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Theory of NMR line broadening by elastic modes in nematic liquid crystals

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The model proposed in [7] to calculate the broadening effect produced by elastic modes on NMR line shapes of nematic liquid crystals, in which all modes with relaxation times longer than a NMR time scale $\Delta\tau$ are static, and infinitely fast in the opposite case, is put on a more rigorous theoretical basis, by considering all modes with their actual relaxation times. The correlation function of the transverse magnetization is calculated and expressed in terms of the self-correlation function of the components n_x and n_y of the local director, assumed to be equivalent and independent gaussian random variables. Formal expressions are given for the general case, and in the one constant, cylindrical and spherical cases, approximations. The general procedure describing how to use this formalism for a NMR spectrum composed of many lines, is given. This formalism is then used to analyse the same data as in [7] concerning a main chain nematic polymer, in the spherical approximation. It is shown that fits with the same quality are obtained. These results provide (i) theoretical support for the model of [7], (ii) an operational way to define $\Delta\tau$ and (iii) a practical example for discussion of the controversial problem of the 'cut-off wavevector(s)' of the modes, which define the size of the elementary uniaxial object in the nematic medium. It is shown that, for this polymer, the smallest size corresponds to a volume between one and four repeat units. The analysis of line shapes provides the viscoelastic parameter $\eta^{1/2}/K^{3/2}$, where η and K are the average viscosity and average elastic constant. Values of η and K can be deduced from the theory. The limitations of the model are discussed. It is shown that the present model and the one of [7] are complementary. It is argued that the present formalism may be useful to analyse NMR line shapes in conventional polymers.

1. Introduction

The study of thermally induced long range orientational fluctuations (the elastic modes) [1, 2] in uniaxial liquid crystals is currently the subject of considerable interest. The main experimental techniques used for this purpose are light scattering [1, 2] and nuclear spin-lattice relaxation [3–6]. While the theory to analyse light scattering data is well established and widely accepted, essentially because this very technique can select a particular wavelength which is always much larger than a molecular length, the situation is more confusing for spin-relaxation because all modes, in particular those with short wavelengths, need to be taken into account. In a recent paper [6 (*a*)], Faber

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discusses a number of important questions on this matter, in particular the central open question about what are the shortest (cut-off) wavelengths (whose actual values are of fundamental importance in the theory) below which the continuous theory breaks down. His conclusion is that "the director field can be defined at any arbitrary length scale" and consequently, that it is justified to assume that "all the misalignment of molecules in a nematic can be described in terms of director fluctuations, even on a microscopic scale" [6(*a*)].

Although this viewpoint is not widely accepted, the very existence of the elastic modes is not questioned, and methods that are sensitive to them can be used to study viscoelastic properties, test the theory and/or estimate the contribution of other mechanisms to the measured quantity. Besides those already mentioned, another possible method is the study of NMR (and ESR) line shapes. A reason why this method is not widely used is that the overwhelming number of NMR studies have concerned low molecular mass liquid crystals, in which the effect of these modes on the NMR line shapes is negligible [4]. In other words, practically all modes are fast compared to the relevant magnetic interactions. In polymer liquid crystals on the contrary, due to the increase in the viscosities by several orders of magnitude, an appreciable fraction of the elastic modes are slow, producing some 'static' broadening of the lines.

In a previous paper [7], the calculation of the corresponding effect was made by introducing a NMR time scale $\Delta\tau$ and assuming that all modes whose relaxation time is larger than $\Delta\tau$ are completely static, and infinitely fast in the opposite case. This assumption naturally led to the introduction of the notion of 'static order parameter' S_{stat}, which could be expressed in terms of an average viscosity η, an average elastic constant K, the NMR time $\Delta\tau$ and the temperature T. This parameter quantifies the amount of orientational disorder introduced by the 'static' modes. This model accounts very well for the experimental variation of the proton NMR line shape of a main chain nematic polymer monodomain with the angle between the axis of the monodomain and the static magnetic field [7]. It also proved to be very useful to analyse the time evolution of line shapes during magnetic reorientation of monodomains, from which accurate values of viscoelastic coefficients could be deduced for a main chain [8] and a side chain [9] nematic polymer.

This model applies only to cases where the static disorder is small ($S_{\text{stat}} \gtrsim 0{\cdot}9$), its main approximation lying in the partition of the modes into (completely) static and (infinitely) fast ones. Moreover, the quantity S_{stat} which is deduced from the experiments is not an intrinsic property of the phase, since it depends on the NMR time scale $\Delta\tau$. Since in addition $\Delta\tau$ is *a priori* ill-defined for broad proton NMR spectra (although this limitation is not too serious, since the dependence on this parameter is only to the power 1/2), it would be very interesting to remove this approximation and consider all the modes in the calculation of the line shape. The main purpose of this paper is to present such calculations.

In § 2, the general theory is presented and close mathematical forms for the correlation function of the transverse magnetization are given, corresponding to the cylindrical and spherical one constant approximations. In § 3, we describe an application of this theory to the analysis of proton NMR line shapes of a main chain nematic polymer, and in § 4 these results are compared to those obtained with the approximate method of [7]. In § 5, the question of length scale and cut-off wavevectors is discussed in the light of the results obtained with this particular polymer. In the conclusion, the approximations of the model are discussed and the possibility of application of the method to conventional polymers is outlined.

2. Theory

2.1. *General formalism for the case when the static magnetic field is parallel to the mean director*

We consider an idealized 'basic molecule' constituted by a segment picturing its (cylindrical) symmetry axis, and oriented at an angle θ with respect to the static magnetic field. For simplicity, its NMR spectrum is assumed to be a single sharp line j at a distance $\omega_j = \omega_{j0} P_2(\cos\theta)$ from the Larmor pulsation ω_0. This distance is a maximum ($=\omega_{j0}$) when the molecule is aligned along the field. If the angle θ fluctuates, the line shape will change according to the time scale and the magnitude of the fluctuations. In the adiabatic approximation, i.e. when the fluctuations are fast compared to the spin-lattice relaxation time, the line shape $I_j(\omega)$ of an ensemble of such magnetically uncoupled molecules is given by the Fourier transform of the function $G_j(t)$ [10]

$$G_j(t) = \mathrm{Re}\,\{\exp(\mathrm{i}\omega_0 t - t/T_2)\langle \exp[\mathrm{i}F_j(t)]\rangle\}, \tag{1}$$

where

$$F_j(t) = \int_0^t \omega_j(t')\,dt' = \omega_{j0} \int_0^t P_2[\cos\theta(t')]\,dt'. \tag{2}$$

$1/T_2$ is a damping coefficient which ensures that $G(t)$ always tends to 0 at infinite time, or equivalently, that the NMR line has a non-zero width (equal to $2/T_2$) in the absence of fluctuations. The brackets stand for an equilibrium statistical average.

The calculation consists of evaluating the above quantities, assuming that the time fluctuations of θ are due to the elastic modes. We will adopt the viewpoint discussed in the Introduction, and identify the local director **n** of the continuous theory with the long axis of our idealized molecule.

In the hydrodynamic theory, a statistical order parameter S at time t' is defined as

$$S = \left\langle 1 - \frac{3}{2}[n_x^2(r,t') + n_y^2(r,t')] \right\rangle, \tag{3}$$

where n_x and n_y are the components of the local director in the laboratory frame, z being along the mean director n_0 (i.e. the axis of the monodomain) and where, here, the brackets stand for a space average at time t'. Invoking the ergodicity theorem (valid in a sufficiently fluid medium), it can also be thought of as a time average performed at a particular point r, where our idealized molecule is situated. Thus, n_x and n_y are the components, in the laboratory frame, of the unit vector along the molecular axis. Consequently, $P_2[\cos\theta(t')]$ in equation (2) is just the value at time t' of the quantity inside the brackets in equation (3). In the following, the explicit dependence on r will be omitted for simplicity, in all formulae.

Defining the real random functions

$$\xi(t') = n_x^2(t') + n_y^2(t') - \langle n_x^2(t') + n_y^2(t')\rangle \tag{4}$$

and

$$X_j(t) = -\frac{3}{2}\omega_{j0} \int_0^t \xi(t')\,dt', \tag{5}$$

we can write

$$\omega_j(t') = S\omega_{j0} - \frac{3}{2}\omega_{j0}\xi(t') \tag{6}$$

and

$$G_j(t)=\mathrm{Re}\left\{\exp\left[\mathrm{i}(\omega_0+S\omega_{j0})t-\frac{t}{T_2}\right]\langle\exp[\mathrm{i}X_j(t)]\rangle\right\}. \tag{7}$$

2.2. *Statistical behaviour $X_j(t)$*

Later, it will be assumed that $n_x(t')$ and $n_y(t')$ are gaussian random functions with the same distribution, and it follows that $n_x^2+n_y^2$ is a random function of the χ^2 type with two degrees of freedom. But whatever reasonable hypothesis is made about the probability distributions of n_x and n_y, or ξ, $X_j(t)$ defined by equation (5) may always be considered as a gaussian random function. The reason is that an integral of a random function behaves just like the sum of random variables, and the gaussian character follows from the central limit theorem. This argument is probably weak when t is small or comparable to the correlation time of ξ, but in this case $X_j(t)$ is always small, and the type of distribution taken for this variable is not likely to affect much the average present in equation (7).

With this gaussian hypothesis for X_j, we have

$$\langle\exp[\mathrm{i}X_j(t)]\rangle=\int_{-\infty}^{+\infty}P(X_j,t)\exp(\mathrm{i}X_j)\,dX_j, \tag{8}$$

where

$$P(X_j,t)=\frac{1}{[2\pi\langle X_j^2(t)\rangle]^{1/2}}\exp\left[-\frac{(X_j-\langle X_j\rangle)^2}{2\langle X_j^2(t)\rangle}\right]. \tag{9}$$

Noting that $\langle X_j\rangle=0$ (this property follows immediately from equations (4) and (5)) we readily obtain

$$\langle\exp[\mathrm{i}X_j(t)]\rangle=\exp[-\langle X_j^2(t)\rangle/2]. \tag{10}$$

Assuming that $\xi(t')$ is a stationary random function, which is actually the case whenever S does not depend on time, it can be shown after some mathematical manipulation that we have

$$\langle X_j^2(t)\rangle=\frac{9}{4}\omega_{j0}^2\int_0^t d\tau(t-\tau)C_\xi(\tau) \tag{11}$$

where $C_\xi(\tau)$ is the self-correlation function of ξ

$$C_\xi(\tau)=\langle\xi(t')\xi(t'-\tau)\rangle. \tag{12}$$

2.3. *An expression for $C_\xi(\tau)$*

From equation (4), it follows that

$$C_\xi(\tau)=\langle[n_x^2(t')+n_y^2(t')-\langle n_x^2+n_y^2\rangle][n_x^2(t'-\tau)+n_y^2(t'-\tau)-\langle n_x^2+n_y^2\rangle]\rangle, \tag{13}$$

where we have used the property that $\langle n_x^2+n_y^2\rangle$ does not depend on t' and τ. Using the fact that n_x and n_y are equivalent random variables (same statistical properties), we obtain

$$C_\xi(\tau)=2\langle n_x^2(t')n_x^2(t'-\tau)\rangle+2\langle n_x^2(t')n_y^2(t'-\tau)\rangle-\langle n_x^2+n_y^2\rangle^2. \tag{14}$$

To go further with the calculation, we shall follow [5] and assume that (i) the fluctuations in x and y are uncorrelated and (ii) n_x and n_y are gaussian random variables with the same distribution. The first assumption makes it possible to write

$$\langle n_x^2(t')n_y^2(t'-\tau)\rangle = \langle n_x^2(t')\rangle\langle n_y^2(t'-\tau)\rangle$$

and the second assumption leads to

$$\langle n_x^2(t')n_x^2(t'-\tau)\rangle = \langle n_x^2(t')\rangle\langle n_x^2(t'-\tau)\rangle + 2\langle n_x(t')n_x(t'-\tau)\rangle^2$$

Inserting these two relations into equation (14), we arrive at the following simple result:

$$C_\xi(\tau) = 4\langle n_x(t')n_x(t'-\tau)\rangle^2. \tag{15}$$

2.4. *Formalism for the case when the static magnetic field is at an angle Θ to the mean director*

The laboratory frame is chosen such that the z axis is along n_0, as before, and the static field H is in the xz plane. In this frame, the polar and azimuthal angles of the field and of the molecular axis n are Θ, 0, and Ω, φ, respectively. The relevant formulae are still as in equations (1) and (2), but now $\theta = (n, H)$ becomes a function of Θ. We have

$$P_2(\cos\theta) = \tfrac{3}{2}(n_x^2\sin^2\Theta + n_z^2\cos^2\Theta + 2n_xn_z\sin\Theta\cos\Theta) - \tfrac{1}{2} \tag{16}$$

and taking $\langle n_x^2\rangle = \langle n_x^2 + n_y^2\rangle/2$, $\langle n_xn_y\rangle = 0$, it follows that

$$\langle P_2(\cos\theta)\rangle = SP_2(\cos\Theta). \tag{17}$$

Writing $\omega_j(t') = \langle\omega_j(t')\rangle + [\omega_j(t') - \langle\omega_j(t')\rangle]$, and using equation (17), we arrive at

$$\omega_j(t') = S\omega_{j0}P_2(\cos\Theta) - \tfrac{3}{2}\omega_{j0}\xi_\Theta(t'), \tag{18}$$

where

$$\xi_\Theta(t') = \tfrac{2}{3}SP_2(\cos\Theta) - (n_x^2\sin^2\Theta + n_z^2\cos^2\Theta + 2n_xn_z\sin\Theta\cos\Theta) + \tfrac{1}{3} \tag{19}$$

is a random function which generalizes $\xi(t')$, given by equation (4), to the case where $\Theta \neq 0$, i.e. $\xi_0(t') \equiv \xi(t')$, and also satisfies $\langle\xi_\Theta(t')\rangle = 0$.

Similarly, defining the random variable

$$X_{\Theta,j}(t) = -\tfrac{3}{2}\omega_{j0}\int_0^t \xi_\Theta(t')\,dt' \tag{20}$$

the lineshape $I_{\Theta,j}(\omega)$ in the presence of fluctuations, when the director is rotated at an angle Θ with respect to the field, is given by the Fourier transform of $G_{\Theta,j}(t)$

$$G_{\Theta,j}(t) = \mathrm{Re}\left\{\exp\left[\mathrm{i}(\omega_0 + S\omega_{j0}P_2(\cos\Theta))t - \frac{t}{T_2}\right]\langle\exp[\mathrm{i}X_{\Theta,j}(t)]\rangle\right\}. \tag{21}$$

Invoking the same arguments as for $X_j(t)$, we shall assume that $X_{\Theta,j}(t)$ is a gaussian variable, and we can write a set of equations similar to equation (8) through equation (12), the only difference being that $X_j(t)$, $C_\xi(\tau)$ and $\xi(t')$ are now replaced by $X_{\Theta,j}(t)$, $C_{\xi_\Theta}(\tau)$ and $\xi_\Theta(t')$.

The calculation of the self-correlation function $C_{\xi_\Theta}(\tau)$ is made in three steps. First, using equation (19), and all statistical properties of n_x and n_y previously assumed to hold, we obtain

$$\begin{aligned}\langle\xi_\Theta(t')\xi_\Theta(t'-\tau)\rangle = {} & (4-12\sin^2\Theta+10\sin^4\Theta)\langle n_x(t')n_x(t'-\tau)\rangle^2\\ & +4\sin^2\Theta\cos^2\Theta\langle n_x(t')n_z(t')n_x(t'-\tau)n_z(t'-\tau)\rangle\\ & -4\sin\Theta\cos\Theta\left(\frac{2S+1}{3}-S\sin^2\Theta\right)\langle n_x(t')n_z(t')\rangle\\ & +4\sin^3\Theta\cos\Theta\langle n_x^2(t')n_x(t'-\tau)n_z(t'-\tau)\rangle\\ & +4\sin\Theta\cos^3\Theta\langle n_z^2(t')n_x(t'-\tau)n_z(t'-\tau)\rangle. \qquad (22)\end{aligned}$$

This equation is exact, but unuseful because most of its bracket expressions are not expressable in terms of model parameters such as S or the viscoelastic parameters referred to below. To proceed, we assume that the fluctuations are small (n_x^2 and $n_y^2 \ll 1$); then we can replace n_z by $1-\frac{1}{2}(n_x^2+n_y^2)$. Noting that $\langle n_x^3(t')\rangle = \langle n_x^2(t')n_x^3(t'-\tau)\rangle = \langle n_x^2(t')n_x(t'-\tau)\rangle = 0$, and neglecting terms of the third order in n_x^2, we can write

$$\begin{aligned}\langle\xi_\Theta(t')\xi_\Theta(t'-\tau)\rangle = {} & 4\langle n_x(t')n_x(t'-\tau)\rangle^2\\ & +(\sin^2\Theta-\sin^4\Theta)\Bigg[\left(\frac{S+5}{3}\right)^2\langle n_x(t')n_x(t'-\tau)\rangle\\ & -2\frac{S+5}{3}\langle n_x^3(t')n_x(t'-\tau)\rangle-10\langle n_x(t'-\tau)\rangle^2\Bigg]\\ & -2\sin^2\Theta\langle n_x(t')n_x(t'-\tau)\rangle^2. \qquad (23)\end{aligned}$$

In the Appendix, we show that the gaussian hypothesis for $n_x(t')$ leads to the relation

$$\langle n_x^3(t')n_x(t'-\tau)\rangle = 3\langle n_x^2\rangle\langle n_x(t')n_x(t'-\tau)\rangle \qquad (24)$$

so we find

$$\begin{aligned}\langle\xi_\Theta(t')\xi_\Theta(t'-\tau)\rangle = {} & \frac{(S+5)(7S-1)}{9}(\sin^2\Theta-\sin^4\Theta)\langle n_x(t')n_x(t'-\tau)\rangle\\ & +[4-2\sin^2\Theta-10(\sin^2\Theta-\sin^4\Theta)]\langle n_x(t')n_x(t'-\tau)\rangle^2. \qquad (25)\end{aligned}$$

For $\Theta=0$, we recover all equations of the previous sections.

It is interesting to note that, in the general case, the correlation function of ξ_Θ is the sum of two terms, the first one being proportional to the correlation function of n_x and the second one to its square. For $\Theta=0$ and 90° on the contrary, only the square term survives. Because this latter function is basically a quantity (much) smaller than 1, and the coefficients of proportionality are usually comparable when Θ is around 45° (otherwise the coefficient of the square term largely dominates), we conclude that the effects of the elastic modes on NMR line shapes are stronger when the director of the nematic monodomain makes a large angle (say, 40 to 60°) with the static field. This result constitutes the theoretical support for the qualitative arguments invoked in [7] to justify the corresponding experimental results. The only thing that is now needed to perform a practical calculation is a formal expression for the self-correlation function of n_x in terms of the parameters of the hydrodynamic theory.

2.5. *Calculation of* $\langle n_x(t')n_x(t'-\tau)\rangle$

In the hydrodynamic theory of nematics [1, 2], we introduce the space Fourier transform of n_x, limited to the volume V of the nematic monodomain

$$n_x(r,t)=\frac{V}{(2\pi)^3}\int dq\, n_x(q,t)\exp(-\mathrm{i}q.r). \tag{26}$$

Using the normal splay–bend ($\alpha=1$) and twist–bend ($\alpha=2$) modes $n_\alpha(q,t)$, the correlation function of n_x can be expressed as

$$\langle n_x(0)n_x(\tau)\rangle=\frac{1}{2}\frac{V}{(2\pi)^3}\sum_{\alpha=1}^{2}\int dq\langle|n_\alpha(q,0)|^2\rangle\exp\left[-\frac{\tau}{\tau_\alpha(q)}\right] \tag{27}$$

showing that the two kinds of modes contribute additively to this function. Neglecting the diamagnetic contribution to the free energy (see below), the $\langle|n_\alpha(q,0)|^2\rangle$ and the $\tau_\alpha(q)$ can be written [2]

$$\langle|n_\alpha(q,0)|^2\rangle=\frac{k_\mathrm{B}T}{(K_\alpha q_\perp^2+K_3q_z^2)V};\quad \tau_\alpha(q)=\frac{\eta_\alpha(q)}{K_\alpha q_\perp^2+K_3q_z^2}, \tag{28}$$

where

$$\eta_1(q)=\gamma_1-\frac{\alpha_3^2\rho^4-2\alpha_2\alpha_3\rho^2+\alpha_2^2}{\eta_\mathrm{b}\rho^4+(\alpha_1+\eta_\mathrm{b}+\eta_\mathrm{c})\rho^2+\eta_\mathrm{c}}, \tag{29 a}$$

$$\eta_2(q)=\gamma_1-\frac{\alpha_2^2}{\eta_\mathrm{a}\rho^2+\eta_\mathrm{c}}. \tag{29 b}$$

In these expressions, the symbols have their usual meanings. The K_i are the Frank elastic constants, the α_i are the Leslie viscosity coefficients and the η_i are the Miesowicz viscosity coefficients. The quantities $q_\perp$ and q_z are the components of q perpendicular and parallel to the director z, and $\rho=q_\perp/q_z$.

Introducing the two functions

$$f_\alpha(\rho)=K_\alpha\rho^2+K_3 \tag{30}$$

and

$$F_\alpha(\rho)=f_\alpha(\rho)/\eta_\alpha(\rho) \tag{31}$$

equation (27) can be rewritten

$$\langle n_x(0)n_x(\tau)\rangle=\frac{k_\mathrm{B}T}{16\pi^3}\sum_{\alpha=1}^{2}\int dq\frac{\exp[-q_z^2\tau F_\alpha(\rho)]}{q_z^2f_\alpha(\rho)}. \tag{32}$$

This equation gives the most general expression for the correlation function of n_x. The value of this function for $\tau=0$ is

$$\langle n_x^2(0)\rangle=k_\mathrm{B}T/2E_\mathrm{e}, \tag{33 a}$$

where E_e is a quantity, with the dimension of an energy, given by

$$\frac{1}{E_\mathrm{e}}=\frac{1}{8\pi^3}\sum_{\alpha=1}^{2}\int\frac{dq}{q_z^2f_\alpha(\rho)}. \tag{33 b}$$

This energy may be thought of as an elementary elastic energy associated with the modes, and stored in the nematic phase. It must be sufficiently large compared to the 'quantum' of thermal energy $k_BT/2$ so that a nematic phase exists at temperature T. The energy E_e is related to the order parameter S via the evident relation

$$S=1-\frac{3k_BT}{2E_e}. \tag{34}$$

So far, nothing has been assumed concerning the molecules, except that they are necessarily objects with cylindrical symmetry. If we assume that the nematic domain contains N such objects, a condition concerning the integration volume in q space can be written. This condition is that the number of modes in this monodomain is equal to the total number of orientational degrees of freedom associated with the (linear) molecules, namely $2N$ [6]. Noting that the density in q space, of modes of polarization α ($\alpha=1,2$), in a sample of volume V, is $V/8\pi^3$, the above condition writes

$$\frac{V}{8\pi^3}\sum_{\alpha=1}^{2}\int dq=2N. \tag{35}$$

Introducing the number of molecules per unit volume n_v, the density ρ, the 'molecular mass' M (the quotes emphasize the fact that the idealized molecules are not necessarily the true molecules) and the Avogadro number N_a, this condition can be rewritten

$$\sum_{\alpha=1}^{2}\int dq=16\pi^3n_v \quad \left(=16\pi^3N_a\frac{\rho}{M} \text{ for a pure sample}\right). \tag{36}$$

The integration volume in q space has necessarily cylindrical symmetry around the mean director. The lower limit corresponds to the inverse of the sample dimensions. It can be taken as zero for a macroscopic sample, in normal magnetic fields, provided the upper limit is sufficiently high (of the order of the inverse of the molecular dimensions), as is actually the case. The reason is that the contribution to the integrals in equation (27), of all modes whose wavelengths are longer than the magnetic coherence length (a few microns in our magnetic field), turns out to be completely negligible. This result also justifies that the diamagnetic term in the free energy can be neglected, as previously assumed. The upper limit of the integration volume is more interesting. It cannot extend to infinity in all directions since equation (36) imposes that this volume be finite. The upper limit of the integration volume thus defines two cut-off wavevectors $q^c_{\theta\alpha}$ for each orientation θ of q with respect to the mean director.

To proceed with the calculation, some volume shape should be assumed. We choose the simplest shapes, namely circular cylinders. In this case, there are, in all, four cut-off parameters, $q^c_{\perp\alpha}$ and $q^c_{z\alpha}$. The volume element in q space being $dq=2\pi q_\perp dq_\perp\, dq_z$, equation (32) can be rewritten:

$$\langle n_x(0)n_x(\tau)\rangle=\frac{k_BT}{8\pi^2}\sum_{\alpha=1}^{2}\int_{-q^c_{z\alpha}}^{+q^c_{z\alpha}}\frac{dq_z}{q_z^2}\int_0^{q^c_{\perp\alpha}}q_\perp dq_\perp\frac{\exp[-q_z^2\tau F_\alpha(\rho)]}{f_\alpha(\rho)}. \tag{37}$$

The integral in $q_\perp$ being performed at constant q_z, we have $dq_\perp=q_z\,d\rho$. Noting that the integrand is an even function of q_z, the change of variables $(q_\perp,q_z)\to(\rho=q_\perp/q_z, v=q_z)$ leads to

$$\langle n_x(0)n_x(\tau)\rangle=\frac{k_BT}{4\pi^2}\sum_{\alpha=1}^{2}J_\alpha(\tau), \tag{38}$$

where the $J_\alpha(\tau)$ are double integrals defined as

$$J_\alpha(\tau)=\int_0^\infty \frac{\rho d\rho}{f_\alpha(\rho)}\int_0^{g^\alpha(\rho)} dv \exp[-v^2\tau F_\alpha(\rho)]. \tag{39}$$

The upper limit of the second integral is given by:

$$g_\alpha(\rho)=q^{\rm c}_{z\alpha} \qquad \text{for } \rho\leqslant q^{\rm c}_{\perp\alpha}/q^{\rm c}_{z\alpha} \tag{40 a}$$

and

$$g_\alpha(\rho)=q^{\rm c}_{\perp\alpha}/\rho \qquad \text{for } \rho> q^{\rm c}_{\perp\alpha}/q^{\rm c}_{z\alpha}\cdot \tag{40 b}$$

Introducing the error function erf, which verifies the identity

$$\frac{1}{A}\int_0^A \exp(-Bu^2)\,du=\frac{\pi^{1/2}}{2}\frac{\operatorname{erf}(AB^{1/2})}{AB^{1/2}}, \tag{41}$$

we get

$$\begin{aligned}J_\alpha(\tau)=&\frac{\pi^{1/2}}{2}q^{\rm c}_{z\alpha}\int_0^{q^{\rm c}_{\perp\alpha}/q^{\rm c}_{z\alpha}} d\rho\frac{\rho}{f_\alpha(\rho)}\frac{\operatorname{erf}\{q^{\rm c}_{z\alpha}[\tau F_\alpha(\rho)]^{1/2}\}}{q^{\rm c}_{z\alpha}[\tau F_\alpha(\rho)]^{1/2}}\\&+\frac{\pi^{1/2}}{2}q^{\rm c}_{\perp\alpha}\int_{q^{\rm c}_{\perp\alpha}/q^{\rm c}_{z\alpha}}^{\infty} d\rho\frac{1}{f_\alpha(\rho)}\frac{\operatorname{erf}\{q^{\rm c}_{\perp\alpha}[\tau F_\alpha(\rho)]^{1/2}/\rho\}}{q^{\rm c}_{\perp\alpha}[\tau F_\alpha(\rho)]^{1/2}/\rho}.\end{aligned} \tag{42}$$

It can be easily seen that both integrals converge for all τ values, but their evaluation can be made only numerically. However, for $\tau=0$, a close form exists. One way to perform the calculation is to put $\tau=0$ in equation (32) and follow the procedure used in [7]. The final result, expressed in terms of the elementary elastic energy $E_{\rm e}$ of equation (33), is

$$\frac{1}{E_{\rm e}}=\frac{1}{2\pi^2}\sum_{\alpha=1}^{2}\frac{q^{\rm c}_{z\alpha}}{K_\alpha}\left[\frac{1}{2}\log(1+m_\alpha)+m_\alpha^{1/2}\arctan\left(\frac{1}{m_\alpha^{1/2}}\right)\right], \tag{43 a}$$

where

$$m_\alpha=\frac{K_\alpha(q^{\rm c}_{\perp\alpha})^2}{K_3(q^{\rm c}_{z\alpha})^2}, \quad \alpha=1,2. \tag{43 b}$$

It is worth noting that, from the purely computational point of view, the model implies eleven parameters, namely the five independent viscosity coefficients, the three elastic constants, and the four cut-off wavevectors related by equation (36). This is certainly too much in most practical cases, where little is known about the viscoelastic constants. Moreover, the numerical evaluation of the J_α for finite values of τ is rather difficult. Some further simplification should thus be made.

2.5.1. *The cylindrical, one constant approximation*

The next simplification that can be made corresponds to the one constant approximation, in which only one viscosity (η) and one elastic constant (K) are considered, and no distinction between the splay–bend and twist–bend modes is made, so that the index α becomes irrelevant. Defining perpendicular and parallel 'cut-off relaxation times' $\tau^{\rm c}_\perp$ and $\tau^{\rm c}_z$ as

$$\tau^{\rm c}_\perp=\frac{\eta}{K(q^{\rm c}_\perp)^2}, \qquad \tau^{\rm c}_z=\frac{\eta}{K(q^{\rm c}_z)^2}, \tag{44}$$

we obtain, after a rather lengthy algebraical manipulation, the following final (exact in this approximation) result:

$$\langle n_x(0)n_x(\tau)\rangle=\frac{\pi^{1/2}}{2}\frac{1}{4\pi^2}\frac{k_BT}{K}q_z^c\int_{\tau/\tau_\perp^c}^{\infty}du\,\frac{1-\exp(-u)}{u}\,\frac{\operatorname{erf}[(q_z^c/q_\perp^c)u^{1/2}]}{(q_z^c/q_\perp^c)u^{1/2}}. \tag{45}$$

This integral is easily evaluated numerically for any set of values of the two viscoelastic parameters and the two cut-off wavevectors. In this approximation, equations (43) and (36) become

$$\frac{1}{E_e}=\frac{1}{\pi^2}\frac{q_z^c}{K}\left\{\frac{1}{2}\log\left[1+\left(\frac{q_\perp^c}{q_z^c}\right)^2\right]+\left(\frac{q_\perp^c}{q_z^c}\right)\arctan\left(\frac{q_z^c}{q_\perp^c}\right)\right\} \tag{46 a}$$

and

$$q_z^c(q_\perp^c)^2=4\pi^2n_v\quad\left(=4\pi^2N_a\frac{\rho}{M}\quad\text{for a pure sample}\right). \tag{46 b}$$

In this cylindrical approximation, the number of parameters is reduced from eleven to three. It is possible to simplify the problem slightly further with the spherical approximation.

2.5.2. *The spherical, one constant approximation*

This is the usual approximation that is found in the literature [4–6]. No distinction is now made between modes propagating parallel and perpendicular to the director. The integral in equation (36) is calculated in a sphere whose radius is the modulus q_c of the single cut-off wavevector. The result of this calculation is well known [5]

$$\langle n_x(0)n_x(\tau)\rangle=\frac{\pi^{1/2}}{4}\frac{1}{\pi^2}\frac{k_BT}{K}q_c\frac{\operatorname{erf}(\tau/\tau_c)^{1/2}}{(\tau/\tau_c)^{1/2}}. \tag{47}$$

The single cut-off relaxation time τ_c is given by

$$\tau_c=\frac{\eta}{Kq_c^2} \tag{48}$$

and equations (43 *a*) and (36) become

$$\frac{1}{E_e}=\frac{1}{\pi^2}\frac{q_c}{K} \tag{49 a}$$

and

$$(q_c)^3=6\pi^2n_v\quad\left(=6\pi^2N_a\frac{\rho}{M}\quad\text{for a pure sample}\right). \tag{49 b}$$

The two free parameters of the model, to be determined by comparison with experiment, are the cut-off relaxation time τ_c and the order parameter S. In terms of these parameters, equations (47) and (34) can be rewritten

$$\langle n_x(0)n_x(\tau)\rangle=\frac{\pi^{1/2}}{6}(1-S)\frac{\operatorname{erf}(\tau/\tau_c)^{1/2}}{(\tau/\tau_c)^{1/2}} \tag{50}$$

and

$$S=1-\frac{3k_BT}{2\pi^2}\frac{\eta^{1/2}}{\tau_c^{1/2}K^{3/2}}. \tag{51}$$

These two equations are the central ones for practical use in the framework of the spherical approximation. They will be used below to analyse proton NMR line shapes of a nematic polymer. But, before, we shall summarize the procedure to be followed to perform the complete calculation for an aligned NMR spectrum (basic spectrum) constituted by a single line, and then for a more realistic basic spectrum composed of many lines.

2.6. *The calculation procedure*

In short, the calculation of the NMR line shape in the presence of elastic modes, when the director is rotated at an angle Θ to the static field, for a basic spectrum composed of a single line at ω_{j0}, can be made in six or seven steps:

(i) choose an expression for the correlation function of $n_x(t')$, namely either equation (32) (general case), or (45) (cylindrical, one constant approximation), of (47) (spherical, one constant approximation);
(ii) select numerical values for the parameters of the model and the angle Θ;
(iii) calculate the correlation function of n_x for all τ values between 0 and about $5T_2$;
(iv) insert these values into equation (25) to calculate the correlation function of ξ_Θ;
(v) use equation (11) to calculate $\langle X^2_{\Theta,j}(t)\rangle$, and equation (10) to calculate $\langle \exp[iX_{\Theta,j}(t)]\rangle$;
(vi) use equation (7) to calculate $G_{\Theta,j}(t)$, and perform the time Fourier transform.
(vii) Possibly, if the sample is a polydomain, with a distribution function $F(\Theta,\Phi)$ for the mean directors, the relaxation function $[G_j(t)]_{\text{av}}$ to be Fourier transformed is

$$[G_j(t)]_{\text{av}} = \int d\Omega G_{\Theta,j}(t)F(\Theta,\Phi). \qquad (52)$$

The isotropic 'powder' corresponds to $F(\Theta,\Phi)=\frac{1}{4}\pi$.

2.7. *Generalization to complex spectra of real molecules*

So far, our molecules are idealized objects with cylindrical symmetry which are reduced to their long axis. Real systems are composed of real molecules which generally have no symmetry at all, and their NMR spectra are composed of many lines. A central question to be discussed is which object should be identified with the idealized molecule of the theory. Whatever this object is, we shall suppose that the perfectly aligned (basic) spectrum of the idealized molecule is the same as that of the real molecule (this assumption will be discussed below).

To know this spectrum, it is generally necessary to conduct experiments using anisotropic fluid phases in order to determine the structure, conformation and order tensor. The principal axes $OXYZ$ of this tensor are the most reasonable choice for the molecular axes. For molecules as large as those of usual low molecular mass nematics, it is expected that these axes do not change much with temperature and with the medium in which they are embedded, so that they can reasonably be considered as rigidly attached to the molecule. If such experimental results are not available, then the directions of these axes, the structure and conformation should be guessed.

Two possibilities arise, depending on whether the order tensor is uniaxial or biaxial. If it is uniaxial, the basic spectrum of the idealized molecule can be identified with that of the real molecule, calculated with OZ along the field, using magnetic interactions that are averaged over internal motions only. These averages are perfectly defined in the framework of the single conformation model [12, 13].

If the tensor is (suspected to be) biaxial, we may proceed as follows. The overall motion described by the order tensor is split into a fluctuation (described by angle χ) of principal axes OX and OZ in their own plane (X and Y defined such as $S_{XX}-S_{YY}\geqslant 0$), and a uniaxial motion of the frame defined by OX', OY' and OZ', where OX', OY' and OZ' are the average orientations of OX, OY and OZ over the fluctuations χ. The magnitude of this fluctuation is related to the anisotropy of the orientational order $\eta_S=(S_{XX}-S_{YY})/S_{ZZ}$ by

$$[P_2(\cos\chi)]_{\mathrm{av}}=\frac{1}{1+\eta_S}=\frac{S_{ZZ}}{S_{ZZ}+S_{XX}-S_{YY}}\left(=-\frac{S_{ZZ}}{2S_{YY}}\right). \tag{53}$$

The uniaxial order parameter to be associated with the long axis OZ' is related to the principal values of the order tensor by

$$S=S_{ZZ}/[P_2(\cos\chi)]_{\mathrm{av}}=S_{ZZ}+S_{XX}-S_{YY}(=-2S_{YY}). \tag{54}$$

For uniaxial order, we recover $\chi\equiv 0$ and $S\equiv S_{ZZ}$.

The basic spectrum $I(\omega)$ to be considered is now the one calculated with OZ' along the field, using the magnetic interactions that are partially averaged by the internal motions, as in the uniaxial case, but also by the fluctuations χ. This procedure, which applies under the assumption that the fluctuations χ are fast but not too large ($|\chi|_{\mathrm{av}}<\pi/4$), and uncorrelated with the fluctuations described by the elastic modes, has been briefly justified in two previous papers [12, 13]. The paper presenting the detailed calculations is in preparation.

It is also worth mentioning that the real molecules may (but not necessarily) be identified with the idealized molecules if their orientational order can be considered as uniaxial. However, strictly speaking, they can definitely not, if the order is biaxial. Since there is increasing evidence that the molecular order is generally biaxial in real systems, this means that the idealized molecules of the theory should necessarily be identified with entities larger than one molecule.

Let $I(\omega)$ be the basic NMR spectrum of one molecule, calculated with the field along OZ', according to the above prescription. This spectrum is composed of L lines j of intensities I_j and distances ω_{j0} from the Larmor pulsation ω_0. We can write

$$I(\omega)=\sum_{j=1}^{L} I_j\delta(\omega_{j0}-\omega_0). \tag{55}$$

The rotation around OZ' is uniform by definition. If it can be considered fast enough on the NMR time scale, all the averaged (by the internal motions and the uniform rotation) magnetic interactions are scaled by the factor $P_2(\cos\theta)$. The rotated spectra have exactly the same shape as the aligned spectrum, but are narrower by this factor. In this case (and, strictly speaking, only in this case), each line j keeps its identity when the angle is changed, and can thus be considered as independent of all the other lines.

Now, if the molecule is embedded in a nematic phase, it is evident that, because of this independence, the lineshape $I_\Theta(\omega)$ in the presence of elastic modes is the time Fourier transform of $G_\Theta(t)$ given by

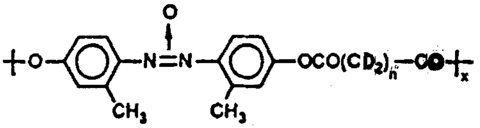
$$G_\Theta(t)=\sum_{j=1}^{L} I_j G_{\Theta,j}(t), \tag{56}$$

where $G_{\Theta,j}(t)$ is the relaxation function associated with line j of the theoretical spectrum, given by equation (21).

In all this discussion, it is assumed that the fluctuations χ and the rotation around OZ' are fast compared to the largest magnetic interactions. If they are not, equation (56) does not apply, although it may be a reasonable approximation if the amplitude of χ is small and the order sufficiently large.

3. Application to a nematic polymer

The theory is now applied to the analysis of the proton NMR line shape of a main chain nematic polymer of the type $(RF)_x$, where R is a mesogenic unit and F a flexible spacer, labelled AZA9d14, whose chemical formula is



$n = 7$

$x \sim 10$

This sample is the same as the one used in previous work [7, 8], in particular, the work in which the concept of 'static order parameter' was introduced [7]. Here, we repeat the analysis of the same data, namely the angular (Θ) dependence of the proton spectrum of a monodomain of this polymer, at 393 K, using the present theory. For this analysis, we use the spherical, one constant approximation, which will prove to be sufficient for our purpose.

According to § 2.7, we need as a starting point the theoretical proton NMR spectrum of the idealized basic molecule, with the long axis along the field (basic spectrum). For polymer AZA9d14 (deuteriated on the spacer), we assume that this spectrum is the same as that of its azoxybenzene moiety. The exact simulation of the corresponding twelve spin 1/2 spectrum has been the subject of previous work, recently published [14], in which the structure and conformation of the azoxybenzene moiety, and the direction of the principal axis OZ and associated principal value S_{ZZ} of the order tensor, were determined. Although there is some independent evidence that the order is biaxial [15], no significant information about the biaxiality can be extracted from this simulation alone, because the effect of introducing a finite value of η_S can be very easily compensated by slightly changing the geometrical parameters [14].

However, because the existence of biaxiality also changes the width of the aligned ($S = 1$) spectrum, two basic spectra will be considered, one for $\eta_S = 0$, and one (almost identical, but narrower, since some dipolar interactions have been reduced by the χ fluctuations) for $\eta_S = 0{\cdot}272$ (corresponding to $|\chi|_{\mathrm{av}} = 22{\cdot}17°$), which is probably closer to the actual situation, as shown by a recent, more detailed, analysis (performed in our laboratory) of the whole set of existing data concerning this polymer. These two basic spectra are reproduced in figures 1 (A) and (B).

The order parameter S_{ZZ} of AZA9d14 is known over the whole nematic range [7, 14]. At 393 K, its value is $\approx 0{\cdot}54$. The values of the uniaxial parameter S of the theory, given by equation (54), are $S = 0{\cdot}54$ with basic spectrum 1 (A) and $S = 0{\cdot}69$ with basic spectrum 1 (B). In the spherical, one constant approximation, the single remaining parameter to be determined from the analysis is the cut-off relaxation time τ_c.

We have performed the calculation as prescribed in § 2.6 for the same values of the angles as in [7], using a UNIX computer. The enormous number of lines of the theoretical spectra have been gathered into 800 packets of width $\Delta\omega_{j0}$ around ω_{j0}. The

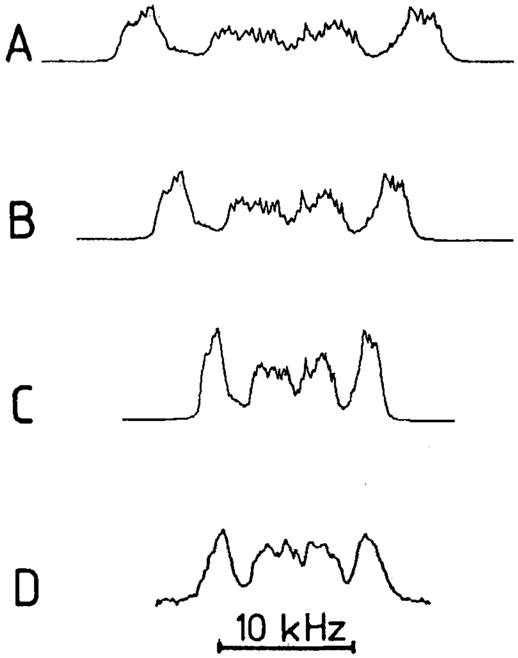


Figure 1. Basic proton NMR spectra of AZA9d14 polymer used in the analysis. (A) calculated for no biaxiality ($\eta_S=0$): this spectrum is identical to spectrum 1 (*b*) of [14]; (B) calculated with $\eta_S=0{\cdot}272$: this spectrum is narrower than (A) by the factor $(1+\eta_S)^{-1}$; (C) calculated for a large basic molecule such that $S=0{\cdot}962$: this spectrum is narrower than (A) by a factor 0·54/0·962; (D) reference spectrum used in the approximate method of [7]: this is the experimental aligned ($\Theta=0°$) spectrum at $T=120°\mathrm{C}$ for the nematic phase.

intensity I_j associated with packet j is the sum of the corresponding intensities of the individual lines inside this packet, and this packet is identified with line j of the spectrum used in the computation.

The results of the simulation, with $T_2=0{\cdot}25\times10^{-2}\,\mathrm{s}$, are shown in figures 2 (A) and (B) for the two basic spectra. Comparison with the experimental spectra (see figure 2 (E)) shows that good fits, of nearly equal qualities, are obtained in both cases. For the case $\eta_S=0$, the best fit is obtained for $\tau_c=(0{\cdot}43\pm0{\cdot}15)\times10^{-6}\,\mathrm{s}$. The simulation is rather sensitive in the sense that values of τ_c outside the range mentioned can be excluded. The situation is slightly different for the case $\eta_S=0{\cdot}272$, where the uncertainty range is broader, although the central value is certainly larger than for the case $\eta_S=0$. Figure 2 (B) corresponds to the simulation with $\tau_c=0{\cdot}95\times10^{-6}\,\mathrm{s}$.

Introducing in equation (51) the values of S and τ_c for the case $\eta_S=0$ yields $\eta^{1/2}/K^{3/2}=(1{\cdot}13\pm0{\cdot}21)\times10^{9}\,\mathrm{kP}^{1/2}\,\mathrm{dyne}^{-3/2}$ ($1\,\mathrm{kP}=10^{2}\,\mathrm{Pa\,s}$; $1\,\mathrm{dyne}=10^{-5}\,\mathrm{N}$). Exactly the same value is obtained for the case $\eta_S=0{\cdot}272$. This quantity is the only information on the viscoelastic parameters that can be extracted from the simulation of the line shapes.

It is possible to go further and find the actual values of η and K, using equation (49 *b*). Consider the case $\eta_S=0$. The smallest uniaxial object is then the repeat unit (the object attached to the $OXYZ$ frame of § 2.7). The corresponding molecular mass is 426 g. With $\rho=1\,\mathrm{g\,cm}^{-3}$, equation (49 *b*) yields $q_c=4{\cdot}37\times10^{7}\,\mathrm{cm}^{-1}$. Combining equations (34) and (49 *a*), we obtain $K=0{\cdot}78\times10^{-6}$ dyne, and from the above value of $\eta^{1/2}/K^{3/2}$, we deduce $\eta=(0{\cdot}61\pm0{\cdot}22)\,\mathrm{kP}$.

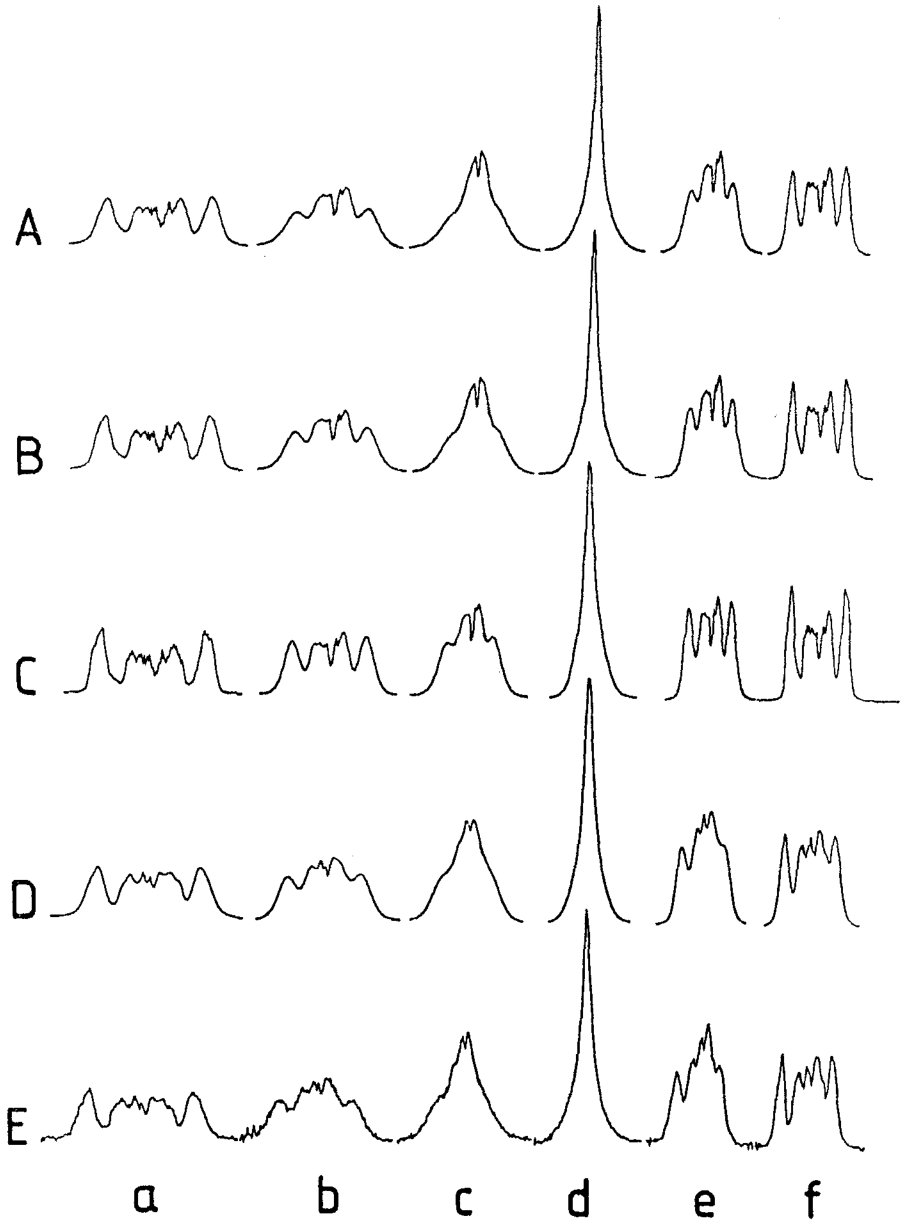


Figure 2. 90 MHz proton NMR spectra of a nematic monodomain of AZA9d14 polymer, at 393 K, for different angles Θ between the mean director and the static magnetic field: (*a*) 0°, (*b*) 25·5°; (*c*) 37°; (*d*) 47°; (*e*) 76·5°; (*f*) 90°. Spectra (A), (B) and (C) are calculated in the spherical, one constant approximation: (A) using basic spectrum 1 (A), $S=0{\cdot}54$ and $\tau_c=0{\cdot}43\times10^{-6}$ s (case uniaxial); (B) using basic spectrum 1 (B), $S=0{\cdot}69$ and $\tau_c=0{\cdot}95\times10^{-6}$ s (case biaxial); (C) using basic spectrum 1 (C), $S=0{\cdot}962$ and $\tau_c=0{\cdot}64\times10^{-4}$ s (large basic molecule). Spectra (D) are calculated with the approximate method of [7], using reference spectrum 1 (D) and $S_{\mathrm{stat}}=0{\cdot}962$ (reproduced from [7]). Spectra (E) are experimental, obtained at $T=120°\mathrm{C}$ for the nematic phase (reproduced from [7]).

It is instructive to compare these values with the results from magnetic reorientation measurements [8]. Concerning the elastic constants, it has been found [8] that $K_1 \approx 1 \times 10^{-6}$ dyne and that $0{\cdot}3 \leqslant K_3/K_1 \leqslant 0{\cdot}5$. Nothing is known about K_2. If we assume that the value of the latter is comparable to that of the two other constants, it is seen that the value obtained for K may be considered as a reasonable average value. The agreement is better (more accurate) for the viscosities, which can be classified into small and large [8], differing by about two orders of magnitude. The small ones are η_{bend}, η_b and probably η_a, and the large ones are η_{twist} ($=\gamma_1$), η_{splay} and η_c. The viscosities with indices bend, twist and splay are given by equations (29). They correspond to those of the three fundamental modes, and are equal to $\eta_1(0)$ ($=\eta_2(0)$), $\eta_2(\infty)$ and $\eta_1(\infty)$, respectively. For the present purpose, it is natural to focus on the viscosities of the three fundamental modes, whose values are (in kP) [8]: $\eta_{\text{bend}} = 0{\cdot}17 \pm 0{\cdot}02$, $\eta_{\text{splay}} = 11 \pm 5$, and $\eta_{\text{twist}} = 15{\cdot}7$. The harmonic average (average of the inverses) of these three viscosities is $\eta_{\text{harm}} = (0{\cdot}50 \pm 0{\cdot}07)$ kP. It is remarkable that η_{harm} and η, which have been obtained independently from one another, are found to be equal within experimental accuracy. In a situation in which the three elastic constants are of the same order of magnitude, the harmonic average of the three fundamental viscosities is proportional to the (arithmetic) average of the relaxation rates of the three fundamental modes. And it is clearly this average rate which is the most reasonable candidate to be identified with the single average rate of a one constant approximation model.

The fact that the simplest possible version of the model (one constant, spherical), with one free parameter only (τ_c), allows us to describe satisfactorily the experimental results, and that the values deduced for the viscoelastic parameters are in complete agreement with what is expected, suggests that the physics introduced in the theory (the elastic modes) is probably correct. However, the analysis is heavy and the amount of information about the viscoelastic properties extracted from the analysis of the line shapes (the value of $\eta^{1/2}/K^{3/2}$), is rather weak. From this point of view, it may be asked if the simpler method of [7], when applicable, does not give in fact the same amount of information. This is what is explored in the next section.

4. Comparison with the approximate method of [7]

As stated in the Introduction, the approximate method described in [7] introduces a NMR time scale $\Delta\tau$ which is not only a function of the system under study, but also of its NMR features. In this description, the disorder associated with the slow modes is characterized by a 'static order parameter' S_{stat} given by the same expression (51), but with τ_c replaced by $\Delta\tau$ [7].

An important question in this method is how to define accurately $\Delta\tau$ when dealing with broad (proton) NMR spectra, such as that of our polymer. All that could *a priori* be said is that "$\Delta\tau$ is of the order of the inverse of the spectral width" [7]. This statement can now be made much more accurate using the above results. Combining the two expressions for S and S_{stat}, we obtain

$$\Delta\tau = \tau_c \left(\frac{1-S}{1-S_{\text{stat}}}\right)^2. \tag{57}$$

With the above values of S and τ_c associated with either $\eta_S = 0$ or $0{\cdot}272$, and $S_{\text{stat}} = 0{\cdot}962$ [7], we obtain $\Delta\tau = (0{\cdot}63 \pm 0{\cdot}22) \times 10^{-4}$ s, which is about the value 10^{-4} s guessed in [7].

It is interesting to relate $\Delta\tau$ to the full extension $\Delta\nu_{\text{ref}}$ of the reference spectrum of figure 1 (D). This spectrum extends over ~ 15 kHz, corresponding to $(\Delta\omega_{\text{ref}})^{-1}$

$=(2\pi\Delta\nu_{\mathrm{ref}})^{-1}\sim 1{\cdot}1\times 10^{-5}\,\mathrm{s}\sim 0{\cdot}17\,\Delta\tau$. This result means that, for broad NMR lines such as those of the AZA9d14 polymer, the value of $\Delta\tau$ to be chosen, in an analysis in terms of static order parameter, is about $6\,(\Delta\omega_{\mathrm{ref}})^{-1}$. Thus, with this prescription for the choice of $\Delta\tau$, the approximate method of [7], when applicable, yields the same viscoelastic information as the more rigorous method presented here. This fact justifies *a posteriori* its use in the analysis of line shapes in magnetic reorientation experiments [8, 9].

5. The problems of the cut-off wavevector and of the nature of the basic molecule

In this section, we use the above results to discuss the questions of the value of the cut-off wavevector and the nature of the basic molecule in the AZA9d14 polymer, in order to see if it is possible to shed new light on this controversial [6 a] matter.

In a matter like this, the most important point is to separate properly the quantities introduced in the model into quantities with direct physical meaning, that is, which are directly accessible to experiment, and those which are only convenient concepts introduced in the theory. The order tensor of the mesogenic unit (which can be measured directly from simulation of the NMR spectrum, if the structure and conformation are known), the viscosities and elastic constants (which both can, in principle, be measured directly by well-established methods, independent of NMR), and the density belong to the first class. The cut-off wavevector(s), the cut-off correlation time(s) τ_c, the uniaxial order parameter S, the basic molecule and its associated theoretical NMR spectrum, on the contrary, belong to the second class. These latter parameters can *a priori* have any values, the only restrictions being that calculation of the measurable quantities in terms of them should always yield the same results. The restrictions on S, τ_c, q_c and n_v (or M) can be written in the form

$$(1-S)\tau_c^{1/2}=\frac{3k_BT}{2\pi^2}\frac{\eta^{1/2}}{K^{3/2}}, \tag{58}$$

$$q_c^2\tau_c=\frac{\eta}{K}, \tag{59}$$

$$q_c^3n_v^{-1}=6\pi^2 \quad (\text{or } q_c^3M=6\pi^2\rho N_a \quad \text{for a pure system}). \tag{60}$$

These equations show that the choice of the cut-off (and thus of the associated basic molecule) is almost completely arbitrary. The smallest possible basic molecule corresponds to the smallest entity in the nematic monodomain which can be considered as having uniaxial symmetry, and the upper limit is the size of the sample monodomain.

This statement can be made more clear if we remember the definition of the theoretical NMR spectrum of the basic molecule: it is the spectrum of this molecule, assuming that its symmetry axis is fixed along the field. However, in order to calculate this spectrum, we have to consider the real magnetic interactions in the real molecular units inside this basic molecule, which are averaged by the real molecular motions. The larger the basic molecule, the larger the number of motions which need to be considered (in particular if the size is large, some short wavelength modes should be considered as internal motions). The more and more averaged the magnetic interactions are, the narrower will be the basic NMR spectrum. The difference to the experimental spectrum decreases, and this is equivalent to an increase in the uniaxial order parameter S. For a basic molecule equal to the monodomain, all motions are internal motions, the basic spectrum is identical to the experimental one, and $S=1$. Correlatively, the slower the motions associated with the (remaining) modes to produce the observed broadening, the larger τ_c. For $S\rightarrow 1$, $\tau_c\rightarrow\infty$ in agreement with equation (58) and, according to equations (59) and (60), $q_c\rightarrow 0$ and $n_v\rightarrow 0$ (or $M\rightarrow\infty$). To summarize, we have the following scaling laws (valid in the spherical, one constant approximation):

$$q_c^{-3}\propto\tau_c^{3/2}\propto(1-S)^{-3}\propto n_v^{-1} \quad (\text{or} \propto M \quad \text{for a pure system}). \tag{61}$$

This statement is consistent with the results obtained for our polymer. We have indeed seen above that, with the introduction of the biaxiality, which is equivalent to including more disorder inside the basic molecule (and thus less disorder in the modes), an almost equivalent fit is obtained, as with no biaxiality, but with a larger value of τ_c. According to the above scaling laws, the basic molecule, which, in the uniaxial case, corresponds to one repeat unit, corresponds now to ~3·3 repeat units. The basic molecule is now larger because each unit performs its biaxial fluctuations inside the uniaxial frame $OX'Y'Z'$ (cf. §2.7). This frame is necessarily attached to an entity larger than one repeat unit. Let us now increase the scale by a large factor, and assume that the internal motions include a very large number of modes. The basic NMR spectrum is now much narrower, almost equal but not quite, to the experimental spectrum. This means that the order parameter S associated with the remaining modes is very large. Suppose we choose for S the value of $S_{\text{stat}}=0{\cdot}962$. According to the scaling laws, the associated value of τ_c is now increased to $0{\cdot}63\times10^{-4}$ s, q_c is reduced to $5{\cdot}29\times10^{6}\ \text{cm}^{-1}$ and M increased to $\sim 7{\cdot}6\times10^{5}$ g. The basic molecule of the theory corresponds to a volume of $\sim(100\ \text{Å})^3$, containing ~1800 repeat units. Figure 2(C) shows the corresponding calculated spectra. It is seen that, although still reasonable in the sense that the main features are reproduced, the fit obtained is significantly worse than before (see figures 2 (A) and (B)), and also worse than the fit obtained with the analysis in terms of 'static order parameter' (see figure 2 (D)): the spectra are too well-resolved compared to the experimental spectra. The reason for this is clear: the basic NMR spectrum (see figure 1 (C)) has been deduced from spectrum 1 (A), assuming that all the internal motions are infinitely fast. With a basic molecule as large as that chosen here, the modes included as internal motions are not infinitely fast, and consequently the basic NMR spectrum is too well-resolved. This illustrates the practical limitation of the choice of a small q_c in the present method, and correlatively the power of the appropriate method of [7] for this particular system.

It is seen that, in the problem of the broadening of NMR line shapes by the elastic modes, although the cut-off wavevector is in principle arbitrary, in practice it is not. In practice, we must choose as the basic molecule the smallest possible object which can reasonably be considered to have the uniaxial symmetry, in order to avoid the problem of slow internal motions. This object is one single molecule (in the case of uniaxiality) or, more likely, a small group of molecules (in the case of biaxiality). On the other hand, even if there is no problem with slow internal motions, it is not reasonable to choose too large a basic molecule. The reason is that it is not natural to split the modes arbitrarily into short wavelength modes, which would be considered as internal motions, and long wavelength modes, which would be the 'true' elastic modes. Unless there is some good reason for not doing so, all modes must be considered as 'true' modes. This is another argument favouring the choice, for the basic molecule, of a small (molecular size) object with uniaxial symmetry. It follows from this discussion that, in practice, the choice is rather limited. Only careful analysis of relevant experimental results can tell what is the 'best' basic molecule in each particular case. We have seen that for our polymer, the best results are obtained with an object whose size ranges between one to four repeat units. Similar situations are suggested by spin-lattice relaxation results in several systems [4–6]. All these results are consistent with Faber's view that "all the misalignment of molecules in a nematic can be described in terms of director fluctuations, even on a microscopic scale" [6 (a)], keeping in mind that the microscopic scale is probably, in real systems, larger than one molecule; larger in order to account for the probable biaxial motions which, by nature, cannot be described by these fluctuations.

6. Concluding remarks

To conclude, we wish to make some remarks on two points, namely the limits to the applicability of this theory, and the possibility of its use to study viscoelastic properties of soft, isotropic materials such as conventional polymers.

The limits of the theory are associated with the several unavoidable simplifications that have been made, mainly (i) the assumption of small amplitude fluctuations, (ii) the gaussian statistics and the non-correlation between n_x and n_y. and (iii) the gaussian character of $X_j(t)$. First, the small amplitudes are essential approximations of the hydrodynamic theory which leads to equations (26) through (29). It turns out that the most severe numerical approximation in all the calculation lies in the identification of the overall mean square amplitude fluctuation $\langle\theta^2\rangle$ to $\langle\sin^2\theta\rangle$: the relative error made is of the order of $\theta^2/3$. On the other hand, equation (25) suggests that S cannot be smaller than $1/7=0{\cdot}14\ldots$. Other considerations, not developed here, show that this limit is in fact $1/4=0{\cdot}25$. Suppose we fix the lower limit of S to $\sim 0{\cdot}429$ (the lowest value of the Maier–Saupe theory). This value corresponds to an average angle of $\sim 38°$, that is $\sim 0{\cdot}66$ rad, yielding $\theta^2/3\sim 15$ per cent. Second, the gaussian character is used to establish equations (15) and (23). In fact, since the values of n_x and n_y are limited to the range $[-1, +1]$, the statistics cannot be exactly gaussian, so that the two equations are exact only in the limit $S=1$. To have an estimation of the error made, we have calculated the ratio $R=\langle n_x^4\rangle/3\langle n_x^2\rangle$ as a function of S, using a gaussian distribution function truncated at ± 1. We find that R decreases from 1 to 0·84 when S decreases from 1 to 0·429. If the truncation is made at $\pm 0{\cdot}85$, to take into account the (small) correlation introduced by the condition $n_x^2+n_y^2\leqslant 1$, the lower limit decreases from 0·84 to 0·78. It is seen that the error made here is of the order ~ 20 per cent.

An overall precision of ~ 15–20 per cent in this problem is quite reasonable in view of all the simplifying assumptions that were made, and the accuracy in the measurement of the viscoelastic parameters, in particular in polymeric systems. Thus, we can reasonably expect that the present description may be useful for systems in which the degree of (dynamical) disorder corresponds to S as small as 0·4–0·5, that is for all liquid crystals. It is worth noting however that this problem of a small value of S is in fact not too serious, since S can be increased by choosing a larger basic molecule, whose size, we have seen, is somewhat arbitrary.

Third, the approximation concerning the gaussian character of $X_j(t)$, pointed out in § 2·2, is a good one only for t sufficiently larger than the correlation time of ξ. This means that this correlation time should be short. This condition limits, in practice, the applicability of the method to samples with average viscosities that are not too high. There is however a way to escape this limitation, namely the approximate method in terms of 'static order parameter' [7], since no such condition is invoked. In the range where it applies (S_{stat} sufficiently large), this method is (or rather has become since, now we know how to choose accurately the NMR time scale $\Delta\tau$) as accurate as the more detailed method presented in this paper, to extract viscoelastic information from the NMR line shapes.

This discussion shows that the two methods are in fact complementary. This method presented here is rather suitable to analyse systems that are not too viscous, with possibily rather small order parameters, while the method of [7] is adapted to more viscous and more ordered systems.

As a possible extension of this work, we would like to point out that, although developed for (polymer) liquid crystals, the formalism presented may also be useful to analyse NMR line shapes of conventional polymers. The reason for this is the following. In conventional, rather soft (amorphous, melts, solutions, gels...) polymeric systems, there is certainly no long range order at a macroscopic scale as in nematic systems, but some order at a mesoscopic scale (larger than, say ~100 Å) certainly exists, as revealed by the slight birefringence that is often observed for many of these systems. Our point is to say that, for NMR, these systems must be considered as anisotropic. But since the medium is generally macroscopically isotropic, an additional 'powder average' must be performed. Work along these lines is currently being performed in our laboratories.

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Appendix

To establish equation (24), we use the property that if n_x is a random gaussian variable with zero average value, the probability density for a given pair of values $n_x(t') \equiv x_1$ and $n_x(t'-\tau) \equiv x_2$ is given by the bidimensional gaussian distribution [16]

$$W(x_1, x_2) = \frac{1}{2\pi\sigma^2(1-\rho^2)^{1/2}} \exp\left[-\frac{x_1^2 + x_2^2 - 2\rho x_1 x_2}{2\sigma^2(1-\rho^2)}\right],$$

where

$$\sigma^2 = \langle x_1^2 \rangle = \langle x_2^2 \rangle \quad \text{and} \quad \rho = \langle x_1 x_2 \rangle / \sigma^2.$$

The use of the relation

$$\langle x_1^3 x_2 \rangle = \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 x_1^3 x_2 W(x_1, x_2)$$

leads, upon resolution of the double integral, to equation (24) of the text.

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