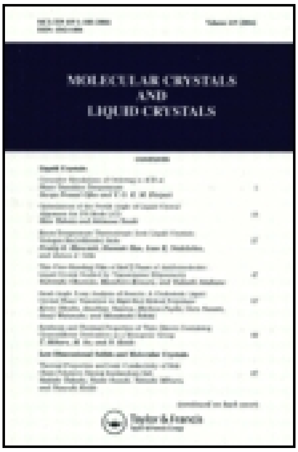

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F. Volino [a] & D. Galland [a]

[a] DRF/SPh/PCM, CENG - 85X, 38041 F, GRENOBLE Cedex

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ON THE MODELISATION OF NON-RIGID MOLECULES IN LIQUID PHASES

F. VOLINO* and D. GALLAND
DRF/SPh/PCM - CENG - 85X - 38041 F-GRENOBLE Cedex
*Member of CNRS
(*Received March 14, 1991*)

CONTENTS

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INTRODUCTION

In this paper, we would like to discuss the problem of the modelisation of the structure and dynamical behaviour of liquids, more generally of dense fluid phases composed of and/or containing in solution, non-rigid molecules. More specifically, we shall focus on the problem of the interpretation of NMR data in anisotropic media, which is of direct relevance in this field of research, keeping in mind that the concepts and ideas presented here may be used for the interpretation of other kinds of (spectroscopic) data. In such a broad and difficult subject, there are many researchers and different schools of thought. We shall try here to present two different models that are used in this field, and which are based on two rather opposite pictures of a liquid, the solid-like picture and the gas-like picture. Emphasis will be particularly put on the former one, giving reasons why we believe it is (much) better than the other. This may upset several people who are supporters of the latter. For this we apologize, but we prefer the reader to draw his own conclusions.

GENERAL BACKGROUND

Non-rigid molecules will be defined here as molecules composed of at least two rigid chemical moieties (phenyl ring, methylene group...) linked by single covalent bonds. In a large number of such molecules, it is generally accepted that the height of the internal potential V_i hindering the rotations around these bonds is of the order of a few k_BT, where T is about room temperature and k_B the Boltzmann constant. Thus, at such temperatures, and when the molecules can be considered as isolated, as for example in gas phases, rotational jumps around the single bonds can occur frequently, thus the name non-rigid. Expressed in another manner, it can be said that the molecule can exist in several conformations with a probability given by a suitable Boltzman factor. Complete knowledge of the internal state of the isolated molecule is contained in the detailed shape of the potential $V_i(\varphi_1, \varphi_2, \ldots, \varphi_i, \ldots, \varphi_N)$, where the φ_i are angles defining the rotations around the N single bonds i. This potential may be calculated by quantum mechanical methods. The values of φ_i for which V_i is an absolute minimum define the most probable conformation in the gas phase.

In a condensed phase, the situation is significantly different because of the existence of the intermolecular potentials. In the case of solid phases, these latter potentials are very high. Indeed, the crystallographic studies of single crystals show that the structure and the conformation of the molecules are well defined, which means that the effective rotational potentials around the bonds are virtually infinite (much larger than k_BT). This conformation may be different from the most probable conformation of the gas. The case of a liquid phase is more complicated in that sense that it may be considered either as an ordered gas phase or as a disordered solid phase. In fact, each picture is correct depending on whether long or short range aspects are considered. Concerning the long range order, an isotropic liquid is similar to a gas. For the short range order, which is the aspect we are interested in here, the situation is more similar to that of a solid. Indeed, the density of a liquid is almost the same (only a few % smaller) as that of the lower temperature solid, which means that the molecular packing is similar in both cases. Moreover, diffraction experiments on pure molecular liquids invariably reveal the existence of diffuse scattering at the same angles as the Bragg peaks of the lower temperature solid. This means that also the average arrangement at the scale of a few molecules is very similar. Concerning the conformations of the molecules, we thus expect that they are rather well defined, but possibly (sligthly) different from those in the solid, when the latter are not identical to the most stable conformation in the isolated state.

Other aspects such as fluidity, high values of self-diffusion coefficients...show that disorder also exists at the molecular level, implying fast molecular motions. Thus, these motions must be such that they keep the average molecular arrangement unchanged. In the next section, we briefly review the various types of motions and phenomena which specifically characterize the liquid state, in spite of its analogy with the solid state.

MOLECULAR ASPECTS IN A LIQUID

Let us consider for example the structure of a crystal formed by intrinsically non-rigid molecules composed of several non-chiral moieties linked by single covalent bonds. There are plenty of such studies, in particular of crystals which exibit liquid crystalline phases at higher temperature. In all cases (there is, to our knowledge, no counter-example), the symmetry of the crystal is low and the unit cell contains an even number of molecules (generally four), whose conformations are two by two images of one another in a mirror. This shows that although the molecule is chiral (because each conformation has generally no symmetry plane), there is no global chirality left at the scale of the unit cell, explaining the absence of optical activity of the crystals. Since the liquid is also optically non-active, neither shows corresponding fluctuations, this means that the chirality is also compensated at the molecular scale in the liquid. The simplest manner to realize this situation is that the average molecular arrangement in the liquid is that of the unit cell of the solid, exactly as suggested by diffraction. The only way to concile molecular motions with well defined average local arrangement is to imagine that, at the molecular level, these motions are either of small amplitude or, if of large amplitude, such that they leave the molecules or the arrangement in the unit cell unchanged.

For non-rigid molecules, the molecular motions may be split into two kinds, namely internal and external motions. The internal motions are those which involve time dependence of the angles φ_i around the single bonds. Some motions leave the conformations unchanged. These motions are purely symmetry operations, and are relevant only when some rigid moieties in the molecules have a symmetry larger than merely one symmetry plane. Methyl group rotation around the 3-fold axis and π-flips of phenyl rings around their para-axis are typical such motions. Once such motion has occured, the final conformation is undiscernable from the initial one. Another important symmetry operation is the motion corresponding to the exchange with the mirror image conformation (racemization motion). In the framework of the picture presented, such exchange is necessarily coupled with the reverse exchange of a neighboring molecule in order to keep the integrity of the unit cell. There is plenty of direct (that is, independent of any model analysis) evidence, in particular from NMR in anisotropic media, that such symmetry internal motions occur in fluid phases. In particular, in molecules with aliphatic chains, such racemization motion is implied by the observation that the two deuterium spins of a deuterated methylene group are always found to be magnetically equivalent in a deuterium NMR experiment. Note that this is generally no more true if the molecules are intrinsically chiral (for example if one of the rigid moieties itself is chiral, as in molecules involved in cholesteric phases).

Internal motions that do not leave the conformation unchanged are rotational fluctuations (mean amplitude $\Delta\varphi_i$) around the single bonds, about the mean values φ_i. These fluctuations will be called librations, to discriminate them from the vibrations which also exist in solid phases. The amplitude of the librations are expected to be small, although larger than that of the vibrations. Because these amplitudes are small, it is reasonable to define the molecular conformation as the average over these librations, in the same manner as "rigid moieties", out of which the molecules are made, are averages over the vibrations. (We refer here to the vibrations which are conveniently pictured by the so-called normal modes of vibrations, and which are detected by optical methods, mainly infra-red absorption and Raman scattering of light, and by inelastic neutron scattering.)

In the present picture, these internal motions, mainly the racemization motion, may be identified with the isomerization motion, including the very popular trans-gauche rotational jumps in aliphatic chains (RIS model), that are often invoked in the literature to caracterize the "flexibility" of such molecules. Here, the molecules essentially exchange between only two states: the laevo and dextro conformations. (This motion is sufficient to produce significant averaging in NMR). Here, there is no such thing as trans-gauche jumps in aliphatic chains, caracterized by torsional angles of 0 and 120°. There is only (quasi) simultaneous jumps of the dihedral angles between φ_i and $-\varphi_i$, on which librations are superimposed. These angles can have a priori any value since the packing forces can bring them away from the minima of the isolated molecule, as often occurs in solid phases.

The external motions are those which involve the molecules as a whole. They may be split into translational and rotational motions. Both kinds of motions involve a large spectrum of time and length scales. Short time scales (nano to pico-seconds) are reasonably associated with small length scales (fractions of molecular dimensions) and may be thought as mainly individual motions. They are easily detected, together with the above mentioned librations, for example by (incoherent) neutron quasi-elastic scattering. These motions can be pictured as translational and rotational fluctuations about the average positions within the unit cell. These motions (possibly coupled between themselves) are responsible for loss of the long range order that existed in the solid phase (because they are not fully in phase with those of the neighbouring molecules). Longer time scale motions (from nano to millisecond or even seconds) must be associated with collective motions of longer length scales (from a molecular length to microns or even macroscopic lengths). Such kinds of motions require a continuous description in terms of acoustic waves, rotational modes... They are detected for example, by methods such as dielectric absorption and light scattering (Rayleigh and Brillouin scattering), performed in various geometries for the polarization of the electromagnetic waves. In the particular case of nematic phases, the so-called elastic modes must be included in this category of motions, (and can also be detected by light scattering).

In this picture, the translational or rotational single particle diffusion coefficients (or associated correlation times) that are often deduced from certain types of experiments (low momentum transfer neutron quasi-elastic measurements, field gradient NMR, ...) must be thought as phenomenological transport coefficients which reflect these collective motions, as seen by a particular molecule (or incoherently to use the terminology of neutron scattering). This is conceptually analogous to the so-called "density of states" measured by incoherent neutron inelastic scattering which reflects (at least in part), the collective motions represented by the phonons, as seen by a particular atom in the crystalline lattice.

This discussion shows that complete description of the structure and behaviour of a liquid phase made of complex molecules is a priori rather involved. Such a complete description certainly requires a large number of different experimental data obtained by various methods, each of them being more sensitive to a particular aspect. However, since it is out of question to analyze these data in terms of a theory using only first principles (this can be done, only approximately, with very simple liquids), models must be elaborated which will allow to transform the raw experimental data (e.g. NMR splittings) into quantities of physical significance (e.g. the average value of the dihedral angle between two rigid moieties). Such a model, to be scientifically acceptable, should not only be able to describe the set of experimental data considered (this is generally possible with models with many adjustable parameters), but also not to be in contradiction with other data. A good model must moreover be simple and have a reasonable predictive character.

In the following, we shall show how the above ideas may be used to analyze very simply NMR data of non-rigid molecules in a liquid phase. Emphasis will be put on the case of (uniaxial) anisotropic liquids, because the latter contain much more information than similar data in isotropic phases (which, from a purely operational point of view, can be considered as particular cases of anisotropic phases). The main advantage of NMR is that it is essentially sensitive to rotational aspects, making the analysis a priori easier than, for example, neutron scattering data which reflects both rotational and translational aspects. The inconvenience of NMR is clearly that practically no information can be obtained about these translational aspects.

THE ANALYSIS OF NMR DATA

a) General

The subject of NMR in anisotropic media has been discussed in much detail over the last twenty years or so, in particular in several review papers and books[1-5] and it is not intended to repeat once again all this here. In fact, the formalism is rather complicated and it seems to us that the underlying physics is often obscured by the mathematics. Here, we shall rather focus on the question of which kind of information is contained in NMR data in anisotropic (and eventually isotropic) media, how it can be extracted and how reliable this information is. This last question is relevant because the number of data is necessarily limited, and since the a priori knowledge of some important parameters involved in the problem is also limited, the required information is ultimately the result of an often complex mathematical procedure, in which the (sometimes not unique) output depends on an essential way of the assumed input. It turns out, in fact, that the disputes and controversies that exist nowadays in this field is just the result of the use of different inputs to analyse the same or similar data.

From the computational point of view, it is clear that the larger the number of adjustable free parameters n_p of the model for a given number of independent data n_d, the greater the chance to find a set of values for these parameters which constitute an answer to the problem. As often occurs, in particular when only deuterium NMR (DMR) data are available, n_p is larger than n_d, and solutions are found for several models.

To improve this scientifically unsatisfactory situation, it is necessary to reverse the above condition concerning n_p and n_d, by acting on both numbers. Recently, technological and computational progress is allowing to increase significantly the number of data using proton NMR (PMR). On the other hand, it is necessary to keep the models sufficiently simple in order to reduce the number of free parameters. It might be expected that these facts are contributing to improve the situation concerning the number of solutions. It seems however that this is not the case yet, even, as we shall see later, in situations where n_p is sizably smaller than n_d.

b) Basic considerations on NMR

Basically, an NMR spectrum is the time Fourier transform of the correlation function of the transverse magnetisation of the sample under study. Its calculation from the first principles requires knowledge of the detailed time dependence of the so-called spin-hamiltonian of the whole sample, which involves both spin and spatial dynamical variables of all the molecules. The formal theory of NMR is mathematically involved and abstract, and is developped in fundamental books such as that of Abragam [6]. Fortunately, in the case of low viscosity fluids, whether anisotropic or not, in high static magnetic fields, the formalism simplifies considerably, and may be reduced to a few mathematical and physical concepts.

The low viscosity allows to neglect in a first approximation the magnetic interactions between the different molecules, (and in a second approximation to lump all these interactions into a single "broadening parameter"), and the high field justifies the use of perturbation theory to perform the detailed calculations.

Nevertheless, the problem is still complicated since the correlation function is the sum of the correlation functions of the N molecules of the sample. A further great simplification occurs if the system is ergodic, in which case the total correlation function is just N times the correlation function of one molecule. Ergodicity is related to the existence of fast motions in the system under study. The system will be ergodic if the statistical average (i.e the average over all the particles of the sample, at a given time), is the same as the time average (i.e. average over all the possible states that are explored many times by each particle during the time scale of the experiment). For NMR, this time scale ranges between ms and μs according to the nature of the spins and to the most important magnetic interactions.

The ergodicity hypothesis usually holds in the case of conventional low molecular mass isotropic and nematic liquids (in the form of monodomains in the latter case), and this is why the NMR data can be described in terms of monomolecular properties. It is clear that if all these conditions are not simultaneously fullfilled, for example in polymers where some important motions are not sufficiently fast, or/and all the molecules non equivalent (polydispersity, microphase separation,...), the analysis is more complicated. If these aspects are not properly taken into account, misinterpretations and errors may occur. These complications will not be considered here. Rather, we want to focus on the methodology of NMR data analysis and this is why we shall consider here the simplest case of low molecular mass nematic monodomains.

c) The data extracted from the NMR spectrum of a nematic monodomain

In high magnetic field, what is measured is basically the projection along the direction of the static magnetic field $\underline{H}$, of the average (over the fast - as defined above - motions, and over all the molecules of the sample if ergodicity does not apply) of specific molecular tensors, such as dipolar, quadrupolar, ... tensors. For more details, the reader is referred to the above mentioned reviews or textbooks on NMR [1-5]. It turns out that these tensors are either exactly (dipolar tensor between protons) or nearly (quadrupolar tensor acting on the deuterium spin in a C-D bond) axially symmetric around some "principal" direction $\underline{u}$. In this case, this projection is just proportional to $< P_2(\cos \underline{u}.\underline{H}) >$ where P_2 is the second Legendre polynomial and the brackets note the average. In case of dipolar and quadrupolar interactions, the direction of $\underline{u}$ in the molecule is well defined and the proportionality constant is known with reasonable or good accuracy. In this way, a number of averages values of P_2 associated with various directions in the molecule can be deduced from the data. These values are often baptized "order parameters" (a much better name would be "orientational parameters"). There are plenty of examples in the literature in which is given the variation of the "order parameter" along the terminal chains in liquid crystals molecules with deuterated such chains, which inform about the average orientation of the various C-D bonds with respect to $\underline{H}$. When the molecular tensor is not axial (e.g. chemical shift tensor, nitrogen 14 quadrupolar tensor, ...), the expression of the projection is more complicated since it involves the three principal axes of the tensor. The information is less direct, but the data are intrinsically of the same quality.

To summarize, from analysis of NMR spectra, (such analysis may be rather involved as in the case of PMR spectra), one can obtain the values of a number of physical quantities related to the molecule itself (structural parameters) and to its average orientation with respect to static magnetic field (orientational parameters). This number may be identified with the number of data n_d mentioned above. Obtention of these data constitutes the first stage of the work.

THE INTERPRETATION OF NMR DATA

The second stage consists in the interpretation of these data in terms of the physics of the system under study. The data relate a very local quantity, namely one or several molecular directions attached to the frame in which the molecular tensor is defined, to a single laboratory direction (not the complete laboratory frame), namely the static field direction. There are several intermediate levels between these two extreme space scales. Going from small to large scales (presumably associated with short to long time scales, respectively) , these levels are (i) the rigid moieties, (ii) the molecules, (iii) several molecules (this level corresponds to the short range order introduced previously), (iv) the semi-macroscopic (mesoscopic) level corresponding to the wavelengths of the modes describing the collective motions, in particular the elastic modes of the nematics, (v) the macroscopic level corresponding to the size of the monodomains, again for nematics, and finally (vi) the level of the sample used in the experiment.

a) The rigid moiety level

We have already mentioned the most elementary level with "the order parameter distribution" along alkyl chains,which relate only one direction in rigid moieties (the CD bonds) to the laboratory direction (the static field). The second level is that of the rigid moieties. A rigid moiety being a three dimensional object, its orientation with respect to the field is described by two parameters. These parameters may be either the polar and azimuthal angles Θ, Φ of the field in some orthogonal frame Oxyz attached to the rigid moiety, or equivalently the three angles θ_i ($i=x,y,z$) of the field with the frame axes (these angles are not independent, but such as $\Sigma \cos^2\theta_i = 1$). The average orientation of the rigid moiety is fully described by a distribution function f (θ_i). The orientational information contained in the NMR data must thus be transformed into an information on the function f. The experimental data being of second rank tensorial nature, tensorial algebra tells us that the projection along some direction (the field direction is the only relevant one to NMR) Q_{HH} of any tensor Q defined in the moiety frame Oxyz is given by

$$Q_{HH} = \frac{1}{3} \Sigma Q_{ii} + \frac{2}{3} \Sigma Q_{ij} S_{ji} \qquad (i,j = x,y,z) \qquad (1)$$

where the summation runs over repeated indices. Here, Q_{ij} are the components of Q in the moiety frame and S_{ij} are the components of the so-called order tensor of the moiety frame with respect to the field, given by

$$S_{ij} = < \frac{3}{2} \cos\theta_i \cos\theta_j - \frac{1}{2} \delta_{ij} > \qquad (2)$$

where the brackets stand for the average, using distribution f, of the corresponding quantity. This order tensor being traceless and symmetric, it is completely determined by the knowledge of only five S_{ij} values. These quantities describe the average orientation of the moiety frame with respect to the static field direction. Eq. (1) shows that knowledge of Q_{HH} can give information about S. Since there are five components of S, if the components of Q in the moiety frame are perfectly known (a situation that is seldom met in practice), one needs at least five independent Q_{HH} values (that is five splittings or magnetic interactions) associated with the same moiety to determine completely the order tensor of this moiety with respect to the field. It must be said here that this is almost never the case in practice for all moieties of non-rigid molecules, and if the further step in the modelisation does not want to be made, the final output of the study is a limited number of moiety order parameters (more often only relations between them). This situation is slightly frustrating because even if one knows some partial (and often abstract since the numerical value of a tensor order component is of not direct intuitive physical significance) information about one or several moieties in a molecule, there is not yet information on the molecule itself (except, clearly if the molecule is constituted by one single rigid moiety). To get this molecular information, one must go to the next level of modelisation.

b) From moiety to molecule

So far, what has been described above is well established and accepted. The reason is that the kind of analysis required is mathematically relatively rigourous and the rare hypotheses that are made concerning the symmetry of some motions such as flips of phenyl rings or methyl group rotations are implied by the very nature of the NMR data (e.g. the number of lines in a spectrum is always reduced by symmetry). The step from the moieties to the molecule is more delicate due to the non-rigidity. The tremendous complication is that, in the molecules, the angles φ_i around the single bonds can fluctuate so that there a priori exists, strictly speaking, not only one, but an infinite number of conformations n (conformers) defined by a set of dihedral angles $\varphi_i{}^n$ and a probability of occurence p_n. Each such conformer can be considered as a rigid object, and one can thus define an order tensor S^n per conformer. S^n would correspond to an average over the orientations with respect to the field, of all the molecules that are in conformation n. Thus, each conformer is characterized by six quantities, one p^n and five Q^n_{ij}. In a frame attached to this conformer, the components of the molecular tensor of interest are Q^n_{ij}. Making the reasonable assumption that the trace of Q is independent of n, one can define an average of Q_{HH} by the quantity

$$Q_{HH} = \frac{1}{3}\Sigma Q_{ii} + \frac{2}{3}\Sigma p^n \Sigma Q^n_{ij} S^n_{ji} \qquad (3)$$

Eq. (3) is simply a mathematical generalisation of Eq. (2). If the exchange between all the conformers is fast on the NMR time scale, then this expression may be thought as representing the measured physical quantity . Yet, the quantities p^n and S^n_{ji} are only mathematical symbols (exactly as the coefficients of a mathematical expansion) since they are not directly measurable quantities. If no further hypothesis is made, or if no other information is introduced in the problem, this step is of little interest as such. The only progress is that it allows to deal with tensorial quantities associated with the whole molecule which could not be accounted for in the previous level of description (we think here to dipolar interactions between spins located on different moieties). Since it is not possible to deal with the six infinities of mentioned quantities as free parameters, it is necessary to modelize further the problem to go ahead with the analysis.

It is at this level that a picture of the liquid must be introduced, and consequently where the various models differ. In the following, we develop the argumentation along the lines drawn in the first section of this lecture, in which a liquid is pictured as a disordered solid, and then we briefly describe the more popular picture, (and the corresponding various models), in which a liquid is pictured as a perfect (for isotropic) or partially ordered (for nematic) gas.

THE SOLID-LIKE PICTURE

According to the first section, the large amplitude internal motions are symmetry operations, and there are only two different conformations which are symmetrical under the parity operation. In NMR, the only relevant physical quantity is the spin hamiltonian. This spin hamiltonian being invariant under such operation (because only second rank tensors are involved in it: parity changes only odd rank tensors such as vectors which are first rank tensors), the orientations of the two conformations are described by the same order tensor. The introduction of librations only slightly blurrs the concept of conformation in that sense that the latter is not only defined by the set of angles φ_i (or $-\varphi_i$ for the mirror image) but also by a set of libration amplitudes $\Delta\varphi_i$. With this model, Eq. (3) is rewritten

$$Q_{HH} = \frac{1}{3} \Sigma \ll Q_{ii} \gg + \frac{2}{3} \Sigma \ll Q_{ij} \gg S_{ji} \tag{4}$$

where the double brackets stand for an average over the (symmetry) internal motions and over the librations $\Delta\varphi_i$. This equation correspond to what we call the "single conformation model" to emphazise the fact that knowledge of one of them implies knowledge of the other. (A better, but more abstract name would be "single order tensor model")

The fundamental result is that Eq. (4) is formally identical to Eq. (1). The frame attached to the rigid moiety is replaced by a frame attached to one conformation (say the dextro conformation) and the molecular tensor components are replaced by averages over the mentioned internal motions, including the racemization (details on how these internal averages can be made in practice are given in[7] in a particular case). What needs to be determined from the data is the conformation, namely N angles φ_i, N libration amplitudes $\Delta\varphi_i$ and the five elements of the order tensor S, that is $n_p = 5+2N$ adjustable parameters (assuming the geometry of moieties are perfectly known; if not this number is larger). In fact, the fluctuations can often be lumped into the value of effective dihedral angles φ_i so that the number of parameters can often be reduced to 5+N.[10] Thus, from a purely computational point of a view, at least the same number of independent data n_d is required to determine univocally all these parameters. The condition $n_d > n_p$ is practically always fulfilled for rigid molecules (N=0), sometimes realized for N=1, much more difficult to achieve for $N \geqslant 2$.

The case N=0 is treated in detail in[2], and in fact NMR of small rigid molecules in nematic phases turns out to be a powerful method to determine the structure of such molecules in liquid phases. The case N=1 has also been extensively studied experimentally [2], but to our knowledge never analyzed systematically with the present approach. In a paper presented in this conference[8], some published NMR data for such molecules (including the controversial case of anisole) are reanalyzed in this manner. It is found that not only this single conformation model can describe very well the data, but for the particular case of anisole at least, the mathematical solution is not unique. Essentially two different, but equally good, solutions are found, corresponding to one nearly planar and one nonplanar conformations. One main reason for the non-unicity is that it is never really possible to realize $n_d > n_p$ because some ill-known structural quantities should in fact be considered as free parameters.

The case N=2 is more interesting when the above condition is fulfilled. Molecules based on the ethoxybenzene moiety have been considered in detail by us[7] using published data[9]. The number and quality of these data, mainly dipolar interactions obtained from PMR spectra, allowed to realize the condition $n_d = n_p + 2$ for two molecules. For both, but also for the other molecules where the number of data was less, very good fits were obtained, with values of the parameters in good agreement with what is expected. This result shows that, in addition to be simple, this model has also a reasonable predictive character since only $n_d - 2$ could have been used to determine the values of the parameters, which in turn would have allowed to predict the values of the remaining two interactions.

The fact that it works very well in this particular situation is not sufficient to prove that this model is good. To be really good, it must be general, namely it must allow to describe similar kinds of data in very different situations. So far, we know no example where this model is unable to describe NMR data of non-rigid molecules in an anisotropic phase. The fact that the cases corresponding to N=1 explored by us can be analyzed by this model constitutes in fact only a weak evidence for its validity due to the necessary limited number of data. Besides the case N=2 considered above, which in itself constitutes a much stronger support, we have explored in the past the more complicated case of para-azoxyanisole[10] with the same approach, trying to describe the maximum number of data with the minimum number of parameters. We could demonstrate without any doubt that the molecular order tensor was biaxial in the bulk nematic phase. This was done by assuming no biaxiality and showing that this hypothesis was not in agreement with the data (mainly the shape of PMR spectra and diamagnetic susceptibility data). But, despite the large number of data available, the problem could not be solved completely due to the complexity of the molecule, which in our nomenclature, corresponds to N=4.

THE GAS-LIKE PICTURE

The view that in an isotropic liquid, the molecules are free to move and adopt all the conformations as if they were isolated, is apparently widely spread among the liquid crystal community. In fact, this idea comes from NMR of small molecules dissolved in usual solvents (a powerful method for chemical analysis) which shows very well resolved spectra that can be analyzed in terms of single particles properties. This situation holds because the translational and rotational motions at all length scales are sufficiently fast to average out to zero all the anisotropic parts of the magnetic interactions. This does not imply however, that the motion of one molecule is uncorrelated with that of its near neighbours, and in fact the existence of the short range order revealed by diffraction demonstrates that this is not the case. Thus what the global structure of NMR spectra in isotropic phases really reveals is that the overall motion of the molecule is fast and isotropic, but does not say much about what occurs at the molecular scale, in particular about the conformations. Clearly, some conformational information is contained in the spectra, in the form of the actual values of chemical shifts or JJ coupling constants, but extraction of this information is delicate. Since in addition, these quantities involve similar second rank tensors as in the anisotropic case, the quality of the information concerning the structure and conformation in the isotropic phase is basically of the same nature as that obtained in anisotropic phases. In particular, this information is also model dependent.

Nevertheless, with the picture of an isotropic phase identical to a gas phase, an anisotropic phase becomes a (partially) oriented gas phase. In this approach, two basic assumptions are made (i) some less elongated conformations are less probable and (ii) the molecules are oriented in average along some preferred direction (the nematic director). In terms of Eq. (3), this means that (i) the p^n are different from those of the isotropic phase and (ii) the tensors S^n are a priori all different.

As stated earlier, numerous models have been proposed to simplify Eq. (3) in order to avoid the determination of all these quantities considered as adjustable parameters. It is not possible here to detail all these models, but what can be said is that they can roughly be classified into two kinds: those which make hypotheses about the possible conformations and/or the properties of the order matrices (in some sense these models share the same philosophy as the solid-like model), and those in which theoretical concepts about the phase are introduced early in the analysis. Numerous relevant references are given in [1-5] , in particular in the most recent reviews 5a,b.

Let us discuss briefly these two kinds of models. For the first kind, a popular assumption is for example to assume that all the conformers which can be contained in a cylinder (whose radius is taken as an adjustable parameter) exist with the same probability as in the gas phase and the other conformations are forbidden. Another assumption concerning the order is that the tensors S^n are proportional to the inertial tensor (a very relevant concept in gas phases!), or to the molecular polarizability tensor, of the corresponding conformer n. Such assumption allows to reduce the number of parameters for every tensor order from five to only one (the proportionality constant). Note that these models depend in a crucial manner of the knowledge of the properties of the isolated molecule. For the second kind of models, the presently most popular one is that which makes use of the so-called ELS theory [11] . This theory is a generalisation of the well-known mean field theories of Maier and Saupe, and of Straley (developed for nematic phases made of rigid objects), to nematic phases of non-rigid objects. The basic ingredient in the ELS theory is that the nematic mean field potential not only governs the long range orientational order, but also the probability of occurence of the various conformations. Thus, when going to the isotropic phase, the mean field potential vanishes, and the conformations are governed by the intramolecular potential only, as in a (diluted) gas phase. The main parameters of the model are (i) coefficients in the expansion of the mean field potential in terms of generalized Legendre polynomials and (ii) parameters concerning the conformations such as Fourier coefficients of the expansion of the rotational potential around single bonds. An example of the application of this model concerns the NMR data of ethoxybenzene cited earlier [9], which were reanalyzed in terms of the single conformation model in[7].

All these gas-like models allow to describe satisfactorily NMR data, in that sense that they reproduce at least qualitatively the experimental data. For the particular case of ethoxybenzene, the agreement is quantitatively very good with both models, so that it is not possible, on the basis of NMR data only, to decide which of the solid-like picture of[7] or of the gas-like picture of[9], is the best. We thus have to discuss in more detail the model themselves and the modelisation process.

DISCUSSION ABOUT MODELISATION

From a purely operational point of view, as soon as a model can describe accurately data, it can be considered as valid since it allows to replace experimental quantities (the data) by the values of a limited number of other values (those of the adjustable parameters of the model). To be physically acceptable, these latter values should not contradict other data. In particular, they should be reasonable when they represent simple physical quantities (e.g. the exact value of a valence angle or of an interatomic distance which is refined by the model). Other parameters, such as coefficients of the expansion of the mean field, may or may not be acceptable according to the confidence one puts in the model. However, independently of this, the various assumptions must be mutually consistent within the framework of each model. An example where this is not the case is when the single order tensor approximation is made in models which permit several different conformations.

Another important aspect is the unicity of the solution, which is particularly relevant when the number of parameters is relatively large. The case of anisole mentioned earlier is examplary in this respect. The corresponding NMR data are available since many years, and have been found to be consistent with a most probable planar conformation [11,12] . To our knowledge, non-planar conformations have never been looked for systematically . As stated above, we have made this research [8] using the single conformation model and found that these data are consistent with a planar and a nonplanar conformation. Thus, it is not possible to decide on the basis of these NMR data only which of these different conformations the anisole molecule adopts in the corresponding nematic solvent. The arguments given in[8] in favor of the nonplanar conformation are supported by results obtained from other sources.

This also shows that it cannot be claimed that NMR demonstrates that non-rigid molecules exist in several conformations in a liquid phase. Our search for cases in which the single conformation model cannot be used to describe such data has not be successful so far, so that we can rather claim that there is no evidence that non-rigid molecules exists in more than two conformations (which exchange via the racemization motion). Now, if (possibly several times) two conformations constitute a solution, it is not very surprising that combining many conformations, such as those of the isolated molecule, other solutions can be found. This is merely a mathematical property: it is equivalent to increase the number of parameters, and it is easier to find solutions with more parameters. In other words, one finds many conformations because one looks for many conformations! This is somewhat analogous to what God said to the French philosopher (and scientist) Pascal "Tu ne me chercherais point si tu ne m'avais pas déjà trouvé". Thus, the many conformation solution does not prove anything about the existence of these conformations, and a fortiori about exchange between them. It can be concluded that there is so far no convincing evidence (from NMR at least) that non-rigid molecules exist in many different conformations in a liquid phase. Clearly, the same thing can be said for two conformations. This simply means that NMR alone can say almost nothing about this aspect, except probably that there are at least two conformations! Our preference for the solid-like picture is based on the idea, developed above, that at the molecular scale, a liquid is not a perfect (or partially oriented in case of nematics) gas, but rather a disordered solid, with significant short range order. Moreover, it has the considerable advantage of simplicity, which is an important quality for any good model.

GOING FURTHER WITH THE SOLID-LIKE PICTURE

In the best cases, as that of ethoxybenzene[7], the (single) order tensor could determined completely. Diagonalisation of this tensor allows to determine the principal frame OXYZ and the principal values (the usual axial and biaxial "order parameters" S_{ZZ} and $S_{XX} - S_{YY}$, respectively). These quantities together with the values of the dihedral angles φ_i constitute the final output of the problem (in general the libration amplitudes can be assumed to be zero, which means that the corresponding disorder is lumped into the values of φ_i, which should be thought as effective values close to the actual values).

One can go further into the physics in the following manner: instead of using the two above mentioned order parameters, it is equivalent to use two new parameters S_0 and $<P_2(\cos\chi)>$, related to the former by

$$S_0 = -2\,S_{YY} \tag{5}$$

and

$$< P_2(\cos\chi) > = 1 / (1 + \eta_S) \tag{6}$$

where $\eta_S = (S_{XX} - S_{YY})/ S_{ZZ}$ is the anisotropy of the orientational order (disorder). These new parameters are as general as the former ones on the condition that the labeling of the principal directions satisfy the following ordering relationship

$$S_{YY} \leqslant S_{XX} \leqslant S_{ZZ} \qquad (7)$$

The interest of these new parameters is that they support a deeper physical significance. Indeed, consider a cylindrical object, of axis labeled OZ, and inside it, a smaller rigid moiety able to perform internal rotational fluctuations around some diameter OY of the cylinder. Let $\chi(t)$ be the current angle describing the rotation around OY and let S_0 be the axial orientational order parameter of the cylinder. If we assume that this motion (external motion) is uncoupled with the fluctuations $\chi(t)$ (internal motion), then it is easy to show that the orientational order, at the smaller scale of the moiety, remains diagonal, but becomes biaxial according to the relations

$$S_{ZZ} = S_0 \langle P_2(\cos\chi)\rangle \qquad (8)$$

and

$$S_{XX} - S_{YY} = S_0(1 - \langle P_2(\cos\chi)\rangle) \qquad (8)$$

Inversion of the expressions yields relations (5,6). The quantity $\langle P_2(\cos\chi)\rangle$ is thus a purely biaxial order parameter. Note that although Eq.(8) expresses the main order parameter as the product of two order parameters, the meaning of this decomposition is completely different from similar formal decompositions that are sometimes found in the literature[17].

This description allows us to separate the disorder into biaxial and axial components. Since what is biaxial are the molecules (a microscopic concept), and what is axial is the phase (a macroscopic concept), one can reasonably make the assumption that the time scales of the motions represented by these two quantities are different and that they can be considered as decoupled. In our opinion, separation of the motions at this level is much better than the one which consists in describing the disorder in terms of rotation around the long axis (OZ) and fluctuations of this axis about the laboratory direction, as is often made in some dynamical models. The biaxial angle χ may be considered as molecular, and eventually be treated on the same footing as the librations angles $\Delta\varphi_i$ in more elaborated models, in which it is necessary to introduce these librations. This approach is used to analyze NMR data of dimer model compounds of nematic polymers and is presented on a poster at this conference[13]. The axial order parameter S_0 on the other hand, may be used to test continuum theories, such as that describing the orientational disorder in terms of thermally excited elastic modes. Such studies are currently performed in our laboratory, in connection with small molecular mass nematics as well as polymers.

CONCLUDING REMARKS

This paper has been mainly devoted to the problem of the description of liquid phases at the molecular scale. Two somewhat opposite pictures have been presented, namely the solid-like picture in which a liquid (whether isotropic or nematic or even smectic) is regarded as a disordered solid, and the gas-like picture in which an isotropic phase is identified to a perfect gas phase and a nematic phase to a partially oriented gas phase. An important difference between the two pictures lies in the fact that for the former, there is essentially no difference between nematic and isotropic phases. The number of conformations is the same in both phases and these conformations are probably very similar at least near the clearing transition. On the contrary, in the latter model, the change in the number of conformations measured via the change in their probabilities of occurence, varies significantly at the transition.

The basis of the solid-like picture lies on the diffraction experiments which show that the local molecular packings are "quite similar in nematic and isotropic phase"[14] . The aligned nematic phases give diffraction patterns different from those of isotropic phases for basically the same reason that single crystals give different patterns from that of the corresponding crystal in powder form: this a purely macroscopic property. In this sense, it may be roughly said that a nematic phase is a partially oriented powder of an isotropic phase. A consequence of the solid-like picture is that there is no contribution of the conformations to the transition entropy, prediction which seems to be supported at least in one particular case[15] . Finally, the existence of well defined conformations excludes the possibility that, in aliphatic chains, defects such as gauche defects, are delocalized on the chain. If some defect is somewhere, it stays there and only exchanges with the symmetrical defect via the racemization motion.

The gas-like picture does not seem to be supported by anything else than NMR. It is inconsistent with the existence of the short range order. Moreover, this picture is completely misleading concerning what a nematic phase is. It suggests that the ordering process that appears when going from isotropic to nematic is due to the onset of a mysterious potential (the "mean field potential", or "potential of mean torque") which would act on the molecules, and would force them to align along a preferred direction (the nematic director). In fact, a phase transition is not a molecular process, but a global process. This mean field potential is not a true potential, but only a pseudo-potential which is introduced in mean field theories to describe the properties of the phase. As such, it does not act directly on the molecules and consequently cannot be added to the intramolecular potential, which is a true potential, as is done in the ELS theory.[11]

The nematic transition is characterized by the appearance of a long range orientational order along some direction (breaking of a symmetry). The order parameters calculated in mean-field theories just reflect this property: they describe the long range orientational correlation of the molecular axes of the 10^{20} or so molecules of the monodomain, and consequently, they are not molecular quantities, but macroscopic quantities, of the same nature as, for example, the heat of transition. In phenomenological descriptions such as those made in Landau-De Gennes theories, the ordered phase is characterized by a second rank (because the phase is non-polar) order parameter tensor with axial symmetry around the director. This tensor is only accidentally of the same mathematical nature as the order tensors of NMR. The tensors of NMR are of second rank because the magnetic interactions are second rank tensorial quantities. This feature is clearly independent of symmetry of the molecules (which generally have no symmetry at all) and of the macroscopic state of the sample under study. Now, if the field is directed along the director of the monodomain, as is generally the case, the single order parameter of the phase may be chosen proportional to the average value of the projection of any molecular tensor along the field. Since there are many different such tensors, the definition is not unique. A popular tensor is the diamagnetic susceptibility tensor, which is not accessible by NMR, but by magnetic measurements. Other tensors are also chosen. All these tensors have a priori not the same temperature dependences, so that it is not possible to test accurately any theoretical model which does not take into account the details of the particular system under study. These details may certainly be found in the structure of the isolated molecule, but also, and more importantly, in the molecular arrangement in the unit cell of the lower temperature solid. This fact has since long been pointed out by several researchers[16], who suggest the the study of the structure of solid phases may be a clue to understand nematic phases.

To conclude, we have given arguments to support the idea that, at the molecular scale, a liquid phase should be considered as a disordered solid, and that there is no essential difference between isotropic and nematic states. We have also given arguments against the idea that a liquid can be considered as a (perfect or partially ordered in case of nematics) gas.

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