

CHAPTER 14

ESR STUDIES OF MOLECULAR DYNAMICS AT PHASE TRANSITIONS IN LIQUID CRYSTALS

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ABSTRACT. Order parameter fluctuations at mesomorphic phase transitions modulate the molecular dynamics of spin probes, thereby affecting spin relaxation. The anomalous relaxation rates at the phase transitions (T^*) often diverge as $|T - T^*|^\gamma$, where γ is a critical exponent, and has been noted to be universal. For N-I transitions, $\gamma = -1/2$, and for S_A -N transitions, $\gamma = -1/8$. Theoretical models are discussed that provide a unified framework for rationalising the experimental results.

1. Introduction

Owing to the wide variety of ordered phases seen in liquid crystals [1,2], they often exhibit several kinds of phase transitions involving phases differing from each other in their degree of order and symmetry [3]. Accordingly, several experimental methods, which include light scattering [4,5], NMR [6,7,8], X-ray diffraction [9,10,11,12] and adiabatic calorimetry [3,13,10,14,15] (each of which is sensitive to some characteristic property of the liquid crystal), have been used to study mesomorphic transitions. Such transitions have typically been noted to be heralded by characteristic pretransitional effects (i.e., divergences in heat capacities, viscosities, elastic constants, correlation lengths) that can often provide insight leading to the nature of the transition.

The pretransitional effects, which are manifested as critical anomalies in magnetic resonance relaxation measurements, are caused by fluctuations in the order parameter appropriate to the particular transition [16,17,18]. Thus, for example, although the long range order vanishes abruptly at the nematic-isotropic transition, there is evidence to indicate that a short range order analogous to the nematic order persists in the isotropic phase just above the transition [4]. Similarly, in liquid crystals exhibiting an underlying smectic A phase, at temperatures just above $T_{S_A,N}$ there are small domains of so-called cybotactic clusters, i.e., regions with local smectic order [2,19]. As the transitions are approached from the higher temperature phase, the regions of local order (that characterise the lower temperature phase) grow. Also, since the symmetry of the smectic phase requires twist and bend deformations to become forbidden, the associated elastic constants must diverge as the S_A phase is approached from above.

The fluctuations in the order parameter(s) that occur at the phase transitions result in a slowly fluctuating orientational potential at the site of the probe molecule, thus modulating the rotational reorientation of the probe. Such modulations have been shown to lead to anomalous effects in spin relaxation, manifested as critical type divergences for the hyperfine lines [16,20]. Detailed studies of electron spin relaxation and orientational ordering at liquid-crystalline phase transitions using a variety of spin probes therefore provides important complementary information to that obtained

using the more traditional techniques, shedding light on the subtle molecular features that usually characterise these transitions, which are usually weakly first order to second order. The nature of the linewidth divergences at these transitions can also be useful in addressing how the molecular dynamics of the spin probes couples to the collective modes. The critical exponents describing the divergence in the relaxation rates provide a useful indication of the nature of this coupling [17,21].

2. Models of Collective Dynamics: Director Fluctuations

2.1. HYDRODYNAMICS

In mesomorphic phases of liquid crystals, just below the transition temperature, each deformation of the ordered structure is opposed by a restoring force. Such forces are described in terms of elastic constants for curvature strain, and the minimum number of such constants are given by symmetry considerations. For example, for a nematic liquid crystal (which has uniaxial symmetry), there are three non-vanishing elastic constants corresponding to splay, twist and bend deformations [22]. Such deformations (of the ordered structure) are typically induced by temperature fluctuations that tend to randomise the ordering of the molecules. The collective motions due to the order director fluctuations that tend to restore the symmetry of the phase to its equilibrium value affect the spin relaxation rates of spin probes dissolved in the liquid crystal solvent, since they modulate the local (i.e., instantaneous) orientation of the directors with respect to the magnetic field [23,16]. Therefore, as discussed by Freed [17], a complete description of molecular dynamics in liquid-crystalline phases must include both the single particle variables as well as the collective variables of the liquid crystal.

The instantaneous director $\mathbf{n}(\mathbf{r},t)$ can be specified in terms of a mean director $\mathbf{n}_0(\mathbf{r})$ and the deviation from the mean $\delta\mathbf{n}(\mathbf{r},t)$, i.e.,

$$\mathbf{n}(\mathbf{r},t) = \mathbf{n}_0(\mathbf{r}) + \delta\mathbf{n}(\mathbf{r},t), \quad (1)$$

where $\delta\mathbf{n}(\mathbf{r},t) \equiv \mathbf{n}(\mathbf{r},t) - \mathbf{n}_0(\mathbf{r})$. The mean director defines the direction of preferred alignment at \mathbf{r} . In the limit of small director fluctuations, $\delta\mathbf{n}(\mathbf{r},t)$ is orthogonal to $\mathbf{n}(\mathbf{r},t)$, and we have the result

$$\langle n(\mathbf{r}_0)_\pm^* n(\mathbf{r})_\pm \rangle = \langle \theta_0 \theta \exp[\pm i(\phi_0 - \phi)] \rangle, \quad (2)$$

where $\mathbf{n}_\pm = n_x \pm i n_y$, and n_x and n_y are the x and y components of $\delta\mathbf{n}(\mathbf{r})$; and (θ, ϕ) denote the polar coordinates of the unit vector along $\mathbf{n}(\mathbf{r})$. The time dependent disturbance in equation (1) can be analysed in terms of the Fourier modes

$$\delta\mathbf{n}(\mathbf{q},t) \equiv V^{-1} \int dV \delta\mathbf{n}(\mathbf{r},t) \exp(-i\mathbf{q} \cdot \mathbf{r}), \quad (3)$$

where V is the sample volume. Since these Fourier modes decay slowly, their time evolution can be treated in the hydrodynamic limit. Such an analysis leads to a purely viscous type of relaxation for the q th Fourier mode (which is also a normal mode), and is given by

$$\partial \delta n_\alpha(\mathbf{q}) / \partial t = -\tau_\alpha(\mathbf{q})^{-1} \delta n_\alpha(\mathbf{q}), \quad (4)$$

with $\alpha = 1$ or 2 corresponding to distortions in the xy plane, but with $n_1(\mathbf{q})$ parallel to the projection of \mathbf{q} in the xy plane, and $n_2(\mathbf{q})$ normal to $n_1(\mathbf{q})$. If, for simplicity, we ignore the

anisotropy in the restoring forces and viscosities, then the rate constant for the decay τ_q^{-1} is given by $\tau_q^{-1} = Kq^2/\eta$, where K is the average elastic constant of the liquid crystal and η is an average viscosity [22].

The fluctuations in the x and y components of $\mathbf{n}(\mathbf{q})$ each contribute a quadratic term for each normal mode to the free energy. The use of the equipartition theorem leads to the results [24]

$$\langle |n_x(\mathbf{q})|^2 \rangle = \langle |n_y(\mathbf{q})|^2 \rangle = \langle |\theta(\mathbf{q})|^2 \rangle = 2k_B T / Kq^2 V, \quad (5)$$

which, when combined with equation (2), now becomes [25,26]

$$\langle \mathbf{n}(r_0) \cdot \mathbf{n}(r) \rangle = \frac{V}{2\pi^3} \int_0^{\omega_c} \frac{2k_B T}{Kq^2 V} \exp\left(-\frac{Kq^2 t}{\eta}\right) 4\pi q^2 dq = At^{-3/2} \Phi[(\omega_c t)^{1/2}], \quad (6)$$

where $\omega_c = Kq_c^2/\eta$ is the cut-off frequency, which is introduced since the hydrodynamic theory should break down for wavelengths $\lambda_c = 2\pi/\omega_c$ comparable to molecular dimensions. Also $\Phi[\chi]$ is the error function [27], and

$$A = k_B T \eta^{3/2} / 2\pi^{3/2} K^{3/2}. \quad (7)$$

The spectral density calculated using the correlation function in equation (6) exhibits a divergence as $\omega \rightarrow 0$. This divergence can be removed by recognising that the correct value of $\tau_q^{-1} = (K/\eta)[q^2 + \xi_B^{-2}]$, where $\xi_B^{-2} = K/\Delta\chi B^2$, with ξ_B the correlation length due to the presence of the magnetic field B , and $\Delta\chi$ the anisotropic part of the diamagnetic susceptibility. Also, the mean square values of equation (5) become $2k_B T / K V [q^2 + \xi_B^{-2}]$.

Equation (7) can be corrected for the effects of finite translational diffusion by replacing $1/K^{3/2}$ with $1/[K(K + \eta D_T)^{3/2}]$ as discussed by Pincus [23], and later demonstrated formally by Freed [17] (see later). Also, the use of a finite cut-off q_c is somewhat arbitrary, and improvements on this approximation have been discussed by Zientara and Freed [28].

2.2. SPECTRAL DENSITIES

As shown in Chapter 12, section 1, the orientation dependent part of the spin hamiltonian $H_1(\Omega)$ can be written as

$$H_1(\Omega) = \sum_{\mu j} \sum_{L, m, k} (-1)^k F_{\mu j}^{(L, k)} D_{m, -k}^L(\Omega) A_{\mu j}^{(L, m)}, \quad (8)$$

where Ω specifies the orientation of the molecular axis system relative to the laboratory fixed frame. The introduction of a director frame into the hamiltonian requires the use of two further transformations with the following Euler angles [17]: (i) Ψ , the orientation of the mean director $\mathbf{n}_0(\mathbf{r})$ with respect to the laboratory, (ii) Ξ , the instantaneous orientation of the director $[\mathbf{n}(\mathbf{r}, t)]$ relative to the mean director and it is, in general, a set of variables for the collective effects of all the \mathbf{q} modes. The typical perturbation terms in equation (8) require $L = 2$. As a result, the reorientational motion relative to the fluctuating director, $H_1(\Omega)$ will be partially averaged, and its average value is given by

$$\langle H_1(\Omega) \rangle = \sum_{\mu j} \sum_k \sum_m (-1)^k \langle D_{m, -k}^2(\Omega) \rangle F_{\mu j}^{(2, k)} A_{\mu j}^{(2, m)}, \quad (9)$$

where

$$\langle D_{mk}^2(\Omega) \rangle = \int d\Xi \int d\Omega P(\Omega, \Xi) D_{mk}^2(\Omega). \quad (10)$$

In this equation $P(\Omega, \Xi)$ is the equilibrium probability distribution function in orientations Ω and Ξ . We shall invoke the assumption, based on the hypothesis that the collective motions associated with director fluctuations and those associated with single particle reorientations have different characteristic time scales (i.e., a molecule reorients many times during a normal mode period), the $P(\Omega, \Xi)$ can be factored into the equilibrium distributions $P_{\Xi}(\Omega)$ and $f(\Xi)$, so that [17]

$$P(\Omega, \Xi) = P_{\Xi}(\Omega) f(\Xi). \quad (11)$$

This equation is analogous to the Born-Oppenheimer approximation in quantum mechanics so that $P_{\Xi}(\Omega)$ is the equilibrium distribution in Ω for arbitrary values of Ξ . When substituted into equation (10), this leads to

$$\langle D_{mk}^2(\Omega) \rangle = \int d\Xi f(\Xi) \int d\Omega P_{\Xi}(\Omega) D_{mk}^2(\Omega). \quad (12)$$

The spin relaxation in the motional narrowing regime is determined by the correlation function for the hamiltonian in equation (9). But to the extent that the entire time dependence in $\langle H_i(\Omega) \rangle$ is contained in $\langle D_{m-k}^2(\Omega) \rangle$, it is sufficient to study the correlation functions for the latter, i.e.,

$$C_{m-k, m', -k'}(t) \equiv \langle D_{m-k}^2(\Omega) D_{m'k'}^{2*}(\Omega_0) \rangle - \langle D_{m-k}^2(\Omega) \rangle \langle D_{m'k'}^{2*}(\Omega_0) \rangle. \quad (13)$$

The calculation of these correlation functions is performed using equation (12), and leads to the result that $C_{m-k, m', -k'}(t)$ in equation (13) can be written as the sum of three terms [17]: (i) $C_{m-k, m', -k'}^{(1)}(t)$, which describes molecular reorientation under the potential $U(\Omega)$; (ii) $C_{m-k, m', -k'}^{(2)}(t)$, which is due to relaxation caused by fluctuations in Ξ (i.e., director fluctuations); and (iii) $C_{m-k, m', -k'}^{(3)}(t)$, which represents a (negative) cross term between these two processes, but which bears a simple relation to (ii) [17].

The spectral density terms relevant to the present discussion arise from (ii) and (iii). If we include director fluctuations to lowest order, it can be shown that only terms with $k = k' = 0$, and $m = m' = \pm 1$ will enter the expressions for $C_{m-k, m', -k'}^{(2)}(t)$ and $C_{m-k, m', -k'}^{(3)}(t)$. With these substitutions, we obtain with some simplifying approximations (e.g. considering fluctuations in Ξ to lowest order) [17]

$$\begin{aligned} C_{mk}(t) &= C_{mk}^{(1)}(t) + C_{mk}^{(2)}(t) + C_{mk}^{(3)}(t), \\ &= \kappa(m, k) \exp(-t/\tau_R) + \delta_{k0} \delta_{m\pm 1} (3/2) S^2 A t^{-3/2} \\ &\quad \times \Phi[(\omega_c)^k] [1 - \exp(-t/\tau_R)]. \end{aligned} \quad (14)$$

It is important to recall that for this model the time scales obey the inequalities

$$\tau_R^{-1} \gg \omega_c \geq \tau_g^{-1}.$$

Thus it follows from equation (14) that initially $C_{mk}(0) = C_{mk}^{(1)}(0)$, but for $t \gg \tau_R$ the rotational motion has relaxed and $C_{mk}(t) \approx C_{mk}^{(2)}(t)$, and further relaxation is due to the director fluctuations.

The spectral density is then obtained as

$$\begin{aligned}
 J_{mk}(\omega) &= \sum_{i=1}^3 \operatorname{Re} \int_0^{\infty} dt C_{mk}^{(i)}(t) \exp(-i\omega t), \\
 &= \kappa(m,k) \tau_R / (1 + \omega^2 \tau_R^2) + (3/2) S^2 A \delta_{k,0} \delta_{m,1} \\
 &\quad \times \left[\sqrt{\frac{\pi}{2}} \frac{u(\omega/\omega_c)}{\sqrt{\omega}} - \left(\tau_R / (1 + \omega^2 \tau_R^2) \right) \frac{2}{\sqrt{\pi}} \omega_c^{3/2} \right],
 \end{aligned} \tag{15}$$

where

$$u(\omega/\omega_c) = 1 - \frac{1}{2\pi} \ln \left| \frac{1 + \sqrt{2\omega/\omega_c} + \omega/\omega_c}{1 - \sqrt{2\omega/\omega_c} + \omega/\omega_c} \right| - \frac{1}{\pi} \tan^{-1} \left(\frac{\sqrt{2\omega/\omega_c}}{1 - \omega/\omega_c} + \rho \right) \tag{16}$$

and

$$\kappa(m,k) \equiv \int d\Omega P(\Omega) \left(|D_{mk}^2|^2 - \langle D_{00}^2(\Omega) \rangle^2 \delta_{k,0} \delta_{m,0} \right). \tag{17}$$

Also $\rho = 0$ if $\omega/\omega_c < 1$ but $\rho = 1$ if $\omega/\omega_c > 1$. These expressions assume that the mean director lies parallel to the magnetic field. When, however, the former is rotated by an angle Ψ relative to the magnetic field, the new spectral densities, which are now functions of Ψ , are related to the former spectral densities by the expressions given in Chapter 12.

The following points may be noted about the result in equation (15):

(i) For small (ω/ω_c) , $u \rightarrow 1$, while for large (ω/ω_c) , $u \rightarrow 0$. Therefore, the effect of (ω/ω_c) is to suppress the high frequency spectral densities.

(ii) $J_{mk}(\omega)$ shows an unphysical divergence as ω approaches zero. This divergence implies a lack of restoring potential as $q \rightarrow 0$. However, when the free energy associated with alignment by the magnetic field, $\Delta\chi/B^2$, is included in the denominator on the right hand side of equation (5), this divergence is removed as discussed previously [17]. (Another way to prevent this divergence is to introduce walls with strong anchoring to the director.)

(iii) The wavelength associated with a director distortion mode (q) cannot be made shorter than the molecular dimensions. Therefore, either a high frequency cut-off q_c should be used, or molecular dimensions should be used explicitly as shown by Zientara and Freed [28].

(iv) In this model, the strong dependence of J_{mk} on Ψ implies that in smectic liquid crystals, the observed ESR relaxation rates (i.e., linewidths) should be highly orientation dependent. The extent of such dependence is proportional to the square of the order parameter, so that more ordered probes should exhibit a larger orientational dependence than weakly ordered probes (i.e., CSL as opposed to perdeuterated tempone- d_{16}). Whereas in NMR the director fluctuations are an important relaxation mechanism, in ESR they are found to be unimportant and possibly too slow for spin relaxation.

(v) Note that the spectral density for order director fluctuations $J_{0,\pm 1}^{(2)}(\omega)$ used in equation (15) neglects corrections due to the magnetic coherence length and finite translational diffusion. When these effects are included, the spectral density becomes [17]

$$J_{mk}^{(2)}(\omega) \approx \left(\frac{1}{4\pi} \right) \left(\frac{S_{NI}^{(p)}}{S_{NI}} \right)^2 \frac{k_B T \xi_B}{K} \delta_{k,0} \quad (18)$$

$$\times \left[\frac{D_T [1 - (1/\sqrt{2}) \sqrt{x^2 + (\omega/a')^2} + x] + (\omega \xi_B^2 / \sqrt{2}) \sqrt{x^2 + (\omega/a')^2} - x}{\omega^2 \xi_B^4 + D_T^2} \right]$$

with $a' \equiv K'/v\xi_B^2$, $K' \equiv K + vD_T$, and $x = K/K'$. Note that in [17] a typographical error was made in equations (B4) and (4.14), which have been corrected here. The respective equations appear here as equations (18) and (36). In the limit where a highly ordered molecule, such as a labelled liquid crystal molecule, then expressions appropriate for the high order limit are readily obtained from a simple modification of the model of Zientara and Freed [28]. In this case the assumptions of a separation of time scales and lowest order in fluctuations are not invoked.

3. The Nematic-Isotropic Phase Transition

3.1. LANDAU-DE GENNES THEORY AND IRREVERSIBLE THERMODYNAMICS

The starting point of the Landau-de Gennes theory is an expansion of the free energy near the N-I phase transition in terms of the nematic order parameter Q [22]. We first consider the isotropic phase. Neglecting the tensorial features for simplicity, this may be written as

$$F = F_0 + (\frac{1}{2})\tilde{A}Q^2 - (\frac{1}{6})\tilde{B}Q^3 + (\frac{1}{4})\tilde{C}Q^4 + (\frac{1}{2}) \int d^3r L(\nabla Q)^2, \quad (19)$$

where F_0 is the orientation independent part, $\tilde{A} = a(T - T^*)$ following Landau, while \tilde{B} , \tilde{C} and L are only slowly varying with temperature, and L is a force constant for distortions. If it were not for the term in Q^3 in equation (19), then there would be a second order phase transition at T^* . Since $\tilde{B} \neq 0$, the transition will always be first order [1]. If F is minimised with respect to Q (but neglecting L), then we obtain the value of Q in the nematic phase

$$Q_N = (\tilde{B}/2\tilde{C}) [1 + (1 - 4\tilde{A}\tilde{C}/\tilde{B}^2)^{1/2}]. \quad (20)$$

The first order phase transition occurs at T_{NI} such that

$$\tilde{A} = a(T_{NI} - T^*) = 2\tilde{B}^2/9\tilde{C}$$

and $Q_N = 2\tilde{B}/3\tilde{C}$. Thus $T_{NI} > T^*$.

When the tensorial features are included, then to lowest order in Q (i.e., neglecting the terms \tilde{B} and \tilde{C}), we have after Fourier transforming [29]:

$$\Delta F = (\tilde{A}V/3) \sum_{\mathbf{q}} \left[|Q^{(20)}(\mathbf{q})|^2 + (|Q^{(21)}(\mathbf{q})|^2 + |Q^{(2-1)}(\mathbf{q})|^2) \right. \\ \left. + (|Q^{(22)}(\mathbf{q})|^2 + |Q^{(2-2)}(\mathbf{q})|^2) \right] (1 + \xi^2 q^2), \quad (21)$$

where $\overline{\Delta F} \equiv \overline{F - F_0}$, and

$$Q^{(20)} = \sqrt{3/2} Q_{xx}, \quad (22)$$

$$Q^{(2\pm 1)} = \mp Q_{xx} - iQ_{xy}, \quad (23)$$

and

$$Q^{(2\pm 2)} = (1/2)(Q_{xx} - Q_{yy} \pm 2iQ_{xy}). \quad (24)$$

In equation (21), $Q^{(2m)}(\mathbf{q})$ denotes the m th component of the tensor order parameter $\mathbf{Q}(\mathbf{q})$ associated with the q th Fourier mode, and for simplicity we have utilised a single correlation length for order fluctuations ξ . Also, ξ^2 is given by

$$\xi^2 \equiv L/\tilde{A} = L/a(T - T^*), \quad (25)$$

where T^* is the N-I transition temperature when the transition is approached from the isotropic phase. The equipartition theorem leads to the result

$$\langle |Q^{(2,m)}(\mathbf{q})|^2 \rangle = (3/2) \langle |Q(\mathbf{q})|^2 \rangle = (3k_B T / 2\tilde{A}V)(1 + \xi^2 q^2)^{-1}. \quad (26)$$

At equilibrium, the value of $Q(\mathbf{q})$ is determined by the requirement that the free energy $\overline{\Delta F}$ be a minimum with respect to variations in $Q(\mathbf{q})$, i.e., $\partial(\overline{\Delta F})/\partial Q(\mathbf{q}) = 0$. Owing to fluctuations in $Q(\mathbf{q})$, however, this condition is not satisfied, and therefore a relaxation process occurs in which $Q(\mathbf{q})$ varies with time and tends to $\overline{Q}(\mathbf{q})$. In states not far from equilibrium, i.e., when $\partial(\overline{\Delta F})/\partial Q(\mathbf{q})$ is small but not zero, the relaxation rate $dQ(\mathbf{q})/dt$ is also small. In Landau theory the relation between these two derivatives is assumed to be a simple proportionality [30] and leads to $dQ(\mathbf{q})/dt = -\tau_q^{-1} \partial(\overline{\Delta F})/\partial Q(\mathbf{q})$, where τ_q^{-1} is a characteristic relaxation rate associated with the relaxation of the q th normal mode (cf. section 1.1). Utilising equation (21) leads to

$$dQ^{(0)}(\mathbf{q})/dt = -\tau_q^{-1} Q^{(0)}(\mathbf{q}), \quad (27)$$

where

$$\tau_q^{-1} = L(\xi^{-2} + q^2)/\nu. \quad (28)$$

In this equation, ν is the associated viscosity. Furthermore, the use of equations (21) and (26) shows that the fluctuations of different tensor components of $Q(\mathbf{q})$ are uncorrelated, i.e.,

$$\langle (Q^{(2m')}(q))_0 (Q^{(2m)}(q))_l \rangle = \langle |Q^{(2m')}(q)|^2 \rangle \exp(-l/\tau_q) \delta_{m,m'}. \quad (29)$$

Below the N-I phase transition, i.e., in the nematic phase, Q is replaced by $Q_N + \Delta Q$, (where $\Delta Q \equiv Q - Q_N$), and where Q_N is the nematic value of Q given by equation (20). Then, to the same level of accuracy as the simple approach in the isotropic phase, we obtain [17]

$$(2/3) \langle |\Delta Q^{(2,m)}(\mathbf{q})|^2 \rangle = \langle |\Delta Q(\mathbf{q})|^2 \rangle = \tilde{A}V/k_B T (1 + \xi^2 q^2) \quad (30)$$

and

$$\tau_q^{-1} = L_N(\xi^{-2} + q^2)/\nu_N, \quad (31)$$

with $\xi^2 \equiv L_N/\bar{A}$, where T^\dagger is the (hypothetical) N-I transition temperature when the latter is approached from the nematic phase and

$$\bar{A} \equiv \tilde{A} - 2\tilde{B}Q_N + 3\tilde{C}Q_N^2 \rightarrow 3a(T^\dagger - T),$$

where the arrow shows the limit for small \tilde{A} . In this limit $T^\dagger = T_{NI} + (1/2)(T_{NI} - T^*)$. Note that in general, $L_N \neq L$, and $v_N \neq v$ at T_{NI} , the N-I transition temperature. The important point in these cases is that from the N and I sides of the N-I transition, we obtain the result that $\xi^2 \propto (T^\dagger - T)^{-1/2}$ and $\xi^2 \propto (T - T^\dagger)^{-1/2}$ respectively, i.e., the correlation length diverges according to a $(1/2)$ power law. It also follows from this result that the N-I transition temperature when approached from the nematic phase appears to be slightly higher than that from the isotropic phase. In a more careful analysis, Rao et al. showed that in the range $-0.4 \text{ K} \leq (T - T^*) \leq 0.7 \text{ K}$, $T^\dagger = T_{NI} + 0.6(T_{NI} - T^*)$ [16].

3.2. MOLECULAR SPECTRAL DENSITIES

The analysis of the fluctuations in the order parameter that occur near the N-I phase transition proceeds in an analogous manner to that for director fluctuations (cf. section 1.2). Freed [17] has shown that the correlation functions describing such fluctuations (when they are small) near the N-I transition are given by

$$C_{m, \pm m', \pm'}^{(2)}(t) = \frac{1}{25} \langle \bar{\lambda}(t=0) D_{m',0}^{2*}(\Psi_0) \bar{\lambda}(t) D_{m,0}^2(\Psi) \rangle \delta_{0,k} \delta_{0,k'}, \quad (32)$$

above the transition, and below the transition it is only necessary to replace $(1/25)$ by $\kappa(m,0) \kappa(m',0)$. In this equation, $\lambda(t)$ is the (time dependent) ordering potential, and Ψ denotes the instantaneous orientation of the local director in a laboratory fixed frame (i.e., the mean director). For a weakly ordered probe molecule with order parameter $S^{(p)}$ and ordering potential $\bar{\lambda}^{(p)}$, the approximate substitution $\bar{\lambda}^{(p)}/S^{(p)} \approx \bar{\lambda}/S$, which holds when $\bar{\lambda}$ is small, leads to

$$C_{m, \pm m', \pm'}^{(2)}(t) \approx \left(S_{NI}^{(p)}/S_{NI} \right)^2 \langle (Q_{m'})_0 (Q_m)_t \rangle \delta_{k,0} \delta_{k',0}. \quad (33)$$

The ratio $(S_{NI}^{(p)}/S_{NI})$ in this equation can be estimated from the measured order parameters for the probe and the liquid crystal just below the N-I transition. The fluctuations in $Q_m(\mathbf{q})$ (the nematic order tensor) appearing in equation (33), are described by Landau-de Gennes mean field theory as we have discussed (cf. section 2.1, equation (29)). This leads to the result that the spectral densities for the order parameter fluctuations are given by [17]

$$J_{m, \pm m', \pm'}^{(2)}(\omega) \approx \left(\frac{S_{NI}^{(p)}}{S_{NI}} \right)^2 \frac{k_B T}{4\pi\sqrt{2}} \sqrt{\frac{v}{L^3 \omega \xi}} \sqrt{\frac{1}{1 + \sqrt{1 + (\omega/\omega_\xi)^2}}} \delta_{k,0} \delta_{k',0} \delta_{m,m'}. \quad (34)$$

with

$$\omega_\xi = L/(v\xi^2). \quad (35)$$

For small order fluctuations, ξ^2 is inversely proportional to $(T - T^*)$ according to Landau-de Gennes theory, $\xi^2 = L/a(T - T^*)$. Equation (34), which applies above the N-I transition may be

used below the transition by multiplying by $[5\kappa(0,m)]^2$ and letting $\nu \rightarrow \nu_N$, $L \rightarrow L_N$, and $\xi \rightarrow \xi_N$.

The effects of finite translational diffusion can be incorporated into equation (34) by procedures described in detail in Appendix B in [17]. We then have the result

$$J_{mk}^{(2)}(\omega) \approx \left(\frac{1}{4\pi}\right) \left(\frac{S_{N1}^{(0)}}{S_{N1}}\right)^2 \frac{k_B T \xi}{L} \delta_{k,0} \times \left[\frac{D_\tau [1 - (1/\sqrt{2})\sqrt{x^2 + (\omega/\omega'_\xi)^2 + x}] + (\omega \xi^2/\sqrt{2})\sqrt{x^2 + (\omega/\omega'_\xi)^2 - x}}{\omega^2 \xi^4 + D_\tau^2} \right] \quad (36)$$

with $\omega'_\xi \equiv L'/\nu \xi^2$, $L' = L + \nu D$ and $\chi = L/L'$. Note that the secular spectral densities are given by

$$\begin{aligned} J_{m0}^{(2)}(0) &\approx \left(\frac{1}{4\pi}\right) \left(\frac{S_{N1}^{(0)}}{S_{N1}}\right)^2 \frac{k_B T \xi}{L} \left(\frac{1 - \sqrt{\chi}}{D_\tau}\right) \\ &= \left(\frac{1}{4\pi}\right) \left(\frac{S_{N1}^{(0)}}{S_{N1}}\right)^2 \frac{k_B T \xi}{LD_\tau} \left(1 - \frac{1}{\sqrt{1 + \nu D_\tau/L}}\right). \end{aligned} \quad (37)$$

Equations (34) and (36) show that $J^{(2)}(\omega)$ is largest at zero frequency; therefore, the secular spectral densities for order fluctuations are the dominant contributors to the anomalous part of spin relaxation. The anomalous contributions to the linewidth parameters B and C (cf. Chapter 12), i.e., B_{anom} and C_{anom} , are given by [26,17]:

$$B_{\text{anom}} = \frac{-\gamma_c B_0}{9} (A_{xx} + A_{yy} - 2A_{zz}) (2g_{zz} - g_{xx} - g_{yy}) J_{00}(0) \quad (38)$$

and

$$C_{\text{anom}} = \frac{\gamma_c}{72} (A_{xx} + A_{yy} - 2A_{zz})^2 [8J_{00}(0) - 3J_{10}(\omega_s)], \quad (39)$$

where the spectral densities in these equations are given by equation (34), and ω_s is the frequency of nuclear spin flips. These substitutions lead to:

$$B_{\text{anom}} = k_B (T - T^*)^{-\alpha} \quad (40)$$

and

$$C_{\text{anom}} = k_C (T - T^*)^{-\alpha}, \quad (41)$$

where k_B and k_C are given by (neglecting translational diffusion and the cross term $J_{mk}^{(3)}$):

$$k_b = \left[-\frac{\gamma_e B_0}{9} (A_{xx} + A_{yy} - 2A_{zz})(2g_{zz} - g_{xx} - g_{yy}) \left(\frac{S_{NI}^{(p)}}{S_{NI}} \right)^2 \right] \left[\frac{k_B T \nu}{8\pi L^{3/2} a^{3/2}} \right] \quad (42)$$

and

$$k_c = \left[\frac{\gamma_e}{72} (A_{xx} + A_{yy} - 2A_{zz})^2 (N_C) \left(\frac{S_{NI}^{(p)}}{S_{NI}} \right)^2 \right] \left[\frac{k_B T \nu}{8\pi L^{3/2} a^{3/2}} \right] \quad (43)$$

In equation (43), N_C is a factor which takes values between 8 and 5; ($2N_C = 8 - 3J_{10}(\omega_s)/J_{00}(0)$). The former extreme corresponds to the case when $J_{10}(\omega_s) < J_{00}(0)$ (which is the case for slow fluctuations and/or molecular diffusion), whereas the latter extreme corresponds to $J_{10}(\omega_s) \approx J_{00}(0)$ (which occurs in the case of rapid fluctuations). The quantities appearing within the first set of braces in these equations for k_b and k_c depend solely upon the properties of the spin probe, while the second set contains parameters characteristic of the liquid crystal. Using the parameters for MBBA, i.e., $L \approx 10^{-1}$ N, $a \approx 6 \times 10^{-2}$ J cm⁻³ K, $\nu = 0.3$ P [29,16], we estimate the quantity within the second set of braces to be about 1.05×10^{-9} at $T_{NI} \approx 78^\circ$ C, which is the N-I transition temperature for 4O.6 or 6OCB-8OCB at the composition studied. k_b and k_c can thus be calculated from a knowledge of the probe ordering and magnetic tensors. Note however, that when the more general expression i.e., equation (37), is used, we find that the secular spectral densities (including translational diffusion) are $2x/(1 + \sqrt{x})$ times those calculated neglecting the effects of D_T .

We note that C_{anom}/B_{anom} lies between $(8/5)(C_0/B_0)$ and (C_0/B_0) depending on the value of N_C . Equations (38) and (39) also show that the temperature dependence of both B_{anom} and C_{anom} can, alternatively, be described by

$$\frac{B_{anom}}{5B_0} = \frac{C_{anom}}{N_C C_0} = k(T - T^*)^{-x}, \quad (44)$$

where

$$k = \left(\frac{S^{(p)}}{S} \right)^2 \frac{k_B T}{4\pi L^{3/2} a^{3/2} D_T} \left(1 - \frac{1}{\sqrt{1 + \nu D_T/L}} \right) \tau_R^{-1}. \quad (45)$$

k can be calculated from the order parameters $S^{(p)}$ and S (i.e., for the probe and liquid crystal solvent, respectively) at the N-I transition, the physical properties of the liquid crystal, and the rotational correlation times of the spin probe near T_{NI} . The latter are obtained by linear extrapolation of $\ln \tau_R$ versus $1/T$ (i.e., Arrhenius-like behaviour for τ_R as a function of temperature is assumed) to the critical regions. The method of data treatment based on these equations is described in section 7.

3.3. EXPERIMENTAL RESULTS

The variation of B and C with temperature is shown in figures 1 and 2 for perdeuterated tempone- d_6 in 4O.6 and 6OCB-8OCB. Here, we clearly note that as the phase transitions are approached,

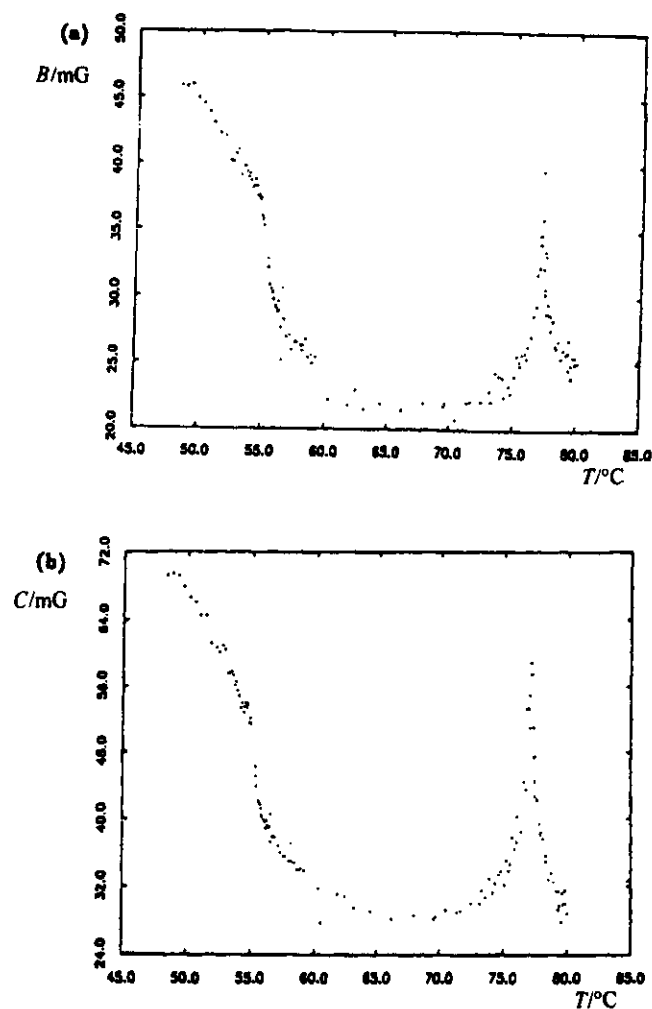


Figure 1. Temperature variation of B and C for perdeuterated tempone in the I, N and S_A phases of 4O.6. (From [49]).

the relaxation parameters exhibit anomalous behaviour in that they appear to diverge as the transitions are approached. A closer look at these effects is presented in figures 3 to 6, where we show B and C for the transitions occurring in perdeuterated tempone- d_{16} in 6OCB-8OCB as an example, together with the error bars associated with the linewidth measurements. The curves shown through the data points represent non-linear least squares fits using the relations

$$B_{\text{max}} \text{ or } C_{\text{max}} = k |T - T^*|^\gamma \quad (46)$$

to yield values of k , T^* and γ after subtracting the background contributions to B_0 or C_0 . The

physical justification for using the expression in this equation has been discussed; the results, shown in tables 1 and 2 together with the standard deviations, are discussed here for the N-I transition.

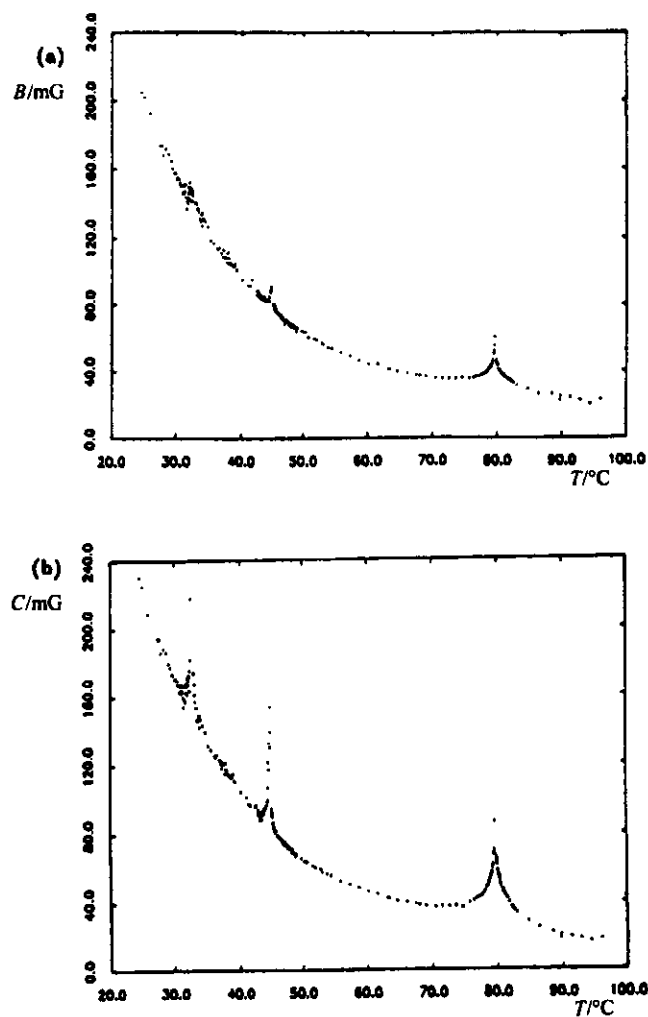


Figure 2. Temperature variation of B and C for perdeuterated tempone in I, N, S_A and N_R phases of 6OCB-8OCB. (From [49]).

The results of the analysis at the N-I transition (cf. table 1) indicate that (i) in all cases, $\gamma = -\frac{1}{2}$; (ii) at a given transition, the value of T^* is higher at the lower temperature phase than that obtained from the analysis at the higher temperature phase; and (iii) for a given liquid crystal solvent, the values of k , and their ratios obtained from the B and C analysis, depend on the spin probe. The exponent of $(-\frac{1}{2})$ has been rationalised in terms of the fact that it is the secular spectral densities which contribute most to relaxation, and for nematic order fluctuations, these diverge as

ξ. The observed divergence in the linewidth parameters is explained by invoking the result that for the coherence length of the order fluctuations, $\xi^2 \sim |T - T^*|^{-1}$. The observation that T^* appears to be higher for the analysis from the nematic than the isotropic side is consistent with previous studies of critical effects at the N-I transition seen with perdeuterated tempone- d_{16} in MBBA (see table 1 and [16]). In the limit when $|T - T^*| < |T_{NI} - T^*|$, Rao et al. [16] show that if T^\dagger and T^* denote the transition temperatures when the analysis at the N-I transition is performed from the N and I phases, respectively, then $T^\dagger = T_{NI} + (T_{NI} - T^*)/2$. Thus, when $(T_{NI} - T^*) \approx 1^\circ\text{C}$, we expect $(T^\dagger - T_{NI}) = 0.5^\circ\text{C}$, which is of the order of the observed difference.

Table 1. Non-linear least squares analysis of fits to $B, C, = k(T - T^*)^\gamma$ for perdeuterated tempone- d_{16} , MOTA and P in 4O.6, 6OCB-8OCB and perdeuterated tempone- d_{16} in MBBA at the N-I transition.

System	Phase	B or C	$k/\text{mG } ^\circ\text{C}^\gamma$	$T^*/^\circ\text{C}$	γ
PDT/6OCB-8OCB ^a	I	B/mG	14.2±1.9	79.43±0.09	-0.43±0.09
		C/mG	46.4±2.2	79.27±0.05	-0.40±0.03
	N	B/mG	16.20±0.03	79.93±0.02	-0.50±0.01
		C/mG	29.90±0.03	80.02±0.01	-0.56±0.01
PDT/MBBA ^b	I	B/mG	36.0±20.0	40.0±1.50	-0.60±0.20
		C/mG	35.0±5.00	40.9±0.30	-0.43±0.10
	N	B/mG	52.0±10.0	42.1±0.60	-0.50±0.10
		C/mG	76.0±20.0	41.8±0.50	-0.50±0.16
PDT/4O.6 ^c	I	B/mG	7.6±1.7	76.7±0.2	-0.49±0.11
		C/mG	17.4±2.1	77.0±0.2	-0.45±0.09
	N	B/mG	4.46±0.05	77.17±0.02	-0.48±0.01
		C/mG	9.7±0.2	77.24±0.01	-0.54±0.02
MOTA/6OCB-8OCB ^a	I	B/mG	42.0±4.9	78.5±0.5	-0.48±0.08
		C/mG	39.0±15.7	78.3±1.0	-0.48±0.04
	N*	-	-	-	
MOTA/4O.6 ^a	I	B/mG	58.4±5.4	77.2±0.1	-0.47±0.02
		C/mG	68.3±5.7	77.2±0.1	-0.50±0.02
	N	B/mG	43.0±0.2	77.90±0.02	-0.48±0.01
		C/mG	44.0±0.2	77.93±0.03	-0.50±0.01
P/4O.6 ^a	I	B/mG	160.7±49.1	76.6±0.2	-0.49±0.12
		C/mG	66.3±37.3	76.9±0.1	-0.50±0.15
	N	B/mG	209.8±1.0	77.71±0.01	-0.51±0.01
		C/mG	125.4±1.5	77.77±0.03	-0.49±0.02

* No divergence in B or C observed

^a [49]. ^b [16]. ^c [20].

The relative contributions of the critical effects to spin relaxation are, as noted in equations (44), measured by the parameters k_B and k_C . Using the magnetic tensors for the three spin probes in table 1 and the parameters for MBBA in equations (44) and (45), and equating the results (for the three spin probes) to the values of k_B and k_C at the N-I transition in 4O.6 (cf. table 2), we find that $S_{NI}^{(p)}/S_{NI} \approx 0.06, 0.09$ and 0.30 for perdeuteriated tempone- d_{16} , MOTA and P respectively. These numbers are in fair agreement with what we expect for these three probes based on using the order parameter for CSL in 4O.6 near the N-I transition (about 0.4) as a model for the overall liquid crystal ordering. On the other hand, the order parameter for MOTA in 6OCB-8OCB is actually lower than that of perdeuteriated tempone- d_{16} (near T_{NI} , $S \approx 0.04$ for MOTA and about 0.08 for perdeuteriated tempone- d_{16} [31]). Consistent with decreased ordering, we note a very small critical divergence for MOTA in the isotropic phase near the N-I transition.

Table 2. Non-linear least squares analysis of fits to $B, C = k(T - T^*)^\nu$ for perdeuteriated tempone- d_{16} , MOTA and P in 4O.6 and 6OCB-8OCB at the S_A -N transition^a.

System	Phase	B or C	$k/mG \text{ } ^\circ C^\nu$	$T^*/^\circ C$	γ
PDT/6OCB-8OCB [†]	N	B/mG	16.8 ± 2.7	43.93 ± 0.03	-0.30 ± 0.02
		C/mG	12.5 ± 1.2	44.97 ± 0.01	-0.36 ± 0.03
	S_A [‡]	B/mG	19.2 ± 2.7	32.75 ± 0.01	-0.33 ± 0.02
		C/mG	32.4 ± 3.0	32.74 ± 0.01	-0.38 ± 0.02
PDT/4O.6 [†]	N	B/mG	4.1 ± 1.7	55.21 ± 0.03	-0.33 ± 0.07
		C/mG	6.0 ± 0.8	55.15 ± 0.04	-0.38 ± 0.06
MOTA/6OCB-8OCB [†]	N	B/mG	74.6 ± 8.5	45.4 ± 0.5	-0.37 ± 0.02
		C/mG	76.8 ± 6.3	44.7 ± 0.3	-0.35 ± 0.02
	S_A [‡]	B/mG	207.3 ± 9.6	30.45 ± 0.01	-0.13 ± 0.01
		C/mG	262.3 ± 32.7	30.49 ± 0.01	-0.13 ± 0.02
MOTA/4O.6 [†]	N	B/mG	8.0 ± 0.2	55.89 ± 0.01	-0.32 ± 0.01
		C/mG	5.2 ± 0.4	55.97 ± 0.02	-0.33 ± 0.02
P/4O.6 [*]	S_A	B/mG	713.3 ± 2.9	56.84 ± 0.40	-0.21 ± 0.03
		C/mG	702.8 ± 0.7	56.96 ± 0.01	-0.23 ± 0.02

^a References as in table 1

[†] N_R - S_A transition

[‡] No critical divergence at $S_A \rightarrow N$ transition

^{*} No critical divergence at $N \rightarrow S_A$ transition

The values of k_B and k_C at the nematic side of T_{NI} are obtained by replacing $\xi[\xi^2 \approx L/a(T - T^*)]$ by $\xi[\xi^2 \approx L/3a(T^* - T)]$ in equation (35). Since the spectral densities are

proportional to ξ (cf. equation (34)) this substitution implies a reduction in the k values in the nematic phase by a factor of $\sqrt{3}$ [16]. The other factors that can cause changes in k during phase transformation are τ_R and D_T (cf. equation (45)). However, the former do not change very much upon passing from I to N [32], and for $10^{-7} < D_T/\text{cm}^2 \text{ s}^{-1} < 10^{-6}$ and typical values of v (0.3 P) and L (10^{-1} N), equation (45) shows that $k \approx (S^2/S)^2 k_B T v / 8\pi L^{3/2} a^{3/2} \tau_R^{-1}$, i.e., k is independent of D_T to first order. This matter has been discussed in greater detail elsewhere [49]. Although we note that for perdeuterated tempone- d_{16} in 4O.6 k in the nematic phase is lower than in the isotropic phase, the values of k seem to be comparable in the two phases in the other systems, and for P in 4O.6 they are actually higher in the N phase. The apparent discrepancy may be due to the fact that at the weakly first order N-I transition, the changes in L and v with temperature may occur in a way as to offset the decrease in k by the factor of $\sqrt{3}$. The difference in the behaviour of the P probe could be caused by the tendency of the latter to pack with the cores rather than the chain regions in 4O.6 [33], thus causing its relaxation to be modulated differently; (see [49] for further discussion).

4. The Smectic A-Nematic Phase Transition

The basic mean field theories of the smectic A-nematic phase transition are due to McMillan [34] and de Gennes [22]. Though these mean field models have been further refined by many authors [35,36], we shall mainly consider these theories partly because the renormalisation group methods [37,38] as applied to this problem have met with only partial success; and to date, many problems involving the critical behaviour of the S_A -N transition remain unsolved.

4.1. MEAN FIELD THEORIES

We shall first describe the McMillan molecular field theory, which is an extension of the well-known Maier-Saupe [39] theory for the nematic-isotropic transition. The theory gives more insight into the molecular properties that govern the order of the S_A -N transition. Some of the remarkable successes of this theory are: (i) prediction of the S_A -N-I phase diagram as a function of molecular parameters; (ii) identification and calculation of relevant order parameters (i.e., for the S_A -N transition); (iii) prediction of a tricritical point at the S_A -N transition.

The form of the anisotropic interaction potential used by McMillan for the interaction between two molecules in the smectic A phase is given by [34]

$$U_{12}(r_{12}, \cos \theta_{12}) = (\epsilon/N r_0 \pi^{3/2}) \exp(-r_{12}/r_0) [P_2(\cos \theta_{12}) + \delta] \quad (47)$$

where r_{12} is the distance between the centres of molecules 1 and 2; and r_0 is of the order of the length of the rigid section of molecule. Then, Fourier analysing this interaction, and using the fact that there is periodicity in the z direction (i.e., the molecules are arranged in two dimensional liquid-like planes separated by the distance d) we obtain the single particle molecular field potential as

$$U_1(z, \cos \theta) = -\epsilon [S + \alpha \sigma \cos(2\pi z/d)] P_2(\cos \theta) + \gamma \delta \cos(2\pi z/d), \quad (48)$$

where S and γ are the orientational and positional order parameters and σ is the order parameter that describes the coupling between position and orientation. These order parameters are

$$\begin{aligned}
S &= \langle P_2(\cos \theta) \rangle = \langle (3 \cos^2 \theta - 1)/2 \rangle, \\
\sigma &= \langle [P_2(\cos \theta) \cos(2\pi z/d)] \rangle, \\
\gamma &= \langle \cos(2\pi z/d) \rangle,
\end{aligned} \tag{49}$$

where

$$\alpha = 2 \exp\{-\pi r_0/d\}.$$

The only molecular quantities that appear are α and ϵ . The latter is determined by the N-I transition temperature (i.e., $T_{NI} = 0.2202 \epsilon$, from the Maier-Saupe theory), while the former is determined by the dimensionless ratio r_0/d . When the self consistent equations for the order parameters in equation (49) are solved, ignoring the δ term in equation (48), we can calculate the phase diagram as a function of α and the N-I transition temperature (equivalently ϵ). Physically, α ($0 < \alpha < 2$) governs the order of the S_A -N transition (second order for $\alpha < 0.88$, first order for $0.88 < \alpha < 1.1$ with $\alpha = 0.88$ being the tricritical point). It may be looked upon as a ratio of steric interactions to anisotropic dispersion interactions. The larger values of α lead to a larger extent of the S_A phase at the expense of the extent of the nematic phase. For the values of $\alpha > 1.1$ the nematic phase disappears and the smectic phase transforms directly into the isotropic phase. The theory predicts a change in the order of the S_A -N transition in a homologous series, as the alkyl chain length is increased. Near $\alpha = 1.1$, but for $\alpha > 0.88$, $M = T_{sA-N}/T_{NI}$ varies linearly with α . One of the legacies of the McMillan theory is that all the liquid crystals that have been explored in the study of the S_A -N transition are characterised by the parameter M and we shall use the symbol α^M for α where it conflicts with other notations.

The McMillan molecular field model suffers from the well-known drawback of the neglect of fluctuations. We may incorporate the fluctuations in a mean field approach using Landau theory. We shall come back to the McMillan theory in Chapter 13 where we describe some of the equilibrium studies at the S_A -N transition. In order to set the stage for our spin relaxation models near the S_A -N transition, we will review the Landau-de Gennes theory for the S_A -N transition [22].

Liquid crystal molecules in the S_A phase are arranged in a one dimensional periodic structure. For a monolayer smectic A phase, the molecular length gives the period of the one dimensional mass density wave, which can be written as

$$\rho(z) = \rho_0(1 + 2^{-\alpha} |\Psi| \cos(q_s[z - u(\mathbf{r})])), \tag{50}$$

where ρ_0 is the average density of the liquid crystal, $q_s \equiv 2\pi/d$, and d is its periodicity; $|\Psi|$ is the strength of the density modulation and is identified as the amplitude of the complex S_A order parameter

$$\Psi \equiv |\Psi| \exp(i\phi) \equiv |\Psi| \exp(iq_s u(\mathbf{r})). \tag{51}$$

In these equations, $u(\mathbf{r})$ represents the displacement of the smectic layers along the $z \parallel \mathbf{n}_0$ axis. In the Landau theory, we expand the free energy density as a power series in Ψ about its value in the nematic phase where $|\Psi| = 0$

$$F_{s_A} - F_N = \alpha |\Psi|^2 + \beta_0 |\Psi|^4 + \gamma |\Psi|^6 + \dots \tag{52}$$

with α usually written as $a_0(T_{s,N} - T)$ with a_0 positive, and the sign of β_0 governs the order of the transition, i.e., if β_0 is negative (positive), a first (second) order transition results; for $\beta_0 = 0$ a tricritical phase transition is observed. The sixth order term is added to ensure stability of such an expansion. In this model, a cross over from a second order phase transition (i.e., $\beta_0 < 0$) to the tricritical point is accomplished by finding a mechanism that changes β_0 to its tricritical value of zero. In general, such an effect can be achieved by coupling the order parameter to density variables. In the case of the S_A -N transition, we introduce the coupling of the nematic order parameter to the smectic A order parameter. Upon entering the S_A phase, we generally observe an enhancement in S , so we include a coupling term of the type $-C |\Psi|^2 \delta S$ to the lowest order in $|\Psi|^2$ and δS ; this term implies a reduction in the S_A free energy with positive change in δS . However, the enhancement of the nematic order in the smectic phase occurs at the expense of an increase in the nematic free energy since $\delta S \neq 0$ is consistent with minimising just the nematic free energy. Hence we add a positive term $\delta S^2/2\chi_N$ to the free energy to account for this effect. We also note that in Landau or mean field theory χ_N , the nematic susceptibility, diverges near the N-I transition with a power law

$$\chi_N \approx \frac{\chi_0 T_{NI}^d}{(T_{NI}^\dagger - T)} \quad (53)$$

and T_{NI}^\dagger is the apparent second order transition temperature which is slightly higher ($\sim 0.6 - 1.0^\circ\text{C}$) than that actually observed for the first order transition at T_{NI} . (Note that T^\dagger in section 2 is now T_{NI}^\dagger). Near T_{NI} , the $\delta S^2/\chi_N$ term permits larger deviations in S (from its equilibrium value S_0) than deeper into the nematic phase ($T - T_{NI} > 1$). Minimising the total free energy with respect to δS , and collecting terms, we obtain

$$F_{s_A} = F_0 + \alpha |\Psi|^2 + \beta |\Psi|^4 + \gamma |\Psi|^6 + \dots, \quad (54)$$

where

$$\beta = \beta_0 - \frac{1}{2} C^2 \chi_N \quad (55)$$

and

$$\delta S = \chi_N C |\Psi|^2. \quad (56)$$

It is clear from the form of β in equation (55) that it can become negative, thereby leading to a first order S_A -N transition, when either χ_N is large or the coupling coefficient C is large. It may be noted that up to this stage, the de Gennes theory essentially gives the picture of the S_A -N transition that is comparable to the McMillan model in that $\alpha^{\text{McMillan}} \equiv \alpha^M$ is closely related to $\frac{1}{2} \gamma C^2$. The theory outlined, is suited for spatially homogeneous systems. The spatial fluctuations in the order parameter can be more easily incorporated in the Landau theory in the following way [24]

$$F_{s_A}^{\text{fluct}} = f((\nabla \Psi)(r), T) \approx (\nabla \Psi)^* \mathbf{M}^{-1} (\nabla \Psi), \quad (57)$$

where ∇ is the gradient operator and \mathbf{M} is the mass tensor. Note, the first order contribution vanishes because the free energy cannot be a complex quantity. Furthermore, we are keeping only the lowest order scalar term in the gradient expansion, which means that only long wavelength (i.e., $q \ll q_c = 2\pi/d$) fluctuations are considered. Recalling that, even in the simplest version of

S_A -N theory (i.e., McMillan model) there is a coupling between the nematic and the smectic A order parameters, we must modify equation (57), by the long wavelength fluctuations in the components of the tensorial nematic order parameter $Q_{ij}(\mathbf{r}) = S_{ij}(\mathbf{r}) (3\mathbf{n}_i(\mathbf{r}) \cdot \mathbf{n}_j(\mathbf{r}) - 1)/2$. However, the general problem of incorporating fluctuations in Q induced by Ψ has not been solved (but see [49] appendix D). The usual approach is to associate the small length scale fluctuations in Q with S , and the large length scale fluctuations with \mathbf{n} [40]. In equation (56) we have taken into account the fluctuations in S , while the fluctuations in the director $\mathbf{n}(\mathbf{r})$ can be taken into account following de Gennes [19].

In the S_A phase, away from the S_A -N transition, we have to consider fluctuations in the phase of the complex order parameter (cf. equation (51)), since in the smectic phase the amplitude $|\Psi|$ is just a slowly varying function of temperature. Thus, from equation (57) gradient terms of Ψ such as $\partial\Psi/\partial s$, where $s = z, x, y$ must be considered. The first term corresponds to uniform dilation of the layers, and associated with it is the smectic elastic constant B . The derivatives with respect to x and y correspond to the rotations of layers about the y and x axis, respectively. For example, $(1/q_y)(\partial\Psi/\partial x)$ is the angle of rotation of the layers about the y axis, leading to a molecular rotation by an angle $-\delta n_x$. The net tilt angle is the difference of the two. From such considerations we modify the gradient term in equation (57) as follows [19]

$$F_s^{\text{nem}} = (\nabla + iq_s \delta \mathbf{n}) \Psi^* \mathbf{M}^{-1} (\nabla - iq_s \delta \mathbf{n}) \Psi. \quad (58)$$

Thus the overall Landau free energy which is applicable above and below the S_A -N transition is written as

$$F - F_0 = \alpha |\Psi|^2 + \beta |\Psi|^4 + (\nabla + iq_s \delta \mathbf{n}) \Psi^* \mathbf{M}^{-1} (\nabla - iq_s \delta \mathbf{n}) \Psi + F_N, \quad (59)$$

where F_N is the usual nematic director distortion (on a macroscopic scale i.e., wavelengths $\gg d$) free energy given by Frank [22]

$$F_N = \frac{1}{2} [K_1 (\text{div } \mathbf{n})^2 + \tilde{K}_2 (\mathbf{n} \cdot \text{curl } \mathbf{n})^2 + \tilde{K}_3 (\mathbf{n} \times \text{curl } \mathbf{n})^2], \quad (60)$$

where the $K_i (i = 1, 2, 3)$ are the elastic constants associated with the splay, twist and bend distortion modes, respectively. The smectic phase does not easily accept bend and the twist deformations; (we have represented this effect by the renormalised elastic constants \tilde{K}_2, \tilde{K}_3), and therefore the associated elastic constants become large, and they show pretransitional anomalies given by [19]:

$$\begin{aligned} \tilde{K}_2 &= K_2 + (\pi k_B T / 6 M_\tau d^2) \sqrt{M_\nu / \alpha} \\ \tilde{K}_3 &= K_3 + (\pi k_B T / 6 d^2) / \sqrt{M_\nu \alpha}, \end{aligned} \quad (61)$$

where M_ν and M_τ are components of the mass tensor in the direction parallel and perpendicular to \mathbf{n} . The excess contribution to these elastic constants is seen to diverge as the S_A -N transition is approached from the nematic phase, since $\alpha \rightarrow 0$ (cf. equation (52)). Actually, this divergence is associated with the divergence of the correlation length (ξ) of the smectic A order parameter. The correlation length is defined by the positional correlation function of Ψ [41]

$$\langle \Psi(0) \Psi(r) \rangle = \langle |\Psi(0)|^2 \rangle r^{-1} \exp(-r/\xi). \quad (62)$$

The Landau theory predicts a $1/2$ power law divergence for the correlation length (i.e.,

$\xi \propto |T_{NA} - T|^{-\nu}$). The free energy associated with the fluctuations of Ψ at the S_A -N transition (cf. equation (57)) is similar to the normal to superfluid (NS) transition found in $^3\text{He}/^4\text{He}$ mixtures; that is, they have similar forms for the complex order parameter. In addition, in both the cases, coupling to the auxiliary order parameters (i.e., nematic order parameters for the S_A -N, and the mole fraction of ^4He for the NS transition,) drives the S_A -N and NS transitions first order [42]. Then, the more general theory of critical exponents (the renormalisation group), predicts a $3/2$ power law for the correlation length divergence [42]. Thus the problem of analysing the fluctuations can be solved by the conventional methods.

4.2. THE BROCHARD-JAHNIG ANALYSIS: DYNAMIC SCALING

Following Brochard [43], we Fourier analyse the smectic free energy (cf. equation (59)). Then, applying the equipartition theorem, we obtain the amplitudes of the \mathbf{q} dependent fluctuations associated with Ψ and the other auxiliary order parameters for $T < T_{s,N}$

$$\langle |\Psi(\mathbf{q})|^2 \rangle = k_B T / \left(2\alpha + \frac{q_z^2}{M_V} + \frac{q_\perp^2}{M_T} \right) \quad (63)$$

$$\langle |n_1(\mathbf{q})|^2 \rangle = k_B T / \left(K_1 q_\perp^2 + \tilde{K}_3 q_z^2 + \frac{\Psi_0^2 q_\perp^2 q_z^2}{q_\perp^2 M_V + q_z^2 M_T} \right) \quad (64)$$

$$\langle |n_2(\mathbf{q})|^2 \rangle = k_B T / \left(\tilde{K}_2 q_\perp^2 + \tilde{K}_3 q_z^2 + \frac{\Psi_0^2 q_\perp^2}{M_T} \right) \quad (65)$$

$$\langle |u(\mathbf{q})|^2 \rangle = k_B T / \left[q_\perp^2 (K_1 q_\perp^2 + \tilde{K}_3 q_z^2) + \frac{\Psi_0^2 q_\perp^2 q_z^2}{M_V} \right] \quad (66)$$

where $\Psi_0 = -\sqrt{\alpha/\beta}$ is the equilibrium S_A order parameter. For $T > T_{s,N}$, we have

$$\langle |\Psi(\mathbf{q})|^2 \rangle = k_B T / \left(2\alpha + \frac{q_z^2}{M_V} + \frac{q_\perp^2}{M_T} \right) \quad (67)$$

$$\langle |n_1(\mathbf{q})|^2 \rangle = k_B T / (K_1 q_\perp^2 + \tilde{K}_3 q_z^2) \quad (68)$$

$$\langle |n_2(\mathbf{q})|^2 \rangle = k_B T / (\tilde{K}_2 q_\perp^2 + \tilde{K}_3 q_z^2). \quad (69)$$

The $n_1(\mathbf{q})$, and $n_2(\mathbf{q})$ are the director fluctuation components perpendicular to \mathbf{n}_0 (such that $n_1(\mathbf{q})$ is in the plane formed by \mathbf{n}_0 and \mathbf{q} , and $n_2(\mathbf{q})$ is perpendicular to this plane). It is clear from these equations that the director fluctuations are suppressed near the S_A -N transition due to the divergences in \tilde{K}_2, \tilde{K}_3 . In the smectic phase, these elastic constants are large but not infinite, which is due to the presence of edge dislocations [22]. $u(\mathbf{q})$ is the Fourier transform of $u(\mathbf{r})$, and is associated with the amplitude of vertical displacement modes of molecules in a smectic phase.

However, the general experimental as well as theoretical picture is far more complicated than the Landau model outlined here. For example, the X-ray studies of the correlation lengths due to the MIT group [45,46] have shown that not only are the correlation lengths in the directions parallel and perpendicular to the director (i.e., $\xi_{\parallel}, \xi_{\perp}$) different, but they diverge with different power law critical exponents. This effect can be incorporated into the Landau theory [44] by modifying equation (60) to give

$$\langle |\Psi(\mathbf{q})|^2 \rangle = \chi / (1 + q_z^2 \xi_1^2 + q_{\perp}^2 \xi_{\perp}^2), \quad (70)$$

where we have now identified $\xi_1^2 = 1/(2\alpha M_v)$, $\xi_{\perp}^2 = 1/(2\alpha M_r)$ and $\chi \equiv k_B T/2\alpha$. The latter may be called a generalised smectic susceptibility. In the Landau description we have critical exponents $-1/2(\equiv \nu_{\parallel})$, $-1/2(\equiv \nu_{\perp})$ and $-1(\equiv \gamma)$ for the two anisotropic correlation lengths and for the susceptibility, respectively. From the superfluid analogy, we still expect isotropic correlation length exponents, but with a higher numerical value i.e., $3/4$. Experimentally, however, we find that these exponents vary from -0.9 to -0.5, which is, as yet only partially explained by the renormalisation group calculations which predict a cross over in critical exponents near the tricritical point [42].

Magnetic resonance may not appear to be well suited for measuring these critical exponents accurately. At first glance, magnetic resonance spectral densities should not be sensitive to the S_A order parameter fluctuations, since the amplitudes of the director fluctuation modes are reduced near the S_A -N transition. Unlike the N-I transition, where there is a direct modulation of the orienting potential due to critical effects, at the second order S_A -N transition there is no direct way to influence the spectral densities. However, we have found that as the smectic layers begin to form, small probe molecules often tend to be expelled from the relatively higher density at the core of liquid crystals to the alkyl chains, where the packing density is lower [32]. In other words, these probe molecules are directly affected by the formation of the smectic mass density wave. Furthermore, it is well-known from numerous magnetic resonance studies that the orientational ordering decreases from core to the alkyl region [47]. Thus, fluctuations in Ψ , (cf. equations (60) and (70)), modulate the probe expulsion effect, thereby affecting the probe dynamics. We shall return to these considerations later, but now we consider the relaxation of the S_A order parameter (i.e., the time correlation function of the order parameter) in the spirit of Landau-Khalatnikov theory [30]

$$\langle \Psi(\mathbf{q}, t) \cdot \Psi(\mathbf{q}, 0) \rangle = \langle |\Psi(\mathbf{q})|^2 \rangle \exp(-t/\tau_q), \quad (71)$$

where $\Psi(\mathbf{q}, t)$ is the Fourier transform of $\Psi(\mathbf{r}, t)$, and τ_q is the q dependent relaxation time of the smectic order parameter given by

$$\tau_q = \tau_m / (1 + q_z^2 \xi_1^2 + q_{\perp}^2 \xi_{\perp}^2)^x. \quad (72)$$

τ_m is a relaxation time that is independent of \mathbf{q} and is expected to vary as $|T - T_{S_A N}|^{-1}$ [43]. The exponent x is determined from dynamic scaling arguments and the dynamic scaling argument, due to Brochard goes as follows. The τ_q is considered to be a homogeneous function of τ_m and $(\mathbf{q} \cdot \xi)$.

At $T = T_{s,N}$, τ_m diverges, i.e., the $q = 0$ mode becomes infinitely slow; this is the so-called critical slowing down of the order parameter. For larger q , τ_q does not diverge as $T \rightarrow T_{s,N}$, but it becomes temperature independent as $q \rightarrow \infty$, i.e.,

$$\tau_q = f(\tau_m, \mathbf{q} \cdot \xi) \equiv \tau_m f(0, q\xi) \propto [1/(T - T_{s,N})] f(0, q\xi). \quad (73)$$

Thus, in order to have a non-divergent τ_q for $q\xi \rightarrow \infty$ near the S_A -N transition, we estimate x as follows

$$\tau_q \approx \tau_m / (q\xi)^{2x} \approx |T - T_{s,N}|^{-1+2x\nu} q^{-2x}.$$

Hence, we must have $2x\nu = 1$; if $\nu = 2/3$ (from the superfluid analogy) we have $x = 3/4$; or if $\nu = 1/2$ (Landau theory) then $x = 1$. Note also that $\tau_q \propto 1/q^{2x}$ for $q \rightarrow \infty$ which is independent of temperature. Having determined both the amplitude as well as the decay rates of Ψ , we now proceed to show how the probe expulsion couples the fluctuations in Ψ to the relevant molecular spectral densities associated with $H_1(\Xi)$.

4.3. COUPLING OF MOLECULAR DYNAMICS AND HYDRODYNAMIC MODES

We have proposed the following model to explain our principal results at the S_A -N transition [20,21,48,49]. It has some similarities to the SRLS model described in Chapter 4, section 4. The probe has a preference to be located in the lower density regions of the smectic layer, i.e., the alkyl chain region [32]. As the smectic phase is approached from above, and smectic layering forms as a pretransitional phenomenon (i.e., smectic-like clusters), there is an expulsion of the probe to the lower density regions of the transitory smectic layer. Molecular parameters which affect spin relaxation (i.e., the nematic order parameter S_p and/or τ_R , the rotational correlation time) are affected by this expulsion effect. The onset of smectic layers near the transition is described by density fluctuations: $\rho(\mathbf{r}, t)$ which also affects the translational motion of the probe. Since the critical fluctuations in $\rho(\mathbf{r}, t)$ occur on a much longer time scale than probe dynamics, there is a time scale separation of the two types of motions, and this simplifies the analysis. Thus, as smectic-like clusters form and break up in different regions, molecular dynamics and therefore the spin relaxation of the probe is modulated.

In our formal approach [20,21] we first expand the relevant relaxation parameter Q (which is equal for example to S_p or τ_R) as a Taylor's series in the deviation of the density from its mean value ρ_0 , i.e., $\Delta\rho(\mathbf{r}, t) \equiv \rho(\mathbf{r}, t) - \rho_0$

$$\langle \Delta Q(\mathbf{r}_B, t) \Delta Q(\mathbf{r}_B, 0) \rangle \propto \langle \Delta\rho(\mathbf{r}_B, t) \Delta\rho(\mathbf{r}_B, 0) \rangle, \quad (74)$$

where (\mathbf{r}_B, t) refers to the position of the (probe) particle at time t . The translational diffusion of the probe is taken to obey a Smoluchowski equation with a time dependent potential of mean force (see Chapter 4) on the probe, which is a functional of the density fluctuations, (i.e., $U(\mathbf{r}, t) = U[\Delta\rho(\mathbf{r}, t)]$). Then $\Delta\rho(\mathbf{r}, t)$ is related to the complex smectic order parameter $\Psi(\mathbf{r}, t)$ in the usual manner [43] (also see equation (45)).

In the spirit of a Landau expansion, we have considered only the lowest order terms in $\Delta\rho(\mathbf{r})$ to represent the time dependent fluctuations in the spin relaxation parameters. The method of approach for calculating the relevant correlation functions and spectral densities including the critical hydrodynamics of the phase transition and the translational diffusion of the probe is given in detail elsewhere [21]. We assume that $\xi_{\perp} = \xi_{\parallel}$; $D_{\perp}^{\dagger} = D_{\parallel}^{\dagger}$ and the dynamic critical exponent

$x = 1$. Consider the case where $q_s \rightarrow 0$, (Note that this does not mean that the interlayer spacing goes to zero, but it is the mathematical limit in which we can obtain a simple analytical form for the spectral density. That it is physically relevant is discussed later.) we obtain for $J(\omega)$:

$$J(\omega) = (M k_B T \xi / 16\pi) \left\{ D_T \left[1 - (z/2)^x \left((1 + \omega^2 \tau_m^2)^x + 1 \right)^{1/2} \right] + \frac{1}{\sqrt{2}} \omega \xi^2 z^x \left((1 + \omega^2 \tau_m^2)^x - 1 \right)^{1/2} \right\} \frac{1}{\omega^2 \xi^4 + D_T^2}, \quad (75)$$

where $z \equiv (1 + D_T \tau_m / \xi^2)^{-1}$ measures the relative importance of translational diffusion over the correlation length ξ versus relaxation of the order parameter in providing averaging of the fluctuations in Q . Next we consider the spectral density at zero frequency since it makes a dominant contribution to the ESR linewidth

$$\begin{aligned} 4J(0) &= (M k_B T / 4\pi) z \tau_m / \xi (1 + z^x) \\ &= M k_B T \tau_m / 8\pi \xi \propto \xi^x \propto (T - T_{s,N})^{-x} \quad \text{for } z \approx 1 \\ &= M k_B T \xi / 4\pi D_T \propto \xi \propto (T - T_{s,N})^{-x} \quad \text{for } z \ll 1. \end{aligned} \quad (76)$$

The case $z \approx 1$ corresponds to relaxation dominated by the order parameter fluctuations while the other case $z \ll 1$ corresponds to relaxation dominated by translational diffusion.

On the other hand if we let $q_s = 2\pi/d$ and let $D_T^\perp \tau_m / \xi_p$, $D_T^\perp \tau_m / \xi_\perp$ approach zero, we obtain for the zero frequency spectral density [20,21]

$$J(0)^{\text{int}} \approx \frac{M k_B T \tau_m}{16\pi \xi} \frac{\sqrt{1+c} - 1}{c}. \quad (77)$$

Here, c measures the relative importance of averaging out the effects of density fluctuations $\Delta\rho(\mathbf{r})$ in a single smectic-like layer through diffusion of the probe in the direction normal to the layer versus the relaxation of the smectic layers. (In the formal theory, $c = q_s^2 D_T^\perp \tau_m$). As $c \rightarrow 0$, corresponding to probe diffusion being unimportant, we have $J(0) \propto \tau_m / \xi \propto \xi^x \propto |T - T_c|^{-x}$. This is equivalent to the result of equation (76) in the limit $z \rightarrow 1$. For $c \gg 1$, $J(0) \propto \tau_m / \xi \propto \xi^{-x}$, and it does not diverge, but rather goes to zero. Based upon measurements of ξ_1 [45,46] and D_T [55,56] in somewhat related materials, we estimate $\xi_1 \approx 10^{-5}$ cm for $|T - T_c| = 0.1$ K and $D_T \approx 10^{-7}$ cm² s⁻¹. Also we estimate $\tau_m \approx 10^{-5}$ s at $T - T_c = 0.1^\circ$ C [20], so $D_T^\perp \tau_m / \xi^2 \approx 10^{-2}$ to 10^{-3} (for $T - T_c \approx 0.1^\circ$ C), while $D_T^\perp \tau_m q_s^2 \approx 10^3$ to 10^2 [49]. Thus, while it may be reasonable to ignore the averaging effects of translational diffusion over the distances of ξ_p , it is questionable for diffusional averaging over a single smectic layer thickness d .

However, if U is a very sensitive functional of $\Delta\rho(\mathbf{r})$, then as $\Delta\rho(\mathbf{r})$ diverges as the critical point is reached, we may expect virtually no diffusion parallel to the normal to the smectic phases in the smectic-like clusters, (i.e., D_T^\perp would be significantly reduced). Instead, the probe would reside entirely in the alkyl chain regions in such clusters, i.e., the expulsion effect referred to previously. Thus, the modulation of the spin relaxation would be primarily determined by the formation and break-up of the smectic-like clusters, with the probe rapidly adjusting its location within the layers accordingly. This effect would be measured by the correlation function

$\langle \Psi(\mathbf{r},t) \Psi(\mathbf{r},0) \rangle$ for which equations (75) and (76) are the appropriate solutions, and give the correct critical exponent for $z \rightarrow 1$. A more complete discussion of these matters including a detailed comparison with experiment may be found in [21] and [49].

It is interesting to point out that the predicted value of the critical exponent is a very sensitive function of the details of the model. Thus, for example, it follows from equation (77), that as $c \rightarrow \infty$, there is no divergence. Similarly, our considerations of higher order correlation functions [i.e., the quadratic $\langle |\Psi(\mathbf{r},t)|^2 |\Psi(\mathbf{r},0)|^2 \rangle$] show that they yield contributions to $J(0)$ which go to zero approximately as ξ^{-2} rather than diverge. Thus, we believe that the experimental observation of the critical exponent provides a very sensitive test of the nature of the dynamics at the phase transition.

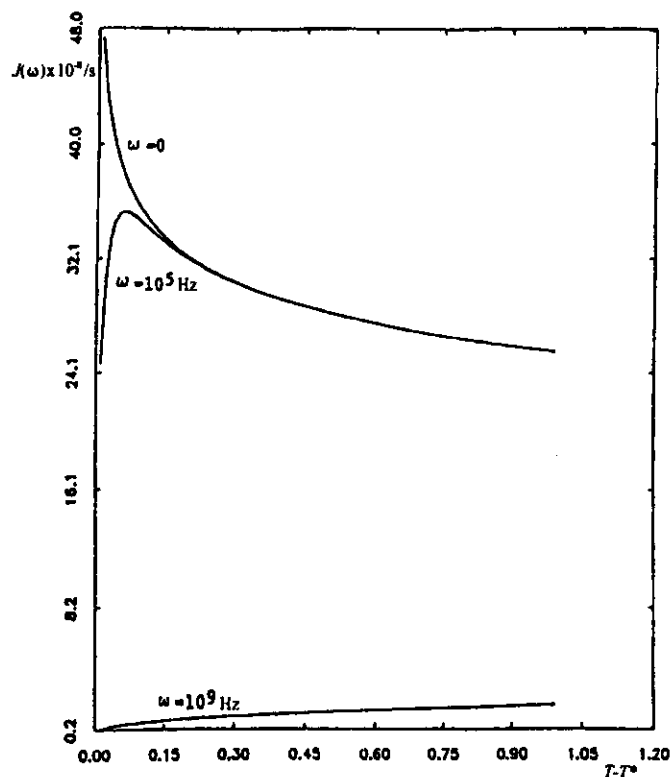


Figure 3. Temperature dependence of the spectral density $J(\omega)$ at frequencies corresponding to: (i) secular ($\omega=0$); (ii) pseudosecular ($\omega \sim 1.3 \times 10^8 \text{ s}^{-1}$); and (iii) non-secular ($\omega \sim 5.8 \times 10^{10} \text{ s}^{-1}$); (From [49]).

Another example of how delicate and sensitive is the critical exponent from spin relaxation studies comes from an examination of $J(\omega)$ for $\omega = 0$. We show in figure 3, $J(\omega)$ for three values of ω corresponding to secular, pseudo-secular and non-secular spectral densities, calculated using the more general form for $J(\omega)$ than equation (75) which considers the temperature dependence of the (unequal) correlation lengths ξ_{\perp} and ξ_{\parallel} (i.e., $\xi_i = \xi_i^0 (T - T^*)/T^*$, where $i = \parallel$ or \perp), and allows for anisotropic diffusion $D_{\parallel}^{\perp} \neq D_{\perp}^{\parallel}$ [49]. The calculations, which use experimental data from

temperature studies of ξ_1 and ξ_2 in 6OCB-8OCB [11] demonstrate clearly that only the secular spectral density [i.e., $J(0)$] shows the critical divergence. Near the phase transition, the pseudo-secular $J(\omega_s)$ and the non-secular $J(\omega_c)$ show little or no tendency to diverge and they are much weaker in magnitude.

5. The Dynamic Cluster Model

Our past ESR analyses in terms of local cooperativity were based upon the slowly relaxing local structure (SRLS) model, described in Chapter 4, section 4. However, in the highly ordered phases typical of liquid crystals, the cooperativity in reorientation may be too great to be modelled in terms of such a simple model. With the recent theoretical and computational advances, it could be feasible to analyse more realistic models of cooperative dynamics for the longer time scales (i.e., > 1 ps) that are important for our magnetic resonance studies [50]. In this sense, such methods could be a useful alternative to full molecular dynamics calculations [51,52].

The particular model we have studied is a dynamic cluster model [48,50], which is based on a form of Bethe's cluster method. In this treatment, a central molecule is surrounded by γ nearest neighbours, which form the outer shell. The central molecule interacts with this cluster through pairwise potentials $U(\Omega_0, \Omega_i)$, $i = 1, 2, \dots, \gamma$, with Ω_i being the Euler angles for the i th molecule. While the γ molecules do not interact with each other, they all feel an orienting potential $U(\Omega_s)$ representing the mean potential of the fluid. Then a self-consistency relation is introduced so that the central molecule orders exactly in the same way as do the other shell molecules. This leads to non-trivial integral equations for solving for $U(\Omega)$. Ypma and Vertogen [53] obtained the best results for this model when $\gamma = 3$ or 4.

The dynamic cluster model we have studied is just the dynamical version of this. We model the $(\gamma+1)$ particle system by the appropriate set of coupled Smoluchowski equations for the joint probability distribution $P(\Omega_0, \dots, \Omega_\gamma, t)$. These coupled Smoluchowski equations are then solved for correlation functions such as

$$\langle Y_{2,0}[\Omega_0(t)] Y_{2,0}[\Omega_0(0)] \rangle - \langle Y_{2,0}[\Omega_0(0)] \rangle^2$$

by means of the Lanczos algorithm (cf. Chapter 15). If we regard the central molecule as a probe, then in a sense, it is not necessary to achieve self-consistency. However, the matter of self-consistency is conveniently dealt with by solving numerically the Ypma-Vertogen integro-differential equations. These equations then give us the self-consistent values of $U(\Omega_s)$ for a given value of $U(\Omega_0, \Omega_s)$. In our solution of the several body diffusion equation $\partial P/\partial t = \Gamma P$, (actually we use the symmetrised form), we use the analogy to the problem of the quantum mechanics of a many electron atom. Let us call the operator Γ for the dynamic cluster problem Γ_{cluster} , while the standard problem of the operator Γ_{MF} (and is typically given in the form of equation (1) in Chapter 4. We first solve the conventional mean field problem for $P^1(\Omega, t)$ in the usual manner (i.e., equation (1) in Chapter 4) to yield the single particle mean field eigenvalues and eigenvectors appropriate for a given mean field potential. We then select the mean field solution corresponding to order parameter $S = \langle Y_{2,0} \rangle$ which is (nearly) equal to that for the cluster problem to be solved. That is, we regard these Γ_{MF} as the differential analog of Hartree SCF theory, i.e., as an approximation to the best single particle solution. Then, we solve for Γ_{cluster} by methods analogous to configuration interaction starting with these single particle solutions of Γ_{MF} . That is, the basis states are products of the single particle states from Γ_{MF} , and we can diagonalise Γ in this basis.

The problem with this method, as in any configuration interaction, is whether we have chosen enough excited configurations for the calculation to converge. Utilising approximate basis sets, initial results have been obtained for the correlation function for $Y_{2,0}(\Omega_1)$, and we have compared them to the mean field results, as shown in figure 4. Interestingly enough, it is noted that for the nematic phase, the results for the full dynamic cluster mode lie rather close in shape to those of the simple mean field approach. However, this is not so for the isotropic phase, especially for the phase transition region for $\gamma = 3$ or 4.

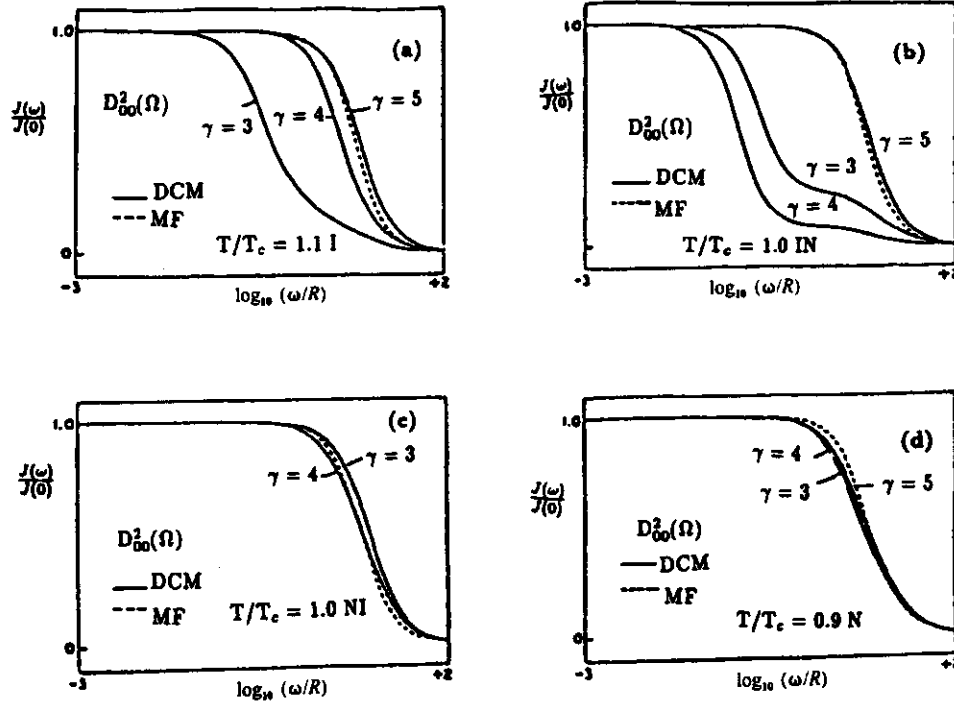


Figure 4. Dimensionless spectral densities $J(\omega)/J(0)$ versus dimensionless frequency ω/R plotted logarithmically for the dynamic cluster model; (a) $T/T_c = 1.1$, i.e., in the isotropic phase just above the liquid crystal phase; (b) $T/T_c = 1.0$, in the isotropic phase at the phase transition; (c) $T/T_c = 1.0$, in the liquid crystal phase at the phase transition; (d) $T/T_c = 0.9$, deep in the liquid crystal phase. Dashed line is the mean result and solid lines are for $\gamma = 3, 4$ and 5 cluster particles. (From [48]).

6. Fast versus Slow Collective Motions

A general question which exists with regard to a spin relaxation theory involving director fluctuations pertains to the validity of the motional narrowing approach. This concern becomes especially relevant when in the critical region, and a slowing down of the q modes occurs. That is, if each q mode contributes to spin relaxation independently, and if $H_{1,q}$ is the component of H_1 which is modulated by the q th mode of director fluctuations, then the condition $|H_{1,q}|^2 \tau_q^2 < 1$ (which is a requirement for motional narrowing theory to apply) may no longer hold. In this case,

we may write

$$|H_{1,q}|^2 \sim f^2 \omega_s^2 \alpha_q^{-1}, \quad (78)$$

where f measures the extent of coupling of the probe to the critical modes, ω_s is the magnitude of the typical terms in the spin hamiltonian, and α_q^{-1} is the mean square fluctuation of the q th mode of the smectic order parameter near the S_A -N transition (cf. section 3). A similar result can also be written for the nematic order fluctuations near the N-I transition [17]. From equation (78), it follows that the cross over from fast to slow motion should occur at

$$1 = |H_{1,q}|^2 \tau_q^2 \approx \frac{k_B T}{2AV} \frac{f^2 \omega_s^2 \tau_m^2}{(1 + q^2 \xi^2)^{1+2x}}. \quad (79)$$

Here, x is a dynamic scaling parameter which we shall assume to be unity. Although we initially interpreted V as the sample volume [17], it is more appropriate that $V \sim \xi^3$, where ξ denotes the length over which correlations in order persist [24,21]. Thus, V may be regarded as the natural volume within which to expand the fluctuations.

A more rigorous analysis of this matter can be performed in terms of a more complete slow motional theory [17,21], but does not appear warranted here. Suffice it to say that a preliminary treatment (utilising the partial time ordered cumulant method) gives the result that the cross over from fast to slow motion should occur when (letting $x = 1$)

$$\frac{k_B T}{2A} \frac{f^2 \omega_s^2 \tau_m^2}{(32\pi)\xi^3} \approx 1, \quad (80)$$

and, by comparison with equation (79) (with V replaced by ξ^3), the important q modes for motional narrowing are those for which $q^2 \leq \xi^{-2}$. Since, as we discussed in section 3, $\xi^2 \sim (T - T_c)^{-\nu}$, we have the result that as $T \rightarrow T_c$, the slow motional condition would be achieved. Note that in this discussion the effect of finite diffusion has been neglected. The results from the treatment in section 3 suggest that this may be included by replacing ω_m by $\tau'_m \equiv z\tau_m$ (where z is defined in equation (73)).

7. Treatment of Data

The parameters A , B and C are directly related to the tumbling motion of the spin probe. Our results for B and C with temperature for perdeuterated tempone- d_{16} in 6OCB-8OCB are shown in figures 5-8. It is clear from these figures that the values of B and C at the phase transitions are anomalous in the sense that they appear to diverge as T^* , the phase transition temperature, is approached from either one or both sides of the transition. The anomalous contributions to B and C (B_{anom} and C_{anom}) are obtained by subtracting out the main contributions to B and C (B_0 and C_0), i.e., those that arise due to rotational motions away from T^* , in the following way. In regions away from critical effects, the linewidth parameters B and C were compared to values of B and C that were calculated using a range of values of τ_r , N (if D_R^+ and D_R^- are the perpendicular and parallel components of the rotational diffusion tensor, $\tau_r^{-1} = 6\sqrt{D_R^+ D_R^-}$ and $N = D_R^+ / D_R^-$), and the probe order parameter S . The magnetic parameters for the different systems studied here are shown

in table 2 in Chapter 12. From such comparisons, the set of simulation parameters that best represent the experimental data was selected. In order to obtain τ_R in the critical regions, a linear extrapolation of $\ln\tau_R$ versus $1/T$ was performed. From a knowledge of the order parameters near T^* measured using the hyperfine splittings [32,31], N , and the values of τ_R thus obtained, B ($=B_0$) and C ($=C_0$) were calculated using a brownian diffusion model. Finally B_{anom} and C_{anom} were obtained by subtracting B_0 and C_0 from the experimental values of B and C . The anomalous

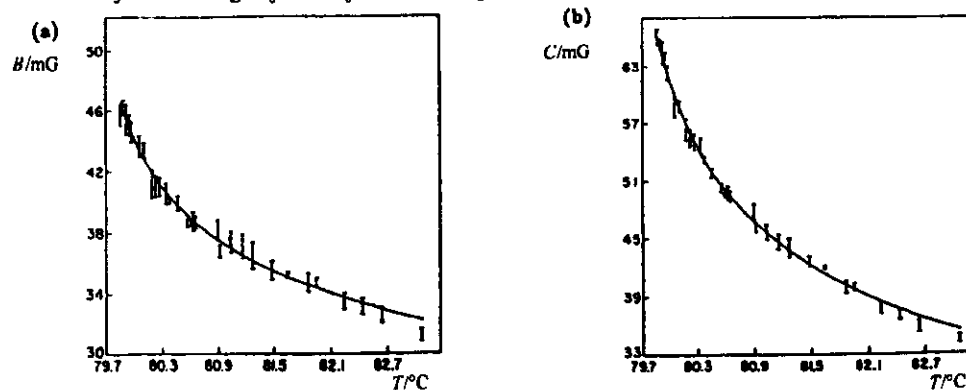


Figure 5. Temperature variation of B and C for perdeuterated tempone in 6OCB-8OCB at the N-I transition. The curve through the data points represents the best five-parameter fit (see text). (From [49]).

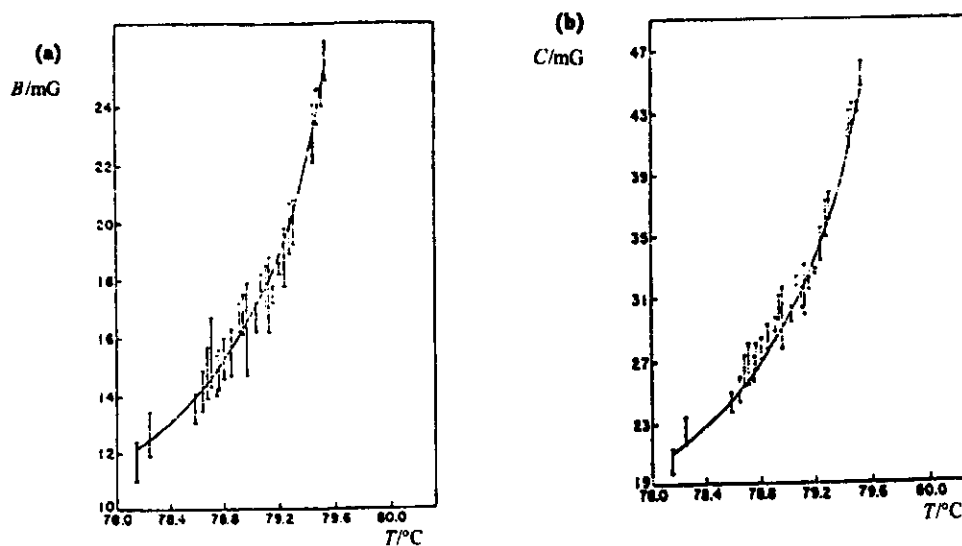


Figure 6. Temperature variation of B and C for perdeuterated tempone in 6OCB-8OCB at the N-I transition. (From [49]).

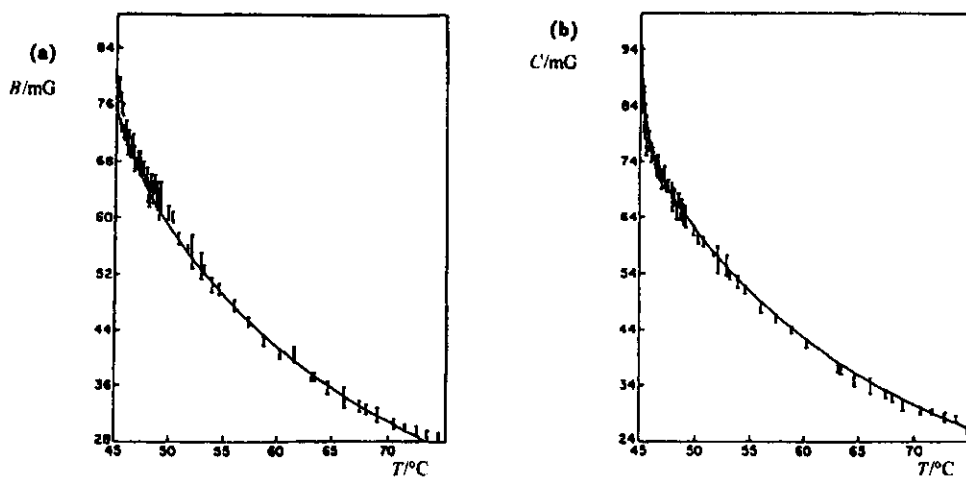


Figure 7. Temperature variation of B and C for perdeuterated tempone in 6OCB-8OCB at the S_A -N transition. (From [49]).

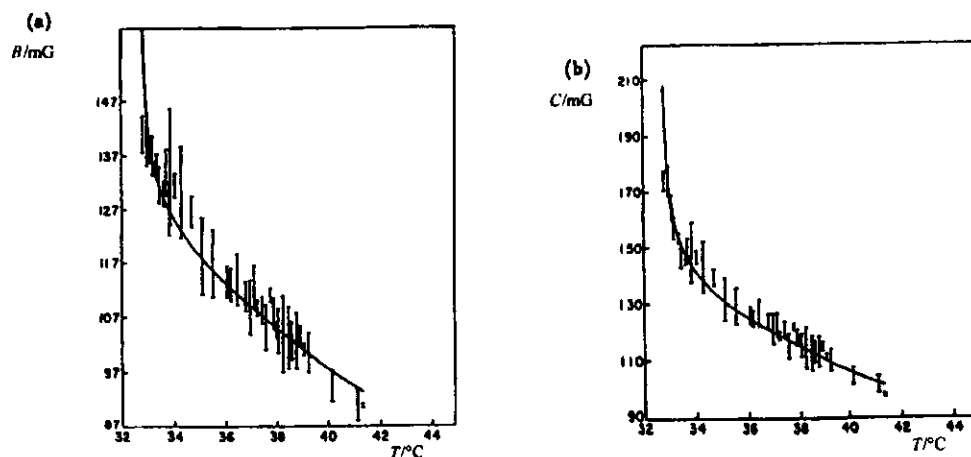


Figure 8. Temperature variation of B and C for perdeuterated tempone in 6OCB-8OCB at the N_R - S_A transition. (From [49]).

contributions to B and C thus obtained were then fitted to an expression of the form B_{anom} or $C_{\text{anom}} = k |T - T^*|^\gamma$ (cf. equations (35) and (36)), using a non-linear least squares routine based on the Marquardt algorithm [54], to yield values of k , T^* , and γ . In certain cases, however, where the order parameter did not change much with temperature (i.e., near the S_A -N transition) a five parameter fit was performed. This used an expression of the form $B, C = k(T - T^*)^\gamma + A \exp(-B/T)$, where the second term on the right hand side models the temperature variation of the secular spectral densities arising from simple rotational diffusion. The program also provided uncertainties

in the values of the parameters associated with the fits to the data, as shown in tables 1 and 2.

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