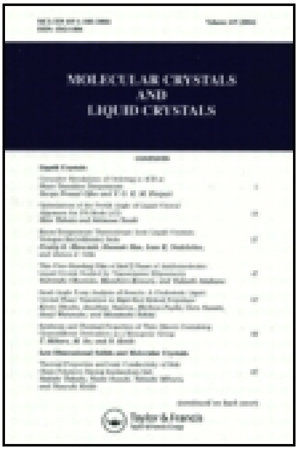

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Impurity Diffusion in the Smectic *A* and Smectic *B* Phases†‡

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Abstract—Using NMR pulsed gradient techniques, we have measured the diffusion constants of the impurity molecule tetramethylsilane (TMS) dissolved in the ordered nematic, smectic *A* and smectic *B* phases of the compound 4-*n*-butoxybenzylidene-4′-*n*-octylaniline. The molecular diffusion is shown to be strongly anisotropic in the smectic phases with the diffusion constant perpendicular to the molecular director, $D_\perp$ (diffusion within the smectic layers) being more than an order of magnitude larger than $D_\parallel$ in these phases. The average value of D in the smectic *A* phase is the same as that in the nematic phase of this compound. The measurements in the smectic *B* phase are consistent with the de Gennes–Sarma model for that phase.

The term smectic usually implies a layered structure.(1,2) In the smectic *A* phase, there is no spacial order within these layers and each layer is often thought of as a two-dimensional nematic liquid. In contrast, the smectic *B* phase does have order within each layer.(3) It has not been clear whether or not this is the only difference between these two phases. In fact, it has not been understood how the smectic *B* phase differs from that of a solid and several different theories have been proposed.(4)

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Needless to say, these structures imply unusual diffusion properties. Although the literature has been devoid of diffusion measurements in them, simple observations suggest that the diffusion be highly anisotropic. For example, a carefully melted smectic *A* sample on a surface will form a terraced droplet with visible tiers that slide easily over one another whereas an unordered bulk sample is itself quite viscous. We report here NMR measurements of the diffusion constant of a " spherical " impurity molecule tetramethylsilane (TMS) dissolved in a uniformly aligned liquid crystal which exhibits both the smectic *A* and *B* phases. In the smectic phases, the diffusion constant is indeed found to be strongly anisotropic. It is interesting, however, that although the smectic *A* phase is quite viscous as compared to the nematic phase, the average diffusion constant for the TMS molecules dissolved in this phase is equal to that in the nematic. In addition, it is found that there is little difference in impurity diffusion in the smectic *A* and smectic *B* phases.

Pulsed NMR in the presence of a pulsed or continuously applied magnetic field gradient is a well-known and powerful technique for the measurement of the diffusion constant in normal liquids.(5) The application of the technique to liquid crystals, however, is not at all obvious. The measurement of the diffusivity in normal liquids relies on the translational diffusion to be the principal mechanism to destroy the imposed transverse nuclear spin polarization. This is not the case in liquid crystals or, for that matter, solids. In these systems there exists a competing mechanism, namely, the nuclear magnetic dipole–dipole interactions which dominate the effects of diffusion and hence make the diffusion constant unmeasurable.

In liquid crystals we have been able to overcome this problem in two ways. One is by dissolving in an impurity molecule in which the dipole interactions are motionally averaged to a sufficiently small value so that its diffusion can be observed. The other technique is to use a specially prepared smectic *A* sample where the spin interactions can be reduced nearly to zero by orientation in the magnetic field.(6) It is the former which we discuss in this paper.

NMR in liquid crystals is unique in that the intermolecular nuclear dipole interactions are motionally averaged to zero while the intramolecular interactions are not.(3) Because the molecules are partially ordered, the magnitude of the transverse relaxation time,

T_2, is very similar to that seen in solids. Normally, if one dissolves an impurity molecule into a liquid crystal, it, too, will become partially ordered by the liquid crystal host, and its value for T_2 will likewise be small. A molecule with tetrahedral symmetry on the other hand obviously will not order unless, of course, the molecule should become distorted. Such a molecule is TMS. It will only slightly distort(7) to give a T_2 which is sufficiently large to allow a measurement of the diffusion constant.

In order to measure the diffusion constant, it is necessary to have a uniformly aligned smectic. This can often be done by cooling into the smectic phase from the nematic phase in the presence of a large magnetic field ($\sim 15{,}000$ G). Often it happens, depending upon the length of the alkyl chain on the molecule, that a compound will exhibit both the nematic and smectic phases with the nematic phase appearing at the higher temperature. While in the nematic phase, the preferred direction of orientation of the molecules will be parallel to the direction of the field. Upon cooling and transforming into the smectic phase, the molecules will retain this parallel alignment. As a matter of fact, a smectic *A* sample once prepared in this manner cannot be easily distorted. Unlike a nematic, once the smectic *A* phase is formed, a large magnetic field competes very little with the container walls in the alignment of the molecules. In the smectic phase no twist or bend deformations are allowed.(8) Thus, as will be illustrated later, a sample can be rotated in the presence of a 15,000 G field with little distortion. This is contrasted with the nematic phase where the deformation constants are so small that the alignment from the container walls is only realized over a distance of a few microns into the sample.

To illustrate the uniformity of alignment as well as the absence of distortion of a smectic *A* and *B* in the presence of a magnetic field, we observed the NMR line and width and free induction decay. A broad NMR line or short free induction decay is normally observed since the molecules are partially ordered. In the smectic phase, the molecular diffusion is nearly always rapid enough to average out the intermolecular dipole interactions and only dipolar interactions within the molecule contribute.(9) If one has a uniformly aligned smectic *A* or *B*, the dipole interaction then depends strongly on the orientation of the sample in the magnetic field and will be directly proportional to the expression $|(3\cos^2\theta_0 - 1)|$ where θ_0 is the angle between the molecular director and the direction of the magnetic field.(9) This dependence arises because the molecules are rotating rapidly about their long axes and the intramolecular dipole interactions are all, on the average, in the same direction, i.e., along the director. The line width, therefore, follows $|3\cos^2\theta_0 - 1|$ and the time of the free induction decay follows $|3\cos^2\theta_0 - 1|^{-1}$. This is dramatically illustrated in Fig. 1 which shows the angular dependence of the free induction decay in an aligned sample in the smectic *A* and smectic *B* phases. At the magic angle, $\theta \simeq 54°$, the free induction decay is only $\frac{1}{3}$ that observed in the isotropic phase in the same magnetic field gradient illustrating almost complete removal of the dipolar effects and hence near perfect alignment of the sample. Once aligned, the sample was observed to remain aligned for several days. The small amount of dipolar interactions which remain has been discussed elsewhere(10) and may be due to disinclinations(11) in the smectic *A*.

The diffusion measurements were made using the pulsed gradient technique(5) with a Bruker pulsed NMR system. A linear magnetic field gradient was applied parallel to the direction of the large uniform field. The linearity and the direction of the gradient were measured by observing the spin echo from two small capillary water samples. The value of the gradient was then measured from the beats in the echo. The linearity and direction of the gradient were determined by measuring the angular dependence of the gradient, that is, by orienting the capillary tubes at various angles in the field. A plot of this dependence is shown in Fig. 2. A linear gradient should show a straight line dependence on a $\cos\theta$ plot where θ is the angle between the direction of the field and the intercapillary vector. From Fig. 2, it is seen that $g_\parallel^2/g_\perp^2 \sim 100$ where $g_\parallel$ is the gradient parallel to the field and $g_\perp$ is that in a perpendicular direction. This ratio is sufficiently large to measure diffusion anisotropies of about two orders in magnitude.(5) While the magnitude of the gradient was measured by the capillary method these values were checked by measuring the diffusion constant in water and comparing the results with values measured by other workers.(12)

The diffusion constants for TMS in the nematic, smectic *A* and smectic *B* phases of 4-*n*-butoxybenzylidene-4′-*n*-octylaniline is

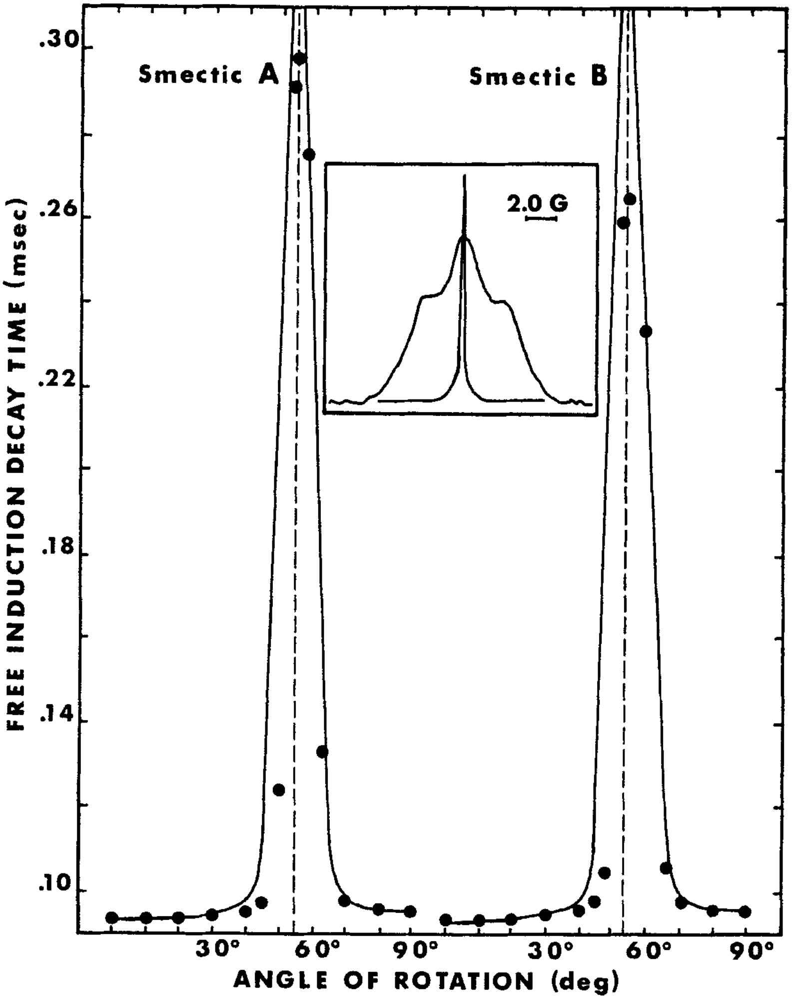

Figure 1. A plot of the time for the free induction signal to decay to $\frac{1}{3}$ of its maximum value vs. the angle the molecular director of a uniformly aligned sample makes with the magnetic field direction. The points are the measured values for 4-*n*-butoxybenzylidene-4′-*n*-octyaniline in the smectic *A* and smectic *B* phase and the solid curve is $|3\cos^2\theta - 1|^{-1}$ fitted at $\theta = 0$. Also shown are the absorption line shapes at $\theta = 0$ and $\theta = 54°$ in the smectic *A* phase.

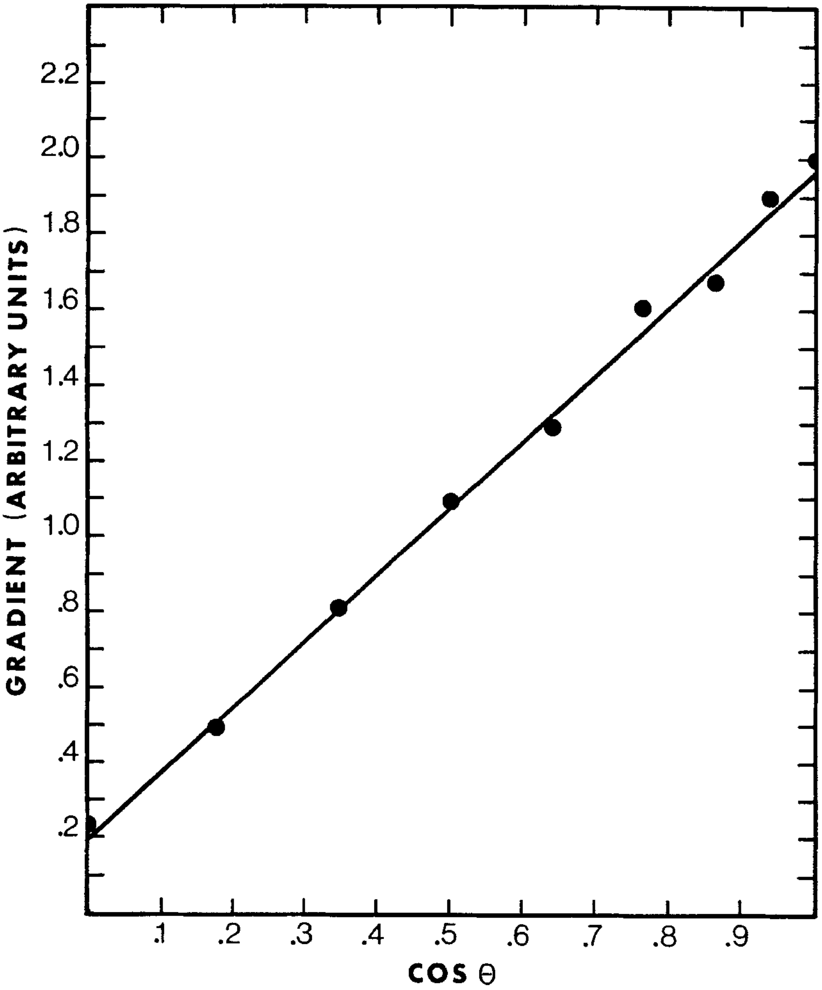

Figure 2. The measured angular dependence of the field gradient used in the experiments.

shown in Fig. 3. As the TMS spin echo was weak, signal averaging was necessary. This was done with a Hewlett–Packard multichannel analyzer and Vidar voltage to frequency converter. The anisotropy of the diffusion constant was measured by orienting the aligned smectic sample in the linear gradient. In the nematic phase only the values of the diffusion constant parallel to the molecular

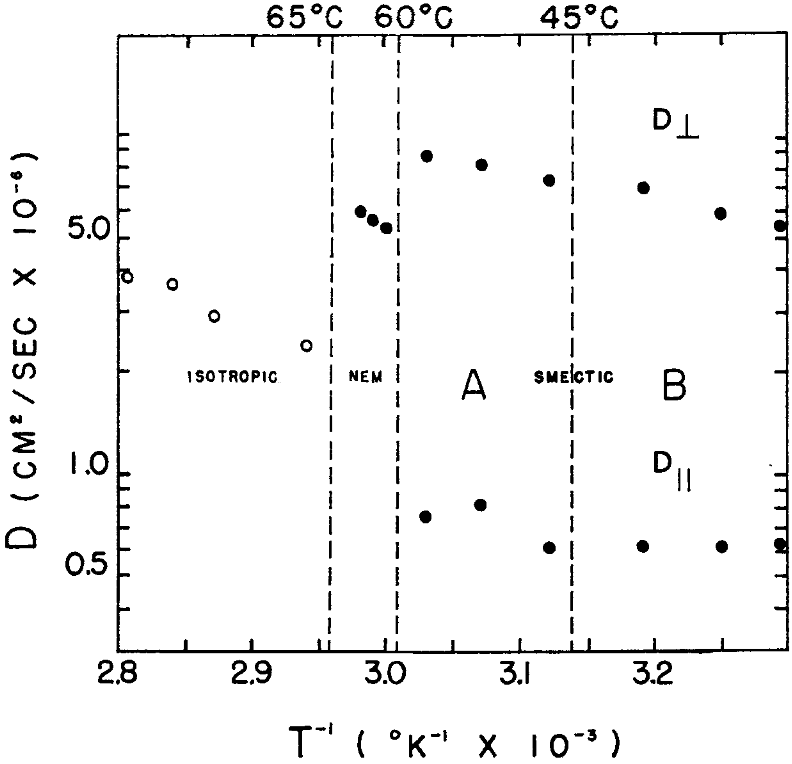

Figure 3. The measured temperature dependence of the diffusion constant of TMS dissolved in the liquid crystalline phases of 4-*n*-butoxybenzylidene-4′-octyaniline. In the smectic phases the large values of the diffusion constant are $D_\perp$ and the small values $D_\parallel$. In the nematic phase are shown the values of $D_\parallel$. The open circles in the isotropic phase are the self diffusion constants of the liquid crystal molecules as opposed to the black circles in the liquid crystal phases which represent the diffusion constant of the TMS molecules.

director, $D_\parallel$, could be measured since the nematic director cannot be altered away from the direction of the field. It has been shown, however, that very little anisotropy is present in the nematic phase.(13) In the smectic phases, on the other hand, both $D_\parallel$ (diffusion along the director) and $D_\perp$ (diffusion within the layers) could be measured. In the smectic phase several values of D were measured at each temperature for different orientations of the sample in the field gradient. In Fig. 4 it is seen that the values obey the expected expression $D = D_\parallel - (D_\perp - D_\parallel) \sin {}^2\theta$.

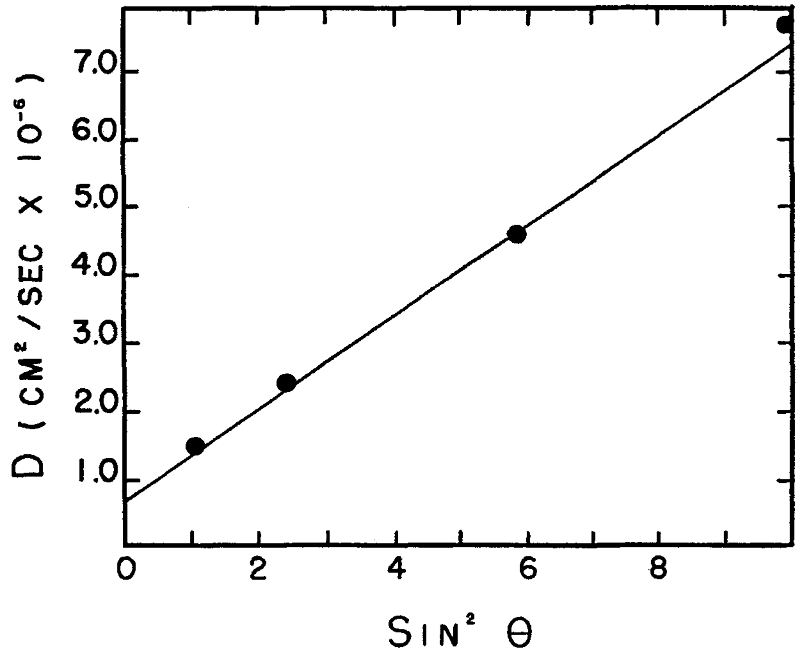

Figure 4. Angular dependence of the diffusion constant of TMS dissolved in 4-*n*-butoxybenzylidene-4′-*n*-octyaniline at a temperature of 48 °C.

It is interesting to note that the average value of D namely $\bar{D} = \frac{1}{3}(2D_{\perp} + D_{\parallel})$ gives a value like that observed in the nematic even though the viscosities in the two phases appear strikingly different. The viscosity in the nematic phase is similar to that in a normal liquid and can, for example, be poured from a container. Upon cooling and transforming into the smectic phase, the liquid crystal appears quite viscous and pouring is impossible yet $\bar{D}$ for TMS is the same as in the nematic phase.

In our preliminary interpretation of these data,⁽¹⁴⁾ we visualize the smectic phase similar to that described by McMillan⁽¹⁵⁾ as consisting of a hard core region made up of the rigid central portion of the molecule and a more fluid-like region made up of the flexible alkyl chains. We believe the TMS molecules to be residing primarily in the soft region. In the smectic *A* phase, the activation energy for $D_{\perp}$ (diffusion within the planes) is 3.0 kcal-mol. It appears that the activation energy for $D_{\parallel}$ has close to the same value even though the magnitude of $D_{\parallel}$ is a factor of 15 smaller. The motion of the alkyl chains are such that the TMS molecules are activated more frequently in the direction of $D_{\perp}$. A TMS molecule, therefore, becomes trapped within the planes even though the activation energy is the same in either direction. In the smectic *B* phase the activation energy appears to change for $D_{\parallel}$. This is expected since the rigid portion of the liquid crystal molecules become ordered in the layers. The fact that $D_{\perp}$ is not changed at the smectic *A*–*B* transition perhaps suggests that the alkyl chains are little affected at this transition. This is consistent with the smectic *B* model proposed by de Gennes and Sarma where the smectic *B* is described by a system of stacked planes with weak forces between the planes in the alkyl end chain region.

Finally, we must state that the mole percentage of TMS was between 5 and 10%. At this percentage the nematic–smectic transition was not appreciably surpressed and yet the spin-echo signal was strong enough for diffusion measurements with the use of signal averaging. The isotropic–nematic transition, on the other hand, was surpressed by 14 °C. For comparison with Fig. 3, the transition temperatures for the pure sample are: isotropic–nematic transition, 79 °C; nematic–smectic transition, 63 °C; and the smectic–smectic transition, 48 °C.

The 4-*n*-butoxybenzylidene-4′-*n*-octylaniline (" 4–8 ")(16) used in this study was prepared by condensing equimolar quantities of 4-*n*-butoxybenzaldehyde and 4-*n*-octylaniline in absolute ethanol and recrystallizing from absolute ethanol (3 X) to a constant melting point. The 4-*n*-octylaniline employed in this synthesis was itself prepared from acetanilide by the sequence: Friedel–Crafts acylation (with octanoyl chloride) then Wolff–Kishner reduction. The overall yield was 25%, b.p. 128–30 °/1.5 tor, η_D^{20} 1.5165; mass analysis indicated no contamination with higher or lower homologues.

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