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Anisotropy of Self-Diffusion in the Smectic-*A* and Smectic-*C* Phases*

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The anisotropy of the translational self-diffusion tensor in the smectic-*A* ($\langle D_\parallel\rangle/\langle D_\perp\rangle = 0.3$) and smectic-*C* phases of terephthal-*bis*-4-*n*-butylaniline has been determined by multipulse NMR. The experimental results are interpreted in terms of a pseudolattice model with anisotropic potential barriers which seems to provide a better description of the physical situation than the "two-dimensional-liquid" model.

In this Letter we report what we believe to be the first measurement of the anisotropy of the self-diffusion tensor of the liquid crystal molecules in the smectic-*A* and smectic-*C* phases. The system investigated was terephthal-*bis*-4-*n*-butylaniline (TBBA).

Smectic-*A* and smectic-*C* liquid crystals[1] are usually considered to be two-dimensional nematic liquids where the molecules are free to move within the smectic layers. Within these equidistant layers the preferred direction of the long axis of each molecule (i.e., the molecular director) is parallel to the plane normals for smectic-*A* systems, whereas it is tilted with respect to the planes of the layers for smectic-*C* systems. In both smectic-*A* and smectic-*C* liquid crystals one would thus expect self-diffusion within the layers to be much larger than perpendicular to the smectic layers.

Murphy *et al.*[2] observed a large anisotropy in the self-diffusion coefficient of the spherical impurity molecule tetramethylsilane dissolved in a smectic-*A* system, but no measurement of the complete self-diffusion tensor of the smectic molecules themselves has been performed so far. Since only such a measurement can provide a quantitative test of the validity of the two-dimensional "free-flow" model within the smectic layers, it seemed worthwhile to use the newly developed multipulse line-narrowing proton-spin-echo technique for this purpose. The simple classical NMR technique for self-diffusion measurements is simply not applicable[3] in liquid crystalline systems because of a too short spin-spin relaxation time T_2.

The pulse sequence used which is similar to the one described earlier[3] is shown in Fig. 1. It consists of a (i) Waugh-type multiple 90° rf pulse sequence removing dipolar interactions: $-P_y-(t-P_x-2t-P_x-t-P_y-2t-P_y)_n$; (ii) a pulsed, linear, magnetic-field-gradient sequence placed between the rf pulses at such intervals that its effect is not averaged out by (i); (iii) a slow, refocusing, Carr-Purcell train of 180° rf pulses.

The echo maxima are given by the same expression as in Ref. 3. The components of the self-diffusion tensor $\underline{D}$ were determined by observing the dependence[3] of the spin-echo maxima at 87 msec on the strength and orientation of the field gradient $\vec{G} = \text{grad}\, H_Z$. The width of the gradient pulses varied between 2 and 8 μsec and the interval t between the 90° rf pulses at 60 MHz

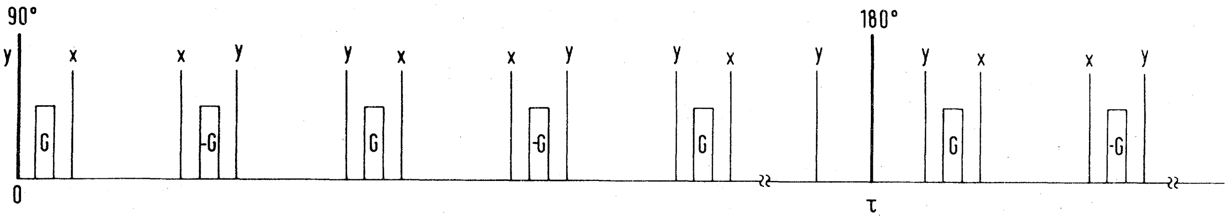

FIG. 1. Pulse sequence used for the determination of the translational self-diffusion tensor in systems with short spin-spin relaxation times T_2.

was 8–12 μsec.

A uniformly aligned uniaxial smectic-*A* sample was obtained[4] by slowly cooling the system from the nematic into the smectic-*A* phase in the presence of a magnetic field of about 15 000 G. The preferred orientation of the molecular directors is parallel to the direction of the field and perpendicular to the smectic layers. The self-diffusion tensor in the smectic-*A* liquid crystalline frame $\underline{D}^0$ is thus diagonal and axially symmetric: One principal axis ($D_\parallel{}^0$) is parallel to the smectic-plane normals, whereas the other two principal axes ($D_\perp{}^0$) lie in the smectic planes and are equal in magnitude.

The situation is more complicated in the biaxial smectic-*C* phase. The smectic layers are not parallel any more throughout the sample, which now consists of a large number of differently oriented "single-liquid-crystal" domains[4] with uniform parallel planes. In each of these domains the smectic planes make an arbitrary azimuthal angle φ with the magnetic field direction. The layers are subject only to the constraint that the molecules within them are tilted at a common angle α with respect to the plane normal. The molecular directors are, on the average, oriented parallel to the direction of the magnetic field in which the sample was cooled.

The self-diffusion tensor $\underline{D}'$ in a single domain is of monoclinic symmetry and has three nonequivalent axes the orientations of which differ in the different domains. $\underline{D}'$ can be characterized by three different components: an out-of-plane one ($D_{z'z'} = D_\parallel{}^0$) and two different in-plane ones ($D_{x'x'} = D_\perp{}^0$ and $D_{y'y'} = D_\perp{}^{0\prime}$). The macroscopic self-diffusion tensor is obtained by a transformation of $\underline{D}'$ into the "sample" frame ($xyz \parallel H_0$) with the help of a rotation around the $x' = x$ axis and by averaging over all possible orientations of the smectic layers in the multidomain sample:

$$\langle \underline{D}^0 \rangle = (2\pi)^{-1} \int_0^{2\pi} R_\alpha^{-1} R_\varphi^{-1} \underline{D}' R_\alpha R_\varphi \, d\varphi . \tag{1}$$

In the process of averaging, all off-diagonal elements vanish and the smectic-*C* diffusion tensor in the "sample" frame is diagonal and axially symmetric around the direction of the magnetic field:

$$\langle D_\parallel{}^0 \rangle = D_\parallel{}^0 \cos^2\alpha + D_\perp{}^{0\prime} \sin^2\alpha , \tag{2a}$$

$$\langle D_\perp{}^0 \rangle = \langle D_\perp{}^{0\prime} \rangle = \tfrac{1}{2}(D_\perp{}^0 + D_\perp{}^{0\prime} \cos^2\alpha + D_\parallel{}^0 \sin^2\alpha) . \tag{2b}$$

The above discussion is valid for a system where the nematic order is perfect. This is not quite the case in smectic-*A* or smectic-*C* liquid crystals. It can be easily shown[5] that the components of the self-diffusion constant tensor in a partially ($\langle \underline{D} \rangle$) and a perfectly ($\langle \underline{D}^0 \rangle$) ordered nematic system are related by

$$\langle D_\parallel \rangle = \langle D \rangle (1 - \eta) + \eta \langle D_\parallel{}^0 \rangle , \tag{3a}$$

$$\langle D_\perp \rangle = \langle D \rangle (1 - \eta) + \eta \langle D_\perp{}^0 \rangle , \tag{3b}$$

where η is the nematic order parameter and $\langle D \rangle$ is the average diffusion coefficient: $\langle D \rangle = \frac{1}{3}(2\langle D_\perp{}^0 \rangle + \langle D_\parallel{}^0 \rangle$. The above relation (3) is as well valid for smectic-*A* and smectic-*C* systems.

A single rotation of the field gradient $\vec{G}$ around an axis which is perpendicular to the preferred axis (i.e., perpendicular to $\vec{H}_0$) is thus sufficient to determine $\langle D_\parallel \rangle$ and $\langle D_\perp \rangle$ in smectic-*A* as well as in smectic-*C* systems. The expected angular dependence in the laboratory frame is

$$D_{11} = \langle D_\parallel \rangle + (\langle D_\perp \rangle - \langle D_\parallel \rangle) \sin^2\theta , \tag{4}$$

where θ is the angle between the field gradient $\vec{G}$ and the preferred axis (i.e., the direction of $D_\parallel$).

The results for TBBA are shown in Fig. 2.

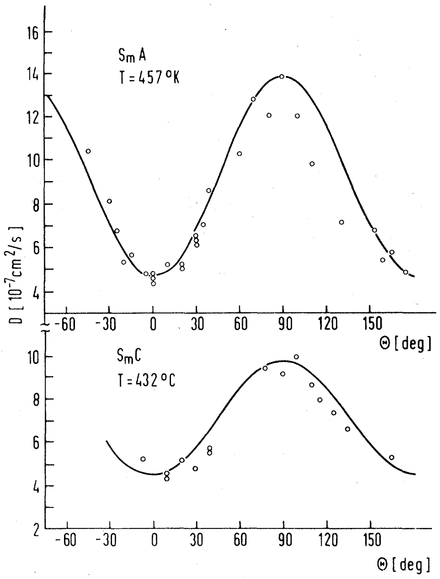

FIG. 2. Angular dependence of the self-diffusion coefficient in the smectic-*A* and smectic-*C* phases of TBBA. The solid curve represents the theoretical angular dependence. φ is the angle between the molecular director and the direction of the field gradient.

Both in the smectic-*A* and in the smectic-*C* phase the diffusion coefficient D_{11} is a linear function of $\sin^2\theta$ in agreement with expression (4).

In the smectic-*A* phase at $T = 183°\text{C}$, $\langle D_\parallel \rangle = 4.6 \times 10^{-7}$ cm²/sec and $\langle D_\perp \rangle = 14 \times 10^{-7}$ cm²/sec. The sense of the anisotropy of the self-diffusion tensor $\langle D_\parallel \rangle / \langle D_\perp \rangle = 0.3$ qualitatively agrees with the two-dimensional "free-flow" model as the in-plane self-diffusion coefficient is larger than the out-of-plane one. The sense of anisotropy is just opposite to that in nematic systems, where, for instance, in N-[*p*-methoxybenzylidine]-*p*-butylaniline,[5] $\langle D_\parallel \rangle / \langle D_\perp \rangle = 1.4$. This can be easily understood, as the height of the potential barrier for out-of-plane diffusion is, following Brochard,[6] proportional the smectic order parameter ψ; $D_\parallel = (D_\parallel)_0 \exp(-c\psi)$, where c is a constant. The magnitude of the observed anisotropy is, however, much smaller than the one expected for a true "two-dimensional liquid." It is also smaller than the one found[2] for diffusion of spherical impurity molecules.

With the help of expressions (3a) and (3b) and the known[7] value of the orientational order parameter in the smectic-*A* phase at $T = 183°\text{C}$ ($\eta \simeq 0.9$) we can obtain the anisotropy in a cluster with perfect nematic order ($\eta = 1$) as $D_\parallel{}^0 / D_\perp{}^0 = 0.27$. The anisotropy is still smaller than expected.

$\langle D_\parallel \rangle$ seems to be thermally activated in the smectic-*A* phase; $D_\parallel{}^0 = D_0 \exp(-Ea/kT)$. The activation energy is $E_a = 0.5 \pm 0.1$ eV.

The apparent anisotropy of the self-diffusion tensor decreases in the smectic-*C* phase. At $T = 158°\text{C}$, $\langle D_\parallel \rangle = 4.5 \times 10^{-7}$ cm²/sec and $\langle D_\perp \rangle = 10 \times 10^{-7}$ cm²/sec, so that $\langle D_\parallel \rangle / \langle D_\perp \rangle = 0.45$. This decrease in the apparent anisotropy is a result of the existence of a finite tilt angle α in the smectic-*C* phase. Using expressions (2a) and (2b), as well as the observed value[4] of the tilt angle α, one can very nearly reproduce the smectic-*C* result $\langle D_\parallel \rangle / \langle D_\perp \rangle = 0.45$ with the assumption $D_\perp{}^0 \simeq D_\perp{}^{0\prime}$ and the value of $\langle D_\parallel \rangle / \langle D_\perp \rangle = 0.33$ observed in the smectic-*A* phase. The smectic-*C* phase in TBBA can be thus described as nearly uniaxial but with a finite tilt angle.

As the anisotropy in $\underline{D}$ is far too small to be understood within a "two-dimensional liquid" model, a quasilattice-type treatment seems to be necessary to describe translational diffusion in smectics. Such a treatment with anisotropic potential barriers may well be appropriate, as the coherence length in smectics is much larger than the molecular jump length.

The principal values of the self-diffusion tensor are now obtained from the well-known expression

$$D_{ii} = \int_0^\infty \langle v_i(0) v_i(t) \rangle \, dt, \quad i = x, y, z. \tag{5}$$

From the work of Rahman,[8] O'Reilly,[9] and others it is known that in classical liquids and molecular solids the velocity autocorrelation function $\langle v_i(0) v_i(t) \rangle$ is of a damped-harmonic-oscillator form. For the present qualitative discussion we approximate $\langle v_i(0) v_i(t) \rangle$ by

$$\langle v_i(0) v_i(t) \rangle \simeq \langle v_i{}^2 \rangle \exp(-t/\tau_i) p_i, \tag{6}$$

where τ_i is the characteristic molecular jump time into a neighboring vacancy which lies in the *i*th direction, and p_i is the probability for the appearance of such a vacancy. Inserting (6) into (5) we find

$$D_{ii} = \langle v_i{}^2 \rangle \tau_i p_i \tag{7a}$$

and

$$D_{ii} \simeq l_i{}^2 p_i / \tau_i, \tag{7b}$$

with $(\langle v_i{}^2 \rangle)^{1/2} \simeq l_i / \tau_i$, where l_i is the jump length in the *i*th direction. We expect that the diffusion of the molecules is stochastically independent and thermally activated. Thus, we can write

$$\tau_i = \tau_0 \exp(U_i / kt), \tag{8a}$$

$$p_i = n_i p, \tag{8b}$$

where U_i is the potential barrier for motion in the *i*th direction, n_i is the number of nearest neighbors, and $p \propto e^{-w/kT}$ is the probability for the creation of a vacancy. We further assume that the molecules can be described as rigid rods of length l and diameter d. As n_i is proportional to the molecular cross section in the *i*th direction we find the ratio of diffusion coefficients parallel to the long molecular axis and perpendicular to it as

$$(D_\parallel{}^0 / D_\perp{}^0) = (l/d) \exp[-(U_\parallel - U_\perp)/kT]. \tag{9}$$

As $l > d$ and $U_\perp \gtrsim U_\parallel$ in nematics, whereas $U_\perp \ll U_\parallel$ in smectic-*A* systems, we can easily understand the change from $D_\parallel{}^0 / D_\perp{}^0 > 1$ in nematics to $D_\parallel{}^0 / D_\perp{}^0 < 1$ in smectic-*A* systems. The relatively small anisotropy in smectics is the result of two competing factors working in opposite directions: The factor l/d tends to increase $(D_\parallel{}^0 / D_\perp{}^0)$, whereas the exponential factor, which depends on the smectic order parameter, tends to decrease this ratio.

The activation energy for $(D_\parallel{}^0 / D_\perp{}^0)$ is thus expected to be much smaller than that for $D_\parallel$. This is indeed observed.

The ratio of the two in-plane diffusion coefficients in smectic-C systems is finally obtained as

$$(D_\perp^0/D_\perp^{0\prime}) = \exp[-(U_\perp - U_\perp{}')/kT] \qquad (10)$$

and is expected to be relatively close to 1.

It should be mentioned that within a "free-flow" model of the smectic-A phase the ratio of the "out-of-plane" (D^0) diffusion constants is obtained as

$$\left(\frac{D_\parallel{}^0}{D_\perp{}^0}\right) = \left(\frac{l_\parallel}{l_\perp}\right)^2 \exp\{-[(U_\parallel - U_\perp)/kT]\}, \qquad (11)$$

where $l_\parallel$ and $l_\perp$ stand for the mean free path for the "out-of-plane" and "in-plane" motion. If the two-dimensional free-flow model should have any meaning $l_\perp$ should be much longer than $l_\parallel$ so that the ratio $(D_\parallel{}^0/D_\perp{}^0)$ should be much smaller than observed experimentally or predicted by Eq. (9).

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Evidence for Upward or "Anomalous" Dispersion in the Excitation Spectrum of He II

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The dispersion and attenuation of superthermal phonons ($\hbar\omega \gg kT$) in He II at 0.1 K are remeasured and reinterpreted as a function of pressure. We find evidence for the existence of the three-phonon process and an upper energy cutoff to this process implying anomalous dispersion. Our earlier conclusion on the absence of anomalous dispersion at saturated vapor pressure is shown to be incorrect.

In order to explain ultrasonic data,[1] it was first suggested by Maris and Massey[2,3] that the $\omega(k)$ relation in He II at saturated vapor pressure (SVP) had a small but finite upward curvature in the energy range up to ~8 K. Recently, we reported group-velocity measurements[4] ($v_g = d\omega/dk$) of propagating phonons generated by a superconducting Al film and it was concluded that the dispersion relation was linear below 4.5 K. This result disagreed not only with other data,[5] but also with theoretical[3,6] estimates of the mean free path for these phonons [under decay via the allowed three-phonon process (3pp) where one phonon decays into two] which should be substantially shorter than our propagation length (a few millimeters) at SVP. It remained vital, then, to show that the phonons measured were indeed of the energy range 0.5 K to 4 K. We report here new measurements and a reappraisal of these earlier measurements which imply that phonons of energy *greater* than this, generated by quasiparticle relaxation, escape from the Al film and are long lived in the He II. It is these higher-frequency phonons which were detected and measured.

By studying the response of a detector superconducting tunnel junction as a function of the bias of a generating junction separated by a medium, one can determine whether phonons of energy $\hbar\omega = 2\Delta$ (the superconducting energy gap) propagate through that medium. At generator