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On the Influence of Director Fluctuations on NMR Relaxation in Liquid Crystals

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Abstract. — We investigated and extended models describing the influence of director fluctuations (DF) on the orientational dynamics of individual (dissolved) molecules. The models are divided in two categories. On one hand the traditional models, relying on a separation in time scales between the DF and the individual motion of the molecule. On the other high ordering models, which assume the motion of the individual molecule is very similar to the DF. The spectral densities calculated from all models were fitted to NMR relaxation data. It is found that virtually all result in acceptable fits for the frequency dependence of $J_1$. Comparison to (sparsely available) $J_2$ data proves to be a much more severe test of the different models. From this we see high ordering models are inadequate. The traditional model gives a slightly better fit, although the calculated frequency dependence in $J_2$ is generally too small, which is actually caused by an overestimation of the effect of DF on $J_1$. Only the extended traditional model result in reasonable agreement between experimental and calculated curves.

1. Introduction

NMR relaxation experiments on (probe) molecules in liquid crystals, show that relaxation is faster at lower spectrometer frequencies, $\nu_0$ [1–19]. This implies the presence, in a nematic liquid crystal, of motional components on the time scale of $\nu_0^{-1}$, i.e. much slower than molecular reorientation in an ordinary, isotropic, liquid.

It is generally assumed that these long correlation times result from the coupling to cooperative orientational motion of the liquid crystal molecules, i.e. director fluctuations, of which those with the shortest wavelength decay on a nanosecond time scale [20–22].

Experimentally, the focus has been on the frequency dependence of spectral density $J_1$, however, some experiments have also made that of $J_2$ available. The main objective of our investigation was to discover why the observed frequency dependence of $J_2$ was much larger than could be accounted for [22–24].

The suggestion that director fluctuations are responsible for the frequency dependence was first made by Pincus [25], and theoretical development of this idea has lead to numerous papers on the subject [25–35]. In practically all these models it is assumed that the time-scales for orientational dynamics of individual molecules is much different from that of the, collective,

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director fluctuations. This time scale separation allows the separation of transition probabilities into contributions due to molecular motion in a fixed director field, coupled to the much slower motion of this field. Thus the problem is split into essentially two independent parts. The only model that does not make this time scale separation approximation is that proposed by Gertner and Lindenberg [35]. Instead they assume that the orientation of the molecule is at all times very close to that of the local director orientation. This approach will be referred to as high ordering. It allows one to write the problem as a set of coupled damped harmonic oscillators, which can of course be solved. For the high ordering models it is thus not necessary to assume time scale separation. However, we will show that it is in fact valid in this case also, when parameters are used in the range giving agreement with experiment.

Two quantities play an essential role in the development of theoretical expressions for the spectral densities. The first quantity, which we denote by parameter $\alpha$, characterizes the magnitude of the director fluctuations. All models use a Gaussian distribution for the director field modes, i.e. the free energy of the fluctuating director field is given by the usual Frank–Oseen expression [20], and $\alpha$ is directly related to the width of this Gaussian distribution. The second quantity characterizes the interaction between the probe molecule and the director. The simplest possible interaction is of the form $U(\Omega) = \lambda D_{60}^2(\Omega)$, where $\Omega$ denotes the set of Euler angles of the molecular frame with the director frame. Thus the interaction is fully specified by the single parameter $\lambda$, which can be found by measuring the order parameter. More complex models, where $\lambda$ is not just one parameter, but a set of parameters, allowing for non–axial molecules have also been proposed [22]. We show in this paper that within the time scale separation approximation, the specific form of the interaction is in fact irrelevant as far as the frequency dependence of the spectral densities is concerned.

Calculations within the time scale separation approximation all use some form of expansion. Thus Freed [30], apart from other approximations, expands in the interaction potential, and therefore in $\lambda$, to lowest order, obtaining a frequency dependence in $J_1$ only. Vold et al. [24] carried out a similar expansion to higher order, which gives a frequency dependent contribution to $J_2$. Van der Zwan and Plomp [22], expand in the fluctuating part of the interaction potential only, which is effectively an expansion in $\alpha \lambda^2$, and obtain frequency dependent terms in $J_2$ as well. In both cases the frequency dependent terms in $J_2$ were found to be too small to explain experimental results.

The high ordering model, which can be viewed as the large $\lambda$ limit of $U(\Omega)$, is characterized by a harmonic interaction potential between director field and molecule. The model is used by Gertner and Lindenberg [35] to calculate frequency dependent contributions to $J_1$, but as we will show in this paper the model can be used to get contributions to $J_2$ also. In view of the length of the calculations, calculational aspects of the high ordering models are attended to in the appendix. We use a slightly different Hamiltonian than the one proposed by Gertner and Lindenberg [35]. It is symmetric in the interaction, and does not lead to a modification of the director field free energy. A comparison is made, however, with the original Gertner/Lindenberg calculations. In practice, experimental values for the parameters used in these models both lead to acceptable fits for $J_1$.

In this paper we use the different models to calculate both the frequency dependent terms in $J_2$, and, in a consistent manner, the frequency dependent terms in $J_1$. Thus, in the next two sections we use time scale separation to calculate director fluctuation contributions to $J_2$ to lowest, i.e. second order, and consequently we also take the expansion of $J_1$ to a higher order than was done by Vold et al. [24]. In that section we also point out a serious shortcoming of the Frank–Oseen approximation to the free energy, when used to calculate director fluctuation autocorrelation functions. The use of the Gaussian approximation leads to divergences resulting from the fact that the director $\mathbf{n}$ is not a vector of unit length in this approximation.
In Sections 4 through 6, we study various aspects of the correlation functions. Thus, Section 4 is devoted to time correlation functions, Section 5 to the spectral densities that can be calculated from these, and Section 6 to initial values.

In the subsequent section, Section 7, all models are fitted to experimental data from the literature. Although it can be argued that the results derived in this paper are more general, we restrict ourselves to quadrupolar relaxation of deuterons in rigid probe molecules dissolved in nematics. In that case only rotations of the probe molecule contribute to the relaxation, intermolecular and internal motions may be neglected. In addition we only took experimental results for liquid crystals which orient parallel to the magnetic field, and for probe molecules which orient parallel to the director. The reason for this is that the relation between experimental and theoretical results is most direct, and not confused by the introduction of more parameters, and that the values of $J_1$ and $J_2$ can be determined independently [19, Chap. 6]. We also tried to restrict ourselves to probe molecules for which the molecular frame coincides with the local field gradient frame for similar reasons. Even though most systems for which the experiments have been carried out fulfill the above conditions the number of systems useful for evaluation of data remains small. Therefore we have included two systems for which the local frame does not coincide with the molecular frame. Based on these experimental results we show that, although $J_2$ data are not abundant, they provide a much more crucial test of the models than $J_1$ data alone.

The final section is devoted to remarks and conclusions.

2. Time Scale Separation

Under the restrictions set down in the introduction the spectral densities obtained from NMR quadrupolar relaxation measurements are the real part of the Fourier transform of the rotational correlation functions [36,37]

$$\begin{equation}
C_k(t) = \langle D_{k0}^2(\Psi_0)D_{k0}^{2*}(\Psi_t) \rangle
\end{equation}
$$

where $\Psi_0$ and $\Psi_t$ represent the set of Euler angles transforming the laboratory frame into the molecular frame at time 0 and $t$ respectively, and $D_{kl}^2$ are the Wigner rotation matrices [38]. A straightforward way to introduce the time scale separation is by using an additional coordinate frame attached to the instantaneous, local director. We use the Euler angles $\Xi$ to relate this frame to the laboratory frame, and $\Omega$ to give the orientation between the molecule and this local director. Using the addition theorem [38, Chap. 3], we can then write:

$$\begin{equation}
C_k(t) = \sum_{m,n} \langle D_{km}^2(\Xi_0)D_{kn}^{2*}(\Xi)D_{m0}^2(\Omega_0)D_{n0}^{2*}(\Omega) \rangle
\end{equation}
$$

We have assumed here that the local, deuteron, frame, and the molecular coordinate frame coincide. This is not essential, but makes the notation less complicated. The angular brackets define an average in the following way:

$$\begin{equation}
\langle \cdot \rangle = \int d\Omega_0 d\Omega d\Xi_0 d\Xi P(\Omega,\Xi,t|\Omega_0,\Xi_0)P_{eq}(\Omega_0,\Xi_0)
\end{equation}
$$

In this equation $P_{eq}(\Omega_0,\Xi_0)$ is the equilibrium probability of finding sets of angles $\Omega_0,\Xi_0$, and the transition probability for finding angles $\Omega,\Xi$ at time $t$ is given that the angles were $\Omega_0,\Xi_0$ at time 0 is denoted by $P(\Omega,\Xi,t|\Omega_0,\Xi_0)$. In using this expression it is implicitly assumed that the stochastic processes are stationary [39].
We now apply the time scale separation approximation, i.e. assume the orientational dynamics of the molecule to be fast compared to director fluctuations. The probabilities can then be split into two independent parts [34]

\[ P(\Omega, \Xi, t|\Omega_0, \Xi_0) \approx f(\Xi, t|\Xi_0)\tilde{f}(\Omega, t|\Omega_0) \]  

(2.4)

\[ P_{eq}(\Omega_0, \Xi_0) = P_{eq}(\Xi_0)\tilde{P}_{eq}(\Omega_0) \]  

(2.5)

where the probabilities with the \( \tilde{\} \) are with respect to the local director frame. We also assumed the probabilities for \( \Omega \) to be independent of the instantaneous director orientation, \( \Xi \), i.e. a molecule sees only its local environment. We note here that the details of the dynamics governing \( f \) and \( \tilde{f} \) are irrelevant for this separation. The only requirement is that the time scales are separated.

Inserting the above relations into the correlation functions gives

\[ C_k(t) = \sum_m \langle D_{km}^2(\Xi_0)D_{km}^{2*}(\Xi) \rangle \langle D_{m0}^2(\Omega_0)D_{m0}^{2*}(\Omega) \rangle \]  

(2.6)

The functions \( \langle D_{km}^2(\Xi_0)D_{km}^{2*}(\Xi) \rangle \) depend only on the director dynamics, they will be referred to by DCF, and \( \langle D_{m0}^2(\Omega_0)D_{m0}^{2*}(\Omega) \rangle \) depend on the dynamics of the molecule with respect to a static director (along the laboratory z-axis, MCF).

Dozov et al. [34] claim that equation (2.6) is correct only for high ordering (however, without using this in their calculation). This does not do them justice, as time scale separation is more naturally applied to low ordering. Actually, for very high ordering Gertner and Lindenberg [35] have proposed a method which does not require assumptions about time scales. It is discussed in Appendix A.

Rewriting equation (2.6) so that the long time limit appears explicitly we get

\[ C_k(t) = \sum_m \langle D_{km}^2(\Xi_0)D_{km}^{2*}(\Xi) \rangle \{ \langle D_{m0}^2(\Omega_0)D_{m0}^{2*}(\Omega) \rangle - S_0^2\delta_{m,0} \} + S_0^2 \langle D_{k0}^2(\Xi_0)D_{k0}^{2*}(\Xi) \rangle \]  

(2.7)

In this expression the terms in parenthesis reduce to zero for times long compared to the correlation time of the MCF.

According to Freed [30, 40] equation (2.7) (and thus (2.6)) is incorrect. He argues that even for a “spherical” probe, i.e. one with zero order parameter, the DF contribute to the correlation functions, as is seen from the first term. However, the expression is only valid when the time scales of the intrinsic dynamics of probe and director are different. This means there is no intermediate time scale, i.e. the MCF has attained its equilibrium value before the DCF starts to differ from its initial value. Therefore, in the first term on the right hand side of equation (2.7), the director fluctuation correlation functions may be replaced by their initial values, and we get

\[ C_k(t) = \sum_m \langle |D_{km}^2(\Xi)|^2 \rangle \{ \langle D_{m0}^2(\Omega_0)D_{m0}^{2*}(\Omega) \rangle - S_0^2\delta_{m,0} \} + S_0^2C_k^d(t) \]  

(2.8)

where the director fluctuation correlation function, DCF, is written as

\[ C_k^d(t) = \langle D_{k0}^2(\Xi_0)D_{k0}^{2*}(\Xi) \rangle \]  

(2.9)

From equation (2.8) we see that the short time behaviour is totally determined by the dynamics of the molecule with respect to a fixed director. The long time behavior is determined only by the director dynamics. Since this last term is multiplied by the square of the order parameter,
it disappears for spherical probes. Freed's reservations with respect to the validity of (2.7) are therefore not justified. Moreover, equation (2.7) is, within the time scale separation approximation, equivalent to Freed's results. Beyond this approximation, when the time scales of the director motion and the probe motion show non-negligible overlap, neither Freed's results nor equation (2.7) is correct.

From equation (2.8) it is clear that the slow contributions to the correlation functions, $C_k(t)$, are fully determined by the director dynamics if there is sufficient difference in the time scale of the intrinsic dynamics of the probe molecule and the dynamics of the director. Thus, for the frequency dependence of the spectral densities, which is determined by these slow contributions, the intrinsic molecular dynamics is of no importance, only its order parameter, $\left< D_{66}^2(\Omega) \right>$, is.

Therefore, within the time scale separation approximation, only the dynamics of the director field plays a role in the frequency dependence of the spectral densities at NMR frequencies. In the next two sections we describe equilibrium and time dependent properties of the director field.

3. Probability Distribution for Director Fluctuations

In this section we calculate the equilibrium distribution function and the transition probability for director fluctuations within the small DF approximation.

The starting point is the free energy of deformation of the director field. In the one-constant approximation (all elasticity constants equal to $K$), which includes all essential features, this is the Frank–Oseen expression [20]:

$$ F = \frac{K}{2} \int \text{d}r \left\{ (\nabla \cdot \mathbf{n}(r))^2 + (\nabla \times \mathbf{n}(r))^2 \right\} \quad (3.1) $$

Since NMR experiments are carried out in a magnetic field, the interaction energy between director and field should be included in the free energy. However, it has been shown [41], that a magnetic field mainly reduces the long wavelength fluctuations, thus defining a preferred direction, with negligible influence on the much shorter fluctuations observed by NMR relaxation.

The $z$-component of the director at each position, $r$, may be written in terms of its $x$- and $y$-components. We choose the laboratory $z$-axis to lie along the average director. Then for small deviations we may expand to second order in the $x$- and $y$-components:

$$ n_z(r) = \sqrt{1 - n_x^2(r) - n_y^2(r)} $$
$$ \approx 1 - \frac{1}{2} (n_x^2(r) + n_y^2(r)) \quad (3.2) $$

Note that we have chosen a definite sign for the square root in the previous equation, this is permitted because the director is symmetric under inversion. The free energy can now be written as

$$ F = \frac{K}{2} \int \text{d}r \left\{ (\nabla n_x)^2 + (\nabla n_y)^2 + [1 + \frac{1}{2} (n_x^2 + n_y^2)] (n_x \nabla n_x + n_y \nabla n_y)^2 \right\} \quad (3.3) $$

For small director fluctuations, $n_{x,y}^2 \ll 1$, the last term may be neglected. After Fourier transformation of the director components we get,

$$ F = \frac{1}{V} \sum_k \frac{K k^2}{2} \left\{ |n_x(k)|^2 + |n_y(k)|^2 \right\} \quad (3.4) $$
Notice that in the small DF approximation, fluctuations of the $z$-component of the director have negligible contribution to the free energy. However, they are not assumed to be strictly zero.

An expression for the probability distribution of the director field deformation can be obtained from this free energy. Except for a normalization constant it is

$$P_{\text{eq}}\{n_x(k), n_y(k)\} = \exp \left[ -\frac{\beta}{V} \sum_k \frac{K k^2}{2} \left( |n_x(k)|^2 + |n_y(k)|^2 \right) \right]$$ \hspace{1cm} (3.5)

As usual, all modes are assumed independent. Then the range of values for each mode $n_{x,y}(k)$ is extended to infinity. This is allowed since the probability for a mode of large amplitude is very small. We are now left with a Gaussian distribution for each of the different modes. However, if more than one mode is present in the sample at the same time, the normalization condition imposed on the director effectively introduces an interaction between the modes. In assuming the modes in equation (3.5) to be Gaussian, this interaction is ignored.

In addition to the equilibrium distribution, a transition probability is required for calculating time correlation functions. Assuming each mode to be adequately described using an independent stationary Gaussian Markov process, we get [39]

$$P(n_t(k), t|n_{x}^0(k), 0) = \exp \left[ -\frac{|n_x(k) - n_x^0(k)|^2}{2\sigma_{\tau k}(1 - e^{-t/\tau_{\tau k}})} \right]$$ \hspace{1cm} (3.6)

where

$$\sigma_{x k} = \sigma_{y k} = \frac{V}{\beta K k^2}$$ \hspace{1cm} (3.7)
$$\tau_{x k} = \tau_{y k} = \frac{\eta_{x,y}}{\beta K k^2}$$ \hspace{1cm} (3.8)

The $\eta_{x,y}$ are effective viscosities [20]. The transition probability in equation (3.6) is consistent with results obtained from the hydrodynamic equations for a single, small amplitude mode.

Equations (3.5) and (3.6) are the probability distributions generally used to calculate the DF correlation functions. Since a sum of Gaussian variables is itself Gaussian, these equations can be used to obtain expressions for the probabilities of the $x$- and $y$-components of the director at a fixed position $r$. The equilibrium probability is given by (apart from the normalization factor):

$$P_{\text{eq}}(n_x, n_y) = \exp \left[ -\frac{n_x^2 + n_y^2}{2\alpha} \right]$$ \hspace{1cm} (3.9)

where $n_x \equiv n_x(r) = \sum_k e^{-i k \cdot r} n_x(k)$; the transition probability is (again normalization constants were suppressed):

$$P(n_x, n_y, t|n_{x}^0, n_{y}^0, 0) = \exp \left[ -\frac{(n_x - n_x^0 I(t))^2 + (n_y - n_y^0 I(t))^2}{2\alpha(1 - I^2(t))} \right]$$ \hspace{1cm} (3.10)

where $\alpha$, the “fluctuation strength” [22], is given by

$$\alpha = \frac{k_c}{2\pi^2 \beta K}$$ \hspace{1cm} (3.11)
The time dependence in equation (3.10) is governed by the function \( I(t) \):

\[
I(t) = \frac{1}{k_c} \int_0^{k_c} dk \exp \left[ -\frac{K k^2}{\eta} t \right] = \int_0^1 dx \exp \left[ -\omega_c x^2 t \right]
\]

with the cut-off frequency \( \omega_c \) defined as

\[
\omega_c = \frac{K k_c^2}{\eta}
\]

In deriving equations (3.9) and (3.10) the sum over \( k \) was approximated by an integral. The cut-off wave vector, \( k_c \), is introduced to avoid divergence of the equilibrium averages of the even moments of \( n_x \) and \( n_y \). In fact the director is a vector of unit length, so that moments of its components cannot have values greater than unity. Therefore, the need for the cut-off is a direct consequence of the small DF approximation. It is not caused by the breakdown of the continuum model for small wavelengths, which is the motivation generally given to introduce \( k_c \).

In the next section we use the above derived probabilities to calculate the time–correlation functions \( C_{kl}(t) \) of Section 2.

4. Time-Correlation Functions

Having obtained the stochastic properties of director fluctuations in the small DF approximation, the time correlation functions can be calculated. The (transition) probability is expressed in \( n_x \) and \( n_y \) only. Therefore, the correlation functions must also be expressed in these terms.

First we use the well-known relations between Wigner rotation matrices and vector components [42]:

\[
D_{00}^2 = \frac{3}{2} \left( n_x^2 - \frac{1}{3} \right)
\]

\[
D_{\pm 10}^2 = \mp \sqrt{\frac{3}{2}} \left( n_x n_x \pm in yn_x \right)
\]

\[
D_{\pm 20}^2 = \frac{1}{2} \sqrt{\frac{3}{2}} \left( n_x^2 - n_y^2 \mp 2in_x n_y \right)
\]

and subsequently equation (3.2) to obtain the following expressions for the DF correlation functions, equation (2.9):

\[
C_0^3(t) = 1 - 6 \langle n_x^2 \rangle + \frac{9}{2} \langle n_x^2 \rangle^2 + \frac{9}{2} \langle n_x(0)n_x^2(t) \rangle
\]

\[
C_0^4(t) = \frac{3}{2} \sqrt{1 - n_x^2(0) - n_y^2(0)} \sqrt{1 - n_x^2(t) - n_y^2(t)} \left[ n_x(0)n_x(t) + n_y(0)n_y(t) \right]
\]

\[
C_0^2(t) = \frac{3}{4} \langle n_x^2(0)n_x^2(t) \rangle + \frac{3}{2} \langle n_x(0)n_x(t) \rangle^2 - \frac{3}{4} \langle n_x^2 \rangle^2
\]

In addition use was made of the fact that the \( x \)– and \( y \)–components are independent but have similar statistical properties, as can be seen from the probability distributions.

In the usual derivation, the approximation that the fluctuations are small, equation (3.2), is not only made in the derivation of the probabilities but also in the correlation functions.
Retaining only the terms linear in the $x$- and $y$-components of the director, at times 0 and $t$, the only non-zero correlation function is

$$C^d_1(t) = 3 \langle n_x(0) n_x(t) \rangle = 3\alpha I(t) \tag{4.5}$$

In order to study the frequency-dependent behaviour of $J_2$, we need to include higher order terms. Using the (transition) probability for the DF, we are in principle able to calculate any time-correlation function of the director components. We need not make the small DF approximation in the correlation functions. At first sight, refraining from this approximation may seem a useless exercise, since any difference with previous results is of higher order in the DF, and therefore beyond the small DF approximation. However, is not unreasonable to expect that the assumption of small DF is a much better approximation in the (transition) probability (i.e. in the exponent) than it is in the correlation functions.

For our calculation we use the approach by Vold et al. [23], which relies on a property of Gaussian processes known as Wick’s theorem [43, p. 311]. It states that the average of a product of Gaussian variables may be replaced by the sum of products of averages of all possible pairs of variables. Using Wick’s theorem, $C^d_0$ and $C^d_2$ are easily evaluated,

$$\tilde{C}^d_0(t) \equiv C^d_0(t) - C^d_{0,\text{eq}} = 9 \langle n_x(0) n_x(t) \rangle^2 = 9\alpha^2 I^2(t) \tag{4.6}$$

$$C^d_2(t) = 3 \langle n_x(0) n_x(t) \rangle^2 = 3\alpha^2 I^2(t) \tag{4.7}$$

where we subtracted the equilibrium contribution from $C^d_0(t)$, since eventually we are only interested in the time-dependent behavior.

Equations (4.6) and (4.7) were also obtained by Vold et al. [23]. They did not, however, calculate higher order terms in $C^d_1$. Since $C^d_1$ contains half-integral powers, cf. equation (4.3), we cannot apply Wick’s theorem directly. We therefore expand the square roots as a series in $n_x^2 + n_y^2$. After some tedious algebra we arrive at the following expression

$$C^d_1(t) = \sum_{\nu=0}^\infty \sum_{\mu=2\nu}^\infty A_{\mu,\nu} \alpha^{\mu+1} I^{2\nu+1}(t) \tag{4.8}$$

where $A_{\mu,\nu}$ are numbers, which can be calculated using the appropriate expression in Appendix B. Values of $A_{\mu,\nu}$ up to order 10 in $\alpha$ are also given. For $t = 0$, all terms with $\mu > 1$ cancel ($I(0) = 1$), so for the initial value we find

$$C^d_1(0) = \frac{3}{2} \langle n_x^2(0)(n_x^2(0) + n_y^2(0)) \rangle = 3\alpha - 12\alpha^2 \tag{4.9}$$

which is the correct equilibrium value, within the small DF equilibrium probability distribution. Obviously, this result can only be valid for small $\alpha$, since for $\alpha$ greater than 1/4, $C^d_1(0)$ is negative.

Using equation (4.8) to calculate higher order terms in $C^d_1(t)$ we found that the expression does not converge. This is a consequence of the fact that, in the small DF approximation, there is a small probability to find values for the director greater than unity. As a result, the higher moments of $n_x$ and $n_y$ do not tend to zero but become increasingly larger. These higher moments come to dominate expansion (4.8), even though the original expression, equation (4.3), is not defined for $n_x^2 + n_y^2 > 1$.

5. Spectral Densities

In this section we calculate the spectral densities assuming time scale separation applies, using the time correlation functions from the previous section. Spectral densities for high ordering
are calculated in Appendix A, but, since sums over the director field modes occur in the same way for both models, actually similar functions are obtained, albeit with different prefactors.

Spectral densities are defined as the real part of the Fourier transforms of the full time correlation functions, i.e. including the MCF's, described in the previous sections. From the expansion in equation (4.8) it is straightforward to obtain the formal frequency dependence of \( J_1 \) to any order in \( \alpha \). However, we refrain from doing so since the expansion diverges, as was shown in the previous section, and thus leads to nonsensical results. Instead we choose to calculate \( J_1 \) to second order, to be consistent with \( J_0 \) and \( J_2 \) as obtained from equations (4.6) and (4.7).

For the molecular correlation functions we adopt an isotropic rotational diffusion model in an orienting potential. Since molecular correlation times are usually much shorter than NMR times (the "extreme narrowing limit" applies in all cases) in fact the specific model is not important, since it only contributes to the high frequency limiting behavior and not to the measured frequency dependence of the spectral densities. The following spectral densities are obtained

\[
\begin{align*}
J_0(\omega) &= B_0 \tau + S_0^2 \frac{9 \alpha^2}{\omega_c} \text{Re}[L_2(\omega/\omega_c)] \\
J_1(\omega) &= B_1 \tau + S_0^2 \frac{3 \alpha(1-4\alpha)}{\omega_c} \text{Re}[L_1(\omega/\omega_c)] \\
J_2(\omega) &= B_2 \tau + S_0^2 \frac{3 \alpha^2}{\omega_c} \text{Re}[L_2(\omega/\omega_c)]
\end{align*}
\]

where the functions \( L_1 \) and \( L_2 \) are given by respectively:

\[
\begin{align*}
L_1(z) &= \int_0^1 dx \frac{1}{x^2 - iz} \\
L_2(z) &= \int_0^1 dx \int_0^1 dx' \frac{1}{x^2 + x'^2 - iz}
\end{align*}
\]

The integral of \( L_1 \) can be calculated analytically, and expressed in elementary functions which are commonly used,

\[
L_1(z) = \frac{\pi}{2\sqrt{2x}} [U_+ (1/z) + iU_- (1/z)]
\]

where the functions \( U_\pm \) are the more familiar expressions,

\[
U_\pm (x) = \frac{1}{\pi} \left[ \frac{1}{2} \ln \left( \frac{x \mp \sqrt{2x} + 1}{x \pm \sqrt{2x} + 1} \right) + \arctan(\sqrt{2x} + 1) + \arctan(\sqrt{2x} - 1) \right]
\]

The \( B_m \tau \) are the contributions from the MCF, in the extreme narrowing limit \((\omega \tau \ll 1)\). The relaxation time \( \tau \) is of the order of typical orientational correlation times of the fast molecular motion with respect to the director.

Had we not assumed isotropic rotational diffusion, \( B_m \tau \) would be replaced by a sum over different relaxation times, i.e. \( \sum_q B_{mq} \tau_q \). The \( B_{mq} \) are equilibrium averages of the molecular motions only, cf. equation (2.8). They depend only on the model chosen for the orienting potential acting on the molecule in the static director field [22].

Neglecting second order terms in \( \alpha \) in equation (5.2) yields the conventional expression [30] for the frequency dependence of \( J_1 \),

\[
J_1(\omega) = B_1 \tau + S_0^2 \frac{3 \alpha}{\omega_c} \text{Re}[L_1(\omega/\omega_c)] = B_1 \tau + S_0^2 \frac{3 \pi \alpha}{2\sqrt{2\omega_c}} \frac{U_+(\omega_c/\omega)}{\sqrt{\omega}}
\]
Both equations (5.2) and (5.8) will be used to fit available data to, in Section 7.

6. Initial Values of the Correlation Functions

To get some insight into the behaviour and range of validity of the different results, we plotted the initial value of $C_2^d$: $C_2^d(t = 0)$, as a function of the initial value of $C_1^d$ in Figure 1.

Since the initial values are equilibrium averages, they can be compared to expressions obtained using an equilibrium distribution which does not require the small DF approximation:

$$P(\theta) = \frac{1}{N} e^{-\frac{\theta^2}{2\alpha}}$$  

where $\theta$ indicates the deviation of the director from equilibrium, i.e. from the $z$-axis. This is the simplest function with the correct symmetry reducing to the small DF result when $\alpha$ approaches zero. The initial values of the correlation functions, using this probability distribution are

$$C_0^d(0) - C_0^d(\infty) = \frac{9}{4} \left( 2\alpha^2 + \frac{2\alpha(1 - \alpha)}{N_0(\alpha)} - \frac{4\alpha^2}{N_0^2(\alpha)} \right)$$  

$$C_1^d(0) = \frac{3}{2} \left( -\alpha(1 + 3\alpha) + \frac{6\alpha^2}{N_0(\alpha)} \right)$$  

$$C_2^d(0) = \frac{3}{8} \left( 1 + 2\alpha + 3\alpha^2 - \frac{2\alpha(1 + 3\alpha)}{N_0(\alpha)} \right)$$

where

$$N_0(\alpha) = \int_{-1}^{1} dx \ e^{-\frac{1-x^2}{2\alpha}}$$
Unlike the results for the expansion, these are meaningful for all values of $\alpha$.

From Figure 1 we see that the curve resulting from the expansion to second order is very close to that from the symmetric probability distribution when $C_1^d(0) < 0.15$. The largest value of $\alpha$ consistent with the approximation seems to be of the order of 0.1. The curve strongly deviating from the others corresponds to the mode of calculation in which $C_1^d(0)$ is carried to first, and $C_2^d(0)$ to second order in the expansion in $\alpha$. This curve is such that if a calculation of $C_1^d(0)$ were based on a parameter fit of $C_1^d(0)$, $C_2^d(0)$ would be strongly underestimated compared to the calculation resulting in the solid curve (the symmetric potential). Surely values of $\alpha$ greater than say 0.04 cannot be correct. It is therefore not very surprising that previous attempts to explain the frequency dependence in $J_2$ [11,14], which used the first order expansion in $\alpha$ for $J_1$, failed.

Note that $C_1^d(0)$ is very close to this isotropic limiting value, $1/5$, for relatively small values of $\alpha$, i.e., $\alpha \geq 0.1$. Therefore, unless the time dependence of $C_1^d(t)$ depends strongly on $\alpha$, fitting models to $J_1$ cannot be used to distinguish between different values for $\alpha$, when $\alpha$ is close to 0.1 or larger.

7. Comparison with Experiment

In this section the spectral densities, $J_1$ and $J_2$, calculated above are compared with experimental data obtained from the literature. Additionally a high ordering model based on that by Gertner and Lindenberg [35] is compared to the data. The details of this model can be found in Appendix A. To facilitate referencing in what follows, we briefly summarize the different models, which will be referred to by the abbreviations preceding them.

The following two variants of the model assuming time scale separation are compared with the experimental data.

E1 (expansion 1) This is the method which has previously been used in attempts to account for the frequency dependence in $J_2$ [22,23]. For $J_1$ the conventional expression is used, obtained from an expansion of the correlation function to first order in the DF. However, an expansion to second order is used for $J_2$. The equations for the spectral densities using this model are equation (5.8) for $J_1$, and equation (5.3) for $J_2$.

E2 (expansion 2) In this case both $J_1$ and $J_2$ are calculated using an expansion of the correlation function to second order in the DF. The relevant equations are equation (5.2) for $J_1$, and equation (5.3) for $J_2$. Note that the shape of $J_1(\omega)$ for both E1 and E2 is the same, the difference lies in the magnitude of the pre-factor.

Additionally, two variants of the high ordering model are compared with the experimental data.

GL (Gertner and Lindenberg) The expression used for $J_1$ is found in equation (A.25). $J_2$ is calculated by Fourier transforming the complex equivalent of $J_1$, called $P(\omega)$ in the appendix, squaring the result and transforming back.

HS (high ordering, symmetric potential) A slightly different model which avoids changes in the equilibrium distribution of the director due to the addition of a single probe molecule. The relevant equation for $J_1$ is (A.17), $J_2$ is calculated in the same manner as for GL.

Experimental data on the frequency dependence of $J_1$ is scarce, and the frequency dependence of $J_2$ received even less attention. This is reflected in Tables I and II, in which all usable data is compiled, including data for which measurements at only two NMR frequencies were
Table I. — The experimental systems, liquid crystals and probe molecules, used for comparison with calculated spectral densities. Given are, the temperature, $T$, at which spectral densities have been determined; the order parameter, $S$, at this temperature; the nematic to isotropic transition temperature, $T_{NI}$ (if available); the number of different NMR frequencies; the reference from which the data was obtained.

<table>
<thead>
<tr>
<th>System</th>
<th>probe</th>
<th>LC</th>
<th>$T$ (K)</th>
<th>$S$</th>
<th>$T_{NI}$ (K)</th>
<th>freqs.</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>BBA</td>
<td>MBBA</td>
<td>296</td>
<td>0.421</td>
<td>324</td>
<td>2</td>
<td>[23]</td>
</tr>
<tr>
<td>B</td>
<td>toluene</td>
<td>Ph V</td>
<td>304.7</td>
<td>0.139</td>
<td>324.5</td>
<td>5/3(3)</td>
<td>[15]</td>
</tr>
<tr>
<td>C</td>
<td>tolane</td>
<td>Ph V</td>
<td>304.3</td>
<td>0.281</td>
<td>304.9</td>
<td>5</td>
<td>[16]</td>
</tr>
<tr>
<td>D</td>
<td>DCCCN</td>
<td>Ph V</td>
<td>303</td>
<td>0.117</td>
<td>3</td>
<td>3</td>
<td>[6]</td>
</tr>
<tr>
<td>E</td>
<td>DEB</td>
<td>Ph V</td>
<td>304.9</td>
<td>0.326</td>
<td>3</td>
<td>3</td>
<td>[23]</td>
</tr>
<tr>
<td>F(1)</td>
<td>DCCCN</td>
<td>Ph V</td>
<td>303</td>
<td>0.114</td>
<td>3</td>
<td>3</td>
<td>[7]</td>
</tr>
<tr>
<td>G(1)</td>
<td>DEB</td>
<td>Ph V</td>
<td>303</td>
<td>0.330</td>
<td>3</td>
<td>3</td>
<td>[8]</td>
</tr>
<tr>
<td>H(2)</td>
<td>toluene</td>
<td>Ph V</td>
<td>304.7</td>
<td>0.139</td>
<td>324</td>
<td>4</td>
<td>[15]</td>
</tr>
<tr>
<td>I(2)</td>
<td>p-xylene</td>
<td>Ph V</td>
<td>304.7</td>
<td>0.262</td>
<td>329.5</td>
<td>5</td>
<td>[18]</td>
</tr>
</tbody>
</table>

(1) Same systems as in D and E, where spectral densities were given as a function of frequency. In F and G they were calculated from tables with temperature dependent data.

(2) Systems for which the local deuteron frame does not coincide with the molecular frame.

(3) For $J_1$ and $J_2$ respectively.

reported. Table I specifies the systems to which the data refer, some of their properties and the reference from which they are obtained, Table II contains the actual data. For most of these systems the principal axis of the local frame of the deuteron and the principal axis of the molecular frame coincide. However, as mentioned in the introduction, two systems are included in which the local and molecular frames have different principal axes (H and I).

In comparing the spectral densities for the systems in table I to results from the various theoretical models, emphasis was on the frequency dependence. The following method was used in this comparison. First, the model equations for $J_1$ were fitted to the experimental data on $J_1$, at fixed cut-off frequency, $\omega_c$. Subsequently, the fitted parameters were substituted in the equations for $J_2$ and compared with the experimental data on $J_2$. This was repeated for several different $\omega_c$ values. The parameter $\omega_c$ was not used as a regular fit parameter because the result of the fit is generally not very critical of its value. Especially when $\omega_c$ is larger than the highest NMR frequency for the system considered, convergence can be very slow since in that case $U_+ (\omega_c/\omega) \approx 1$.

The described method was preferred over the more straightforward approach of simultaneously fitting the data for $J_1$ and $J_2$, because it could be applied to all models in the same manner. The background for this is that simultaneous fits for the high ordering models are very impractical, as they require very large computer resources. For models E1 and E2 some simultaneous fits were carried out. The results of which were, within experimental error, identical to those obtained using the above-described method. This is caused by the relatively large uncertainty in the $J_2$ data, resulting in fits dominated by the $J_1$ data.

Plots of $J_1$ and $J_2$ for system C gave the impression that the lowest frequency data may be wrong. This is not unlikely, since the experimental signal-to-noise ratio increases with magnetic field strength, and thus with the frequency. Since the spectral densities for system C
Table II. — The experimental spectral density data which was used to test the calculations. The figures in parenthesis are estimated errors.

<table>
<thead>
<tr>
<th>System</th>
<th>$\nu_0$ (MHz)</th>
<th>$J_1$ (ps)</th>
<th>$J_2$ (ps)</th>
<th>System</th>
<th>$\nu_0$ (MHz)</th>
<th>$J_1$ (ps)</th>
<th>$J_2$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>15.40</td>
<td>480 (50)</td>
<td>140 (14)</td>
<td>F</td>
<td>4.60</td>
<td>21.4 (1.0)</td>
<td>6.8 (0.5)</td>
</tr>
<tr>
<td></td>
<td>38.40</td>
<td>256 (20)</td>
<td>78 (8)</td>
<td></td>
<td>9.20</td>
<td>17.4 (0.4)</td>
<td>7.25 (0.3)</td>
</tr>
<tr>
<td>B</td>
<td>27.60</td>
<td>14.1</td>
<td></td>
<td></td>
<td>38.40</td>
<td>11.7 (0.3)</td>
<td>6.4 (0.2)</td>
</tr>
<tr>
<td></td>
<td>30.70</td>
<td>13.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.40</td>
<td>11.6</td>
<td>5.4</td>
<td></td>
<td>9.20</td>
<td>116 (1.7)</td>
<td>22.9 (0.7)</td>
</tr>
<tr>
<td></td>
<td>61.40</td>
<td>10.1</td>
<td>5.24</td>
<td></td>
<td>38.40</td>
<td>67.7 (1.3)</td>
<td>19.9 (0.7)</td>
</tr>
<tr>
<td></td>
<td>76.80</td>
<td>9.2</td>
<td>4.87</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>15.50</td>
<td>156</td>
<td>63</td>
<td></td>
<td>38.40</td>
<td>1.34</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>30.70</td>
<td>136</td>
<td>55</td>
<td></td>
<td>61.40</td>
<td>1.09</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>38.40</td>
<td>124</td>
<td>47</td>
<td></td>
<td>76.80</td>
<td>1.03</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>61.40</td>
<td>107</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>76.80</td>
<td>100</td>
<td>37</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>4.60</td>
<td>23.5 (0.9)</td>
<td>8.0 (1.0)</td>
<td></td>
<td>38.40</td>
<td>3.35</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>9.20</td>
<td>17.7 (0.5)</td>
<td>7.3 (0.4)</td>
<td></td>
<td>61.40</td>
<td>2.72</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>38.40</td>
<td>12.0 (0.8)</td>
<td>6.4 (0.5)</td>
<td></td>
<td>76.80</td>
<td>2.51</td>
<td>0.79</td>
</tr>
<tr>
<td>E</td>
<td>4.60</td>
<td>142 (6)</td>
<td>24 (2)</td>
<td></td>
<td>30.70</td>
<td>3.93</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>9.20</td>
<td>107 (7)</td>
<td>22 (2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.40</td>
<td>65 (2)</td>
<td>19 (2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

were measured at a relatively large number of different frequencies (five), we have fitted both with and without the lowest frequency data.

7.1. The ratio $\Delta J_2/\Delta J_1$. — Before going into more detail, a very crude general impression of the measured frequency dependence for the systems in table I is obtained by plotting $\Delta J_2/\Delta J_1$ as a function of the order parameter, $S$, see Figure 2. The ratio $\Delta J_2/\Delta J_1$, where $\Delta J_2 = J_2(n\omega_{\text{min}}) - J_2(n\omega_{\text{max}})$, can be considered as a rough estimate of the ratio of the frequency dependent parts of $J_2$ and $J_1$.

If the time scale separation approximation holds, and the effect of dissolving probe molecules on the slow (director) fluctuations is small, we see from equation (2.8) that $\Delta J_2/\Delta J_1$ should only depend on the liquid crystal used as a solvent. Except for A, all systems in table I have the same solvent. Keeping in mind the crudeness of the comparison, $\Delta J_2/\Delta J_1$ for this solvent varies little, in line with our prediction, with the exception of systems B and C, for which the ratio is unmistakably larger.

For the models E1 and E2 a range of values for the ratio $\Delta J_2/\Delta J_1$ can be given which is in agreement with the approximations on which these models are based. From equations (5.2) and (5.3) we find for E2 that

$$\frac{J_2^2(2\omega)}{J_1^4(\omega)} = \frac{\alpha}{1 - 4\alpha} \frac{I_2(2\omega/\omega_c)}{I_1(\omega/\omega_c)}$$

(7.1)

Because $I_2(2x)/I_1(x) < 1$, this results in $J_2^2(2\omega)/J_1^4(\omega) < \alpha/(1 - 4\alpha)$. From the initial values...
of the correlation functions it was concluded that $\alpha$ should be smaller than 0.1. In Figure 2 the line corresponding to the upper-bound for $J_2^2(2\omega)/J_i^2(\omega)$, with $\alpha < 0.1$, is drawn (dashed). For E1 a similar argument shows $J_2^2(2\omega)/J_i^2(\omega) < \alpha$. In this model the upper-bound for $\alpha$ is 0.04; the line corresponding to this is also included (dotted).

Most of the systems considered have ratios, $\Delta J_2/\Delta J_1$, between the dashed and dotted lines in Figure 2. This indicates that an explanation of the frequency dependence in $J_2$ in terms of E1 is quite unlikely, but may be possible using E2.

7.2. FITTING OF $J_1(\omega)$. — For models E1 and E2 $J_1$ was fitted using the following equation

$$J_1(\omega) = A_1 + \frac{A_2}{\sqrt{\omega}} U_+(\omega_c/\omega)$$

Satisfactory fits were generally obtained for $\omega_c > 10^8$. In the top two graphs of Figure 3 some typical results of fitting are shown, for systems B and E.

From the values of the fit parameters $A_1$ and $A_2$, the cut-off frequency, $\omega_c$ and the order parameter, $S$, values for $\alpha$ were obtained. This is discussed separately for the two models.

E1 $\alpha$ was obtained by comparing equations (7.2) and (5.8). Since corrections to the order parameter from director fluctuations are small [22], we may replace the order parameter
Fig. 3. — Some examples of fits of $J_2(\omega)$ at different fixed $\omega_c$ to experimental data. For systems B (left) and E (right). The top graphs are for the traditional model (using time scale separation) and the bottom graphs for the high ordering model.

$S_0$ with the experimentally obtained order parameter, $S$. The value for $\alpha$ in each system generally has a minimum when $\omega_c$ is close to the lowest value resulting in an acceptable fit. For large $\omega_c$, outside the experimental NMR frequency range, $\alpha$ is proportional to $\omega_c$. Since these large values for $\omega_c$ generally result in acceptable fits, $\alpha$ can be arbitrarily large. The minimum value of $\alpha$, for each system, is given in the second column of table III. As noted above, the expression used to calculate $\alpha$ is only valid for small $\alpha$ ($\alpha < 0.04$). The range of values of $\omega_c$ which both produce acceptable fits and fulfill $\alpha < 0.05$ is given in the third column of table III.

E2 $\alpha$ was obtained using equation (5.2),

$$\alpha = \frac{1}{8} - \sqrt{\frac{1}{64} - \frac{\sqrt{2\omega_c}}{6\pi S^2} A_2}$$

(7.3)

No value of $\alpha$ could be found for systems A, B, and C, since the value in the square root was negative for fits at all $\omega_c$. For these systems $A_2$ is larger than expected on the basis of this model. For the other systems (D-I) a range of values for $\omega_c$ was found for which the results comply with the small DF approximation. The E2-results are summarized in the fourth and fifth columns of table III.
Table III. — The minimum values of $\alpha$, found by fitting the $J_1$ data by models E1 and E2. The range of values for which $\alpha$ is within the small director fluctuation approximation is given in the columns denoted by ($\omega_c$).

<table>
<thead>
<tr>
<th>Syst.</th>
<th>$\alpha_{min}$ ($\omega_c$) $\times 10^8$</th>
<th>E1</th>
<th>$\alpha_{min}$ ($\omega_c$) $\times 10^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.064</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1)</td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>0.027 1-7</td>
<td>0.030 1-7</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>0.025 1-7</td>
<td>0.027 1-10</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>0.03 2-7</td>
<td>0.035 2-10</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>0.03 2-7</td>
<td>0.036 2-10</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.06</td>
<td>0.1 5</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>0.05 4-8</td>
<td>0.07 4-8</td>
<td></td>
</tr>
</tbody>
</table>

(1) when the lowest frequency data is ignored, $\alpha_{min} = 0.13$

The high ordering models, GL and HS, are only directly applicable to systems A through G. To apply them to systems H and I requires a model for the dynamics of the probe molecule about its principal axis. This would result in one or more extra fit parameters. In view of the already small number of data points, more parameters make it even more difficult to obtain reliable information on the director fluctuation contribution. We have therefore refrained from fitting the high ordering models to the experimental $J_1$ for systems H and I. Also, no fit was attempted for system A, as only two data points are available.

Three fit parameters are necessary for fits using the high ordering models, $A$, $\tau$, and $\omega_c$ (kept fixed). The variables $B$, equation (A.16), and $B'$, equation (A.21), can be expressed in these parameters, and $1/\beta\lambda$ can be expressed in the order parameter, $S = 1 - \frac{3}{2}(\langle p_2^2 \rangle + \langle p_3^2 \rangle)$, and $B$ (or $B'$) since

$$\langle p_i^2 \rangle = \frac{1 - S}{3} = \begin{cases} 
\frac{B}{\beta\lambda} & \text{for HS} \\
\frac{1}{\beta\lambda B'} & \text{for GL}
\end{cases}$$ (7.4)

From this we see that for parallel probe orientation $\beta\lambda$ is always greater than 3, however low the ordering, since the minimum value for $B$ (the maximum for $B'$) is one. This is surprising, as one may think that $\beta\lambda = 3$ already fulfills the condition for high ordering. However, for a high ordered probe $\langle p_i^2 \rangle$ should be small, certainly $\langle p_i^2 \rangle \leq 0.2$ should hold, in which case we find that $\beta\lambda$ should actually be greater than 5. The second column in table IV contains the value of $\langle p_3^2 \rangle$, calculated from the order parameters. From these values it is clear that none of the systems, except possibly A, can be considered high ordered. In spite of this, $J_1$ has been fitted successfully in such systems using a high ordering model [35]. Since it is possible that good fits are obtained even when the parameters are not within the required range, as was found to occur for the models in the time scale separation limit, we too have performed some fits. We found that the fits to $J_1$ from HS and GL were indistinguishable. In the bottom two graphs of Figure 3 some are shown. From the figure it is seen that the fits for all models have the same appearance.
Table IV. — Values of some relevant constants obtained from the order parameter alone. The first column applies to high ordering. The second and third columns contain the constants $B_1$ and $B_2$ of equations (5.2) and (5.3), assuming isotropic rotational diffusion.

<table>
<thead>
<tr>
<th>Syst.</th>
<th>$\langle p_x^2 \rangle$</th>
<th>$B_1$</th>
<th>$B_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.193</td>
<td>0.1990</td>
<td>0.0622</td>
</tr>
<tr>
<td>B</td>
<td>0.287</td>
<td>0.2196</td>
<td>0.1457</td>
</tr>
<tr>
<td>C</td>
<td>0.240</td>
<td>0.2190</td>
<td>0.0992</td>
</tr>
<tr>
<td>D</td>
<td>0.295</td>
<td>0.2179</td>
<td>0.1538</td>
</tr>
<tr>
<td>E</td>
<td>0.225</td>
<td>0.2146</td>
<td>0.0864</td>
</tr>
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<td>F</td>
<td>0.295</td>
<td>0.2176</td>
<td>0.1548</td>
</tr>
<tr>
<td>G</td>
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<td>0.2141</td>
<td>0.0853</td>
</tr>
<tr>
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Table V. — Parameters obtained from fits to $J_1$, for the models using time scale separation ($E1$ and $E2$), for which the calculated $J_2$ are closest to experimental values.

<table>
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<th>$\tau$ (ps)</th>
<th>$\alpha$</th>
<th>$\omega_c$ (s$^{-1}$)</th>
<th>$\tau$ (ps)</th>
<th>$\alpha$</th>
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<tr>
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<td>0.061</td>
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7.3. Comparison of Model Calculations and Experimental Data of $J_2(\omega)$. — Using the parameters from the fits of $J_1(\omega)$ for all models, $J_2(\omega)$ was calculated.

First we consider the time scale separation model for systems D through I, for which values of $\alpha$ within the small DF approximation were obtained from the fits to $J_1$. Only such values were considered in calculating $J_2$. For models $E1$ and $E2$, curves obtained from the calculations of $J_2$ are shown in Figure 4. As explained, the $J_1$ data were fitted for several fixed values of $\omega_c$. In Figure 4 the calculated curves for $J_2$ are shown which are closest to the experimental data. These curves are not necessarily the best possible, but in view of the large experimental errors we need not bother about optimizing the agreement at this stage. The parameters corresponding to the shown curves are found in table V.

From Figure 4 we see that the frequency dependence in $J_2$ for $E1$ is too small, as was pointed out before [11,14]. The extended model $E2$, however, results in curves with frequency dependent contributions of the correct order of magnitude.

For systems A, B and C the parameters from the $J_1$ fits to the data were all outside the small DF approximation. Thus the data cannot be explained using $E1$ or $E2$. 

For the high ordering models there is hardly any frequency dependence in \( J_2 \), using parameters from fits of \( J_1 \). For HS some typical curves at different \( \omega_c \) are also shown in Figure 4. The results of GL are similar.

8. Summary and Conclusions
We have investigated and modified models for the orientational dynamics of individual molecules in nematic liquid crystals. This was motivated by difficulties in explaining the frequency
dependence of spectral density $J_2(\omega)$ obtained from NMR relaxation experiments. The models studied can be characterized by three approximations. All are within the small director fluctuation approximation. Apart from this the models either assumed the dynamics of individual molecules to be fast compared to director dynamics (time scale separation), or the molecular orientation to be only slightly different from the director orientation (high ordering).

In the first part we summarized the crucial steps in calculating spectral densities within time scale separation (the most commonly used model). We found that including terms to second order in the strength of director fluctuations, $\alpha$, in $J_1(\omega)$ results in much better agreement of $J_2(\omega)$ with data from NMR relaxation experiments than has been previously obtained.

Based on the comparison of the experimental and theoretical spectral densities in the second part of the paper, it appears as if any model incorporating small director fluctuations can be used to account for the $J_1$ frequency dependence. In contrast, the frequency dependence in $J_2$ turns out very useful to differentiate between models, even though the experimental data is not as accurate as the data for $J_1$. By using the frequency dependence in $J_2$, we could eliminate high ordering models (described in Appendix A) as a satisfactory description of the considered experiments. And as in previous attempts to explain the frequency dependence in $J_2$ [22,23], the conventional model (E1) is also found to be inadequate. This is not unexpected on the basis of the results obtained in the first part of this paper. Only the extended model (E2) shows reasonable agreement with the experimental results for both $J_1$ and $J_2$. Though there remain some experiments for which the frequency dependence in $J_2$ is larger then can be accounted for.

A short comment on the values of the cut-off wavelength, $\lambda_c$, is in order. From table V we see that $5 \times 10^8 \text{s}^{-1} < \omega_c < 10^9 \text{s}^{-1}$ Using typical values for the elastic constant (5 pN), and the effective viscosity (0.06 Pa s), we find that $\lambda_c$ is 15 to 30 Å. This once again shows the cut-off wavelength to be of the order of the length of a liquid crystal molecule. It it also consistent with the Gaussian approximation cf. Section 3, which requires (using the same numbers) that $\lambda_c \gg 5$ Å.

Unfortunately, spectral density $J_1$ cannot be calculated to arbitrary order in $\alpha$ because of a divergence due to the small director fluctuation approximation (it results in a small but finite probability for director fluctuations larger than unity). In order to deal with this property we would need to include an interaction between the different director modes, resulting from the normalization condition of the director. In that case the director modes can no longer be assumed independent, resulting in an intricate nonlinear problem, which we do not address in this paper.

There appear to be two directions to continue the study of the frequency dependence of the spectral densities. One is by considering more realistic interactions between the probe molecule and the liquid crystal. The other by allowing larger director fluctuations. The latter seems more promising for a number of reasons. First of all, simple estimates and the frequency dependence of $J_1$ indicate that the time scale separation approximation is quite good even for relatively high ordered probe molecules. In which case the form of the interaction is of no importance, as we have shown above. If the time scale separation approximation were not to hold, we would rather expect the high ordering model to do better. Finally, from the form of the correlation functions, equations (4.2)–(4.4), it is clear that larger director fluctuations will enhance the frequency dependence in $J_2$ more than that in $J_1$, as is needed to account for some of the experiments. This is due to $C_2$ being to lowest order quadratic in the fluctuations, whereas the quadratic term in $C_1$ is negative, reducing the effect of larger fluctuations. As remarked above, extending the calculations to allow for arbitrary director fluctuations are not straightforward. One is quickly convinced to adopt computer simulation techniques. Such an
approach, using a lattice model with Langevin type dynamics, shows that indeed the effect of larger fluctuations is mainly to \( J_2(\omega) \) [44].

**Appendix A**

**High Ordering Models**

A model for an axially symmetric molecule strongly coupled to the director field has been proposed by Gertner and Lindenberg (GL) [35]. In contrast to the above calculations, in this model separation of time scales is not a necessary ingredient. However, it is applicable only to molecules for which the motion closely resembles that of the director field, and which consequently have a high molecular order parameter. In this appendix we will discuss both the GL model, and a slightly modified one, based on the notion that the equilibrium distribution for the director fluctuations should not change if a single probe molecule is dissolved in the nematic.

For a probe strongly coupled to the director, the interaction energy may be approximated by the quadratic term in its expansion in the angle \( \gamma \) between the director, \( \mathbf{n} \), and the principal axis of the molecule, \( \mathbf{p} \). Like GL we consider here molecules for which it is favourable to orient parallel to the director. The interaction energy may in this case be written as

\[
U_{\text{int}}(\mathbf{n}, \mathbf{p}) = \frac{\lambda}{2} \sin^2 \gamma + O(\sin^4 \gamma) \approx \frac{\lambda}{2}(\mathbf{n} - \mathbf{p})^2 \tag{A.1}
\]

As in the case of low ordering the director fluctuations are assumed to be small, and the laboratory \( z \)-axis is chosen along the average director. Because the interaction between the probe and the director is strong, they will be nearly parallel at all times. Therefore, the small DF approximation, equation (3.2), may be applied together with a similar approximation for the probe, \( p_z \approx 1 - 1/2(p_x^2 + p_y^2) \). Retaining only terms in equations (A.1) and (3.1) to quadratic order in the \( x \)– and \( y \)-components of \( \mathbf{n} \) and \( \mathbf{p} \), and subsequent spatial Fourier transformation of the expression for the director field, the free energy of the combination probe–director field becomes

\[
F = \frac{1}{V} \sum_k \frac{K k^2}{2} \left\{ |n_x(k)|^2 + |n_y(k)|^2 \right\} + \frac{\lambda}{2} \left\{ \left( \frac{1}{V} \sum_k n_x(k) - p_x \right)^2 + \left( \frac{1}{V} \sum_k n_y(k) - p_y \right)^2 \right\} \tag{A.2}
\]

To obtain this equation we also have replaced \( \text{Re}[n_{z,y}(k)] \) by \( n_{z,y}(k) \). The imaginary part of \( n_{x,y}(k) \) does not couple to \( \mathbf{p} \), and may therefore be omitted. Again all modes are assumed to be independent, and the range of values for the \( x \)- and \( y \)-components of \( \mathbf{n} \) and \( \mathbf{p} \) is extended to infinity. The free energy in (A.2) then describes a system of coupled harmonic oscillators. Except for a normalization constant, the equilibrium probability distribution for the \( x \)- and \( y \)-components of \( \mathbf{n} \) and \( \mathbf{p} \), corresponding to this free energy, is,

\[
P_{\text{eq}}\left\{ n_i(k) \right\}, p_i = \exp \left[ -\beta \left\{ \frac{1}{V} \sum_{i,k} \frac{K k^2}{2} n_i(k)^2 + \frac{\lambda}{2} \left( \frac{1}{V} \sum_{i,k} n_i(k) - p_i \right)^2 \right\} \right] \tag{A.3}
\]

where in the sums \( i \) can take the values \( x \) and \( y \) and \( \left\{ n_i(k) \right\} \) denotes the complete set of director field modes.

In order to calculate the spectral densities, we also need to specify the dynamics of the system. For this purpose Langevin equations consistent with the above free energy are used.
In the over-damped limit these are

\[
\eta_k \frac{\partial n(k, t)}{\partial t} = -Kk^2n(k, t) - \lambda \left( \frac{1}{V} \sum_k n(k, t) - p(t) \right) + f_k(t) \tag{A.4}
\]

\[
\gamma \frac{\partial p(t)}{\partial t} = -\lambda \left( p(t) - \frac{1}{V} \sum_k n(k, t) \right) + g(t) \tag{A.5}
\]

To derive this, we assumed that the probe molecule remains located at the origin of the coordinate frame.

Since the \(x\)- and \(y\)-components are independent and obey the same equations, we could leave out the component index. The variables \(f_k(t)\) and \(g(t)\) are fluctuating forces with the usual Gaussian properties, and which are, by fluctuation-dissipation theorems, related to the viscosities ("friction coefficients") \(\eta_k\) and \(\gamma\).

For \(\lambda = 0\), i.e. no probe, equation (A.4) is equivalent to the transition probability for the director modes, cf. equation (3.6).

After Laplace transforming, substituting \(1/V \sum_k n(k, s) - p(s)\) from the second equation into the first, formally solving that for \(n(k, s)\) and subsequently substituting into the second, we obtain the following equation for \(p(s)\)

\[
\gamma [sp(s) - p_0] = -\lambda \left( p(s) - \frac{1}{V} \sum_k \eta_k n_0(k) - \gamma [sp(s) - p_0] + g(s) + f_k(s) \right) + g(s) \tag{A.6}
\]

where quantities with subscript 0 denote initial conditions.

Equation (A.6) may be used to calculate spectral density component \(J_1\), since for small fluctuations \(J_1(\omega) \approx 3\Re\langle p_0 p(-i\omega)\rangle\), and the high order model is only applicable when fluctuations are very small. Therefore, in contrast to the case of time scale separation this should always be a good approximation here. We now define the complex quantity

\[
P(\omega) = \langle p_0 p(-i\omega) \rangle \tag{A.7}
\]

which will also be used in calculating \(J_2\). Realizing that initial values and fluctuating torques are not correlated, we obtain

\[
P(\omega) = \gamma < p_0^2 > \left( 1 + \frac{\lambda}{V} \sum_k \frac{1}{-i\omega \eta_k + Kk^2} \right) + \gamma \left( 1 + \frac{\lambda}{V} \sum_k \frac{1}{-i\omega \eta_k + Kk^2} \right) - i\omega \gamma \left( 1 + \frac{\lambda}{V} \sum_k \frac{1}{-i\omega \eta_k + Kk^2} \right) + \lambda \tag{A.8}
\]

where we used the following equilibrium averages obtained from equation (A.3)

\[
\langle n(k)n(k') \rangle = \frac{V}{\beta K k^2} \delta_{k, k'} \tag{A.9}
\]

\[
\langle p^2 \rangle = \frac{1}{\beta \lambda} + \frac{1}{\beta K V} \sum_k \frac{1}{k^2} = \frac{1}{\beta \lambda} + \alpha \tag{A.10}
\]

\[
\langle n(k)p \rangle = \frac{1}{\beta K k^2} \tag{A.11}
\]
Using the generally accepted approximation that the viscosity, $\eta$, is independent of $k$, and replacing the sums over $k$ by integrals, the sums in equation (A.8) become,

$$\frac{\lambda}{V} \sum_k \frac{1}{-i\omega + Kk^2} \to A \left\{ \sqrt{\omega} \frac{2\sqrt{2}}{\pi} \left( -\sqrt{\omega} U_-(\omega_c/\omega) + i\sqrt{\omega} U_+(\omega_c/\omega) \right) \right\}$$

(A.12)

and

$$\frac{\lambda}{V} \sum_k \frac{1}{\beta Kk^2} \frac{1}{-i\omega + \frac{Kk^2}{\eta}} \to \frac{1}{\beta} \frac{A}{\sqrt{\omega}} \left[ U_+(\omega_c/\omega) + iU_-(\omega_c/\omega) \right]$$

(A.13)

where the quantity $A$ is defined as:

$$A = \frac{\lambda}{4\pi R} \sqrt{\frac{\eta}{2K}} = \frac{\pi}{2} \beta \lambda \frac{\alpha}{\sqrt{2\omega_c}}$$

(A.14)

For the definitions of $U_+$ and $U_-$ see equation (5.7). To avoid divergence of the first sum, a cut-off wave vector $k_c$ was introduced as before. Using these expressions for the sums, with $\tau = \gamma/\lambda$, equation (A.8) may be written as

$$P(\omega) = \frac{1}{\beta\lambda} \left[ (1 + \omega \tau A \sqrt{\omega} U_+(\omega_c/\omega))^2 + (\omega \tau)^2 [B - A \sqrt{\omega} U_-(\omega_c/\omega)]^2 \right]^{-1}$$

$$\times \left\{ \tau B^2 + \frac{A}{\sqrt{\omega}} U_+(\omega_c/\omega) - 2\tau BA \sqrt{\omega} U_-(\omega_c/\omega) + \omega \tau A^2 [U_2^2(\omega_c/\omega) + U_+^2(\omega_c/\omega)] \right\}$$

$$+ i \left\{ \omega^2 B^3 + \left( \frac{1}{\sqrt{\omega}} - 2\omega^{3/2} \tau^2 B^2 \right) A U_-(\omega_c/\omega) \right\}$$

$$+ 2\tau BA \sqrt{\omega} U_+(\omega_c/\omega) + \omega^2 \tau^2 B^2 [U_2^2(\omega_c/\omega) + U_+^2(\omega_c/\omega)] \right\}$$

(A.15)

where

$$B = 1 + \frac{\lambda k_c}{2\pi^2 R} = 1 + \alpha \beta \lambda$$

(A.16)

Since $J_1(\omega) = 3 \text{Re}[P(\omega)]$, we get

$$J_1(\omega) = \frac{3}{\beta\lambda} \left\{ \tau B^2 + \frac{A}{\sqrt{\omega}} U_+(\omega_c/\omega) - 2\tau BA \sqrt{\omega} U_-(\omega_c/\omega) + \omega \tau A^2 [U_2^2(\omega_c/\omega) + U_+^2(\omega_c/\omega)] \right\}$$

$$\times \left[ (1 + \omega \tau A \sqrt{\omega} U_+(\omega_c/\omega))^2 + (\omega \tau)^2 [B - A \sqrt{\omega} U_-(\omega_c/\omega)]^2 \right]^{-1}$$

(A.17)

Equation (A.17) is somewhat different from the one derived by GL. In their calculations the interaction energy, equation (A.1), is expanded to second order in the $x$- and $y$-components of $p$, but only to first in those of $n$. The free energy then obtained, instead of (A.2), is

$$F = \frac{1}{V} \sum_k \frac{Kk^2}{2} \left\{ |n_x(k)|^2 + |n_y(k)|^2 \right\} + \frac{\lambda}{2} (p_x^2 + p_y^2) - \frac{\lambda}{V} \sum_k (n_x(k)p_x + n_y(k)p_y)$$

(A.18)

To remain consistent with the free energy, the first Langevin equation, (A.4) has to be replaced by

$$\eta \frac{\partial n(k,t)}{\partial t} = -Kk^2 n(k,t) + \lambda p(t) + f_k(t)$$

(A.19)
In a manner similar to above we obtain

\[
P(\omega) = \frac{1}{\beta \lambda B'} \left\{ [B' + A\sqrt{\omega}U_-(\omega_c/\omega)]^2 + [\omega \tau + A\sqrt{\omega}U_+(\omega_c/\omega)]^2 \right\}^{-1} \{B'(\tau + \frac{A}{\sqrt{\omega}}U_+(\omega_c/\omega))
\]

\[+i\{\omega \tau^2 + 2\tau A\sqrt{\omega}U_+(\omega_c/\omega) + \frac{B'A}{\sqrt{\omega}}U_-(\omega_c/\omega) + A^2[U_+^2(\omega_c/\omega) + U_-^2(\omega_c/\omega)] \} \}
\]

where

\[B' = 1 - \frac{\lambda \kappa_c}{2\pi^2 K} = 1 - \alpha \beta \lambda \]  

The following averages obtained from equation (A.18) were used,

\[
\langle p_i^2 \rangle = \frac{1}{\beta \lambda B'} \]  

\[
\langle n_i(k)p_i \rangle = \frac{1}{\beta K_k B'} \]  

\[
\langle n_i(k)n_i(k') \rangle = \frac{V}{\beta K_k^2} \delta_k,k' + \frac{1}{\beta K_k^2 k'^2 B'} \]

Notice that these averages diverge when \(\alpha \rightarrow 1/\beta \lambda\). The free energy in equation (A.2) avoids this problem. Spectral density \(J_1\) now is

\[
J_1(\omega) = \frac{3}{\beta \lambda} \left\{ \tau + A\sqrt{\omega}U_+(\omega_c/\omega) \right\} \left\{ (\omega \tau + A\sqrt{\omega}U_+(\omega_c/\omega))^2 + (B' + A\sqrt{\omega}U_-(\omega_c/\omega))^2 \right\}^{-1} \]

Apart from the notation, this is the result obtained by Gertner and Lindenberg.

So far we have assumed the friction as being defined with respect to the laboratory frame. However, it may be argued that the friction should be with respect to the difference in angular velocities of the probe and of the director field. This has of course no effect on the equilibrium properties, only on the dynamics. The spectral densities can be obtained in a manner similar to what we have just done [44]. Here it is sufficient to note that the results are, over a large range of values for the parameters, hardly distinguishable from those of the modified high ordering model described above.

In the special case that \(\tau^2 \omega^2 \ll 1\) (extreme narrowing) and \(A\sqrt{\omega} \ll 1\), both expressions for \(J_1\), equations (A.17) and (A.25) reduce to the same form

\[
J_1(\omega) \approx \frac{3}{\beta \lambda} [\tau' + A'/\sqrt{\omega}U_+(\omega_c/\omega)] \]

where

\[
\tau' = \tau B^2 \quad A' = A \quad \text{for equation (A.17)} \]  

\[
\tau' = \tau/B' \quad A' = A/B' \quad \text{for equation (A.25)} \]

Note that equation (A.26) has precisely the form of \(J_1\) when time scale separation applies, equation (5.2). This observation supports our idea that in practice the precise probe dynamics is of no real importance to the frequency dependence of \(J_1\).

Figure 5 shows the frequency dependence of \(J_1\) for the high ordering models together with that for the time scale separation model (only calculated in the extreme narrowing limit), for some different values of the parameters. The frequency range in Figure 5 is the one currently available for deuterium NMR experiments. For the graph shown in the top left corner of
Figure 5, the parameters are just within the mentioned limits ($\tau^2 \omega^2 \ll 1$ and $A \sqrt{\omega} \ll 1$). In the top right corner the extreme narrowing condition does not hold, in the bottom left corner $A \sqrt{\omega} \ll 1$ is false, and in the bottom right corner neither limit applies. The difference in $J_1$ by GL and the remaining $J_1$ in the bottom two figures, is a consequence of the divergence in $\langle \hat{p}^2 \rangle$. For the modified high ordering model, $J_1$ is very close to the time scale separation results (considering that extreme narrowing is implied in the latter).

So far we concentrated on $J_1$. However, our aims include comparing calculations of $J_2$ to experimental data. Since all variables are Gaussian, Wick's theorem may again be used to calculate the correlation functions, from which the spectral densities, $J_0$ and $J_2$, are calculated

\[
C_0(t) = 9 \langle p_0 p(t) \rangle^2 \quad (A.29) \\
C_0(t) = 3 \langle p_0 p(t) \rangle^2 \quad (A.30)
\]

The Fourier transform of $\langle p_0 p(t) \rangle$, $P(\omega)$, was already obtained in calculating $J_1$. For $J_2$ the Fourier transform of $\langle p_0 p(t) \rangle^2$ must be calculated. This has been done by numerically Fourier transforming $P(\omega)$, squaring the result, and transforming back.
Appendix B

Expansion Coefficients $A_{\mu,\nu}$

The parameters $A_{\mu,\nu}$ in equation (4.8) may be written as

$$A_{\mu,\nu} = \frac{3}{2} \sum_{r=0}^{\nu} \sum_{p=\nu}^{\mu-\nu} \sum_{s=r}^{p} \sum_{j=r}^{p} c_p c_{\mu-p} \left( \begin{array}{c} p \\ j \end{array} \right) \left( \begin{array}{c} \mu - p \\ j \end{array} \right) G_{p,\mu-p,r,\nu-r,s,j}$$

(A.31)

where $c_m$ are the expansion coefficients of the square root,

$$c_m = \begin{cases} 1 & m = 0 \\ -\frac{1}{2} & m = 1 \\ -\frac{(2m - 3)!!}{2^m m!} = -\frac{(2m - 3)!}{2^{m-2}m!(m - 2)!} & m \geq 2 \end{cases}$$

(A.32)

and

$$G_{p,q,r,s,t,j} = f_r^{s,t} d_s^{p-t,q-j} + f_s^{p-t,q-j} b_r^{t,j}$$

(A.33)

with

$$f_r^{k,l} = \frac{(2k + 1)(2l + 1)!}{(2r + 1)!(k - r)!(l - r)!2^{k+l-2r}}$$

(A.34)

$$d_r^{k,l} = \frac{(2k)!2^l}{(2r)!(k - r)!(l - r)!2^{k+l-2r}}$$

(A.35)

The values for $A_{\mu,\nu}$ to tenth order in $\alpha$ are,

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References


