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Nuclear Magnetic Resonance in the Smectic *C* Phase*

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We have determined the molecular arrangement that results when the smectic *C* liquid-crystalline phase is subjected to large magnetic fields. Furthermore, a simple technique which makes use of the free-induction decay is used to obtain a precise determination of the smectic *C* tilt angle. Uniformly aligned smectic *C* samples are obtained by cooling through the nematic phase into the smectic phase in the presence of a 14 000-G magnetic field. Once aligned, the samples are then oriented at various angles relative to the magnetic field direction and the absorption line shape is recorded. A model is developed to describe the molecular arrangement in the smectic *C* which results from reorientation of the sample in the magnetic field. This model allows for the reorientation of the long molecular axes within the smectic layers subject to the constraint that a constant tilt angle be maintained. The experimental test of the model comes from its ability to predict NMR line shapes and second moments. In terephthal-bis-4(4-*n*-butylaniline), we measure the temperature dependence of the tilt angle to be a $(T_c - T)^\beta$ dependence, where $\beta = 0.40 \pm 0.04$ and T_c is the smectic *A*–smectic *C* transition temperature. This is compared with de Gennes's prediction of $\beta = 0.35$. In addition, a tilt angle of 45° was obtained for 4, 4′-bis-(heptyloxy)azoxybenzene.

I. INTRODUCTION

The term "smectic" encompasses a wide variety of liquid-crystalline phases.[1] Two of these phases which commonly occur in nature are classified as the smectic *A* and smectic *C*. It has been verified[2] that these phases are layered, with each layer resembling that of a two-dimensional liquid. Within these structureless layers the preferred direction of the long axis of each molecule (director) may be parallel to the planar normal (smectic *A*), or tilted with respect to the planes of the layers (smectic *C*), as pictured in Figs. 1(a) and 1(b). Although the difference in the structure of these two phases is subtle, the physical properties are often strikingly different. This difference is a result of the increased orientational mobility of the molecules in the smectic *C* phase. Being tilted within the layers offers the molecules freedom to reorient their long axes within the layers subject to the constraint of a constant tilt angle. The literature[3–7] has been, for the most part, contradictory as to the actual measured value of the tilt angle. It is clear, however, that there exist two types of smectic *C*'s. In one type, the tilt angle is fixed in temperature, and in the other, it is variable. The variable variety is found to occur in compounds which have a smectic *A* phase occurring above the temperature range of the smectic *C*.[8] The theory of the smectic *A*-*C* transition and the temperature dependence of the tilt angle has been discussed by de Gennes.[9] The other variety of smectic *C* appears in compounds which are void of the smectic *A* phase.

In this work we show the use of nuclear magnetic resonance to not only measure the tilt angle in the smectic *C* phase but also study the interesting structure that results when this phase is subjected to a large magnetic field. A particular type of experiment is described. In this experiment the directors of all the molecules are initially aligned parallel to a large magnetic field (~14 000 G). This is accomplished by cooling the sample from its nematic phase into the smectic phase in the presence of the field. The sample is then rotated to some fixed angle in the field and the resonance line shape observed and its second moment determined. The variation of the second moment as a function of sample orientation in the field is found to depend only upon the magnitude of the tilt angle. It is also found to be possible to predict actual NMR line shapes.

To compare the experiment with the theory it was necessary to construct a model for the smectic *C* where the smectic sample resides in a large magnetic field. The model is based upon three assumptions, most of which can be checked in a separate NMR experiment. The real test of the model, however, comes in its ability to predict line shapes and, from the measured second moments, to obtain values for the tilt angles, which are then compared with those measured using optics and other experimental techniques.

II. SMECTIC *C* MODEL

A. Assumptions

As described earlier, the smectic *C* phase consists of structureless layers with the spacing between the layers being less than the over-all length of a molecule. This results from the molecules being tilted within the layers. In our experiments,

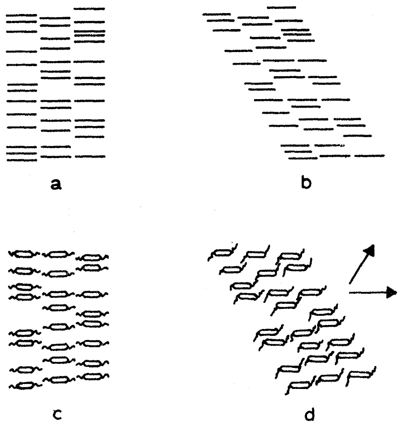

FIG. 1. Sketch of the (a) smectic *A* phase; (b) smectic *C* phase; (c) smectic *A* phase showing the alkyl end chains aligned, on the average, about the same director as the central rigid portion of the molecule; (d) possible smectic *C* structure with the alkyl end chains preferring a different director than that of the molecular central groups.

the smectic sample resides in a magnetic field. This field can have a strong influence on the molecular arrangement in the smectic *C* phase. We construct a model for the smectic *C* based upon three assumptions. These assumptions are first listed then each explained and discussed separately.

(i) Each molecule has *only one* preferred direction of orientation about which each of its groups are, on the average, aligned. This direction may be different for different molecules.

(ii) The magnetic field acts only on the molecular directors and has no influence on the configuration or orientation of the smectic layers, other than through the constraint that the planes of the layers maintain a fixed tilt angle with respect to the director.

(iii) The molecules are free to reorient within the smectic *C* layers, and in a sufficiently large magnetic field, their directors will always align as nearly parallel as possible to the field direction subject only to the tilt-angle constraint.

The textbook picture that is generally drawn for this phase is one of rigid rods lying parallel to one another but uniformly tilted at some angle within the planes as illustrated in Fig. 1(b). However, if one considers the molecular structure in more detail, the above picture appears somewhat naive. The molecule is usually thought of as consisting of a rigid part made up of aromatic rings and a flexible part made up of alkyl end chains.[10] It has been well established that the degrees of order of the two different portions of the molecules are significantly different, with the rigid central portion of the molecule being more ordered than the end chains.[11] In Fig. 1(a) it has been assumed that the preferred direction of orientation (molecular director) is unique for the entire molecule. That is, the end chain and the central portion of the molecule take on the same average direction. In the smectic *A* phase where the molecules are all normal to the planes, this is indeed the case, as can be illustrated by a simple NMR line-narrowing experiment.[12] This will be discussed further in Sec. IV. In the smectic *C* case, on the other hand, it is not obvious that this is the case. For example, one could conceive of the smectic *C* phase as is illustrated in Fig. 1(d), where the director associated with the alkyl end chains is different from that of the aromatic rings. However, it will be shown later that there is some evidence against this particular structure, and in one compound, it will be shown not to be the case. Therefore, the first assumption upon which the smectic *C* model is based is that there exists one unique preferred direction of orientation for the entire molecule. It should be pointed out, however, that it is not important in the model how well different parts of the molecule are ordered about this director, only that all the molecular groups which make up the molecule take on the same director.

The remaining assumptions are concerned with the molecular structure of the smectic *C* in the presence of a strong magnetic field. The smectic *C* samples are made by first heating the liquid crystal into the nematic phase. The sample is then slowly cooled in the presence of a large magnetic field (~ 14 000 G) through the nematic-smectic phase transition into the smectic *C* phase. In the nematic phase, the anisotropy in the diamagnetic susceptibility will cause the preferred direction of the long axis of the molecule to be parallel to the direction of the field. If the sample is slowly cooled into the smectic *C* phase in fields larger than ~ 10 000 G, this molecular director will remain parallel to the field in the smectic *C* phase. In Sec. III it will be shown how this can be checked experimentally with NMR. It might be worthwhile to mention here that if one does not use sufficiently large magnetic fields, the molecular orientation imposed by the container walls will be influential in aligning the director as the sample is cooled from the nematic to the smectic *C* phase.

At first, one is tempted to visualize a smectic *C* sample in which all of the smectic layers are parallel throughout the sample. However, this is not the case. The only constraint on the smectic *C* layers is that they are formed such that the molecules within them are tilted at some common angle. Two possible directions in which the planes can form are shown in Fig. 2. There are, of course, an infinite number of directions (values of ϕ) that the planes can make about the magnetic field direction. We therefore visualize the smec-

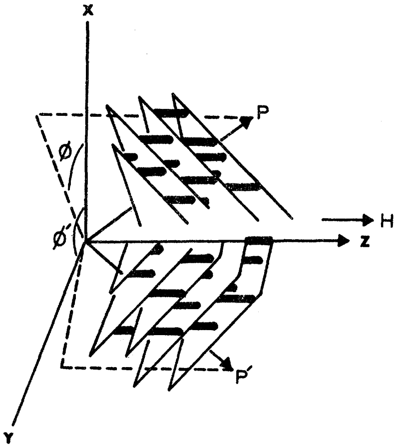

FIG. 2. Diagram illustrating the smectic *C* structure obtained when the sample is cooled from the nematic to the smectic *C* phase in the presence of a large magnetic field. Two single smectic *C* liquid-crystal units oriented at different arbitrary azimuthal angles ϕ about the field direction are illustrated. The dark rods illustrate the molecules tilted in the smectic *C* layers. The vectors $\vec{P}$ are the planar normals.

tic *C* sample which is prepared in this manner as one which consists of regions of small "single liquid crystals" (uniform parallel planes), each of these units making some value of ϕ about the field direction. If the second assumption is correct, then the field will have no influence on the value of ϕ and there will be uniform distribution in ϕ of these single-liquid-crystal units. That is, no value of ϕ will be preferred by the field over any other.

We now concern ourselves with what happens if the direction of the field is changed or, equivalently, if the smectic *C* sample is reoriented in the field. Our second assumption is that in such a case the smectic *C* planes neither distort nor shift. In the smectic *A* this has indeed been demonstrated to be true,[12] and will be illustrated in one compound in Sec. IV. It has been shown that in a smectic *A* compound which exhibits a strong first-order nematic-smectic *A* transition (large transition entropy ~2 cal/deg mole) the sample can be reoriented in a field of 14 000 G without distortion.[11,12] As a matter of fact, from a phenomenological point of view, if one is to retain the planar order, no bend or twist deformations are allowed at all.[13] As the nematic-smectic transition approaches a second-order one (smaller transition entropy), a uniformly ordered smectic *A* will distort in a large magnetic field[11]; however, it is believed that in this case the planar structure is not deformed, but disinclinations are introduced in a manner recently suggested by de Gennes.[14]

The third assumption is perhaps the most interesting of all, since it concerns molecular reorientation within the smectic *C* layers. In the third assumption it is assumed that in the presence of a sufficiently large external force such as a magnetic or electric field, the molecular director can reorient within the smectic *C* layers subject to the constraint that it always maintain a constant tilt angle. This is illustrated in Fig. 3 for two smectic *C* layers, each belonging to two different single-crystal units, and each making a different azimuthal angle ϕ about the field direction. Just how much freedom a particular director has to reorient depends upon the ϕ for its smectic *C* plane and the direction of the external force due to the magnetic field (Fig. 3). As the smectic *C* sample is reoriented in the magnetic field, a director may or may not be able to remain parallel to the field direction depending upon how far the sample is rotated and upon the value of ϕ. If the magnetic interaction is sufficiently large that all molecular directors in the sample remain as parallel to the field direction as possible, subject only to the tilt-angle constraint, then there will occur a redistribution in the direction of the molecular directors as the sample is rotated about the x axis in Fig. 2, with the z axis making some angle δ with the field direction. The resulting distribution of directors depends upon the magnitude of the tilt angle θ and upon the magnitude of δ. Before showing the calculations for these distributions it is first necessary to discuss the interaction of the molecules with the external magnetic field. It must first of all be realized that the interaction energy of a single molecule is insufficient to align the director of that molecule in a field of several thousand gauss.[15] In order to cause the director to follow the direction of the field, the magnetic field must interact

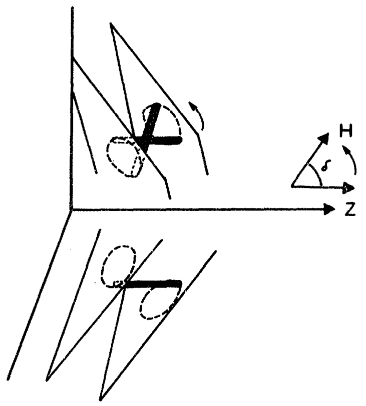

FIG. 3. Illustration of the freedom of the molecular axis for reorientation within the smectic *C* layers. Two planar orientations are illustrated in which the director associated with one set of planes is free to follow the field while the other is not.

collectively with approximately 10^6 molecules. This means that if the director associated with each single-crystal unit is to follow the field direction as closely as possible, the size of each unit or domain must contain enough molecules such that the net magnetic moment is sufficiently large. It turns out, as will be shown in Sec. IV, that fields of ~10 000 G or greater are necessary. In actuality, only about 90% of the sample need to obey the third assumption to give good agreement with the NMR experiment.

B. Distributions in Molecular Director

Using the model described in Sec. II A, we now calculate how the molecular directors will distribute as an aligned smectic *C* sample is oriented in the magnetic field. In Fig. 4(a) we take the director $\vec{N}$ associated with a single-crystal smectic *C* unit which is at some arbitrary azimuthal angle ϕ about the field direction. The tilt angle of the smectic *C* compound is given as θ and the length of the molecule is l. The directors are initially all aligned parallel to the z axis. After the uniformly aligned smectic *C* is formed the sample is rotated in the field to an angle δ. The director $\vec{N}$ then moves to take on the minimum energy configuration [minimum value of η as indicated in Fig. 4(a)]. The unit vectors $\vec{N}$ and $\vec{H}$ are given by

$$\begin{aligned} \vec{H} &= \vec{j}\sin\delta + \vec{k}\cos\delta, \\ \vec{N} &= \vec{i}\cos\xi\sin\beta + \vec{j}\sin\xi\sin\beta + \vec{k}\cos\beta. \end{aligned} \tag{1}$$

We want to minimize η or maximize the value of

$$\cos\eta = \vec{H}\cdot\vec{N} = \sin\xi\sin\beta\sin\delta + \cos\delta\cos\beta. \tag{2}$$

The value of δ is an experimentally determined quantity, as it is the angle through which the sample has been rotated away from the direction of the magnetic field. The values of β and ξ may be obtained in the following manner. The locus of points through which the tip of the vector $\vec{N}$ is constrained to move is a circle, but projects as an ellipse onto the xy plane. We may now pick a point on the ellipse, (x, y), and reexpress Eq. (2) in terms of x and y as

$$\cos\eta = \frac{2y}{l}\sin\delta + \cos\delta\,\frac{(l^2 - 4x^2 - 4y^2)^{1/2}}{l}. \tag{3}$$

Now to determine the values of (x, y) which lie on the ellipse we refer to Fig. 4(b). To form Fig. 4(b), the primed frame is first rotated about the x or x' (initially parallel) axis to an angle θ. The circle of radius $r = \frac{1}{2}l\sin\theta$ in the $x'y'$ plane is the locus of points swept out by the director. The angle θ is constant and is the tilt angle. This particular circle projects as an ellipse into the xy plane with its major axis along the y axis. The primed frame is now rotated about the z axis by an angle ϕ. Each value of ϕ corresponds to the planar orientation of a particular single smectic *C* liquid-crystal unit. The equation for the ellipse is then given by

$$\begin{aligned} &x^2(\cos^2\phi\cos^2\theta + \sin^2\phi) + 2xy(\sin\phi\cos\phi \\ &\quad - \sin\phi\cos\theta\cos^2\theta) + y^2(\sin^2\phi\cos^2\theta + \cos^2\phi) \\ &\quad - 2(\tfrac{1}{2}l)\sin\theta(x\sin\phi\cos\theta + y\cos\phi\cos\theta) = 0. \end{aligned} \tag{4}$$

The procedure now is to pick an x and find the corresponding value of y for a given tilt angle θ and a particular layer orientation ϕ. Then go back to Eq. (3) and compute $\cos\eta$ and check to determine whether it is the largest value. If it is not, then try again until the maximum value of $\cos\eta$ is found for a particular ϕ. Another value of ϕ is picked and the procedure is repeated. We chose 180 values of ϕ between $\phi = 0$ and 2π, and found 180 corresponding values for the maximum value of $\cos\eta$. We could then have the computer tell us how the 180 directors

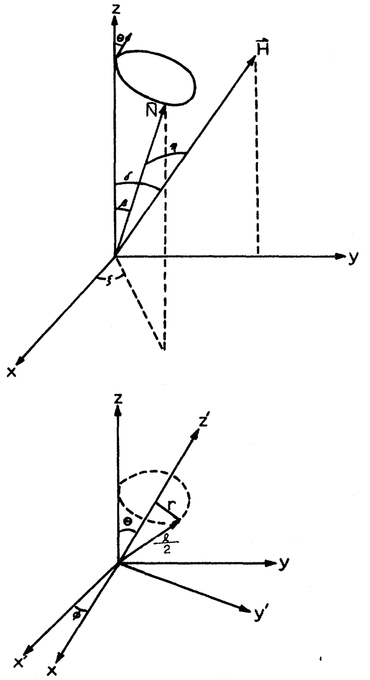

FIG. 4. Diagrams showing the directors and angles discussed in Sec. II. (a) The z axis is the direction along which the smectic *C* was initially aligned in the magnetic field. The direction of the magnetic field $\vec{H}$ is then changed to make angle δ from the z axis. The vector $\vec{N}$ is the molecular director, and the tip of this vector traces out a circle. The plane of the circle is tilted out of the xy plane at the angle θ. This angle corresponds to the tilt angle characteristic of the smectic *C*. (b) With the x and x' axes initially parallel, the primed frame is rotated about the x axis to an angle θ. The primed frame is then rotated to an angle ϕ about the z axis. The circle in the $x'y'$ plane centered about the z' axis projects as an ellipse into the xy plane.

were distributed in η. As will be seen in Sec. III, it turns out to be most useful for NMR purposes to know how the directors are distributed according to $|P_2(\cos\eta)| = \frac{1}{2}|(3\cos^2\eta - 1)|$. In Fig. 5 we illustrate the calculated distribution for the case where the tilt angle $\theta = 45°$. This is shown for several angles of the sample δ in the magnetic field. Similar distributions were calculated for the tilt angles θ varying from 1° to 45°, and for each value of θ the angle δ was varied in steps of 5° from 0° to 90°. It is now necessary to relate these calculated distributions to the experimental line shapes and second moments.

III. THEORETICAL SECOND MOMENTS AND LINE SHAPES

A. Second Moments in Smetic Phase

Nuclear magnetic resonance in liquid crystals is unique in that the intermolecular dipole interactions are averaged to zero while the dipole interactions between spins within the molecule are only partially averaged.[15] Furthermore, even in the very viscous smectic phases there is sufficiently rapid diffusion to average out completely the dipole interactions between spins belonging to different molecules.[12] As the molecules are partially ordered, the intramolecular spin interactions persist and one observes a broad NMR line very similar to that seen in solids. Another interesting and useful property of NMR in liquid crystals results from the fact that the molecules are rapidly rotating about their long axis. Because of this motion all of the dipolar interactions occur, on the average, in the average direction of the long molecular axis. The usefulness of this property will become evident later.

A useful parameter in this study is the second moment defined as

$$\langle\Delta H^2\rangle = \frac{\int_0^\infty (H - \langle H\rangle)^2 F(H)\,dH}{\int_0^\infty F(H)\,dH}\,, \tag{5}$$

where $F(H)$ describes the shape of the resonance line and H is the magnetic field at which resonance occurs. This parameter can be calculated theoretically in a manner originally described by Van Vleck[16] by the expression

$$\langle\Delta H^2\rangle = \frac{3}{4}\,\frac{I(I+1)}{\gamma^2}\,\frac{4\pi^3}{N}\sum_{ij} B_{ij}^2\,, \tag{6}$$

where we have only written down the terms for interaction between spins of the same species such as protons, where I represents the nuclear spins and γ is the gyromagnetic ratio.

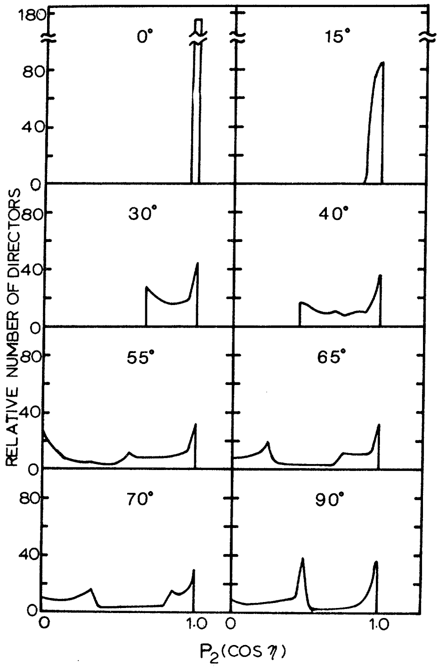

FIG. 5. Graphs illustrating how the molecular directors become distributed in $(\frac{3}{2}\cos^2\eta - \frac{1}{2})$ as a smectic C sample which was initially uniformly aligned parallel to the field direction is then oriented to different angles δ in the magnetic field. These distributions are calculated for the case where the tilt angle $\theta = 45°$.

One must sum over all interactions of N spins in the sample. In the case of a liquid crystal B_{ij} is given as[15]

$$B_{ij} = -(h/2\pi)\gamma^2 \tfrac{1}{2}\,\langle(3\cos^2\alpha_{ij} - 1)/r_{ij}^3\rangle, \tag{7}$$

where α_{ij} is angle between the ith and jth spins and r_{ij} is their separation. As a result of the averaging typical of the liquid crystal,[15,17]

$$\tfrac{1}{2}\langle(3\cos^2\alpha_{ij} - 1)/r_{ij}^3\rangle = (\tfrac{3}{2}\cos^2\eta - \tfrac{1}{2})\tfrac{1}{2}\langle(3\cos^2\alpha'_{ij} - 1)/r_{ij}{}^3\rangle, \tag{8}$$

where η is the angle between the preferred direction of alignment of a given molecule and the magnetic field direction, and α'_{ij} is the angle between this molecular director and the internuclear vector. In a nematic liquid crystal η is typically zero, but in the smectic phase η can be made to vary. The manner in which η varies depends upon the particular smectic phase and the conditions of the experiment. Our experiments were performed at constant temperature, in which case $\langle(3\cos^2\alpha' - 1)/r^3\rangle$ is constant.

The simplest case is that of the smectic A phase. In the smectic A the planes of the layers are all normal to the molecular director. If one forms a smectic A sample by slowly cooling from the nematic phase to the smectic A phase in the presence of a large magnetic field, one can obtain a single smectic A liquid crystal where all the molecular directors are parallel to the field director, and are all normal to the smectic A planes which are all likewise parallel. Upon reorienting the smectic A sample in the field to an angle δ ($=\eta$ in smectic A) and, assuming the smectic layers do not distort, then the second moment will follow the expression

$$\langle \Delta H^2 \rangle = \tfrac{1}{4}(3\cos^2\eta - 1)^2 \langle \Delta H^2 \rangle_0 , \qquad (9)$$

where $\langle \Delta H^2 \rangle_0$ is the second moment at $\eta = 0$, i.e., the second moment before the sample was rotated. The second moment should vanish at the angle $\delta = \cos^{-1} 1/\sqrt{3}$. This is a good test of the validity of the assumptions used in Eq. (8) and has in fact been demonstrated to be true where this procedure was used to remove the dipolar interactions, in order to obtain a measure of the diffusion constant in smectic liquid crystals.[12] To what degree the dipolar interactions can be removed will be shown in Sec. IV.

In the smectic C phase the situation is somewhat more complicated, because η becomes distributed as the sample is reoriented in the field. In Sec. II it was shown how these distributions are calculated. For a particular tilt angle θ and angle of rotation δ of the sample in the field, the directors are distributed in η. For every value of η or, more conveniently, for every value of $\frac{1}{2}(3\cos^2\eta - 1)$ there are M number of directors. To compute the second moment, $\frac{1}{2}(3\cos^2\eta - 1)$ is scaled into P number of values ranging from 0 to 1, and from Sec. II the relative number of directors M_p is determined for each $\frac{1}{2}(3\cos^2\eta - 1)_p$. From Eqs. (6) and (8) the second moment for the smectic C becomes

$$\langle \Delta H^2 \rangle = \tfrac{1}{4} \langle \Delta H^2 \rangle_0 \frac{\sum_p M_p (3\cos^2\eta - 1)_p^2}{\sum_p M_p} . \qquad (10)$$

Since the only unknown is the tilt angle, this is a most useful result, for it provides a method for measuring the tilt angle. For small tilt angles ($\theta \leq 20°$), the technique can be made very simple by just observing where the minimum value of the second moment occurs versus the angle of rotation of the sample. The second moment becomes a minimum at the same angle of sample orientation for which the length of a free-induction decay following a $\frac{1}{2}\pi$ pulse becomes a maximum. Using the calculations described in Sec. II B and Eq. (10), the angle of rotation at which a maximum occurs in the free-induction decay is plotted versus the tilt angle and is shown in Fig. 6. The curve in Fig. 6 is all that is needed to determine the tilt angle from the free-induction decay.

B. Line Shapes in Smectic *C* Phase

It is interesting to try to predict the actual NMR proton line shapes for the smectic C phase that will occur when an aligned sample is rotated to a particular angle δ in the field. Knowing only very little about the specific dipolar interaction which occurs within the molecule, it turns out that one can determine the line shapes with amazing accuracy using the model described in Sec. III A. In general, however, the line shape one obtains for a particular value of δ depends only on two factors: the magnitude of the tilt angle θ and the shape of the NMR line at $\delta = 0$. The simplest case would be for a two-spin system where at $\delta = 0$ one would have a two-line spectrum.[16] In this case the NMR spectrum or line shape for the case of a tilt angle of 45° would be the same as the distributions shown in Fig. 5 folded about the origin. In general, however, the smectic C phase is made up of rather large molecules containing many proton spins giving a broad NMR at $\delta = 0$. Because η becomes so broadly distributed at large values of δ and the tilt angle θ, the line shape becomes rather insensitive to what its shape was at $\delta = 0$. To calculate some line shapes for large values of δ—say, at the magic angle 55°—one can choose the line shape at $\delta = 0$ to be rectangular. That is, each single-crystal unit in the smectic C sample produces a rectangular line shape which has a width depending upon the value of η its director takes on. The number of directors which take on this value of η can be calculated from the model for a given tilt angle and value of δ. For a tilt angle of 45° this can be obtained from Fig. 5. For a particular δ one then has a superposition of rectangular line shapes of a width governed by η and an intensity governed by the distribution of directors. The calculated line shapes for a tilt angle of 45° are shown in Fig. 7. It is interesting to compare the smectic C line shapes with those of the smectic A at the magic angle $\theta \simeq 55°$. A smectic A will show a very narrow line at this angle as is seen from Eq. (9), whereas the smectic C line is broad and has the shape shown in Fig. 7, where the tilt angle is 45°.

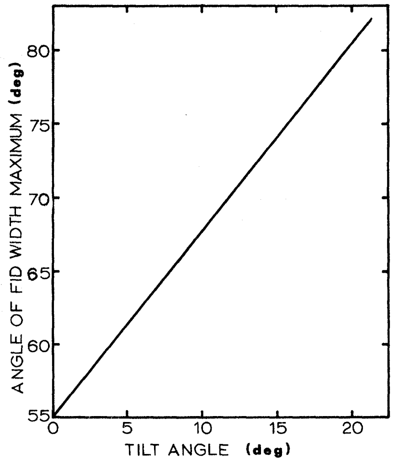

FIG. 6. Calculated angle at which the free-induction decay will be a maximum or the second moment a minimum vs the tilt angle of the smectic C.

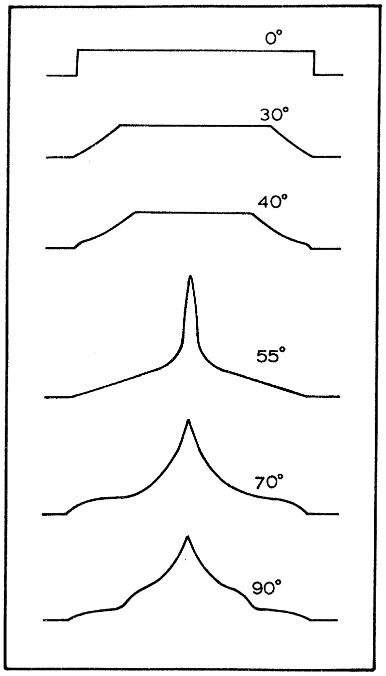

FIG. 7. Predicted variations in the NMR line shapes as an initially aligned smectic C sample with a tilt angle of 45° is oriented to different angles δ in the field. These figures are based on a rectangular line shape at $\delta = 0$, although large changes in this shape such as a triangular shape have little effect on the line shapes at angles near 50°.

IV. EXPERIMENT

A. 4-4′-bis-(heptyloxy)-azoxybenzene (HOAB)

This compound exhibits the nematic and smectic C liquid-crystalline phases and has been studied in numerous experiments.[15] The magnitude of the tilt angle has been reported to be quite large and independent of temperature, although the literature has been contradictory in its actual measured value.[3-7] Optics[3] and some x-ray experiments[4] have reported a value of 45° for the tilt angle, while other x-ray studies[6] as well as studies by other techniques to include electron-spin resonance[5] and the Mössbauer effect[7] have reported significantly lower values near 30°.

In our experiments we prepared the smectic sample in the method described earlier by cooling from the aligned nematic to the smectic C phase in the presence of a 14 300-G field. While in the smectic C phase the sample was then oriented at different angles in the field and the proton-magnetic-resonance line recorded. The absorption line shape was obtained by Fourier-transforming the free-induction decay following a $\frac{1}{2}\pi$ rf pulse. A Bruker model B-KR-322 pulsed-NMR system operated at 61 MHz was used to obtain the free-induction decay. The Fourier transforming was accomplished in a manner originally described by Clark[19] where the boxcar integrator is used to integrate the phase-detected free-induction decay while the magnetic field is continuously swept through the resonant frequency. The absorption line was then traced out on an X-Y recorder and the second moment obtained numerically from the recording.

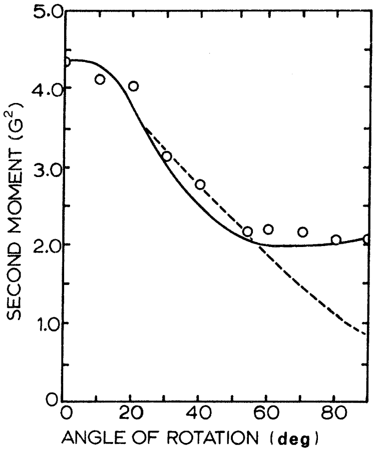

FIG. 8. Measured values of the second moment vs the angle of sample orientation in a magnetic field of 14 300 G for the compound 4-4′-di-n-heptyloxyazoxybenzene at a temperature of 80 °C. The solid curve is that variation calculated for a tilt angle of 45° and the dashed curve for a tilt angle of 30°.

The measured second moments versus the angle of sample orientation are shown in Fig. 8 along with the calculated angular dependence for tilt angles of 45° and 30°. The theory and experiment are in excellent agreement if the tilt angle is taken to be 45°, which is the value obtained in Taylor's optical

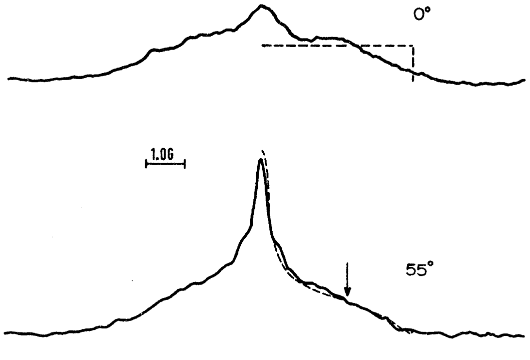

FIG. 9. Line shapes for an initially aligned sample of 4-4′-di-n-heptyloxyazoxybenzene in the smectic C phase at a temperature of 80 °C recorded at the angles of rotation $\delta = 0°$ and 55° in a field of 14 300 G. The dashed curve at 55° is the predicted line shape calculated using a tilt angle of 45° and taking the line shape at $\delta = 0$ to be rectangular. Assuming the line shape at $\delta = 0$ to be triangular has no noticeable effect on the shape at $\delta = 55°$.

experiments[3] and the de Vries x-ray work.[4] A tilt angle of 30° is clearly seen not to be in accord with these second-moment measurements.

It is interesting to compare the actual line shapes with those predicted from the model and shown in Fig. 7. This comparison is made at the angle $\delta = 55°$ in order to contrast the smectic *C* line shape with that of the smectic *A* which becomes a very narrow line at this angle. As explained in Sec. III B, the best agreement with those shown in Fig. 7 would be expected to be near this angle of orientation. The agreement is remarkably good, as is seen in Fig. 9, where the recorded line shape at $\delta = 55°$ is shown. To calculate the curve at $\delta = 55°$ the line shape at $\delta = 0$ was assumed to be rectangular. It should be noted that the line shape at 55° appears to be the sum of two Gaussian lines (one narrow line and one very broad line) superimposed. This gives a very distinct free-induction-decay signal consisting of very fast decay associated with the broad line and a very long decay superimposed for the narrow line. This decay is characteristic of the smectic *C* phase particularly for large tilt angles at $\delta = 55°$.

It is important to note that the data above were taken in large magnetic fields. We found this to be necessary in order for the last assumption in our model to be valid; namely, that all the directors in the sample follow the direction of the field as closely as possible subject only to the tilt-angle constraint. Figure 10 shows the measured second moment in fields near 1500 G, which is not strong enough for all the directors to follow. At this field it is seen that the directors hardly follow the field at all. The curve in Fig. 10 illustrates that if this measurement is not made in large enough fields one could be misled and determine the wrong value for the tilt angle. This could be why the EPR measurement[5] implied too low a value for this angle, as these measurements were made in a 3300-G field.

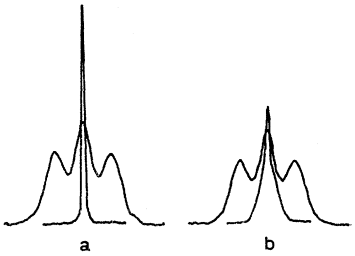

FIG. 11. Recorded line shapes in TBBA at $\delta = 0$ (broad line) and $\delta = 55°$ in the (a) smectic *A* phase at 174 °C and (b) smectic *C* phase at 170 °C (tilt angle of 9°).

B. Terephal-bis-4(4-*n*-butylanaline) (TBBA)

This compound offers a better test of the model, since it has a variable tilt angle. It likewise has been studied by optical techniques. TBBA has three smectic phases in addition to the nematic phase. The transition temperatures are isotropic-nematic 236°, nematic-smectic *A* 200 °C, smectic *A*-smectic *C* 173 °C, and smectic *C*—smectic *B* 144 °C.

The sample was prepared in the same manner as HOAB. Recorded line shapes at $\delta = 0$ and $\delta = 55°$ in the smectic *A* and smectic *C* phases are shown in Fig. 11. It is seen that there is no change in the line shape at $\delta = 0$, indicating no change in the molecular configuration or director, consistent with the first assumption of the model. At $\delta = 55°$ the line becomes broadened, which is typical of the smec-

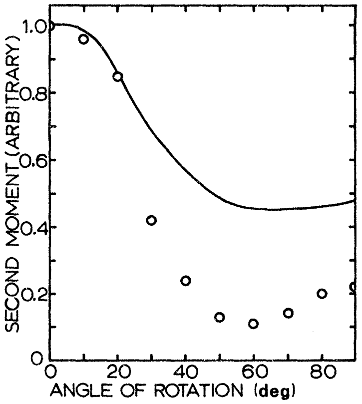

FIG. 10. Variation of the second moment in 4-4′-bis-heptyloxyazoxybenzene in the smectic *C* phase measured at magnetic fields too low (1548 G) for all of the directors to follow (open circles). The solid line is that measured as well as calculated (Fig. 8) for a larger magnetic field strength.

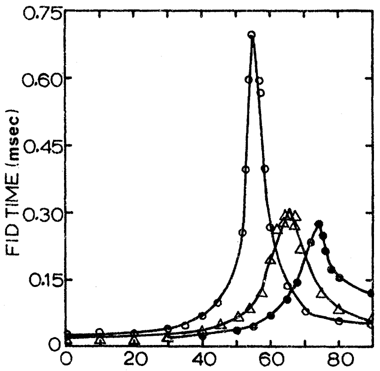

FIG. 12. The time for the free-induction signal to decay to one-third its maximum amplitude vs the angle of orientation of an initially aligned sample of TBBA in the smectic *A* phase at $T = 173$ °C (open circles) and the smectic *C* phase at $T = 170$ °C (triangles) and $T = 164$ °C (closed circles). The sample was aligned and the measurements made in a field of 14 300 G.

tic *C* phase. A more useful observation is the free-induction decay. The length of the free-induction decay (time for the signal to decay to $\frac{1}{3}$ of its maximum value) versus the angle of sample orientation is shown in Fig. 12 in the smectic *A* phase, and for two different temperatures in the smectic *C* phase. The curve in the smectic *A* phase is typical of most aligned smectic *A* compounds in which T_2 increases by more than an order of magnitude at the magic angle. As a matter of fact, if the sample is then cooled into the smectic *A* phase very slowly, it is possible in some cases to get a free-induction decay at the magic angle which differs by less than a factor of 2 of that seen in the isotropic phase of the same compound, indicating nearly complete removal of all of the dipolar interactions. This, therefore, means that for all practical purposes the intermolecular interactions are averaged to zero in the viscous smectic, that the planes of the smectic layers do not distort in the field, and that it is possible to obtain a uniformly aligned smectic.

In the smectic *C* phase, on the other hand, the angle at which the free-induction decay is largest shifts to larger angles. From Fig. 6 the tilt angle can be determined from these free-induction-decay maxima. Figure 13 shows our measured values of the tilt angle along with the average of those obtained optically by Taylor. The agreement is satisfying. The temperature gradients across the sample were 0.5 °C.

For completeness and as an additional check on the model, the second moments of TBBA are plotted in Fig. 14 at various tilt angles. Although the agreement with theory is good, the most precise way of obtaining a measure of the tilt angle is by free-induction-decay maximum rather than by plotting out the entire second-moment curves. We found that our precision in obtaining a value for the tilt angle is limited only by how well one can measure the angle of rotation of the sample in the field. For small tilt angles the largest error arises from temperature gradients in the sample. For small tilt angles the decay maximum is quite distinct and can be determined visually on the oscilloscope. In general, the larger the tilt angle, the less precise is the measurement.

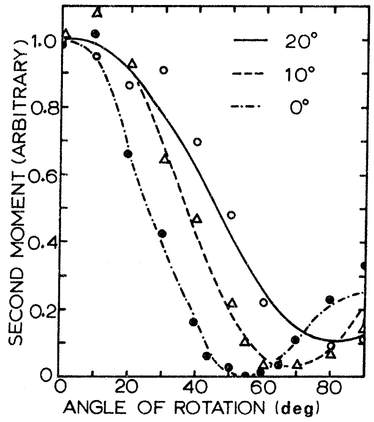

FIG. 14. Variation of the second moment of TBBA vs the angle of sample orientation in the field. The curves are for the smectic *A* phase (closed circles), the smectic *C* phase for a tilt angle of 10° (triangles), and a tilt angle of 20° (open circles). The solid, dashed, and dotted curves are the calculated variation in the second moments for these tilt angles.

Finally, we show in Fig. 15 what happens to the free-induction decay when TBBA is cooled into the smectic *B* phase. The maximum value shifts back to 55°. This can be understood if the molecular directors are no longer allowed to reorient within the layers. Such a behavior might be expected of

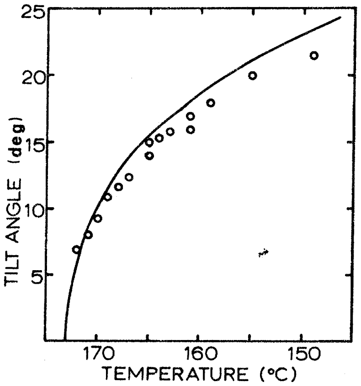

FIG. 13. Measured tilt angle in TBBA as a function of temperature obtained from the free-induction-decay maxima (circles). The solid line represents the average of measured values obtained optically in thin films by Taylor, Fergason, and Arora.

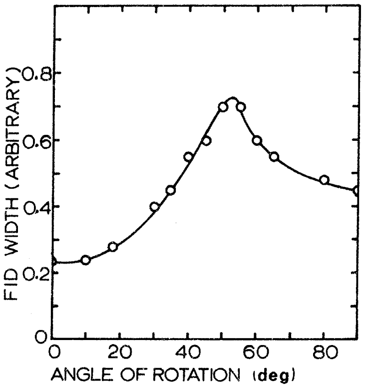

FIG. 15. Variation in the time for the free-induction signal to decay to a fraction of its maximum value as the smectic *B* phase of TBBA is oriented to different angles in the field.

a smectic *B*, since the centers of the molecules become ordered within the layers.[1] It should be noted that the molecules can remain tilted as in the smectic *C*; however, their freedom of reorientation in the planes becomes restricted.

V. DISCUSSION

The model is seen to predict the data remarkably well provided the experiment is performed in magnetic fields greater than 10 000 G. In fact, if one were to use this technique to obtain precise values for the tilt angles, magnetic fields near 15 000 G should be used. The large field is not only necessary to establish the initial condition that all the directors in the sample are aligned parallel at $\delta = 0$, but also as the sample is rotated to other angles in the field, the directors remain as nearly parallel to the field as possible, subject only to the tilt-angle constraint. The latter condition appears to require the largest field strengths. In fact, we found in the case of HOAB that 10 000 G was not quite strong enough to meet this condition, whereas 14 000 G was.

It would be interesting to do this experiment using electric fields to orient the directors instead of the magnetic field. This probably would not be a difficult experiment, since electric fields do not impose the convection problems in smectics that they do in nematics. If the NMR or EPR experiment were done in fields near 3 000 G, it should not require large electric fields to compete with the magnetic field.

In addition to the smectic *C* phase studied here, there are numerous other smectic phases[1] one might study using this technique. The twisted smectic[20] is an example.

Finally, we comment on the temperature dependence of the tilt angle in TBBA. It has been predicted by de Gennes[9] that in liquid crystals which exhibit the smectic *A*–smectic *C* transition the magnitude of the tilt angle θ should vary as $(T_c - T)^{0.35}$, where T_c is the transition temperature in degrees Kelvin. Figure 16 shows a plot of $\ln\theta$ versus $\ln(T_c - T)$ from our measured values of the tilt angle θ in TBBA. The slope of the line gives a measured dependence of $(T_c - T)^{0.40\pm0.04}$. It would be of value not only to measure this in other compounds, but also to make very precise measurements very near (within 2 °C) the smectic *A*-*C* transition. These measurements are possible with this NMR technique if the temperature across the sample is sufficiently uniform.

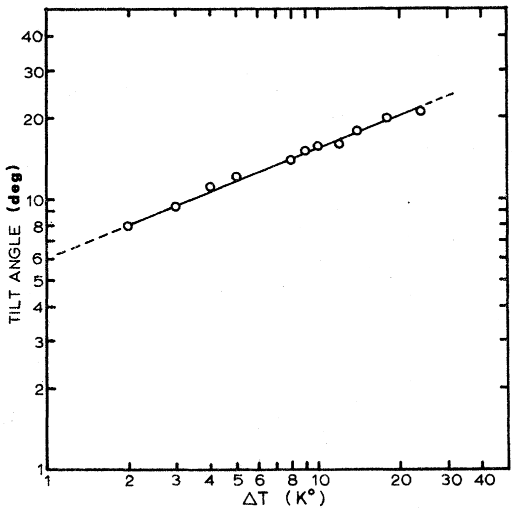

FIG. 16. A plot of $\ln\theta$ (θ is the tilt angle) vs $\ln(T_c - T)$, where T_c is the smectic *A*–smectic *C* transition temperature. The slope of the line gives the temperature dependence of the tilt angle to be $(T_c - T)^{0.40}$.

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Ground State of an Interacting Bose Gas

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The ground-state energy of an interacting many-boson system obtained by Bogoliubov and Zubarev using the collective-coordinate method is shown to be equivalent through second order to the variation-perturbation energy evaluated in the uniform limit by means of the method of correlated basis functions. It is also shown that the wave function derived with a slight modification of the Bogoliubov–Zubarev approach is equivalent to that determined *formally* from the Rayleigh–Schrödinger perturbation theory in the uniform limit.

I. INTRODUCTION

Recently a great variety of microscopic theories have been developed for various interacting many-boson model systems in attempts to determine low-temperature properties of liquid ^{4}He from an atomic viewpoint. Since many of these model calculations are based on different approximation methods and different validity conditions, they do not necessarily yield identical results when the calculations are carried through second or higher order in the weak-coupling expansion. Quite recently, however, it has been shown that the ground-state energy evaluated by Brueckner[1] by summing one- and two-ring diagrams in the Bogoliubov occupation number representation[2] is equivalent through second order to that obtained by the method of correlated basis functions,[3-5] which relies on the variational description of the ground state in the Bijl–Dingle–Jastrow (BDJ)-type wave-function space.[6] The fact that the two approaches, field-theoretic and non-field-theoretic in origin, lead to identical results is significant in that they are valid under different conditions: the weak-coupling limit[2] and the uniform limit.[7] The former is defined by $\beta \equiv (N-N_0)/N \ll 1$ and the latter by $\alpha \equiv 1-g(0) \ll 1$, where N_0 is the number of particles in the zero-momentum state and $g(r)$ is the radial distribution function.

The problem of improving the accuracy of the ground-state solution to second order was first considered by Bogoliubov and Zubarev,[8] who described the collective modes of the system by means of the method of auxiliary variables $\rho_{\vec{k}}$ (which are also called collective coordinates). It is interesting to note that the small many-body parameter used in this approach is not an ordinary small parameter, such as α and β, but a function of wave vector which turns out to be the departure of the liquid structure $S(k)$ from its asymptotic value unity. The purpose of this paper is to give an explicit demonstration of the equivalence (through second order) of the ground-state energy obtained by Bogoliubov and Zubarev[8] to that evaluated in the uniform limit formalism,[6,7,9] thus also establishing the equivalence of the Bogoliubov–Zubarev (BZ) method of collective coordinates and the method of second quantization in the weak coupling limit. It is further pointed out that a slight modification of the BZ perturbation procedure yields a correction to the wave function which contains additional two- (or paired-) phonon components beyond those obtained by BZ, while reproducing their results for the energy and the three-phonon part of the wave function. The wave function derived in this modified-BZ method is also shown to agree exactly, as far as the first three leading terms are concerned, with that obtained *formally* using the Rayleigh–Schrödinger (RS) perturbation theory in the uniform limit.

II. BOGOLIUBOV–ZUBAREV METHOD OF COLLECTIVE COORDINATES

The system under consideration is a collection of N bosons interacting in a box of volume Ω through a two-body potential $v(r)$, whose Fourier transform