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## Liquid Crystals

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## The influence of director fluctuations on molecular reorientation of a small probe molecule in a liquid-crystalline environment

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The influence of director fluctuations on a probe molecule dissolved in a nematic liquid crystal is calculated to all orders using the gaussian properties of the director field. Consequences for the N.M.R. spectrum and relaxation through quadrupolar interaction of the probe molecule are indicated. It is found that the equilibrium distribution of molecular orientations, and consequently quadrupolar spectral splittings are virtually unchanged by fluctuations in the director field. The spectral densities are also obtained and it is shown that in addition to  $J_{01}$  also  $J_{00}$  and  $J_{02}$  become frequency dependent in the N.M.R. frequency range. The frequency dependence of  $J_{00}$  and  $J_{02}$  has a logarithmic contribution; the magnitude of the frequency dependent contribution to  $J_{02}$  is, however, insufficient to explain experimental results.

### 1. Introduction

In the theory of intramolecular N.M.R. spin-lattice relaxation, orientational order and orientational correlation functions play an important rôle. This is especially so when the nucleus under consideration is part of a probe molecule dissolved in a liquid crystal environment. Not only is the ordering high, leading to considerable quadrupolar line splittings in the N.M.R. spectra, but in addition there are slowly relaxing modes present, connected to the director field, which are thought to give rise to the frequency dependent behaviour of the spin-lattice relaxation time [1]. The relaxation behaviour is conveniently described by the Redfield theory [2], which calls for knowledge of the order parameters and orientational correlation functions of the probe molecule. These quantities are influenced to a considerable extent by the presence of a director field. In fact the orientational order is almost totally due to the coupling of the probe molecule to the director field.

For small probe molecules, molecular reorientation can be thought of as resulting from two processes. On a short timescale the reorientation is assumed to take place through orientational diffusion or through collision processes in the presence of a fixed orienting potential [3]. The orienting potential is an interaction potential of mean torque between the probe molecule and the director field. The director field itself changes on a much longer time scale [4-6]. This model implies that we may first calculate order parameters and correlation functions in the presence of a fixed director field and subsequently investigate the influence of fluctuations. This was done in [7] to lowest order in the fluctuations, and to lowest order in the coupling parameter.

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However, experimental results show that the lowest order theory does not suffice [8, 9]. Direct extension of the methods used in [7] to higher orders leads to serious difficulties, both of computational and of a more fundamental nature. The gaussian properties of director fluctuations [10], together with the nature of the orienting potential suggests the possibility of including the fluctuations to all orders.

From this description of the process of molecular reorientation it will be clear that the separation of time scales of molecular reorientation and of the motion of the director field breaks down for large probe molecules. Here large means high ordering, or equivalently, a strong interaction between probe and liquid crystal. In the limiting case of a probe molecule of the same size, or indeed of the same nature, as the liquid crystal molecules the probe participates in the motion of the director field and we may arrive at the opposite description where collisional processes slightly disturb the movement of the probe, which is now almost totally due to the collective motions of the director field. This is not the subject of the present paper [11]. The processes described here can be characterized by two parameters. The first, denoted in this paper by  $\lambda$ , is the coupling strength between the probe molecule and liquid crystal. The second parameter,  $\alpha$ , describes the magnitude of director fluctuations and is consequently related to the elastic constants of the medium and, more importantly, to a cut-off wavelength,  $\lambda_c$ , that has to be introduced to impose a boundary on the application of the macroscopic theory at a molecular level. It is assumed here that there is a regime of parameter values where the lowest order theory alluded to in the first paragraph breaks down, but the separation in time scales can still be made.

In this paper we intend to investigate the influence of director fluctuations to all orders. In §2 we describe the necessary ingredients of the theory, based on the Redfield expressions. In §3 we establish the interaction between a probe molecule and its liquid crystal environment. In §4 we consider the renormalization of the order parameters due to director fluctuations. The time dependent behaviour of the director field is the subject of §5, and its consequences for the correlations functions is studied in §6. The final section is devoted to remarks and conclusions.

## 2. Relaxation by quadrupolar interaction

Although the theory of reorientation motion in a liquid crystal is interesting in its own right, we wish to connect it to the spin relaxation of a nucleus through quadrupolar interaction with its surroundings. The nucleus is part of a probe molecule dissolved in a liquid crystal. The reason for the investigation of this particular problem is a discrepancy between existing theories and experimental data [8, 9] in this field. Also it gives us the possibility to restrict the calculation to a number of correlation functions which are physically interesting, at least in the field of N.M.R. spectroscopy. The basic ingredients of the theory are the following.

The system consists of a nucleus in a probe molecule, immersed in the nematic phase of a liquid crystal and placed in an external magnetic field. The magnetic field has two important effects: the first is to align the liquid crystal and the second is the splitting of the Zeeman energies of the nucleus. Other effects can be shown to be negligible; for instance the probe molecule, if it possesses an anisotropy of its diamagnetic susceptibility tensor, aligns in the magnetic field but to a much smaller extent than the alignment caused by the interaction with the liquid crystal. The magnetic field also changes the spectrum of director fluctuations slightly. It

finally provides us with a reference system, the laboratory frame, to which we refer all our other coordinate frames. The Zeeman hamiltonian of the nucleus is given by

$$\mathcal{H}_0 = -\hbar\omega_0 I_z, \quad \omega_0 = \gamma B_z, \quad (2.1)$$

where  $I_z$  denotes the  $z$  component of the nuclear spin operator,  $\gamma$  is the gyromagnetic ratio of the nucleus and  $B_z$  is the magnetic flux density in the  $z$  direction. The second part of the nuclear hamiltonian is the quadrupolar interaction term  $\mathcal{H}_1$ ; it is given by [12]

$$\mathcal{H}_1 = \hbar\omega_q \sum_m (-1)^m (\mathbb{I})_{-m} \sum_{m'} D_{m'm}^2(\Omega) F_{m'}. \quad (2.2)$$

In this equation  $\omega_q$  denotes the quadrupole coupling constant,  $e^2 q Q V_{zz}$ , multiplied by  $\pi/I(2I-1)\sqrt{3/2}$ ,  $(\mathbb{I})_m$  are the spherical components of the spin product at operators  $\mathbb{I}$ ,  $D_{m'm}^2(\Omega)$  denotes the Wigner rotation matrices (we use the conventions of Rose [13] throughout) and  $\Omega = (-\gamma, -\beta, -\alpha)$ , and  $(\alpha\beta\gamma)$  is the set of Euler angles which transform the laboratory frame to the molecular frame. The molecular frame is some suitably chosen coordinate system in which for instance the electric polarizability tensor is diagonal. The sums over  $m$  and  $m'$  range from  $-2$  to  $2$ . The  $F_m$  are a set of constants completely determined by the molecular geometry; they are given by

$$F_m = D_{0m}^2(\Psi) + \frac{\delta}{\sqrt{6}} \{D_{2m}^2(\Psi) + D_{-2m}^2(\Psi)\}. \quad (2.3)$$

The set of Euler angles  $\Psi$  transform the local frame in which the electric field gradient tensor  $V_{\alpha\beta}$  is diagonal, to the molecular frame;  $\delta$  denotes the asymmetry of the electric field gradient tensor.

The set of angles  $\Omega$  changes with the orientation of the molecule and is therefore a time dependent function. Redfield theory requires two quantities:  $\langle D_{mm'}^2(\Omega) \rangle$ , the ensemble averaged value of the rotation matrices, necessary to calculate transition frequencies. The second set of quantities are the correlation functions  $\langle D_{mm'}^2(\Omega_0) D_{kk'}^2(\Omega) \rangle$  which determine the relaxation behaviour of the quadrupolar nucleus. These averages are defined, respectively, as

$$\langle D_{mm'}^2(\Omega) \rangle = \int d\Omega P_{\text{eq}}(\Omega) D_{mm'}^2(\Omega) \quad (2.4)$$

and

$$\langle D_{mm'}^2(\Omega_0) D_{kk'}^2(\Omega) \rangle = \int d\Omega \int d\Omega_0 P_{\text{eq}}(\Omega_0) P(\Omega_0|\Omega, t) D_{mm'}^2(\Omega_0) D_{kk'}^2(\Omega), \quad (2.5)$$

where  $P_{\text{eq}}(\Omega)$  is the equilibrium distribution of angles  $\Omega$  and  $P(\Omega_0|\Omega, t)$  the conditional probability of finding a set of angles  $\Omega$  at time  $t$ , given that at time zero the angles were  $\Omega_0$ . If there were no director field present,  $P_{\text{eq}}(\Omega)$  would be a constant and the conditional probability could in principle be determined from for instance a collision model or a rotational diffusion model [14]. The presence of a director field changes this in two essential ways. First it provides the molecule with an external field in which it will try to find the orientation of lowest free energy, but secondly this potential of mean torque is itself a fluctuating quantity, governed by its own laws, albeit at a much slower time scale. The inclusion of this potential of mean torque into the Fokker-Planck equation and the consequences of the time scale separation has been studied extensively by Freed [7]. The results of his calculations are essentially that  $P_{\text{eq}}(\Omega)$  can be written, in this limit, as

$$P_{\text{eq}}(\Omega) = \int d\psi f_{\text{eq}}(\psi) P_{\text{eq},\psi}(\Omega), \quad (2.6)$$

where  $\psi = (\phi\theta\chi)$  denotes the set of angles transforming the laboratory frame to the local director field frame of reference,  $f_{\text{eq}}(\psi)$  the equilibrium distribution of this set of angles, which is directly related to the equilibrium distribution of director fluctuations. Finally  $P_{\text{eq},\psi}(\Omega)$  is the equilibrium distribution of angles  $\Omega$  for a given value of  $\psi$  (see, however, Appendix A).

For the transition probability  $P(\Omega_0|\Omega, t)$  the following relation was shown to hold [7]:

$$P_{\text{eq}}(\Omega_0)P(\Omega_0|\Omega, t) = \int d\psi_0 \int d\psi f_{\text{eq}}(\psi_0)P_{\text{eq},\psi_0}(\Omega_0)f(\psi_0|\psi, t)P_{\psi}(\Omega_0|\Omega, t). \quad (2.7)$$

In this equation  $f(\psi_0|\psi, t)$  is the conditional probability of finding a set of angles  $\psi$  at time  $t$ , given that they have values  $\psi_0$  at time zero, and  $P_{\psi}(\Omega_0|\Omega, t)$  the transition probability for the  $\Omega$ s for a given set of values  $\psi$ . The first of these two functions is determined by considering the dynamics of the director field. The second is a consequence of the rotational dynamics of the probe molecule in the external potential provided by the director field. Explicit expressions for these quantities are derived in the subsequent sections. Equation (2.7) shows that the fast rotational motion of the molecule and the motion of the director field have effectively been separated.

### 3. The probe molecule-liquid crystal interaction

The orienting potential of mean torque acting on a molecule at the origin of the coordinate system in a liquid crystal due to the presence of a director field is, to lowest order, given by an expression of the form [3]

$$\mathcal{U} = -\mathbf{Q}:\mathbf{N}(\mathbf{r} = 0), \quad (3.1)$$

where  $\mathbf{Q}$  is some molecular tensor property, for instance the direct product of the molecular dipole moment with itself, or the molecular electric quadrupole moment, and where the tensor  $\mathbf{N}(\mathbf{r})$  describes the director field. Traditionally the director field is described by a vector quantity, usually denoted by  $\mathbf{n}(\mathbf{r})$ , and consequently it might be thought that an interaction term of the type  $\mathbf{q} \cdot \mathbf{n}(\mathbf{r} = 0)$ , where  $\mathbf{q}$  is for instance the molecular dipole moment, would be of a lower order than the one described by equation (3.1). However, the director field in a nematic is invariant under inversion ( $\mathbf{n}(\mathbf{r}) \rightarrow -\mathbf{n}(\mathbf{r})$ ), which would lead to sign change for the latter interaction. We will not specify the character of the tensor  $\mathbf{Q}$ , or the nature of the interaction between probe molecule and director field, but in practice it determines the molecular frame of reference as the coordinate frame in which it is diagonal. The tensor field  $\mathbf{N}(\mathbf{r})$  can be thought of as the direct product  $\mathbf{n}(\mathbf{r})\mathbf{n}(\mathbf{r})$  [15] and its properties can be derived from the properties of the field  $\mathbf{n}(\mathbf{r})$  [4-6, 15].

Now that we have established the form of the interaction, we can proceed to express it in properties of the director field and of the molecule by means of rotations to the molecular and the local director frame. We can write  $\mathcal{U}$  in the following form

$$\mathcal{U} = -(1/3)\text{Tr}(\mathbf{Q})\text{Tr}(\mathbf{N}) - \mathbf{Q}^{(0)}:\mathbf{N}^{(0)}(\mathbf{r} = 0), \quad (3.2)$$

where the superscript 0 denotes the traceless parts of the respective tensors. The first part of  $\mathcal{U}$  is invariant under rotations and we will, henceforth, neglect it since it only represents a shift in zero point energy. The second part can be written as a sum over the spherical components of both the tensors [13]

$$\mathcal{U} = -\sum_m (-1)^m Q_m N_{-m}. \quad (3.3)$$

Transforming the  $Q$ s to the molecular reference frame, and the  $N$ s to the local director frame gives

$$\mathcal{U} = - \sum_m (-1)^m \sum_{m'} D_{m'm}^2(\Omega) Q_m^{(M)} \sum_{m''} D_{m''-m}^2(\psi) N_{m''}^{(D)}. \quad (3.4)$$

In this equation  $Q_m^{(M)}$  denote the spherical components of  $\mathbf{Q}$  in the molecular frame and  $N_m^{(D)}$  the spherical components of  $\mathbf{N}(\mathbf{r} = 0)$  in the local director frame. In general a symmetric traceless tensor has five independent components, three are the Euler angles which refer it to a specific coordinate system, two components remain in the coordinate system in which it is diagonal. Traditionally the largest component is taken to be the  $zz$  component, which leaves one parameter, usually taken to be the difference between the other two diagonal elements. If there are other relations the number of independent parameters is smaller. Such is the case for the director field. The tensor  $\mathbf{N}(\mathbf{r})$  has the additional property that  $\mathbf{N}(\mathbf{r}) \cdot \mathbf{N}(\mathbf{r}) = \mathbf{N}(\mathbf{r})$ . Therefore  $N_m^{(D)} = \delta_{m0} N_0^{(D)}$ . (Note that  $N_0^{(D)} = \sqrt{(2/3)}$ ). For a probe molecule with no further symmetries there are no other relations so that, in general,

$$Q_m^{(M)} = Q_0 \delta_{m0} + \eta (\delta_{m2} + \delta_{m-2}), \quad (3.5)$$

where  $\eta$  denotes the asymmetry of the molecular tensor, which is a measure of the non-uniaxiality of the molecule. This reduces expression (3.4) to

$$\mathcal{U} = -\lambda \sum_m (-1)^m D_{0m}^2(\Omega) D_{0-m}^2(\psi) - \varrho \sum_m (-1)^m \{D_{2m}^2(\Omega) + D_{-2m}^2(\Omega)\} D_{0-m}^2(\psi), \quad (3.6)$$

where  $\lambda = Q_0 N_0^{(D)}$  and  $\varrho = \eta N_0^{(D)}$  are parameters that give the strength of the interaction between the probe molecule and the liquid crystal. Equation (3.6) is a generalization of equation (3.2) of [7] to the case of non-uniaxial molecules. We also note here that the nematic order parameter,  $S$ , has been absorbed into  $\lambda$ .

In addition to the hamiltonians and interaction energies discussed so far, there is also the interaction between the director field and the external magnetic field. This interaction is of the form  $\mathbf{B} \cdot \mathbf{N} \cdot \mathbf{B}$  and using arguments similar to those given for the molecular interaction it is easy to infer that the present interaction can only depend on the angle between the  $z$  axes of the director frame and the laboratory frame. Also the interaction is strong enough to completely align the liquid crystal [4]. Although it is not hard to consider an arbitrary alignment in principle, this would mean the introduction of yet another frame of reference and merely obscure the points to be made in this paper. Our interest is in fluctuations of the director field around its equilibrium value. We will only consider the case where the equilibrium value is (000) for the angles  $(\phi\theta\chi)$ , i.e. alignment along the magnetic field so that  $\psi$  denotes the angles of the fluctuating director field frame.

The procedure followed in previous papers [7–9] is to expand  $\mathcal{U}$  in the set of angles  $(\psi)$ , to try subsequently to express the resulting correlation functions of these angles in the correlation functions of the director field  $\mathbf{n}$ , and finally to use linearized hydrodynamics in combination with equilibrium fluctuation theory to express the latter correlation functions in terms of elasticity constants and viscosities of the medium. This works well for small values of  $\lambda$ , in which case a low order expansion suffices. To include higher order terms, however, turns out to be rather complicated [16]. First of all the theories for equilibrium director fluctuations indicate a gaussian behaviour [17] but obviously this does not mean that the distribution functions for the angles which are obtained in the expansions referred to are gaussians as well. This

implies that in all cases we have to rewrite the angular correlation functions in terms of director correlation functions which is a formidable task [16]. Furthermore, even if we accomplish that task, higher order contributions cannot be neglected. There are two reasons for this. For a gaussian distribution the  $n$ th moment is not necessarily smaller than the  $n + 2d$  [18], and also in this particular situation it turns out that every single term in the expansion diverges [19]. One can show, however, as we will do in the next sections that this is not true if the perturbation series is summed first, or if we do not use a series expansion at all. Finally, the value of  $\lambda$  is for many cases not small, but indeed in many cases larger than  $kT$  [20]. In this paper we propose to use a faster and cleaner procedure by not using equation (3.6) as a starting point, but equation (3.1).

We conclude this section by noting that we have now at least one of the probabilities of interest, the function  $P_{\text{eq},\psi}(\Omega)$ ; it is proportional to  $\exp[-\beta\mathcal{U}(\Omega, \psi)]$  where  $\beta$  is the inverse thermal energy  $1/kT$ .

#### 4. The equilibrium distribution $P_{\text{eq}}(\Omega)$ .

The particular form of  $\mathbf{N}(\mathbf{r})$ , given in §3, suggests that fluctuations of the tensor  $\mathbf{N}(\mathbf{r})$  around its equilibrium value  $\mathbf{N}_0 = \mathbf{n}_0\mathbf{n}_0$  can be written as

$$\delta\mathbf{N}(\mathbf{r}) = \mathbf{n}_0\delta\mathbf{n}(\mathbf{r}) + \delta\mathbf{n}(\mathbf{r})\mathbf{n}_0, \quad (4.1)$$

where, by denoting the deviations from the equilibrium value as a function of  $\mathbf{r}$ , we indicate their positional dependence. The quantities  $\delta\mathbf{n}(\mathbf{r})$  denote deviations of  $\mathbf{n}(\mathbf{r})$  from its equilibrium value  $\mathbf{n}_0$ . The  $\delta$  is omitted in the remainder of this paper as this should not lead to confusion. Use of the classical (Einstein) fluctuation theory for director fluctuations gives a gaussian distribution for  $\mathbf{n}(\mathbf{r})$  [10]. Consistency requires neglecting the second order terms in equation (4.1). Therefore  $\mathbf{N}(\mathbf{r})$  also has a gaussian distribution, which can easily be found from the distribution for  $\mathbf{n}(\mathbf{r})$  [15].

To obtain the distribution for  $\mathbf{n}(\mathbf{r})$  we start from the well-known Frank-Oseen expression for the free energy of a nematic, up to lowest (i.e. second) order in the fluctuations,

$$\mathcal{F} = \mathcal{F}_0 + \frac{1}{2} \int_V d\mathbf{r} \{K_1(\text{div } \mathbf{n})^2 + K_2(\mathbf{n}_0 \cdot \text{curl } \mathbf{n})^2 + K_3(\mathbf{n}_0 \cdot \text{grad } \mathbf{n})^2\}, \quad (4.2)$$

where  $K_1$ ,  $K_2$  and  $K_3$  are the elasticity constants for splay, twist and bend deformations, respectively. In equation (4.2)  $\mathcal{F}_0$  is the free energy of the system in the absence of deformations and  $V$  is the total volume of the system, or rather the volume over which  $\mathbf{n}_0$  is a constant. We introduce the spatial Fourier transform  $\mathbf{n}(\mathbf{k})$  of the fluctuating field  $\mathbf{n}(\mathbf{r})$  as

$$\mathbf{n}(\mathbf{k}) = \int_V d\mathbf{r} \mathbf{n}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (4.3)$$

and its inverse

$$\mathbf{n}(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k}} \mathbf{n}(\mathbf{k}) \exp(-i\mathbf{k} \cdot \mathbf{r}). \quad (4.4)$$

Substitution of equation (4.4) into equation (4.2) gives, after some elementary manipulations, for the free energy difference  $\Delta\mathcal{F} = \mathcal{F} - \mathcal{F}_0$ :

$$\Delta\mathcal{F} = \frac{1}{2V} \sum_{\mathbf{k}} \{K_1|\mathbf{k} \cdot \mathbf{n}(\mathbf{k})|^2 + K_2|\mathbf{n}_0 \cdot (\mathbf{k} \times \mathbf{n}(\mathbf{k}))|^2 + K_3|\mathbf{n}_0 \cdot \mathbf{k}\mathbf{n}(\mathbf{k})|^2\}. \quad (4.5)$$

In a previous paper [15] we showed that, since fluctuations take place in a plane perpendicular to  $\mathbf{n}_0$ , it is advantageous to introduce the orthonormal basis

$$\mathbf{a}_1 = \frac{\mathbf{n}_0 \times (\mathbf{n}_0 \times \mathbf{k})}{k_\perp}, \quad \text{and} \quad \mathbf{a}_2 = \frac{\mathbf{n}_0 \times \mathbf{k}}{k_\perp}, \quad (4.6)$$

where

$$k_\perp^2 = k^2 - k_\parallel^2, \quad \text{and} \quad k_\parallel = \mathbf{n}_0 \cdot \mathbf{k}. \quad (4.7)$$

The fluctuations can then be conveniently expressed as

$$\mathbf{n}(\mathbf{k}) = n_1(\mathbf{k})\mathbf{a}_1 + n_2(\mathbf{k})\mathbf{a}_2 \quad (4.8)$$

and the free energy difference  $\Delta\mathcal{F}$  is given by the diagonal quadratic form [21]

$$\Delta\mathcal{F} = \frac{1}{2V} \sum_{\mathbf{k}} \sum_{\alpha=1,2} \{K_\alpha k_\perp^2 + K_3 k_\parallel^2\} |n_\alpha(\mathbf{k})|^2. \quad (4.9)$$

For every value of  $\mathbf{k}$  the  $n_\alpha(\mathbf{k})$  are two independent modes of the system. The probability of a fluctuation is related to the exponential of the free energy difference, suitably normalized, and consequently the variance of the fluctuating potential of mean torque  $\mathcal{U}$  can be calculated directly: the potential can be written as

$$\mathcal{U} = \mathbf{n}_0 \cdot \mathbf{Q} \cdot \mathbf{n}_0 - \frac{2}{V} \sum_{\alpha=1,2} \sum_{\mathbf{k}} (\mathbf{n}_0 \cdot \mathbf{Q} \cdot \mathbf{a}_\alpha) n_\alpha(\mathbf{k}). \quad (4.10)$$

The first term represents the potential in the fixed director field,  $\mathcal{U}_0$ , and the second term the fluctuations  $\Delta\mathcal{U}$  of this potential around this average value due to director fluctuations. Fluctuations for different values of  $\alpha$  and  $\mathbf{k}$  are uncorrelated and we may write

$$\langle \Delta\mathcal{U} \Delta\mathcal{U} \rangle = \frac{2}{V^2} \sum_{\alpha=1,2} \sum_{\mathbf{k}} (\mathbf{n}_0 \cdot \mathbf{Q} \cdot \mathbf{a}_\alpha)^2 \langle |n_\alpha(\mathbf{k})|^2 \rangle. \quad (4.11)$$

The remaining average can be calculated in the same manner and introduced into equation (4.11); we obtain

$$\langle \Delta\mathcal{U} \Delta\mathcal{U} \rangle = \sum_{\alpha=1,2} \sum_{\mathbf{k}} (\mathbf{n}_0 \cdot \mathbf{Q} \cdot \mathbf{a}_\alpha)^2 \frac{2kTV^{-1}}{K_\alpha k_\perp^2 + K_3 k_\parallel^2}. \quad (4.12)$$

In appendix B equation (4.12) is evaluated for the particular choice of  $\mathbf{n}_0$  indicated in §3:  $\mathbf{n}_0 = \mathbf{z}$ , a unit vector in the  $\mathbf{z}$  direction. The result is that the variance of the potential can be written as

$$\langle \Delta\mathcal{U} \Delta\mathcal{U} \rangle = \frac{kTk_c}{\pi^2 K} \{Q_{zx}^2 + Q_{zy}^2\}, \quad (4.13)$$

where

$$2K^{-1} = \sum_{\alpha=1,2} K_\alpha^{-1} \sqrt{\left(\frac{K_\alpha}{K_3 - K_\alpha}\right)} \operatorname{arctg} \sqrt{\left(\frac{K_3 - K_\alpha}{K_\alpha}\right)}. \quad (4.14)$$

A somewhat simplified derivation can be given if we set  $K_1 = K_2 = K_3 = K = (K_1 + K_2 + K_3)/3$  (the so-called one constant approximation). As can be inferred from equation (4.14) the result for the variance is the same but the interpretation of  $K$  is different [22]. Finally we rewrite equation (4.13) in terms of the spherical



components of  $\mathbf{Q}$  [13], and transform to the molecular coordinate frame to obtain, for axially symmetric molecules ( $\varrho = 0$ , cf. equation (3.6)),

$$\langle \Delta \mathcal{U} \Delta \mathcal{U} \rangle = -3\lambda^2 \frac{kT k_c}{\pi^2 K} D_{01}^2(\Omega) D_{0-1}^2(\Omega). \quad (4.15)$$

This completes our calculation of the variance of the fluctuating potential  $\mathcal{U}$ . If the molecules are not axially symmetric, the distribution acquires additional terms proportional to  $\varrho\lambda$  and  $\varrho^2$ . Here we give explicit expressions only for molecules that do have axial symmetry.

We now come to the calculation of  $P_{\text{eq}}(\Omega)$ . Since  $\mathcal{U}$  is a sum of independently fluctuating quantities, each with a gaussian distribution, cf. equation (4.10), the distribution function for the  $\mathcal{U}$ 's must itself be a gaussian [23]. Using this observation it is relatively easy to calculate the equilibrium distribution for the angles  $\Omega$ ,  $P_{\text{eq}}(\Omega)$ . According to equation (2.6) it can be written as, apart from a normalization constant,

$$P_{\text{eq}}(\Omega) = \langle \exp[-\beta \mathcal{U}] \rangle, \quad (4.16)$$

where the average is over the equilibrium director fluctuations. Using what has been said about the gaussian nature of the fluctuating potential, it is straightforward to derive the equality

$$\langle \exp[-\beta \mathcal{U}] \rangle = \exp[-\beta \mathcal{U}_0] \exp[\frac{1}{2} \beta^2 \langle \Delta \mathcal{U} \Delta \mathcal{U} \rangle]. \quad (4.17)$$

It was obtained by first extracting  $\mathcal{U}_0$ , subsequently expanding the remaining exponential as a series in  $\Delta \mathcal{U}$ , using the gaussian property, and resumming the resulting series expansion [18].

Upon introduction of the explicit expression for  $\mathcal{U}_0$  and equation (4.15) we finally obtain for the equilibrium distribution

$$P_{\text{eq}}(\Omega) = P_0 \exp \beta \left[ \lambda D_{00}^2(\Omega) - \frac{3\lambda^2 k_c}{4\pi^2 K} D_{01}^2(\Omega) D_{0-1}^2(\Omega) \right]. \quad (4.18)$$

The normalization constant  $P_0$  has to be determined by integrating  $P_{\text{eq}}(\Omega)$  over all angles  $\Omega$  and demanding that the result be equal to one. A remark about our treatment of the normalization is in order here. Expression (2.6) was taken from [7] and in that paper the normalized probabilities are taken for  $f_{\text{eq}}(\psi)$  and  $P_{\text{eq},\psi}(\Omega)$ . In contrast we have integrated the unnormalized probabilities and determined the normalization constant at the end. The result of the two procedures is different, since the normalization constant in  $P_{\text{eq},\psi}(\Omega)$  also depends on  $\psi$ . We show in Appendix A that the method we use is in fact the correct one.

In the remainder of this section we discuss some of the properties of the equilibrium distribution given in equation (4.18). First of all it is clear that as a consequence of the occurrence of only  $D_{00}^2$  and the product  $D_{01}^2 D_{0-1}^2$ , the distribution depends solely on the polar angle  $\beta$ . The important consequence is that, in the averages defined in equation (2.4), only  $\langle D_{00}^2(\Omega) \rangle$  is non-zero, which is to be expected for systems with the given symmetry properties. It also implies that the transition frequencies and quadrupolar line splittings can be found immediately, since  $\mathcal{H}_0 + \langle \mathcal{H}_1 \rangle$  is still diagonal [24]. As an application we investigate the molecular order parameter  $S_{zz} = \langle D_{00}^2(\Omega) \rangle$  using this probability density. First we note that, since it depends only on the polar angle  $\beta$ , the distribution can be written as

$$P_{\text{eq}}(\xi) = \frac{\exp[\bar{\lambda} \xi^2 + \alpha \bar{\lambda}^2 \xi^2 (1 - \xi^2)]}{\int_0^1 d\xi \exp[\bar{\lambda} \xi^2 + \alpha \bar{\lambda}^2 \xi^2 (1 - \xi^2)]}, \quad (4.19)$$

Table 1. Experimental data and calculated interaction parameter for isocyanide, toluene-d<sub>8</sub>, xylene-d<sub>10</sub> and toluene-d<sub>10</sub> in Phase V.  $T_s$  = sample temperature,  $T_{NI}$  = nematic-isotropic transition temperature,  $S_{zz}$  = molecular order parameter calculated from spectral splittings. The value of  $\bar{\lambda}$  was calculated by solving the integral equation  $S_{zz} = \int d\Omega P_{eq}(\Omega) D_{00}^2(\Omega)$  for  $\alpha = 0$  (cf. equation (4.19)). For comparison the first order approximation to  $S_{zz}$  using the value of  $\bar{\lambda}$  found in this way is also given. Even for small values of the interaction parameter the difference is noticeable. No change in  $\bar{\lambda}$  is found even for  $\alpha = 0.1$ . Values are taken from [9] and [35]. If non-uniaxiality of the appropriate molecules is taken into account some of the values for  $\bar{\lambda}$  become slightly lower [30].

Probe/measured nucleus	$T_s/^\circ\text{C}$	$T_{NI}/^\circ\text{C}$	$S_{zz}$	$\bar{\lambda}$	$2\lambda/15$
CH <sub>3</sub> NC/15 mol % <sup>14</sup> N	30.4	47	0.074	0.53	0.071
toluene-d <sub>8</sub> /13 mol % <sup>2</sup> H(methyl)	31.7	51	0.139	0.97	0.129
<sup>2</sup> H(para)					
<i>p</i> -xylene-d <sub>10</sub> /10 mol % <sup>2</sup> H(methyl)	31.7	56	0.262	1.77	0.236
toluene-d <sub>10</sub> /10 mol % <sup>2</sup> H(para)	31.3	51.5	0.28	1.89	0.252
Liquid crystal molecules			0.44–0.65†	3–5	

† Order parameters for liquid crystal molecules can be determined in a variety of ways. Maier-Saupe theory [33] gives  $S = 0.44$  at the transition temperature and slightly higher values below that. N.M.R. measurements also give values in the range indicated, and Monte Carlo calculations [32] give similar results.

Table 2. Order parameters as a function of the interaction parameter  $\bar{\lambda}$  and the fluctuation parameter  $\alpha$ . These values were calculated using equation (4.19). For values of  $\bar{\lambda}$  below 3 the fluctuations can be neglected entirely in the equilibrium distribution.  $S_{zz} = \langle D_{00}^2(\Omega) \rangle$ .

$\bar{\lambda}$	$S_{zz}(\alpha = 0)$	$S_{zz}(\alpha = 0.05)$	$S_{zz}(\alpha = 0.1)$
0.5	0.069	0.069	0.069
1.0	0.144	0.144	0.144
2.0	0.297	0.297	0.296
3.0	0.439	0.435	0.432
5.0	0.646	0.626	0.606
7.5	0.777	0.736	0.691

where we have introduced the abbreviation  $\xi = \cos \beta$ . The parameters  $\alpha$  and  $\bar{\lambda}$  are given by

$$\bar{\lambda} = \frac{3}{2} \frac{\lambda}{kT}, \quad \text{and} \quad \alpha = \frac{k_c kT}{2\pi^2 K}. \quad (4.20)$$

For a cut-off wavelength of 25 Å (about the length of a liquid crystal molecule), and a value for the elasticity constant of about 5 pN, we find  $\alpha \approx 0.05 - 0.1$ . For small probe molecules  $\bar{\lambda}$  varies between 0.5 and 2.0, values which can be found from quadrupolar line splittings (see table 1). For liquid crystal molecules themselves  $\bar{\lambda}$  is somewhat larger, equal to about 5 at most.

The general features are also clear from this expression. If the coupling between probe molecule and liquid crystal is weak ( $\lambda < kT$ ), and the fluctuations small (the magnitude of the fluctuations is measured by the parameter  $\alpha$ ) the second term in the

exponential can be neglected and we find the usual expression for the equilibrium distribution of orientations of a molecule in a fixed external field. In the limit  $\lambda \rightarrow 0$  the order parameter  $S_{zz}$  tends to zero, as it should. If we neglect the fluctuations, i.e. take  $\alpha = 0$  and let  $\lambda$  increase, the function  $P_{\text{eq}}(\xi)$  becomes more and more sharply peaked around  $\xi = 1$  and consequently in the limit  $\lambda \rightarrow \infty$ ,  $S_{zz}$  goes to one. This is the correct behaviour, for in that limit the liquid crystal is perfectly aligned along the laboratory axis, there are no fluctuations, and the probe molecule is fixed to the director field. The fluctuations tend to broaden the distribution a little but numerical calculations show that this effect only becomes of importance for rather high  $\bar{\lambda}$  values,  $\bar{\lambda} \gtrsim 3$  (see table 2). This means that for the probe molecules in table 1, fluctuations can be neglected entirely as far as the equilibrium distribution is concerned and the measured order parameters can be used to calculate the interaction parameter  $\bar{\lambda}$  directly. As the nematic–isotropic transition temperature  $T_{\text{NI}}$  is approached the value of  $K$  decreases and consequently  $\alpha$  increases. At values of  $T - T_{\text{NI}} \approx 1 \text{ K}$ , the fluctuations become noticeable even for small probe molecules. Closer to the transition temperature the theory presented here is no longer applicable. The limit of applicability is given by the condition [25]

$$\frac{kT\bar{\lambda}}{\pi K\lambda_c} \ll 1, \quad (4.21)$$

which is satisfied for the values used in this paper for the various constants. The inequality is derived using the requirement that fluctuations should not destroy the nematic order.

### 5. The transition probability

In this section we derive an explicit expression for the transition probability  $P(\Omega_0|\Omega, t)$ , which is given in principle by equation (2.7). To this end we first establish the equivalent of the transition probability  $f(\psi_0|\psi, t)$  in terms of the director field modes found in the previous section. We assume that both the modes  $n_\alpha(\mathbf{k})$  also relax independently towards their equilibrium values, with relaxation times  $\tau_\alpha(\mathbf{k})$  given by

$$\tau_\alpha^{-1} = \frac{K_\alpha k_\perp^2 + K_3 k_\parallel^2}{\eta_\alpha}, \quad \alpha = 1, 2 \quad (5.1)$$

where  $\eta_\alpha$  is an appropriate viscosity [26]. This implies that the time dependent behaviour of each of the modes is given by

$$n_\alpha(\mathbf{k}, t) = n_\alpha(\mathbf{k}) \exp[-t/\tau_\alpha(\mathbf{k})]. \quad (5.2)$$

With the assumption that the different wavevector components of the director field behave as independent gaussian Markov processes we can write down the transition probability for each component. In the previous section we found for the (unnormalized) equilibrium probability  $P(n_\alpha(\mathbf{k}))$  of finding an excitation of the  $\alpha$  mode at wavevector  $\mathbf{k}$ :

$$P(n_\alpha(\mathbf{k})) = \exp\left\{-\frac{|n_\alpha(\mathbf{k})|^2}{2\sigma_\alpha(\mathbf{k})}\right\}, \quad (5.3)$$

where the variance  $\sigma_\alpha(\mathbf{k})$  is given by

$$\sigma_\alpha(\mathbf{k}) = \frac{kTV}{K_\alpha k_\perp^2 + K_3 k_\parallel^2}. \quad (5.4)$$

The transition probability of finding a value  $[n_\alpha(\mathbf{k})]$  at time  $t$ , given that at time zero we have a value  $[n_\alpha(\mathbf{k})]_0$ , is with the previous assumptions, [27]

$$P([n_\alpha(\mathbf{k})]_0|[n_\alpha(\mathbf{k})], t) = \exp - \left\{ \frac{|n_\alpha(\mathbf{k}) - [n_\alpha(\mathbf{k})]_0 \exp(-t/\tau_\alpha(\mathbf{k}))|^2}{2\sigma_\alpha(\mathbf{k})[1 - \exp(-2t/\tau_\alpha(\mathbf{k}))]} \right\}. \quad (5.5)$$

Normalization constants (which depend on  $\mathbf{k}$  and  $\alpha$ ) have been suppressed. The final expression can be normalized by demanding that the integral of  $P(\Omega_0|\Omega, t)$  over  $\Omega$  be equal to one.

We first concentrate on the integration of  $\psi_0$  in equation (2.7), since we do not need a model for the microscopic motion of the probe molecule in order to perform that calculation. We use a somewhat different approach to that in the previous section, but as will become clear, the results in the previous section could equally well have been derived using the methods given here. We rewrite the integral over all the functions containing  $\psi_0$  as

$$\int d\psi_0 f_{\text{eq}}(\psi_0) P_{\text{eq},\psi_0}(\Omega_0) f(\psi_0|\psi, t) = \exp(-\beta\mathcal{U}_0) \prod_{\alpha=1,2} \prod_{\mathbf{k}} \int d[n_\alpha(\mathbf{k})]_0 \exp - \frac{1}{2\sigma_\alpha(\mathbf{k})} \\ \times \left\{ |[n_\alpha(\mathbf{k})]_0|^2 - \frac{2\sigma_\alpha(\mathbf{k})}{kTV} q_\alpha(\Omega_0)([n_\alpha(\mathbf{k})]_0 + [n_\alpha(\mathbf{k})]_0^*) + \frac{|n_\alpha(\mathbf{k}) - [n_\alpha(\mathbf{k})]_0 \exp(-t/\tau_\alpha(\mathbf{k}))|^2}{[1 - \exp(-2t/\tau_\alpha(\mathbf{k}))]} \right\}. \quad (5.6)$$

This expression needs some explanation. First of all we have introduced the abbreviation  $q_\alpha$  for  $\mathbf{n}_0 \cdot \mathbf{Q} \cdot \mathbf{a}_\alpha$ . Secondly we now have to keep track of the angular dependence of the  $\mathbf{Q}$ s, which we indicate by giving the  $q$ s the argument  $\Omega_0$ . Also we have written the exponential of the sums over  $\alpha$  and  $\mathbf{k}$  as a product of exponentials. As will be clear from the previous sections,  $f_{\text{eq}}(\psi_0)$  is nothing but the exponential of the free energy of a deformation ( $\psi_0$ ) of the liquid crystal. This is the first term between the brackets in equation (5.6). The second probability was identified earlier as the exponential of the potential of mean torque of interaction between the liquid crystal and a probe molecule. It is separated into a fixed part, which is the prefactor of the integrals, and a fluctuating part, cf. equation (4.10). Finally the remaining conditional probability is given by equation (5.5). Although the expression looks quite complicated it is just a product of gaussian integrals, one for each value of  $\alpha$  and  $\mathbf{k}$ , which can be performed in the standard way, by completing squares. The result of these integrations is that the right hand side of equation (5.6) reduces to

$$P_{\text{eq}}(\Omega_0) \prod_{\alpha=1,2} \prod_{\mathbf{k}} \exp - \frac{1}{2\sigma_\alpha(\mathbf{k})} \left\{ \left| n_\alpha(\mathbf{k}) - \frac{2\sigma_\alpha(\mathbf{k})}{kTV} q_\alpha(\Omega_0) \exp(-t/\tau_\alpha(\mathbf{k})) \right|^2 \right\} \quad (5.7)$$

where we also used equation (4.17) together with equation (4.12) to separate the  $P_{\text{eq}}(\Omega_0)$ . This shows, by the way, that the procedure followed here provides an alternative way of calculating  $P_{\text{eq}}(\Omega_0)$ .

Equation (5.7) has to be integrated with  $P_\psi(\Omega_0|\Omega, t)$  to obtain the renormalized transition probability  $P(\Omega_0|\Omega, t)$ . We need therefore a model for the transition probability at a fixed orientation of the director field. For this we take a strong collision model, which is rather simple but nevertheless shows the essential features of the theory presented in this paper without the necessity of going into mathematical detail, which for instance a rotational diffusion model would incur. The transition probability can then be written [7] as

$$P_\psi(\Omega_0|\Omega, t) = \delta(\Omega_0 - \Omega) \exp(-t/\tau_R) + P_{\text{eq},\psi}(\Omega)[1 - \exp(-t/\tau_R)], \quad (5.8)$$

where  $\tau_R$  is the mean time between collisions. The first term represents the probability of staying in the initial state  $\Omega_0$ , whereas the second term gives the chance of going to the other state,  $\Omega$ , the probability of which is given by the equilibrium distribution at a fixed potential ( $\psi$ ). We concentrate on the second term. Integration of the first term is trivial.

Introduction of the second term, together with the result (5.7) into equation (2.7) gives, after some elementary manipulations, (we also divided both sides by  $P_{\text{eq}}(\Omega_0)$ )

$$P(\Omega_0|\Omega, t) = \delta(\Omega - \Omega_0) \exp(-t/\tau_R) + [1 - \exp(-t/\tau_R)] \\ \times \exp(-\beta\mathcal{U}_0) \prod_{\alpha=1,2} \prod_{\mathbf{k}} \int dn_{\alpha}(\mathbf{k}) \exp - \frac{1}{2\sigma_{\alpha}(\mathbf{k})} \\ \times \left\{ \frac{2\sigma_{\alpha}(\mathbf{k})}{kTV} q_{\alpha}(\Omega)[n_{\alpha}(\mathbf{k}) + n_{\alpha}^*(\mathbf{k})] + \left| n_{\alpha}(\mathbf{k}) - \frac{2\sigma_{\alpha}(\mathbf{k})}{kTV} q_{\alpha}(\Omega_0) \exp(-t/\tau(\mathbf{k})) \right|^2 \right\}. \quad (5.9)$$

Various normalization factors were not written explicitly. As in the derivation of equation (5.7) from equation (5.6) we notice that these integrations can be performed by completing the square in the exponential. Each of the integrals cancels against normalization factors and what remains is the expression

$$P(\Omega_0|\Omega, t) = \delta(\Omega - \Omega_0) \exp(-t/\tau_R) + [1 - \exp(-t/\tau_R)] P_{\text{eq}}(\Omega) \\ \times \prod_{\alpha=1,2} \prod_{\mathbf{k}} \exp \left\{ \frac{2\sigma_{\alpha}(\mathbf{k}) q_{\alpha}(\Omega) q_{\alpha}(\Omega_0) \exp(-t/\tau_{\alpha}(\mathbf{k}))}{(kTV)^2} \right\}. \quad (5.10)$$

The remaining products are worked out in appendix B. The result of the calculation in the appendix is that  $P(\Omega_0|\Omega, t)$  can be written as (taking axially symmetric molecules for the explicit calculations)

$$P(\Omega_0|\Omega, t) = \delta(\Omega_0 - \Omega) \exp(-t/\tau_R) + P'_0 P_{\text{eq}}(\Omega) [1 - \exp(-t/\tau_R)] \\ \times \exp \frac{-3\lambda^2 k_c \Phi((\omega_c t)^{1/2})}{4\pi^2 K k T (\omega_c t)^{1/2}} \{ D_{01}^2(\Omega) D_{0-1}^2(\Omega_0) + D_{0-1}^2(\Omega) D_{01}^2(\Omega_0) \}. \quad (5.11)$$

In this equation the error integral  $\Phi$  occurs, which is defined in equation (B 13), and a cut-off frequency  $\omega_c$  was introduced, which is related to the cut-off wavevector by

$$\omega_c = \frac{K k_c^2}{\eta}, \quad (5.12)$$

where  $\eta$  is an effective viscosity. The coefficient  $P'_0$  has to be determined by integrating the second term of equation (5.11) over all angles  $\Omega$ , and demanding that the result be equal to  $[1 - \exp(-t/\tau_R)]$ . In that case the transition probability is properly normalized. It is clear that to lowest order in the fluctuations  $P'_0 = 1$ ; see also Appendix A. Equation (5.11) shows that the transition probability after renormalization has the same structure as a collisional transition probability, cf. equation (5.8), however, the probability of acquiring an angle  $\Omega$  at time  $t$ , starting from an angle  $\Omega_0$  at time zero is no longer just  $P_{\text{eq}}(\Omega)$  but a much more complicated expression.

Equations (4.18) and (5.11) are the central results of this paper. We study the properties and consequences of equation (5.11) for the rotational correlation functions in more detail in the next section.

### 6. Rotational correlation functions

In this section we consider the properties of the transition probability derived in the previous section, and especially the consequences for the rotational correlation functions defined in §2, equation (2.5). The time Fourier transforms of these functions are the so-called spectral densities, which determine the relaxation behaviour of the nuclei in the probe molecule [2]. The spectral densities are given by

$$J_m(\omega) = (-1)^m \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle D_{0m}^2(\Omega_0) D_{0-m}^2(\Omega) \rangle. \quad (6.1)$$

It was found [8, 9] that for the lowest order theory as given by Freed [7] the function  $J_{01}$  becomes frequency dependent in the frequency range relevant for N.M.R. spectroscopy, i.e. for frequencies in the neighbourhood of  $\omega_0$  (cf. equation (2.1)). In contrast, the lowest order theory gives functions independent of frequency for  $m = 0$  and 2. Expression (5.11) can easily be used for higher order expansions. Although even for relatively high values of  $\alpha$  the equilibrium distribution functions do not depend very much on the presence of the term proportional to  $\alpha\lambda^2$  in the exponential, it is nevertheless not allowed, *a priori*, to expand the exponential in that parameter since for the relevant values of  $\bar{\lambda}$ ,  $\alpha\bar{\lambda}^2$  is itself not necessarily small enough to allow a successful expansion. In the exponential of the transition probability this factor is, however, further diminished by the error function, which has a maximum of 1, but is much smaller at the relevant frequencies, and by the Wigner rotation matrices, the product of which is also smaller than one. We assume therefore that it is allowed to expand the time dependent exponentials, at least for values of  $\bar{\lambda} \leq 2$ ; this is validated by the final results.

First we consider the normalization factor  $P'_0$ . Up to second order the integral can be written as

$$\int d\Omega P_{\text{eq}}(\Omega) \left\{ 1 - \frac{2}{3} \alpha\bar{\lambda}^2 \frac{\Phi((\omega_c t)^{1/2})}{(\omega_c t)^{1/2}} [D_{01}^2(\Omega) D_{0-1}^2(\Omega_0) + D_{0-1}^2(\Omega) D_{01}^2(\Omega_0)] \right. \\ \left. + \frac{2}{9} (\alpha\bar{\lambda}^2)^2 \frac{\Phi^2((\omega_c t)^{1/2})}{\omega_c t} [D_{01}^2(\Omega) D_{0-1}^2(\Omega_0) + D_{0-1}^2(\Omega) D_{01}^2(\Omega_0)]^2 + \dots \right\}, \quad (6.2)$$

so that  $P'_0$  is given by, using the fact that  $P_{\text{eq}}(\Omega)$  depends solely on  $\beta$ ,

$$P'_0 = 1 - \frac{4}{9} (\alpha\bar{\lambda}^2)^2 \frac{\Phi^2((\omega_c t)^{1/2})}{\omega_c t} \langle D_{01}^2(\Omega) D_{0-1}^2(\Omega) \rangle \langle D_{01}^2(\Omega_0) D_{0-1}^2(\Omega_0) \rangle. \quad (6.3)$$

This term can only give a second order contribution to  $J_{00}$ .

Expansion of the exponential in equation (5.11) again gives the term in brackets under the integral sign of equation (6.2). Introducing these expansions into the expression for the transition probability and subsequent integration with  $P_{\text{eq}}(\Omega_0)$  gives, for the correlation functions of interest,

$$\langle D_{00}^2(\Omega_0) D_{00}^2(\Omega) \rangle = \langle D_{00}^2 D_{00}^2 \rangle \exp(-t/\tau_R) + \frac{4}{9} (\alpha\bar{\lambda}^2)^2 \frac{\Phi^2((\omega_c t)^{1/2})}{\omega_c t} \\ \times [1 - \exp(-t/t_R)] \{ \langle D_{00}^2 D_{01}^2 D_{0-1}^2 \rangle^2 - \langle D_{00}^2 \rangle \langle D_{01}^2 D_{0-1}^2 \rangle \langle D_{00}^2 D_{01}^2 D_{0-1}^2 \rangle \}, \quad (6.4)$$

where we have deleted the arguments of the  $D$ s in the equilibrium correlation functions: it is immaterial whether the integration variable is  $\Omega$  or  $\Omega_0$ . We have used

the fact that combinations of  $D$ s in which the angle  $\gamma$  does not vanish do not contribute to the integrals. Similarly we obtain for the other two functions

$$\begin{aligned} \langle D_{01}^2(\Omega_0)D_{0-1}^2(\Omega) \rangle &= \langle D_{01}^2D_{0-1}^2 \rangle \exp(-t/\tau_R) - \frac{2}{3}\alpha\bar{\lambda}^2 \frac{\Phi((\omega_c t)^{1/2})}{(\omega_c t)^{1/2}} \\ &\times \langle D_{01}^2D_{0-1}^2 \rangle^2 [1 - \exp(-t/\tau_R)] \end{aligned} \quad (6.5)$$

and

$$\begin{aligned} \langle D_{02}^2(\Omega_0)D_{0-2}^2(\Omega) \rangle &= \langle D_{02}^2D_{0-2}^2 \rangle \exp(-t/\tau_R) + \frac{4}{9}(\alpha\bar{\lambda}^2)^2 \frac{\Phi^2((\omega_c t)^{1/2})}{\omega_c t} \\ &\times [1 - \exp(-t/\tau_R)] \langle D_{02}^2D_{0-1}^2D_{0-1}^2 \rangle^2. \end{aligned} \quad (6.6)$$

Apart from the remark that the second order term leads to a frequency dependent  $J_{00}$  we devote no further attention to equation (6.4) since it is only one of the contributions to the spin-spin relaxation time,  $T_2$ , which is hard to measure accurately. We note here that all the equilibrium correlation functions occurring in these and the following expressions can be calculated using the values of  $\lambda$  obtained in §4.

The Fourier transform of the second of these correlation functions is given by

$$J_{01}(\omega) = \frac{-2\langle D_{01}^2D_{0-1}^2 \rangle \tau_R}{1 + \omega^2 \tau_R^2} + \frac{4\alpha\bar{\lambda}^2}{3\omega_c} \langle D_{01}^2D_{0-1}^2 \rangle^2 \left\{ I_1\left(\frac{\omega^2}{\omega_c^2}\right) - I_1\left(\frac{\omega^2}{\omega_c^2} + \frac{1}{\omega_c^2 \tau_R^2}\right) \right\}. \quad (6.7)$$

where the integral  $I_1$  is

$$I_1(x) = \int_0^1 dk \frac{k^2}{k^4 + x}. \quad (6.8)$$

For frequencies  $\omega$  at which N.M.R. transitions take place, which are close to  $\omega_0$ , it is found that  $(\omega\tau_R)^2 \ll 1$  and  $\omega \approx 0.1\omega_c$ . (Collision times, found by taking high frequency values, are in the range of 10–200 ps and  $\omega_c \approx 5.5 \times 10^8 \text{ s}^{-1}$  at a value of 0.06 Pa s for the viscosity and for the values given earlier for  $K$  and  $k_c$ ; note that  $\omega_c\tau_R < 0.1$ , which means that the fundamental assumption of time scale separation is satisfied). This implies that we can neglect the frequency dependence in the first term and in the last, which is referred to as the cross-term, but not in the second. A simple calculation shows that the cross-term can also be neglected compared to the first term. The remaining integral can be expressed in elementary functions but that is not our concern here. Its frequency dependence is the basis of the statement that director fluctuations lead to frequency dependent spectral densities. The value of  $\omega_c$  is compatible with values determined by fitting the experimentally determined values of the function  $J_{01}(\omega)$  [8, 9, 28, 30].

For the probe molecules it is also found experimentally that the function  $J_{02}$ , to which we turn now, becomes frequency dependent. It is given by

$$\begin{aligned} J_{02}(\omega) &= \frac{2\langle D_{02}^2D_{0-2}^2 \rangle \tau_R}{1 + \omega^2 \tau_R^2} + \frac{8(\alpha\bar{\lambda}^2)^2}{9\omega_c} \langle D_{02}^2D_{0-1}^2D_{0-1}^2 \rangle^2 \\ &\times \left\{ I_2\left(\frac{\omega^2}{\omega_c^2}\right) - I_2\left(\frac{\omega^2}{\omega_c^2} + \frac{1}{\omega_c^2 \tau_R^2}\right) \right\}, \end{aligned} \quad (6.9)$$

where the integral  $I_2(x)$  is

$$I_2(x) = \int_0^1 dk_1 \int_0^1 dk_2 \frac{k_1^2 + k_2^2}{(k_1^2 + k_2^2)^2 + x}. \quad (6.10)$$

Table 3. Relative frequency dependence of  $J_{01}$  and  $J_{02}$ . Values are taken from [35] Liquid crystal, probes, measured nuclei and temperatures are the same as those in table 1.

Probe	$\omega_0/2\pi/\text{MHz}$	$J_{01}(\text{DF})\dagger/\text{ps}$	$\Delta J_{02}\ddagger/\text{ps}$	$(\Delta J_{02}/\Delta J_{01}) \times 100\%$ (exp)	(calc)§
CH <sub>3</sub> NC	13.1	3.8	0.4	10	0.5
toluene-d <sub>8</sub>	30.7	5.7	0.6	11	1.6
<i>p</i> -xylene-d <sub>10</sub>	30.7	16.6	2.0	12	3.7
tolane-d <sub>10</sub>	30.7	30	18	60	4.6

† Frequency dependent part of  $J_{01}$  at the lowest measured frequency. Although the first order Freed model was used in [35], these quantities are in fact largely independent of that model.

‡ Estimate for the frequency dependent part of  $J_{02}$ . It is found by subtracting the high frequency value of  $J_{02}$  from the values at the frequencies in the table and assuming that at the highest frequencies director fluctuations no longer contribute. It is likely to be slightly underestimated.

§ Equilibrium correlation functions in equations (6.7) and (6.9) were calculated with  $\bar{\lambda}$ 's from table 1. The integrals in equations (6.8) and (6.10) were calculated with  $\omega_c = 5.5 \times 10^8 \text{ s}^{-1}$ , at the frequencies given in the table. The frequency dependent part of  $J_2(2\omega_0)/J_1(\omega_0)$  was obtained in this way. The calculated values are an order of magnitude too low to explain the observed behaviour.

For this expression the same remarks can be made as for equation (6.8). The cross-term can, in most cases, be neglected entirely and the first term is independent of frequency in the N.M.R. frequency range. The result shows that, due to the second order contribution,  $J_{02}$  does indeed become frequency dependent and furthermore explicit calculation of the integral shows that this frequency dependence has a logarithmic contribution [29].

The relative magnitude of the frequency dependent parts of  $J_{02}$  and  $J_{01}$  can now be determined. We obtain from equations (6.7) and (6.9) for their ratio

$$\frac{J_{02}(2\omega_0)}{J_{01}(\omega_0)} = \frac{2}{3}(\alpha\bar{\lambda}^2) \frac{\langle D_{02}^2 D_{0-1}^2 D_{0-1}^2 \rangle^2}{\langle D_{01}^2 D_{0-1}^2 \rangle^2} \frac{I_2(4\omega_0^2/\omega_c^2)}{I_1(\omega_0^2/\omega_c^2)}. \quad (6.11)$$

For values of  $\omega_0/\omega_c$  between 0.05 and 0.5 the ratio of the integrals  $I_2/I_1$  is approximately constant and equal to 2.3. The same is true for the ratio of equilibrium correlation functions in the range of relevant  $\bar{\lambda}$  values; between  $\bar{\lambda} = 0.5$  and 2.0 it varies between 0.11 and 0.08. This shows that the ratio is generally smaller than 0.05, even for the highest values of  $\bar{\lambda}$ . Some of the results are shown in table 3. The conclusion must be that although direct fluctuations do give rise to a frequency dependent  $J_{02}$ , the observed frequency dependence is nevertheless too high to be explained by these alone.

We defer a complete analysis of the experimental results to a subsequent paper [30].

## 7. Concluding remarks

We have shown in this paper that it is possible to incorporate director fluctuations in the equilibrium distribution of molecular angles and in the angular transition probability to all orders. As a starting point we have used two expressions given by Freed, equations (2.6) and (2.7), both of which were shown only to be valid to lowest, i.e. first order in the fluctuations. It was noted, however, that the equations can be reformulated utilizing elementary probability theory, and that the resulting



expressions have a more general validity, cf. appendix A. The general expression, equation (A 2), can also be used to extend the theory to temperatures closer to the nematic–isotropic transition temperature  $T_{NI}$ . It was noted that fluctuations in the director field only become noticeable in the equilibrium distribution for strongly coupled probe molecules, for instance the liquid crystal molecules themselves, or close to the transition temperature. The liquid crystal hamiltonian  $\mathcal{F}$ , as given by equation (4.2) cannot be used at temperatures closer to the transition temperature than indicated in section 4. Equation (A 2) remains valid and adding mode coupling terms to  $\mathcal{F}$ , may still lead to analytical results.

We have only given explicit calculations for axially symmetric probe molecules. Most of the probes studied have, however, a marked asymmetry, i.e. the parameter  $\varrho$  cannot be taken equal to zero [31]. It can be shown [30] that the general conclusions of this paper remain valid, i.e. to lowest order in the parameter  $\varrho$  there is no contribution to the frequency dependent part of  $J_{0m}$  and inclusion of  $\varrho$  gives an extra contribution to the frequency dependence of  $J_{00}$  and  $J_{02}$  which has the same functional dependence on the frequency as that already found. The conclusion reached at the end of the previous section is not violated. The extra contribution is too small to alter substantially the value of the ratio of the spectral densities.

The general conclusion for the *equilibrium probability* is that director fluctuations influence the equilibrium distribution of angles of a not too large probe molecule only marginally, a few per cent at most. Consequently the order parameter and the interaction parameter  $\bar{\lambda}$  can be determined directly using quadrupolar line splittings. The small difference between the unrenormalized and the renormalized order parameter even for reasonably large probe molecules was not appreciated [9, 16, 28] for two reasons. First of all in the literature all expressions contain only the lowest order contribution to  $S$  in an expansion in the interaction parameter  $\bar{\lambda}$ ,  $S_0 = 2\bar{\lambda}/15$ . For very small values of  $\bar{\lambda}$ , for which Freed's theory was originally formulated, this is correct, but even for values of  $\bar{\lambda} = 0.5$  deviations occur and in fact the values of  $S$  are overestimated so that the effect of fluctuations is overestimated (fluctuations diminish the ordering). The second reason is that attempts to include higher order terms in the expansion [9] include superfluous contributions due to an erroneous expansion of the interaction potential of mean force, which does not take into account a fundamental restriction on the director fluctuations:  $\mathbf{n} \cdot \mathbf{n}_0 = 0$ . This leads to terms proportional to  $\alpha\bar{\lambda}$ , which for small probe molecules ( $\bar{\lambda} < 1$ ) severely overestimate the effect of fluctuations [32].

Since in this paper we are primarily interested in the effect of director fluctuations, and especially its consequence for the spectral densities  $J_{0m}$ , we have left out fluctuations in the order parameter itself completely, since it is to be expected that the time dependence of fluctuations in the order parameter is on a faster time scale than that of director fluctuations [3, 7]. Also, they are decoupled from director fluctuations if the free energy is only expanded to lowest (second) order in both the fluctuating director field and the fluctuating order parameter. We have absorbed the order parameter into the quantity  $\lambda$  and consequently this has now also become an independent fluctuating quantity of which the spectrum is determined by the spectrum of the nematic order parameter. It is rather easy to infer what the result of these fluctuations is. Using a method similar to that given in this paper, the order parameter fluctuations renormalize the potential, cf.  $\lambda SD_{00}^2(\Omega)$  by a factor

$$1 - \frac{1}{2}\lambda D_{00}^2(\Omega) \langle (\Delta S)^2 \rangle, \quad (7.1)$$

so that the effective  $\lambda$  is somewhat smaller. We also note that these fluctuations are not related to the elastic constants at all, but to the expansion parameters in the Landau-de Gennes free energy [4, 5]. Far from the transition temperature  $T_{NI}$  the order of magnitude of  $\langle(\Delta S)^2\rangle$  is about the same as that of  $\alpha$  [33].

The situation with the *transition probability*  $P(\Omega_0|\Omega, t)$  is much more complicated, and the subject of further study. We have modified the expression given by Freed in such a way that also for all orders it has the correct properties and not only to lowest order in the director fluctuations. These properties are that the transition probability is still markovian and properly normalized for integration over the angles  $\Omega$ . The general principles on which it is based remain a little vague, however. It is unclear, for instance, for which interaction strengths the theory breaks down, or even if it does. Also we cannot give a simple extension of the theory closer to the transition point, although this would be interesting since it would allow the study of liquid crystal dynamics in this regime.

In addition to this is the uncertainty in the motional model of the probe molecule itself. We have used a simple strong collision model and the results for the collision times, which can be obtained from the frequency independent part of the spectral densities, are not unreasonable. A variety of other models, all of them more complicated and involving extra parameters is possible [14]. In addition we should include translational diffusion of the probe as well, which leads to yet another variable [7]. These variables are not independent. For instance rotational and translational diffusion constants are in some way related to the viscosities of the medium but expressions relating them are scarce and seldomly go beyond the Stokes–Einstein formula [34].

Another remark concerns the use of the one-constant approximation. We have shown that this approximation is justified for the elastic constants, since the difference between the average elastic constant and  $K$  determined from expression (4.14) is negligible. The following argument can be given for the use of an effective viscosity. It should, in principle, be possible to identify an effective viscosity in the following manner: the appropriate viscosities are substituted into equation (B.10) and the angular integration is subsequently performed numerically, since analytical integration does not appear feasible. Then we try to identify an  $\eta_{\text{eff}}$  such that the relation

$$2K^{-1} \exp -tk^2 K/\eta_{\text{eff}} = \sum_{\alpha} K_{\alpha}^{-1} \int_0^1 d\xi \exp -tk^2 (K_{\alpha}/\eta_{\alpha}) [1 + (K_3/K_{\alpha} - 1)\xi^2] \quad (7.2)$$

is valid. If such an  $\eta_{\text{eff}}$  can be found for all values of  $k^2 t$  the use of an effective viscosity is justified; at present we can only hope this is the case and that the value found is close to the usual viscosities.

Yet another parameter in the theory is the cut-off wavevector  $k_c$ , the presence of which is the result of the application of a macroscopic theory at a microscopic level. Of course, there are ways of ridding oneself of this parameter but at the price of having to specify the behaviour of the liquid crystal at a local scale, or by boundary conditions. Introduction of the cut-off frequency in the time dependent integrals is a more complicated matter. We stated (in appendix B) that this introduction is necessary to insure convergence of the integrals at time zero, but in fact this is an improper limit in view of the fact that for such small times it is not the fluctuating director field but the collisional motion of the molecule that should determine its behaviour. On the other hand there is a physical argument, namely that director field modes cannot have arbitrarily short wavelengths. Also, if the frequency dependence is attributed to

director fluctuations, the observed functional frequency dependence of the spectral densities can only be explained if a cut-off frequency is introduced, the value of which also gives reasonable results for the cut-off wavelength [8, 9, 28, 30].

We conclude therefore by stating that the theory presented in this paper, which is an extension of the ideas proposed by Freed can only be said to be consistent, in the sense that if reasonable values of all parameters are taken, a frequency dependence of both  $J_{01}$  and  $J_{02}$  is obtained. The magnitude of the frequency dependence of  $J_{02}$  appears, however, to be off by an order of magnitude compared to experimental results; the functional dependence of the parameters, as given in equation (6.11) and subsequent equations, seems hardly to allow an improvement. It must be admitted that the magnitude of all effects considered depends rather crucially on the magnitude of the cut-off wavelength  $\lambda_c$ . An increase of this parameter by a factor 3 [32] increases the value of  $\omega_c$  by a factor 9 and the fluctuation parameter  $\alpha$  decreases by a factor 3. This would bring  $\lambda_c$  in a more realistic range, but as a consequence all effects of director fluctuations on the N.M.R. spectra and relaxation behaviour disappears.

The authors would like to thank J. Bulthuis for critical comments regarding our treatment of asymmetric molecules.

### Appendix A

In this Appendix we comment on the procedures followed to obtain the renormalized probabilities. The starting point is the probability of a configuration of the liquid crystal together with the probe molecule. The free energy of deformation  $\mathcal{F}(\psi)$  of the liquid crystal can be considered as that from the hamiltonian of that system, and the energy of interaction  $\mathcal{U}(\Omega, \psi)$ , the hamiltonian of interaction between the probe and liquid crystal environment. The canonical equilibrium probability of a liquid crystal plus probe configuration is then

$$P_{\text{eq}}(\Omega, \psi) = \frac{\exp - \beta[\mathcal{F} + \mathcal{U}]}{\int d\Omega d\psi \exp - \beta[\mathcal{F} + \mathcal{U}]} \quad (\text{A } 1)$$

and from this  $P_{\text{eq}}(\Omega)$  can be simply found by integrating  $P_{\text{eq}}(\Omega, \psi)$  over the angles  $\psi$ :

$$P_{\text{eq}}(\Omega) = \int d\psi \frac{\exp - \beta[\mathcal{F} + \mathcal{U}]}{\int d\Omega d\psi \exp - \beta[\mathcal{F} + \mathcal{U}]} \quad (\text{A } 2)$$

This is exactly the procedure followed in this paper.

The method proposed by Freed [7] is different in the following sense. The respective probabilities used are (cf. equation (2.14 c) of [7])

$$f_{\text{eq}}(\psi) = \frac{\exp - \beta\mathcal{F}}{\int d\psi \exp - \beta\mathcal{F}} \quad (\text{A } 3)$$

and

$$P_{\text{eq},\psi}(\Omega) = \frac{\exp - \beta\mathcal{U}}{\int d\Omega \exp - \beta\mathcal{U}} \quad (\text{A } 4)$$

Clearly

$$\int d\psi \frac{\exp - \beta[\mathcal{U} + \mathcal{F}]}{\left[ \int d\Omega \exp - \beta\mathcal{U} \right] \left[ \int d\psi \exp - \beta\mathcal{F} \right]} \quad (\text{A } 5)$$

is not necessarily equal to the integral in equation (A 2). We maintain that (A 2) is the correct expression. It can be shown, however, by a rather tedious calculation, that to lowest order both expressions yield the same results. We are interested in an expansion up to arbitrary order and consequently make use of equation (A 12), which shows that indeed we can first integrate the unnormalized probability  $\exp - \beta[\mathcal{F} + \mathcal{U}]$  over the angles  $\psi$  and finally fix the normalization constant by integration over  $\Omega$ . A similar situation occurs in the time dependent problem. Again it should be noted that for the probabilities  $P_{\text{eq},\psi}(\Omega)$  occurring in expression (2.7) and the collisional probability function (5.8) the unnormalized probabilities  $\exp - \beta\mathcal{U}$  have to be used in contrast to the equations used by Freed [7]. This can be seen most clearly in the limit  $t \rightarrow \infty$ , when equation (2.7) has to reduce to  $P_{\text{eq}}(\Omega)P_{\text{eq}}(\Omega_0)$ , or, to the square of equation (A 2). The normalization constant can then be fixed at the end by demanding that

$$\int d\Omega P(\Omega_0|\Omega, t) = 1. \quad (\text{A } 6)$$

In view of the symmetry between  $\Omega$  and  $\Omega_0$  in equation (5.11) the markovian property

$$\int d\Omega_0 P_{\text{eq}}(\Omega_0)P(\Omega_0|\Omega, t) = P_{\text{eq}}(\Omega) \quad (\text{A } 7)$$

is then also automatically satisfied by  $P(\Omega_0|\Omega, t)$ .

We note finally that it is allowed to use the normalized probability  $f_{\text{eq}}(\psi)$  as given in equation (A 3). The normalization constant for this function really is a constant and can be taken out of the integrals entirely. This was frequently used in §5, whenever we needed cancellation of gaussian integrals, in order to keep the expressions tractable.

### Appendix B

In this Appendix we evaluate equation (4.12) and derive equations (4.13) and (4.14), and the corresponding expressions for the time dependent problem of section 5. The evaluation takes place in two steps. First we replace the sum over  $\mathbf{k}$  by an integral:

$$\sum_{\mathbf{k}} = \frac{V}{(2\pi)^3} \int d\mathbf{k}. \quad (\text{B } 1)$$

This is allowed for a large enough volume  $V$ . Then we can calculate the resulting integrals, which we write as

$$\mathbf{T}_\alpha = \int d\mathbf{k} \frac{\mathbf{a}_\alpha \mathbf{a}_\alpha}{K_\alpha k_\perp^2 + K_\parallel k_\parallel^2}, \quad \alpha = 1, 2. \quad (\text{B } 2)$$

For the particular choice of  $n_0$  given in §4, the vectors  $\mathbf{a}_1$  and  $\mathbf{a}_2$  are given by

$$\mathbf{a}_1 = \frac{(-k_x, -k_y, 0)}{[k_x^2 + k_y^2]^{1/2}} \quad \text{and} \quad \mathbf{a}_2 = \frac{(-k_y, k_x, 0)}{[k_x^2 + k_y^2]^{1/2}}. \quad (\text{B } 3)$$

There are three different integrals to be considered: those containing respectively  $k_x k_y$ ,  $k_x^2$  and  $k_y^2$  in the integrand. The first is zero, since the integration over the azimuthal angle makes it vanish; the other two are equal:

$$\int_0^{2\pi} d\phi \cos \phi \sin \phi = 0, \quad \int_0^{2\pi} d\phi \cos^2 \phi = \int_0^{2\pi} d\phi \sin^2 \phi = \pi. \quad (\text{B } 4)$$

Next we come to the integration over the polar angle  $\theta$ . The one remaining integral can be written as

$$\int_{-1}^{+1} d\cos \theta \frac{1}{K_x + (K_3 - K_x) \cos^2 \theta} = \frac{2}{K_x} \sqrt{\left(\frac{K_x}{K_3 - K_x}\right)} \operatorname{arctg} \sqrt{\left(\frac{K_3 - K_x}{K_x}\right)}. \quad (\text{B } 5)$$

Finally we have to consider the integration over the length of the vector  $\mathbf{k}$ . This integral is given by

$$\int_0^{k_c} dk = k_c, \quad (\text{B } 6)$$

where we had to introduce a cut-off wavevector,  $k_c$ , to assure convergence of this integral. The rationale for this cut-off is the non-applicability of the macroscopic theory of the director field for small wavelengths. Taking everything together, we find for the tensor  $\mathbf{T}_\alpha$

$$\mathbf{T}_\alpha = \frac{2\pi k_c}{K_x} \sqrt{\left(\frac{K_x}{K_3 - K_x}\right)} \operatorname{arctg} \sqrt{\left(\frac{K_3 - K_x}{K_x}\right)} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \quad (\text{B } 7)$$

The second step in the calculation of  $\langle \Delta \mathcal{U} \Delta \mathcal{U} \rangle$  is to perform the sum over  $\alpha$  which can now be written as

$$\langle \Delta \mathcal{U} \Delta \mathcal{U} \rangle = \frac{2kT}{(2\pi)^3} \sum_{\alpha=1,2} \mathbf{n}_0 \cdot \mathbf{Q} \cdot \mathbf{T}_\alpha \cdot \mathbf{Q} \cdot \mathbf{n}_0. \quad (\text{B } 8)$$

Introduction of equation (B 7) into equation (B 8) gives equations (4.13) and (4.14).

For the time dependent problem cf. equation (5.10) we have a similar integral to calculate; i.e. after replacing the products of exponentials by an exponential of the sum over  $k$  and  $\alpha$ , and subsequently the sum of  $\mathbf{k}$  by an integral, using equation (B 1), we find the tensor

$$\mathbf{T}'_\alpha(t) = \int d\mathbf{k} \frac{\mathbf{a}_\alpha \mathbf{a}_\alpha}{K_x k_\perp^2 + K_3 k_\parallel^2} \exp \left\{ - \frac{t[K_x k_\perp^2 + K_3 k_\parallel^2]}{\eta_\alpha} \right\}. \quad (\text{B } 9)$$

to evaluate. As in the foregoing derivation, we can write  $\mathbf{T}'_\alpha$  in the form of equation (B 7), but now with a time dependent prefactor  $\mathbf{T}'_\alpha(t)$  which is given by

$$\mathbf{T}'_\alpha(t) = \frac{2\pi}{K_x} \int_0^1 d\xi \int_0^{k_c} dk \frac{\exp - tk^2 K_x / \eta_\alpha [1 + (K_3/K_x - 1)\xi^2]}{1 + (K_3/K_x - 1)\xi^2}. \quad (\text{B } 10)$$

A cut-off wavevector,  $k_c$ , was introduced to assure convergence at  $t = 0$ . In the limit  $t \rightarrow 0$  equation (B 10) reduces to equation (B 5), as it should. Further analytical progress is only possible in the one-constant approximation, where all the  $K$ s are taken equal as well as  $\eta_1 = \eta_2 = \eta$ . Then equation (B 10) can be written as

$$\mathbf{T}'_\alpha(t) = \frac{2\pi k_c}{K} \frac{\Phi((\omega_c t)^{1/2})}{(\omega_c t)^{1/2}}, \quad (\text{B } 11)$$

where the cut-off frequency,  $\omega_c$ , is defined by

$$\omega_c = \frac{Kk_c^2}{\eta}. \quad (\text{B } 12)$$

The error integral  $\Phi(z)$  is given by

$$\Phi(z) = \int_0^z dx \exp(-x^2). \quad (\text{B } 13)$$

Finally we perform the sum over the  $\alpha$ s to obtain for the product of exponentials in equation (5.10):

$$\begin{aligned} & \prod_{\alpha=1,2} \prod_{\mathbf{k}} \exp \left\{ \frac{2\sigma_{\alpha}(\mathbf{k})q_{\alpha}(\Omega)q_{\alpha}(\Omega_0) \exp(-t/\tau_{\alpha}(\mathbf{k}))}{(kTV)^2} \right\} \\ &= \exp \frac{k_c}{\pi^2 KkT} \{ Q_{zx}(\Omega)Q_{zx}(\Omega_0) + Q_{zy}(\Omega)Q_{zy}(\Omega_0) \} \frac{\Phi((\omega_c t)^{1/2})}{(\omega_c t)^{1/2}}. \quad (\text{B } 14) \end{aligned}$$

Introduction of the spherical components of the Qs [13] and subsequent transformation to the molecular coordinate frame gives equation (5.11).

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- [24] From the context it should be clear that we use the symbol  $\langle \dots \rangle$  for two different types of averaging. In this section up to equation (4.18) it was used to represent the average over the equilibrium fluctuations of the director field; in this and the following paragraph it symbolizes an average over molecular orientations including director fluctuations.
- [25] In fact this point deserves a more detailed investigation, which is beyond the scope of this paper. The condition is only marginally satisfied for liquid crystal molecules and cut-off wavelengths of the order of magnitude indicated.
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- makes it, however, still too large to explain the experimentally found frequency dependence in the spectral density  $J_{01}$ . It is interesting to note that in the (improper) limit where we let the fluctuating term dominate ( $\alpha\lambda \rightarrow \infty$ ) our molecular order parameter approaches 0.25, whereas Zanoni finds 0.24; see also FABER, T. E., 1977, *Proc. R. Soc. A*, **353**, 247.
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- [34] The translational diffusion constant used in the earlier references is given by  $D_{tr} = kT/6\pi\eta a$ , sometimes taken with corrections for size of the particles, GIERER, A., and WIRTZ, K., 1953, *Z. Naturforschg.*, **A8**, 532; for a different approach see MIYAJIMA, S., NAKAMURA, N., and CHIHARA, H., 1983, *Bull. chem. Soc. Japan*, **56**, 400.
- [35] PLOMP, L., and BULTHUIS, J., 1988, *Liq. Crystals*, **3**, 927.