick cell. The approximate order parameter S is calculated using

$$S \approx \frac{\Delta n}{\Delta n_o} \qquad (5.9)$$

where An, is the birefringence for the fully aligned state. The value of An, was taken to be 0.19 so that the order parameter corresponds to that obtained by magnetic susceptibility measurements in Ref.[33]. The order parameter profile obtained from the measured birefringence data for CP7B (see Fig. 4.8) is fitted to the calculated temperature dependence of the order parameter given by equation 5.8. The fit parameters obtained using coplot software are a=8.85x 10^5 cgs units , B=12.16x 10^6 cgs units, C_1=-1.33x 10^6 cgs units, E=1.002x 10^8 cgs units, T^*=55.1°C. Note that the C_1 term is negative. Both the measured and calculated order parameter profiles are shown in Fig. 5.1. For these set of parameters the value of S_{NI}/S_{T^*} is —0.8 which is in accord with the experiments and the value of T_{NI} is 57.9°C. Further the inclusion of the sixth order term in the free energy expansion has in turn given rise to an effective $\beta \sim 0.25$, as seen in experiments. Inclusion of sixth order term leads to a new possibility. For molecules of arbitrary shape the full tensorial nature of the order parameter has to be retained in the free energy expansion. The free energy contains terms that are invariant combinations of the elements of the order parameter tensor. In such a free energy expansion, as has been discussed by several

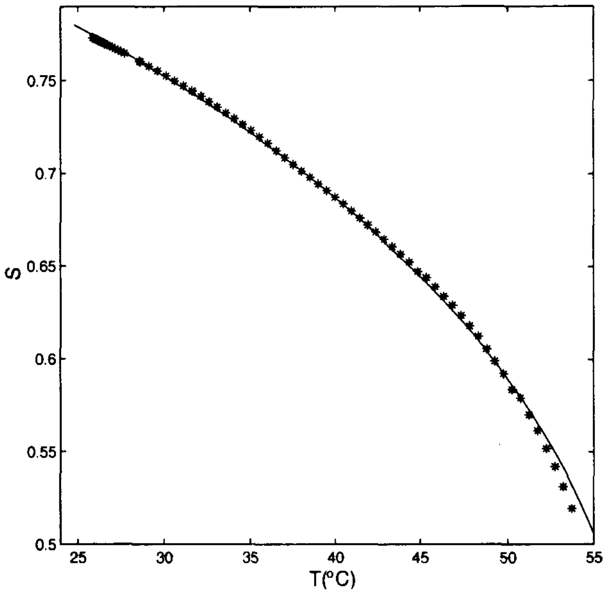

Fig. 5.1: Orientational order parameter as a function of temperature. Solid curves show the theoretical fit to the sixth order Landau theory for the set of parameters mentioned in the text.

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authors earlier, one of the sixth order terms can in principle lead to a biaxial nematic phase [56].

In general, the organic compounds which exhibit the nematic liquid crystalline phase do not have molecules which can be described as cylindrically symmetric rods. The molecules have a much lower symmetry. The next best approximation is to consider them as biaxial objects with reflection symmetry about three mutually orthogonal planes. In the relevant extension of the Landau theory, the macroscopic order in the biaxial nematic phase is represented by *two* independent components of a second rank tensor. However, as has been discussed in several molecular theories, even the *uniazial* nematic phase of biaxial molecules cannot be adequately described by a single order parameter, and requires two independent components of a second rank tensor [57, 32]. A correct description of the biaxial phase requires four independent order parameters which are no longer components of second rank tensors [58]. There has been an attempt to construct an appropriate Landau theory using all the four order parameters [58], but there have not been any detailed calculations in view of the inherent complexities of such a model. We believe that the usual theory used to describe the biaxial nematic phase really offers a good model for a uniaxial phase made of biaxial molecules. We will be describing such a model in the next section.

5.3 Uniaxial nematic made of biaxial molecules

As mentioned above the assumption that the molecules are cylindrically symmetric is not appropriate. As described in section 1.5, for molecules of arbitrary shape the generalised order parameter can be written as:

$$Q_{ij}^{\alpha\beta} = \frac{1}{2} < 3 i_\alpha j_\beta - \delta_{\alpha\beta}\delta_{ij} >, \tag{5.10}$$

where a, β=X, Y, Z refer to a laboratory fixed coordinate system. i, j=ξ, η, ζ refer to the frame linked to the biaxial molecule (see Fig. 1.7). i,, j_β denote the projections of the unit vectors i and j along a and β respectively. Choosing proper coordinate systems for the molecules as well as for the medium, the order parameter tensor can be written in the diagonal form. The non-zero components of the order parameter tensor are $Q_{\xi\xi}$, Q, and $Q_{\zeta\zeta}$. From equation 5.10, the second rank tensor order parameter can now be written as

$$Q = \begin{pmatrix} Q_{\xi\xi}^{zz} & 0 & 0 \\ 0 & Q_{\eta\eta}^{zz} & 0 \\ 0 & 0 & Q_{\zeta\zeta}^{zz} \end{pmatrix} \tag{5.11}$$

The trace is necessarily zero, as the orientational order parameter vanishes in the isotropic phase. A convenient parametrisation of the two independent order parameter components is given by

$$Q = \begin{pmatrix} -\frac{1}{2}(x+y) & 0 & 0 \\ 0 & -\frac{1}{2}(x-y) & 0 \\ 0 & 0 & x \end{pmatrix} \tag{5.12}$$

where $x=Q_{\zeta\zeta}$ is the usual order parameter S given by eq. 1.1 and $y=Q_{\eta\eta} - Q_{\xi\xi}$ is the difference in the two lateral components of the order parameters for the biaxial rod. A convenient method of measuring the orientational order parameters experimentally is through infrared dichroism measurements [59]. Isolated and pronounced bands available in the infrared spectra of the compounds can be used for this purpose, if the orientation of the related transition moment with respect to the molecular geometry is known. If the transition moment chosen for the experiment is not along the long axis, the measured intensity values have contributions from both x and y. In order to determine x and y separately it is essential to have two bonds in the same molecule whose transition moments active in the infrared region make different angles with the long axis.

The Landau theory can now be written in terms of the relevant rotational invariants, which are TrQ^n, where n=2,3... As is well known, for n $\geq$4 the traces can be expressed as appropriate combinations of TrQ^2 and TrQ^3 [56]. The free energy expansion is thus,:

$$\begin{aligned} F \;=\; & F_o + \frac{a'(T - \mathrm{T}*)}{2} Tr(Q^2) + \frac{\mathrm{B}'}{3} Tr(\mathrm{Q}^3) + \frac{C'}{4}[Tr(Q^2)]^2 + \\ & \frac{D}{5}[Tr(Q^2)][Tr(Q^3)] + \frac{E}{6}[Tr(Q^2)]^3 + E'[Tr(Q^3)]^2. \end{aligned} \tag{5.13}$$

Comparing equation 5.13 with equations 5.3 and 5.5 we get a'=$2a/3$, B'=$4B/3$ and C'=$4C_1/9$. It is known that $E' > 0$ leads to a nonzero value of y. Following the arguments of Vause etal [60] we will show in the appendix that D < 0 also leads to y $\neq$0. **As** usual we write equation 5.13 as

$$F(x,y) = \alpha(x) + y^2\beta(x) + y^4\gamma(x) + y^6\delta \tag{5.14}$$

where

$$\alpha(x) \;=\; \frac{3a'(T - \mathrm{T}*)}{4}\mathrm{x}^2 + \frac{\mathrm{B}'}{4}\mathrm{x}^3 + \frac{9\mathrm{C}^1}{16}\mathrm{x}^4 + \frac{9D}{40}x' + \frac{9E}{16}x' + \frac{9E'}{16}x^6 \tag{5.15}$$

$$\begin{aligned}
\beta(x) &= \frac{a'(T-T^*)}{4} - \frac{B'}{4}x + \frac{3C'}{8}x^2 - \frac{3D}{20}x^3 + \frac{9E}{16}x^4 - \frac{9E'}{8}x^4 && (5.16)\\
\gamma(x) &= \frac{C'}{16} - \frac{3D}{40}x + \frac{3E}{16}x^2 + \frac{9E'}{16}x^2 && (5.17)\\
\delta &= \frac{E}{48} && (5.18)\\
& && (5.19)
\end{aligned}$$

The extremum solutions of $F(x, \mathrm{y})$ with respect to y are

$$y = 0 \;\; \mathit{and} \;\; \mathrm{y}^2 = \frac{-\gamma(x) \pm \sqrt{\gamma^2(x) - 3\delta\beta(x)}}{36} \tag{5.20}$$

y=0 corresponds to the isotropic phase and for getting real solutions of y in the nematic phase, it is necessary to have $\gamma^2(x) \geq 3\delta\beta(x)$ and the parameters we consider usually yield $\gamma(x) > 0$ and $\beta(x) < 0$. As such, only the positive sign is relevant. Substituting this back in equation 5.14, the free energy can now be expressed as a function of *x* alone and we get

$$\begin{aligned}
F(x) &= \frac{a'}{2}(T-T^*)\left(\frac{3x^2}{2} + 2N\right) + \frac{B'}{4}x\left(x^2 - 4N\right) + \frac{C'}{4}\left(\frac{3x^2}{2} + 2N\right)^2\\
&+ \frac{3}{20}D\left(\frac{3x^2}{2} + 2N\right)x\left(x^2 - 4N\right) + \frac{E}{6}\left(\frac{3x^2}{2} + 2N\right)^3\\
&+ \frac{9}{16}E'x^2\left(x^2 - 4N\right)^2 && (5.21)
\end{aligned}$$

where

$$\begin{aligned}
N &= \frac{1}{E}\Bigg[\frac{3Ex^2}{4} - \frac{9E'x^2}{4} + \frac{3Dx}{10} - \frac{C'}{4} + \frac{1}{20}\Big(1800\,Ex^4E' - 120\,Ex^3D\\
&+2025\,E'^2x^4 - 540\,E'x^3D + 450\,E'x^2C' + 36\,D^2x^2 - 60\,DxC' + 25\,C'^2\\
&+100\,EB'x - 100\,Ea'T + 100\,ea'T^*\Big)^{0.5}\Bigg]
\end{aligned}$$

Then equation 5.21 is minimised with respect to *x* to get

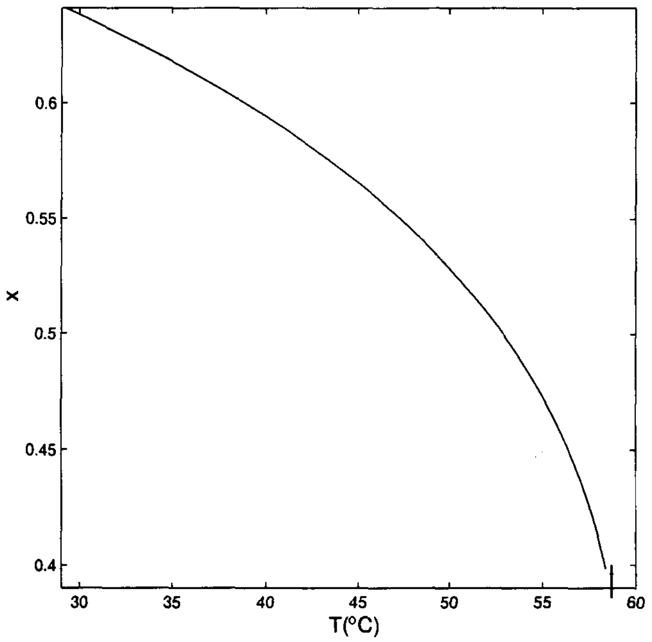

Fig. 5.2: The temperature variation of the order parameters x using the free energy density given by equation 5.14 and the parameter set mentioned in the text. The nematic-isotropic transition point(58.37°C) is indicated in the temperature axis.

$$\begin{aligned} T \;=\; & \frac{1}{45\left(15E'x - D\right)^2 a'}\Big(-125EB'^2 + 675B'x^2E'D - 45B'xD^2 + 45a'T^*D^2 \\ & -1350a'T^*E'xD + 10125a'T^*E'^2x^2 - 4500Ex^3E'B' + 1350x^3E'DC' \\ & -20250x^4E'^2C' - 40500Ex^6E'^2 + 75DC'B' - 1125E'xC'B' - 54x^3D^3 + \\ & 810x^4E'D^2\Big) \end{aligned} \tag{5.22}$$

In the next section, we will show that for an appropriate set of parameters, it is possible to get a stable solution with x $\neq 0$ and with $|y|$ having a relatively small nonzero value in the entire nematic range. This solution obviously describes a uniaxial nematic made of biaxial molecules.

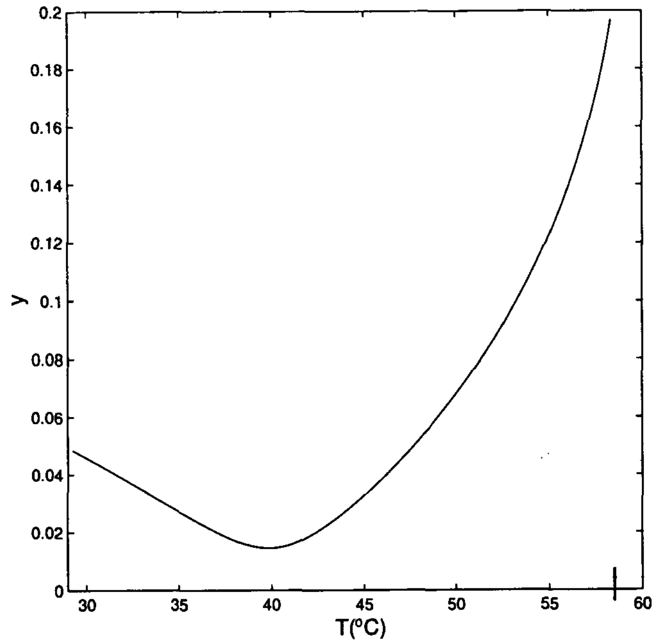

Fig. 5.3: The temperature variation of the order parameters y using the free energy density given by equation 5.14 and the parameter set mentioned in the text. The nematic-isotropic transition point(58.37°C) is indicated in the temperature axis.

5.4 Results

The free energy density given by equation 5.13 admits three solutions: x=0, y=0 which corresponds to the isotropic phase, x $\neq$ 0, y=0 which describes a uniaxial nematic phase and x $\neq$ 0, y $\neq$ 0 which has been usually assumed to represent a biaxial nematic phase [56]. Gramsbergen etal discussed the uniaxial to biaxial nematic phase transition using this expression. They used the following set of parameters: D=E=0, C'=2.7x10^7 cgs units, E'=3.6x10^7 cgs units, $a'(T - T^*)$=-$3C'x^2/2$ and B=-9E'x^3/2. They found that the solution x $\neq$0, y =0 which corresponds to a uniaxial nematic goes over to a 'biaxial' solution in which x $\neq$0 and y $\neq$ 0 as the temperature is decreased.

As we have discussed earlier, equation 5.13 used to describe the biaxial nematic phase usually, really offers a good model for a uniaxial phase made of biaxial molecules. In other words the solution x $\neq$ 0 and y # 0 represents a uniaxial nematic made of biaxial molecules. We looked for a region in the parameter space which gives x $\neq$0 and with $|y|$ a relatively small nonzero value for the entire nematic range. After searching many ranges of parameters, we found that the following set gives the required type of solutions. The value of a' was chosen to be 1.2x10^6cgs units to give a heat of transition of 1kJ/mol. Using T^*=55^{o}C, B'=0.00284x10^6cgs units, C'=$-$62.7x10^6cgs units, D=$-$0.027x10^6cgs units, E=182.6x10^6cgs units and E'=0.006x10^6cgs units, the calculated temperature variations of x and y are shown in Fig. 5.2 and Fig. 5.3 respectively. The free energy becomes zero at 58.37^{o}C, which is hence the nematic-isotropic transition temperature. This temperature roughly corresponds with the T_{NI} of the compound CP7B studied in the last chapter. The B' term is positive and small. However the fifth order D term is negative and relatively large thus giving rise to the required positive order parameter. The negative D term also contributes to nonzero values of y as mentioned above. In order to confirm that the solution is stable, we calculated the Hessian matrix. The Hessian matrix for a function f(x,y) with respect to the variables x and y is defined as

$$H = \begin{pmatrix} \frac{\partial^2 f(x,y)}{\partial x^2} & \frac{\partial^2 f(x,y)}{\partial y \partial x} \\ \frac{\partial^2 f(x,y)}{\partial y \partial x} & \frac{\partial^2 f(x,y)}{\partial y^2} \end{pmatrix} \tag{5.23}$$

For the above mentioned set of parameters we found that the Hessian determinant was positive and all the four elements of the Hessian matrix were also positive and thus the solution was indeed stable for the above mentioned set of parameters over the entire temperature range. The variation of x with temperature is in broad agreement with the experimental curve shown in Fig. 5.1, though the calculated values are slightly lower in the entire nematic range. The order parameter y has been measured for a few nematics using infrared spectroscopy and is shown in Fig. 5.4(taken from Ref.[59]). It has a small value —0.05-0.1, and depending on the compound, it

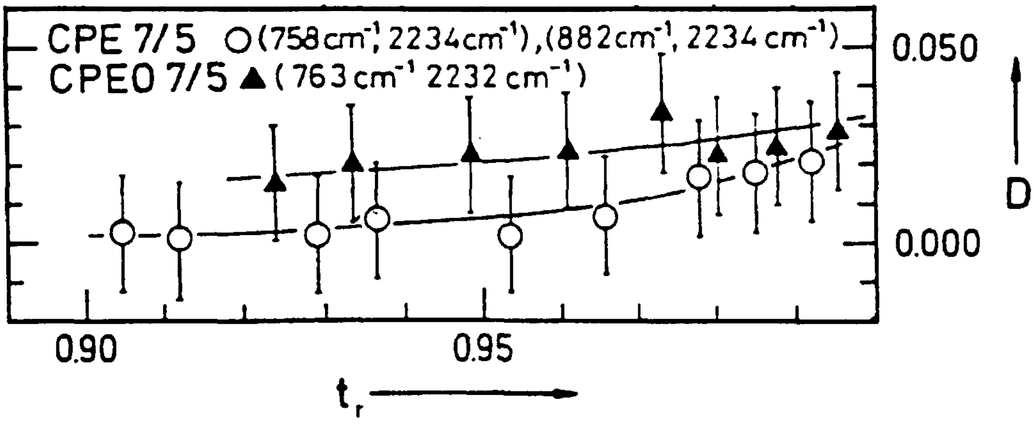

Fig. 5.4: Order parameter y of CPE7/5 and CPEO7/5, two binary mixtures of nematogenic compounds, as a function of reduced temperature t_r=T/T_{NI} in the nematic phase taken from the paper by Keifer [59].

can either increase or decrease as T_{NI} is approached [59]. Our calculated values are in a comparable range.

We shall now take up the question of the effective order parameter in a thin cell in the context of Landau theories. For this purpose, a surface potential which enhances S near the surface is introduced in the Landau-deGennes free energy expansion. The order parameter decays to the bulk value over some length. Ping Sheng [50] has done such a thin cell calculation for a uniaxial nematic. He [50] has used the usual Landau-deGennes theory to calculate the order parameter profile of a nematic near the NI phase transition point in thin cells, by adding the gradient term $L(dS/dz)^2$ to equation 5.3, where z is the distance from the substrate. $L \approx K_{NI}/(2S_{NI}^2) \approx 10^{-6}$dyne [1] where K_{NI} is the average elastic constant at the NI transition point. It was found that the surface induced order parameter decays to the bulk value over a length which is an order of magnitude larger than the correlation length ξ_o for the order parameter S where ξ_o=$(L/aT_{NI})^{0.5}$ —10 $\AA$. The decay length decreases as the temperature is decreased. Ping Sheng restricted the calculations to temperatures between T_{NI} and 0.12^o below T_{NI}. For these calculations,

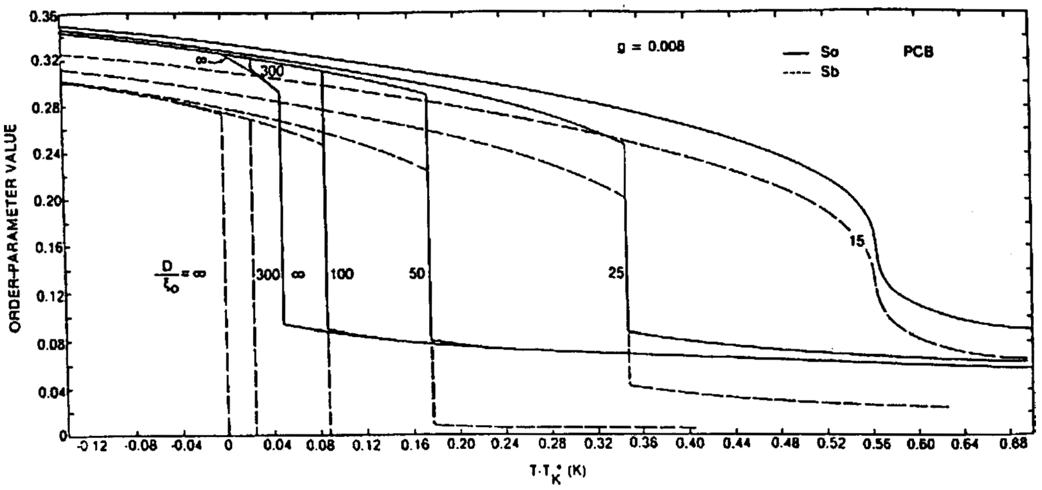

Fig. 5.5: Variation of S_b (order parameter value at the middle of the sample) (dashed curve) and S_o (order parameter value at the surface) (solid curve) as a function of temperature (T – T_K^o), where T_K^o=T_{NI} is the bulk transition temperature as calculated by Ping Sheng [50]. The (half) thickness of the sample is labelled beside each curve. Magnitude of the substrate potential g which is defined by Ping Sheng [50] is taken to be 0.008, in the calculations.

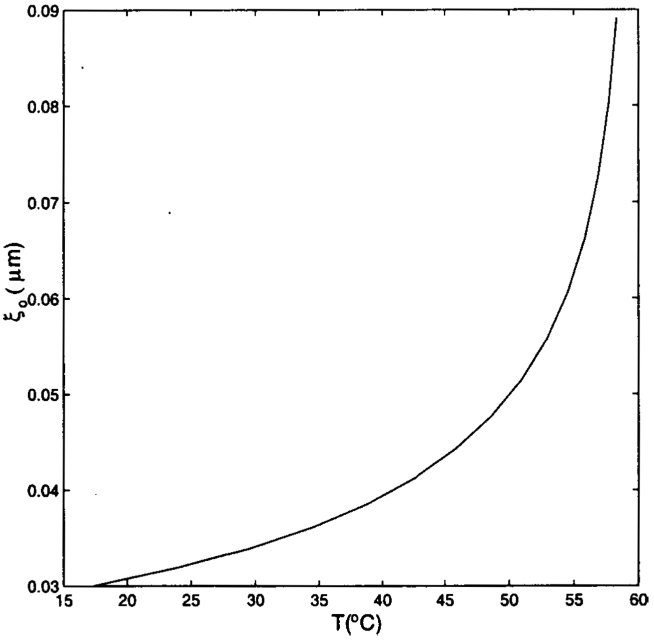

Fig. 5.6: The variation of correlation length ξ_o with temperature using the free energy density given by equation 5.14 and the parameter set mentioned in the text.

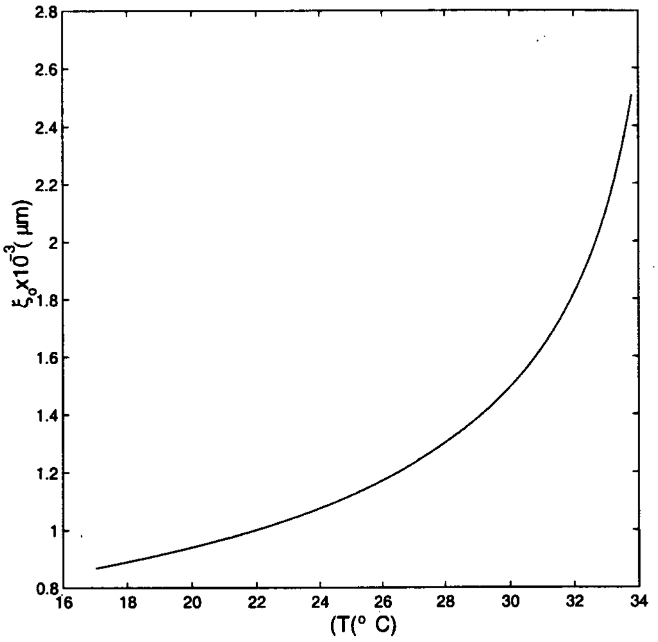

Fig. 5.7: The variation of the correlation length ξ_o with temperature using the Landau free energy density in equation 5.3 for a=1.3x10^6 cgs units, B=-1.6x10^6 cgs units, C=3.9x10^6 cgs units and T^*=34°C. These parameters are taken from the paper by Ping Sheng [50].

the order parameter profile is shown in Fig. 5.5 (taken from Ref.[50]). We tried to extend the calculations to lower temperatures. But at temperatures lower than 3" below T_{NI}, the values of the order parameter obtained from the free energy density were imaginary.

In order to extend the thin cell calculations to a uniaxial nematic made of biaxial particles we have to use appropriate surface potentials for both x and y. These calculations involve solving two coupled second order differential equations simultaneously. We do not intend to take up this problem in this thesis. Using the free energy density given by equation 5.14, the correlation length ξ_o for the main order parameter x is given by $(L/(\partial^2 F/\partial x^2))^{0.5}$. Interestingly for the above mentioned set of parameters the free energy density shows a relatively broad minimum as a function of x which in turn leads to a relatively large correlation length for that order parameter (see Fig. 5.6). For comparison, we have also calculated the correlation length ξ_o using the free energy density in equation 5.3 for the order parameter S (ξ_o= $(L/(\partial^2 F/\partial S^2))^{0.5}$). We have used the parameter set given in Ref.[50] for the calculations (see Fig. 5.7). We can see that the *correlation length* in Fig. 5.6 is much *larger* compared to that in Fig. 5.7. The correlation length for x remains relatively large even 33^o below T_{NI}. Hence in thin cells it can be expected that a higher order parameter induced by the surface potential may not decay to the bulk value. This may be the origin of the large enhancement of the order parameter in thin cells which was found in the experiments described in the last chapter.

It is relatively easier to include the effect of an external magnetic field in the calculations. The field dependent term -$H^2(\Delta\chi x+\delta\chi y)/3$ is added to equation 5.13, where H is the magnetic field, $\Delta\chi=(\chi_\zeta - \frac{\chi_\eta+\chi_\xi}{2})$ and $\delta\chi=(\chi_\eta - \chi_\xi)$. Minimising the free energy density with respect to y and x we get two coupled polynomial equations in the variables which can be solved simultaneously. $\Delta\chi$ and $\delta\chi$ are taken to be

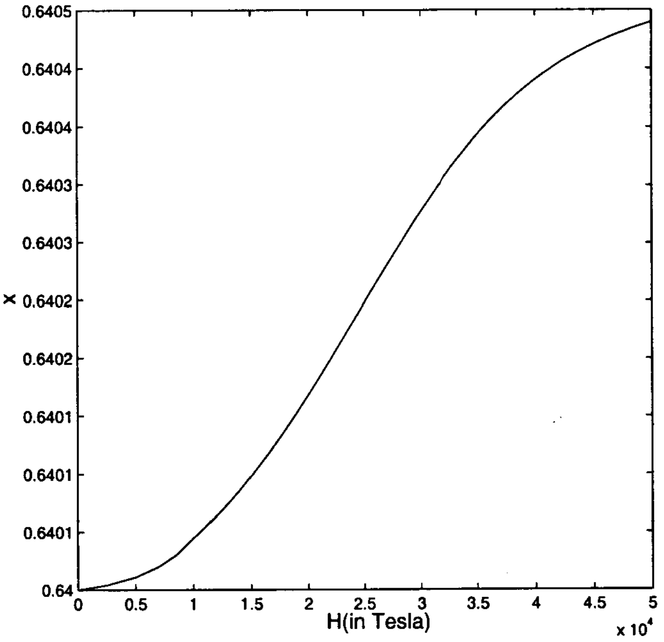

Fig. 5.8: The order parameter x variation with magnetic field at $T_{NI} - T$=30.

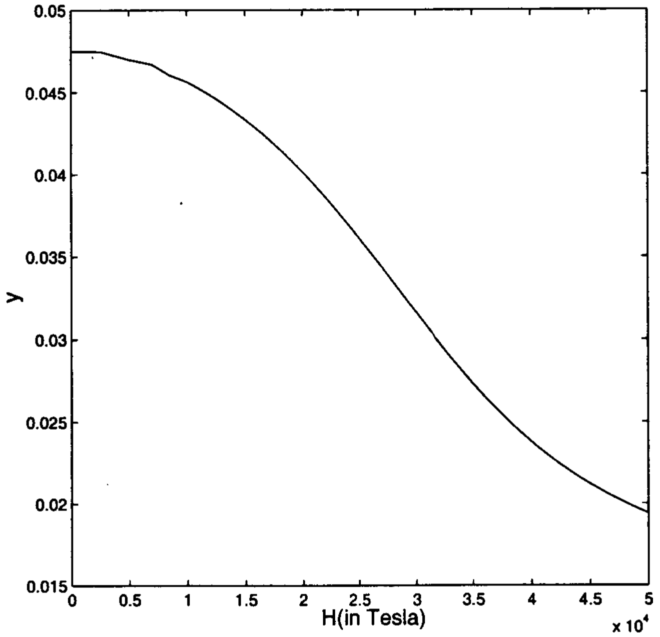

Fig. 5.9: The order parameter y variation with magnetic field at $T_{NI} - T$=30.

1.4x10^{-7} cgs units and 10^{-9}cgs units respectively. For a temperature 30^o below T_{NI}, x and y are 0.64 and 0.048 respectively when H=0. They change to 0.6405 and 0.02 for H=5 Tesla as shown in Fig. 5.8 and Fig. 5.9 respectively. At $T_{NI} - T$=0.6, x and y are 0.42 and 0.175 respectively when H=0. They change to 0.4319 and 0.017 for H=5 Tesla. In the field free case, the same increases in x would have required a decrease of the temperature by ~0.5K and ~0.2K at $T_{NI} - T$=0.6 and $T_{NI} - T$=30 respectively. In the experiments that we described in the last chapter we found that in thin cells the nematic-nematic (N-N) transition temperature which occurred at T_{NI} – T $\simeq$30 increased by a measurable amount under a similar field. This implies a reasonable increase in the order parameter with H. Thus in the extended model the calculated values show the correct trend though they are lower compared to the experimental values. On the other hand using the free energy density given by equation 5.3 the equivalent decrease in temperature obtained for such fields is only ~1mK even close to the NI transition point.

The calculated variations of the order parameter x with the reduced temperature, in the presence and absence of a magnetic field are shown in Fig. 5.10. When a field is applied to the isotropic phase, it induces a weak orientational order in the medium. The NI transition point for H=5 Tesla was calculated by equating the free energies of the weakly ordered paranematic phase and the nematic phase. We found that the NI transition temperature increased by only 0.4mK compared to the field free case. The increase in the order parameter in the presence of a magnetic field hardly affects the NI transition point. However experimentally the N-N transition point shifts considerably (see Fig. 4.12). This implies that the N-N transition temperature depends on the value of the order parameter. The enhancement of the N-N transition temperature seen in thin cells as described in the last chapter, as well as by strong electric fields as mentioned in Ref. [35] are also in accord with this

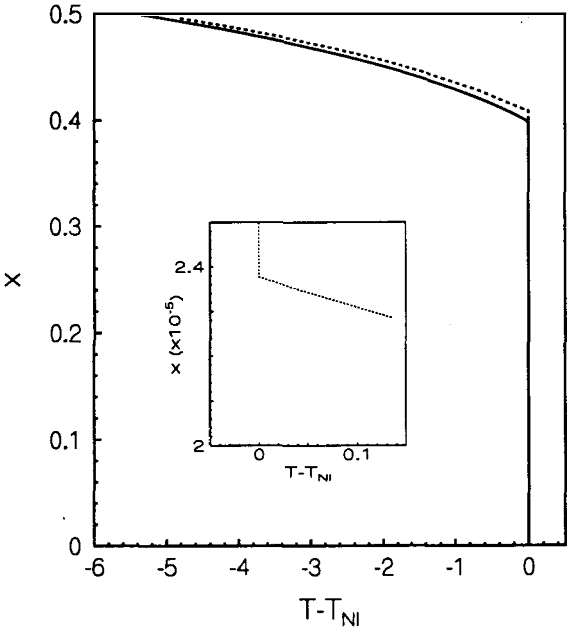

Fig. 5.10: The variation of the order parameter x with temperature. The dashed curve is for a magnetic field of 5Tesla and the solid line is in the absence of any field. The inset shows the weak order parameter in the isotropic phase for a magnetic field of 5Tesla.

dependence.

5.5 Conclusions

In conclusion the Landau-deGennes model has been modified to take into account the coupling of the order parameter with density. This coupling renormalises the coefficient of the fourth order term, making it negative. A sixth order term with a positive coefficient is then required for stability. This in turn leads to a relatively slow variation of the order parameter with temperature as seen in experiments. The Landau theory has also been modified to describe a uniaxial nematic made of biaxial particles which interestingly gives rise to a relatively large value for the correlation length of the order parameter. We believe that the latter model can plausibly explain the enhancement in the order parameter in thin cells as well as the significant increase in the order parameter under the action of a moderate magnetic field, implied by an increase in the nematic-nematic transition point measured in CP7B and described in the previous chapter.

5.6 Appendix

Vause etal have expanded the Landau free energy density in terms of two parameters p and q where $p=-(x+y)/2$ and q=$-$(x $-$ $y)/2$ (see equation 5.12). For $y=0$, $p=q=-x/2$. For rod like molecules, x >0 and p <O. As usual, it is assumed that p=q $\neq 0$ for the uniaxial nematic phase and p $\neq$ q $\neq 0$ for the biaxial nematic phase.

The free energy density is given by

$$\begin{aligned} F(p,q) &= F_o + a'(T-T^*)(p^2+q^2+pq) - B'pq(p+q) + C'(p^2+q^2+pq)^2 \\ &\quad -\frac{6D}{5}pq(p+q)(p^2+q^2+pq) + \frac{4}{3}E(p^2+q^2+pq)^3 \\ &\quad +9E'p^2q^2(p+q)^2 \end{aligned} \tag{5.24}$$

Minimising equation 5.24 with respect to p gives

$$\begin{aligned} a'(T-T^*) - B'q + 2C'(p^2+q^2+pq) - \frac{6D}{5}(q(p+q)^2+p^2) \\ +4E(p^2+q^2+pq)^2 + 18E'pq^2(p+q) &= 0, \end{aligned} \tag{5.25}$$

while minimising equation 5.24 with respect to q results in equation 5.25 with replacement $p \leftrightarrow q$. For D=0 and E'=0 these equations give the uniaxial solution, p=q. Since the E term in equation 5.25 is symmetric in p and q, this term does not lift the degeneracy between p and q. The E' term in equation 5.25 is asymmetric in p and q and will lift the degeneracy between p and q if $E' > 0$. This may be seen as follows. We differentiate the E' term $(9E'p^2q^2(p+q)^2)$ in equation 5.24 twice with respect to p keeping p+q fixed. Finally substituting p=q the second derivative is $-144E'p^4$. If E' <0 the second derivative is positive and hence the free energy is minimum for p=q, i.e. for E' <0 p=q is favoured. When E' >0 the second derivative is negative and hence the free energy is maximum for p=q. The system energetically favours $p \neq q$ for E' >0. This can also be seen from the free energy density given by equation 5.24. If E' <0, the E' term is minimised (keeping p+q fixed) for pq maximum which occurs when p=q. Hence if E' <0 p=q is favoured. For E' >0, the associated term is minimised when pq is minimum which occurs for p=0 or q=0. The system energetically favours $p \neq q$ for positive E'.

Using a similar argument we can see that D < 0 favours $p \neq q$. The D term

$(\frac{6D}{5}pq(p + q)(p^2 + q^2 + pq))$ is differentiated twice and for $p=q$ it is found to be $-\frac{48D}{5}p^3$. For rod like molecules p <O. Hence $D < 0$ favours $p \neq q$.