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Orientation of Nematic Liquid Crystals in Thick Layers

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The electrical conductivity of a thick (1 mm) layer of para-azoxyanisol has been measured during a transient experiment after a magnetic field is removed. The experiments agree with predictions of the Ericksen–Leslie continuum theory and disagree with the predictions of the swarm or statistical theory.

We consider here how far from a surface the orientation imposed by the surface can propagate in the absence of other orienting influences. The continuum theory predicts that the surface orientation can result infinitely far from the surface, provided the boundary conditions imposed on all sides of the container are compatible with that orientation, and no other orienting influence (electric, magnetic, or viscous) are present. The swarm or statistical theory, on the other hand, predicts that the orientation imposed by the surface decays exponentially in the distance from the surface, with the bulk fluid exhibiting properties characteristic of a "random" orientation. Experiments involving only surface orientation forces can thus shed light on the applicability of these theories.

The scattering of light by nematic fluids has been one of the important reasons for postulating the existence of swarms. De Gennes[5] has adequately explained this phenomenon in terms of the continuum theory, and the swarm theory is not now widely accepted.[1] However, on the basis of the orientation behavior of nematic fluids in variable magnetic fields an important argument for the existence of swarms persists.

Yun and Fredrickson[3,1] measured the self-diffusivity of *p*-azoxyanisole (PAA) and found that in the absence of a magnetic field that the measured value was given by

$$D_0 = \tfrac{1}{3}(D_a + 2D_t) \tag{1}$$

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where D_a and D_t are the values measured when the magnetic field (and hence director) was oriented parallel and perpendicular, respectively, to the direction of mass flux. Furthermore a magnetic field of 1000 gauss was necessary to achieve nearly complete orientation in a sample 1 cm on a side. The coherence length from the continuum theory (De Gennes[5])

$$\xi = \left(\frac{k}{\Delta x}\right)^{1/2} \frac{1}{H} \tag{2}$$

for this case is very large, since $\xi H = 1$ gauss-centimeter. Here k is an elastic constant and Δx is the anisotropy of the volume magnetic susceptibility. Substantial orientation parallel to H would be expected for $H \sim 10$ gauss, but this was not found in the measurements. By contrast the swarm theory predicts the surface orientation becomes unimportant at a penetration depth of 10–20 microns from the surface. Since the sample cell was a cube, the possible orienting influence of the side walls cannot be discounted and is examined elsewhere.[16] Other measurement of self-diffusivity of PAA using a neutron scattering technique[11,21] confirm an apparently random self-diffusivity (given by Eq. (1)) in the absence of a magnetic field in aluminum containers with from 1 to 3 mm separation between the walls. Measurements of attenuation of sound in PAA[13] and in MBBA[19] in large sample holders give values at zero magnetic field in accordance with the analogue of Eq. (1), thus suggesting a random orientation of the bulk liquid crystal.

Massen *et al.*[18] measured the diamagnetic susceptibility of PAA and found that for zero magnetic field a value was obtained indicating random orientation.

Jezewski[12] measured the dielectric constant of PAA in a layer 0.7 mm thick, and in the absence of a magnetic field a completely uniform orientation prevails, parallel to the brass surfaces. The half-thickness is 10 times as large as the supposed penetration depth of the swarm theory, and the measurements conflict with the swarm theory. Gruler and Meier[9] measured the resistance of a layer of PAA and found the wall orientation prevailed in a sample thickness of 100 microns. By the swarm theory the inner core (50 microns) should have been random. Gerritsma *et al.*[7] measured the dielectric constant of MBBA between glass rubbed tin oxide conducting plates. The capacitance was the same for all thickness (7 to 106 microns) in the absence of magnetic fields. Indeed the direction of rubbing of the top and bottom plates were perpendicular to each other. The swarm theory would predict a different capacitance (or dielectric constant) in the thickest and thinnest layer, but this was not observed.

Carr[2,3] measured the dielectric loss in PAA in large samples (3.5 × 1.6 cm, and 0.5 × 0.8 cm brass and copper cells). He found the value measured in the

absence of a magnetic field was between the random value and a value corresponding to perpendicular orientation. These data suggest the wall orientation effect propagates quite far from the wall.

In measurements of thermal conductivity Yun *et al.*[32] found that the effective thermal conductivity of *p*-*n*-decyloxybenzoic acid varied as $1/H^2$ as the magnetic field was changed, in agreement with the swarm theory and in conflict with the continuum theory, which predicts a $1/H$ dependence. The authors deduced the thickness of the interfacial layer to be 10 microns. Guyon[10] observed no such effect for MBBA and layer thicknesses up to 700 microns: the surface orientation was obtained throughout the sample, in agreement with the continuum theory. Pieranski *et al.*[23] measured the effective thermal conductivity of MBBA and found they could not differentiate between curves of the form $k_e = 1 - \alpha/H$ and $k_e = 1 - \beta/H^2$ corresponding to the continuum and swarm theories. However, curves for thermal conductivity versus H/H_c gave three separate curves for sample thicknesses of 300, 400, and 500 microns. Since $H_c \propto 1/d$, the axis H/H_c is really Hd and the continuum theory says a single curve should result. In a series of studies[4,22,25,26] the thermal conductivity of PAA was measured in a variable gap device, and the thermal conductivity decreased with gap thickness. Since only surface orienting forces were present (no magnetic or electric fields) the thermal conductivity in the bulk fluid was less than that at the surface. This indicates the surface orientation dies out as the distance to the surface increases, giving a random orientation far from the surface. Such results are not in agreement with the continuum theory. The experimental results are somewhat clouded by the lack of knowledge of the surface orientation and by the fact that the measurements apparently indicate $k_\perp > k_\parallel$ whereas Kessler[14] reports $k_\parallel > k_\perp$ for PAA.

To summarize, based on all the available evidence it is not possible to say conclusively that the continuum theory applies to thick layers. Electrical conductivity measurements were made to elucidate this question.

EXPERIMENTAL DETERMINATION OF ORIENTATION

We have measured the electrical resistance of nematic PAA across a parallel plate cell during changes in the fluid's orientation.[15] The electrical conductivity of the nematic phase is anisotropic, so that the electrical resistance measured across a layer provides a measure of the average orientation over the layer.

Yanno *et al.*[29] have shown that the conductivity tensor may be written

$$\boldsymbol{\sigma} = \sigma_t \boldsymbol{\delta} + (\sigma_a - \sigma_t)\boldsymbol{mm},$$

where σ_t is the transverse conductivity, σ_a is the axial conductivity, $\boldsymbol{m}$ is a unit vector denoting the local symmetry axis, and $\boldsymbol{\delta}$ is the second rank unit tensor.

Our parallel plate cell is thin compared to its width and insulated around its periphery so its electric field is essentially perpendicular to the conducting surfaces, ignoring small perturbations due to the anisotropy of the fluid. Taking "z" to be the coordinate normal to the conducting surfaces and the conductivity tensor to be a function of z (and time) only, which implies homogeneity of the surface orientation, the apparent conductivity $\hat{\sigma}$ across a cell of thickness Δz is

$$\hat{\sigma} = \frac{\Delta z}{\int_0^{\Delta z} \frac{dz}{\sigma_{zz}}},$$

where σ_{zz} is the $z - z$ component of the conductivity tensor. Denoting by ϕ the angle between the local symmetry axis and the x-direction, then

$$\sigma_{zz} = \sigma_t + (\sigma_a - \sigma_t)\cos^2 \phi.$$

Now the cell resistance may be written

$$R = R_t \int_0^1 \frac{d\zeta}{1 + \sigma' \cos^2 \phi}, \tag{3}$$

where

$$\sigma' = \frac{\sigma_a}{\sigma_t} - 1 = \frac{R_t}{R_a} - 1,$$

R_t is the resistance measured when $\phi = 90°$ everywhere, R_a is the resistance measured with $\phi = 0°$, and $\zeta = z/\Delta z$.

By magnetically imposing the orientations $\phi = 0°$ and $\phi = 90°$, thereby obtaining R_a and R_t, the self-imposed cell orientation can be deduced from a resistance measurement in the absence of a magnetic field. The orientation is conveniently expressed in terms of the ratio

$$\beta = \frac{R - R_a}{R_t - R_a},$$

which is insensitive to any constant resistance adding to the cell resistance. β is zero when the nematic fluid uniformly orients perpendicular to the conducting surfaces and unity when a uniformly parallel orientation prevails.

APPARATUS

The resistance cell is shown in Figure 1. The conducting plates were stainless steel, electrolessly nickel plated and then gold plated. The insulating spacers were Teflon. The cell formed two PAA layers, each 1.5 cm wide by 4.9 cm tall. The thicknesses were determined from capacitance measurements to be 0.12 cm. The conducting plates were electrically connected such that the resistances of the PAA layers were measured in parallel; hence, the resistance measurement was effectively that of a single layer of the same thickness but double the area of an individual layer.

The cell was immersed in and flooded with PAA held in a Teflon chamber, and suspended by its electrical connections. The Teflon chamber was tightly fitted into a mortise cut from a cylindrical block of copper, located between the poles of a permanent horseshoe magnet (1500 gauss). The magnet was fitted onto a rotating support such that it could be easily rotated about the cell or quickly removed.

The entire cell and magnet apparatus was mounted in an oven in order to uniformly heat the cell, arranged so that the magnet could be quickly removed through the oven door. The temperature of the PAA in the Teflon chamber was measured by a thermocouple immersed in it and was assumed to be the cell temperature. The temperature of the copper block and the oven air temperature were also measured.

The cell resistance was measured using a John Fluke model 710B impedance bridge, operating at 1000 Hz. The bridge was externally augmented to

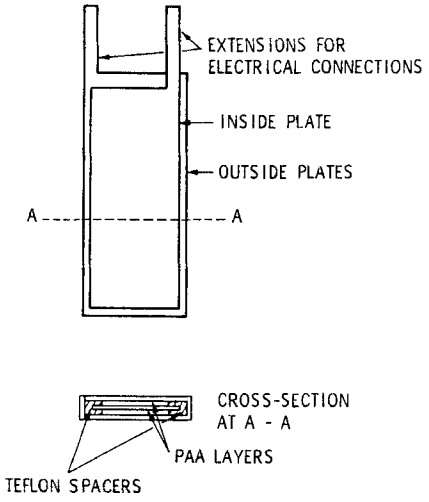

FIGURE 1 Diagram of fixed gap conductivity cell.

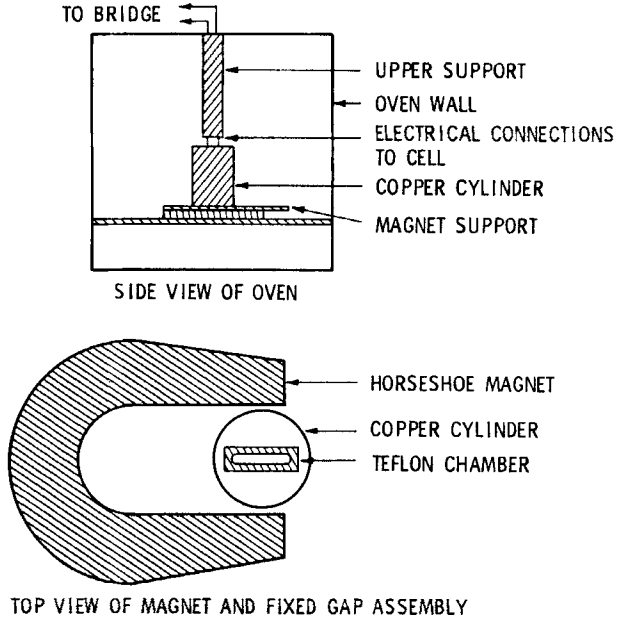

FIGURE 2 Overall view of fixed gap apparatus.

balance the cell capacitance. The maximum voltage appearing across the cell was 0.23 volt, imposing an electric field of only 2 volt/cm. An overview of the apparatus is shown in Figure 2.

The electrical conductivities were

$$\sigma_a = 5.1 - 5.7 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\sigma_t = 3.4 - 3.9 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}.$$

The PAA used in the experiment was purified by first dissolving and filtering in hot acetone, and then recrystallizing three times from absolute ethanol. The successive recrystallizations obtained the same melting point of 118°C.

The orientation of the PAA in the cell was investigated by imposing the uniformly perpendicular and parallel orientations using the rotating magnet. First the two resistances R_a and R_t were obtained, and then the magnet was oriented to facilitate its sudden removal through the oven door. The resistance R_0 measured with the magnet in its final orientation was used to evaluate the actual orientation. Each of the three resistances was measured after waiting about an hour after a new orientation was imposed, in order to damp out small thermal transients introduced by opening the oven door.

The fact that the R_a measured with the magnetic field is in actuality R_a depends on the magnitude of Hd. Pieranski *et al.*[23] have shown that in an

experimental arrangement of this type (director on boundary parallel to surface, magnetic field perpendicular to surface) that the orientation is parallel to the surface everywhere for $Hd < H_c d$, where

$$H_c d = \pi \sqrt{\frac{k_{11}}{\Delta x}}$$

and that for $Hd > H_c d$ the orientation gradually changes to one corresponding to a director perpendicular to the surfaces, everywhere except in a thin boundary layer near the surface. For $Hd \sim 10 H_c d$ the orientation is essentially complete and parallel to the magnetic field and perpendicular to the surface. For PAA, $H_c d$ is 7 gauss-cm, $10 H_c d$ is 70 gauss-cm, whereas we have $Hd = 180$ gauss-cm, thus insuring essentially complete orientation in the measurement of R_a. When measuring R_t the surface effect and magnetic field cause the same orientation, and indeed the presence of the magnetic field made no difference at all, so that R_t was measured with and without H.

An unsteady-state variation in the orientation of the PAA was precipitated by suddenly removing the magnet from the oven and measuring the cell resistance as a function of time until a steady-state resistance R_∞ was obtained. The steady-state results are presented as the ratio β_∞, where

$$\beta_\infty = \frac{R_\infty - R_a}{R_t - R_a},$$

in Table I. All eight experiments showed β_∞ to be nearly unity, indicating an orientation uniformly parallel to the conducting surfaces of the cell.

On removing the magnet the Teflon chamber holding the PAA would rebound slightly, immersing the suspended cell more deeply. In some instances the level of the PAA was low enough initially that the cell was barely covered, so that only upon removing the magnet was the cell fully

TABLE I

Fixed gap experimental runs

Date	T, °C	R_a	R_t	R_∞	β_∞
11/13/73	133.8	1.605	2.403	2.376	0.96
11/14/73	133.8	1.607	2.404	2.370	0.96
11/15/73	133.8	1.571	2.331	2.302	0.96
11/16/73	133.8	1.420	2.074	2.070	0.99
11/19/73	130.4	1.685	2.622	2.616	0.99
11/21/73	125.9	1.893	3.057	2.960	0.92
11/26/73	125.9	1.872	3.051	3.014	0.97
11/28/73	121.9	2.056	3.445	3.451	1.00

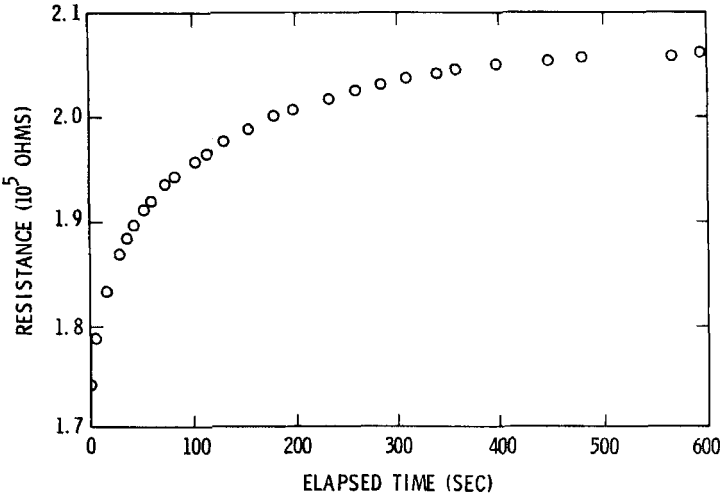

FIGURE 3 Resistance data of run 4.

immersed causing a reduction in the cell resistance. This occured for runs 1, 2, 3, and 6, and probably accounts for the lower values of β_∞ for those runs.

The unsteady-state resistance data of run 4 is shown in Figure 3. The data show little scatter; they indicate the smoothly changing orientation of the PAA in the cell as the surface orientation imposes itself over the bulk of the fluid.

The apparatus, designed originally for steady-state experiments only, necessitated opening the oven door in order to rotate or remove the magnet. Auxillary experiments were conducted to verify that the resulting brief excursion in the oven air temperature did not appreciably affect the unsteady-state resistance data.

COMPARISON OF RESULTS WITH CONTINUUM THEORY

The steady-state results are in agreement with the continuum theory, which predicts a uniform orientation as the state of minimum free energy. We find that the gold plated surfaces orient the PAA parallel to the surface.

Our unsteady-state data can be compared with the orientational behavior predicted by the continuum theory. We resort to the "director equation,"[16] for the case of no velocity gradient or external body force acting. The director

equation then simplifies to

$$\gamma_1 \frac{\partial \boldsymbol{n}}{\partial t} = k_{22}\nabla \cdot \nabla \boldsymbol{n} + (k_{11} - k_{22})\nabla(\nabla \cdot \boldsymbol{n}) + (k_{33} - k_{22})(\nabla \cdot (\boldsymbol{nn} \cdot \nabla \boldsymbol{n}) - \nabla \boldsymbol{n} \cdot (\boldsymbol{n} \cdot \nabla \boldsymbol{n})),$$

where $\boldsymbol{n}$ is the director (a unit vector), γ_1 is a characteristic viscosity, and k_{11}, k_{22}, and k_{33} are the Frank elastic constants.

The director can be expressed in terms of its angle ϕ with the z-axis (the normal to the conducting surfaces) and its angle θ measured in the plane normal to the z-axis. Since σ_{zz} does not depend on θ, the θ orientation is not manifest in our resistance experiments and cannot be determined. Therefore, we conveniently take θ on the surfaces to be uniformly equal to the θ initially imposed over the bulk of the fluid by the magnetic field. Then both spatial and temporal variations in θ vanish, and the director equation becomes altogether independent of θ.

The director equation is made dimensionless by putting

$$t = \left(\frac{L}{2}\right)^2 \frac{\gamma_1}{k_{33}} \tau \tag{4}$$

and

$$\xi = \frac{2z}{L}$$

where L is the thickness of the cell. Assuming that ϕ is a function of ξ and τ only, we finally obtain

$$\frac{\partial \phi}{\partial \tau} = \left[1 + \left(\frac{k_{11}}{k_{33}} - 1\right)\sin^2 \phi\right]\frac{\partial^2 \phi}{\partial \xi^2} - \left(1 - \frac{k_{11}}{k_{33}}\right)\sin \phi \cos \phi \left(\frac{\partial \phi}{\partial \xi}\right)^2. \tag{5}$$

We put $z = \xi = 0$ at the mid-plane of a layer, which is assumed to be a plane of bilateral symmetry. The boundary conditions become

$$\frac{\partial \phi}{\partial \xi} = 0 \qquad \text{at } \xi = 0, \text{ all } \tau$$

$$\phi = 90^\circ \quad \text{at } \xi = \pm 1, \text{ all } \tau$$

$$\phi = \phi_0 \quad \text{at } \tau = 0, \text{ all } \xi \neq \pm 1$$

The boundary condition at $\xi = \pm 1$ is chosen to conform with the condition $\beta_\alpha = 1$ found experimentally; the value of ϕ_0 is found from

$$\phi_0 = \cos^{-1}\left[\left(\frac{R_t - R_0}{R_a - R_0}\right)\frac{R_a}{R_0}\right]^{1/2}.$$

Because of the bilateral symmetry of each PAA layer in the cell, Eq. (3) may be rewritten

$$R = R_t \int_0^1 \frac{d\xi}{1 + \sigma' \cos^2 \phi}$$

The predicted and measured dynamic behavior of the resistance are compared using the ratio

$$\beta_0 = \frac{R - R_0}{R_\infty - R_0} \tag{6}$$

We assume that $R_t = R_\infty$ (as though $\beta_\infty \equiv 1$) so that the predicted β_0 is found from $\phi(\xi)$ by

$$\beta_0 = \frac{(1 + \sigma' \cos^2 \phi_0) \int_0^1 \frac{d\xi}{1 + \sigma' \cos^2 \phi} - 1}{\sigma' \cos^2 \phi_0} \tag{7}$$

Equation (5) is solved numerically to obtain $\phi(\xi, \tau)$; the appropriate quadrature gives $\beta_0(t)$ using Eq. (7). Given ϕ_0 and literature values of k_{11}/k_{33},[8] a table of β_0 vs. t is computed for a given experimental run, and this is fit to the experimental data by applying a scale factor t (real time) $= \alpha\tau$, determined by a least squares fit. A graph of β_0 versus both t (experimental time) and t' (theoretically predicted time), obtained from the data of Figure 3, is presented in Figure 4. Only those β_0 up to about 0.9 were used in the calculation of α, in order to avoid the asymptotic region where the experiment is less accurate.

Literature values of γ_1 and k_{33}[6,8,20,24,28] are used to avaluate predicted values of α. The results of the least squares fit for α for the eight runs are summarized in Table II. The comparison with the literature is presented in Table III.

The calculated values of α are systematically greater than those obtained from the literature, however the discrepancies seem reasonable considering the simple analysis applied. The standard deviations of α of about 15 per cent are due not to scatter in the data, but to the imprecise fit of the theory to the experimental data. This is attributable to experimental error attending the measurement of R_a, R_t, and R_0 (i.e., of ϕ_0), to imperfections in the cell geometry, and to the simplicity of the model adopted for the theoretical analysis (e.g., actually $\nabla\phi \neq 0$). We note that if only the initial portion of the unsteady-state data is fit, better agreement between measured and predicted values of α is obtained.

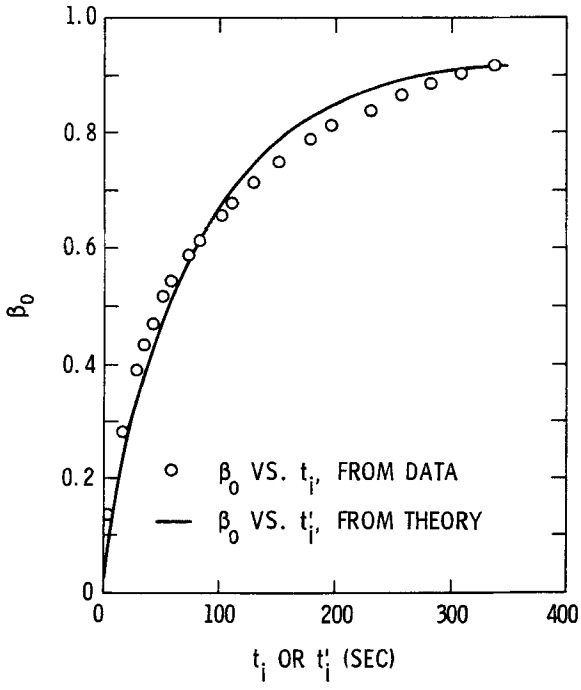

FIGURE 4 Graph of β_0 versus t and t' obtained from the data of Figure 3.

TABLE II

Analysis of unsteady-state data

Date	T, °C	R_a	R_∞	R_0	ϕ_0	$\left(\frac{k_{11}}{k_{33}}\right)_{\text{lit.}}$	$(\alpha_T)_{\text{obs.}}$	Std. dev. $(\alpha_T)_{\text{obs.}}$
11/13/73	133.8	1.605	2.376	1.992	50.7°	0.645	265 sec.	37 sec.
11/14/73	133.8	1.607	2.370	1.995	51.0	0.645	260	32
11/15/73	133.8	1.571	2.302	1.958	52.1	0.645	276	56
11/16/73	133.8	1.420	2.070	1.742	50.1	0.645	259	45
11/19/73	130.4	1.685	2.616	2.149	51.2	0.589	278	29
11/21/73	125.9	1.893	2.960	2.481	54.2	0.526	259	37
11/26/73	125.9	1.872	3.014	2.468	53.0	0.526	233	25
11/28/73	121.9	2.056	3.451	2.769	53.0	0.500	231	25

TABLE III

Comparison of time constants

T, °C	γ_1, g/cm-sec	k_{33}, g-cm/sec^2	$(\alpha_T)_{\text{lit.}}$	$(\alpha_T)_{\text{obs.}}$
133.8	0.030	4–5 × 10^{-6}	220–270 sec.	262 sec.
130.4	0.042	7.7 × 10^{-6}	198	278
125.9	0.058	10.6 × 10^{-6}	198	243
121.9	0.072	12.3 × 10^{-6}	210	231

The steady-state resistance data indicate a completely uniform orientation parallel to the major surfaces of the cell. The agreement with our data of the predictions of the continuum theory regarding both the static and dynamic orientational behavior of the PAA shows that the continuum theory is applicable to "thick" layers.

COMPARISON OF RESULTS WITH SWARM THEORY

In the context of the swarm theory the orientation in a nematic fluid is distributed discontinuously from swarm to swarm, and is described by the local probability of finding a swarm at a given time and position with an orientation falling within a given differential solid angle. Denoting the axis of symmetry of a single swarm by the unit vector $\boldsymbol{m}$, it is assumed that $f(\boldsymbol{m}) = f(-\boldsymbol{m})$ where f is the orientation probability function (i.e., f is an "even" function of orientation). Consequently, $\langle \boldsymbol{m} \rangle$, the orientational probability weighted average of $\boldsymbol{m}$, vanishes. Assuming the properties of swarms to be transversely isotropic about $\boldsymbol{m}$, the nonvanishing averaged dyadic $\langle \boldsymbol{mm} \rangle$ serves to describe the effect of the average swarm orientations on the orientation dependent properties of a nematic fluid.

As discussed above, for layers of PAA much thicker than 35 microns the swarm theory predicts at steady state a random orientation, for which $\langle \boldsymbol{mm} \rangle = \frac{1}{3}\boldsymbol{\delta}$, where $\boldsymbol{\delta}$ is the second rank unit tensor. If a non-random orientation is imposed initially, the orientation would decay to randomness according to

$$\frac{d}{dt}(\langle \boldsymbol{mm} \rangle - \tfrac{1}{3}\boldsymbol{\delta}) = -6D_R(\langle \boldsymbol{mm} \rangle - \tfrac{1}{3}\boldsymbol{\delta})$$

where D_R is the rotational diffusivity of a swarm. Then for our experiments the resistance would decay asymptotically from its initial value to the "random" value, namely

$$R_{\text{random}} = \frac{1}{\dfrac{2}{3R_t} + \dfrac{1}{3R_a}},$$

for which $\beta \sim 0.6$. Clearly, this does not agree with our data.

In addition, the time constant for the decay should be $1/(6D_R)$, which is 2.2 sec when $D_R = 0.075\ \text{sec}^{-1}$.[31] The time response of the data is clearly much slower than this.

The most likely disturbance would be the electric field employed in the resistance measurements. However, there are several indications that the electric field was not the cause of the steady-state orientation. Most importantly, we found that if, after the steady-state orientation resistance were

attained, the electric field were switched off for about 10 minutes and then switched on again, the steady-state value was obtained the instant the field was switched on. The unsteady-state experiments showed that the force causing the uniform orientation required about 10 minutes to orient the nematic fluid. If the electric field were responsible for the maintenance of a non-random orientation, then removing it would allow a return to a supposedly "natural" random orientation. But then its renewed application evidently could not instantaneously obtain the steady-state orientation observed, and so we can conclude that the electric field was not responsible for the uniform orientation.

We also note that from experiments by Carr[4] that audio frequency electric fields of strengths of at least several hundred volts per centimeter are required to obtain a substantially complete orientation in a sample of nematic PAA of the order of 1 cm cubed. Furthermore, the well-known instability of nematic fluids in the presence of electric fields[9] does not occur in PAA for voltages below 9 volts. In our experiment the voltage did not exceed 0.2 volts and the electric field strength did not exceed 2 volts/cm.

One might argue that the orientation of the liquid crystal was caused by the electric field, rather than the surface. In the statistical theory, the relevant parameter determining the orientation is

$$\alpha = \frac{V\varepsilon_0 \Delta\varepsilon E^2}{kT}, \quad \cos^2 \phi = \int_0^1 e^{\alpha x^2} x^2 dx \Big/ \int_0^1 e^{\alpha x^2} dx$$

where V is the volume of the swarm and k is Boltzman's constant. Likewise, with a magnetic field

$$\alpha = \frac{V\Delta\chi H^2}{kT}$$

In our experiments $\varepsilon_0 \Delta\varepsilon E^2 \approx 1.8 \times 10^{-5}$ g cm^{-1} sec^{-2} and, using the analogy $\varepsilon_0 \Delta\varepsilon E^2 = \Delta\chi H^2$ corresponds to the same orienting influence as a 10 gauss magnetic field. Such a small magnetic field is insufficient to cause substantial orientation in the bulk sample (see Ref. 31 where 1000 gauss was required for nearly complete orientation). Thus we can conclude that the orientation parallel to the surfaces was not caused by the electric field. The data disagrees with the swarm or statistical theory.

CONCLUSIONS

A review of the literature reveals that the orientational behavior of nematic fluids has been interpreted in terms of both the "continuum" and the "swarm" theories and that neither theory can explain all of the experimental

data. New experimental results are presented which show that the continuum theory applies to "thick" (~0.1 cm.) layers of nematic PAA. The PAA is found to orient parallel to gold-plated stainless steel surfaces. Both the static and dynamic orientational behavior is adequately explained by the continuum theory. This contradicts the prediction of the swarm theory that the continuum theory would apply only to layers not much thicker than 35 microns.

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References

1. G. H. Brown, *et al.*, *A Review of the Structure and Physical Properties of Liquid Crystals*, C.R.C. Press, Cleveland, 1971.
2. E. F. Carr, *J. Chem. Phys.*, **37**, 104–106 (1962).
3. E. F. Carr, *J. Chem. Phys.*, **39**, 1979–1983 (1963).
4. E. F. Carr, *Mol. Cryst. Liquid Cryst.*, **7**, 253 (1969).
5. P. G. De Gennes, *Mol. Cryst. Liquid Cryst.*, **7**, 325 (1969).
6. H. Gasparoux and J. Prost, *J. Physique.*, **32**, 953 (1971).
7. G. J. Gerritsma, W. H. De Jeu, and P. Van Zanten, *Phys. Letters*, **36A**, 389–390 (1971).
8. H. Gruler, *Z. Naturforschg.*, **28a**, 474 (1973).
9. H. Gruler and G. Meier, *Mol. Cryst. Liquid Cryst.*, **12**, 289–298 (1971).
10. E. Guyon, P. Pieranski, and F. Brochard, *C. R. Acad. Sci., Paris*, **B273**, 486–489 (1971).
11. J. A. Janik, J. M. Janik, K. Otnes, and T. Riste, *Mol. Cryst. Liquid Cryst.*, **15**, 189–195 (1971).
12. M. Jezewski, *Zeitschr. Phys.*, **40**, 153 (1927).
13. K. A. Kemp and S. V. Letcher, *Phys. Rev. Lett.*, **27**, 1634–1636 (1971).
14. J. O. Kessler, private communication (1974).
15. W. L. Kuhn, Ph.D. Dissertation, Univ. of Washington (1974).
16. W. L. Kuhn and B. A. Finlayson, submitted for publication.
17. F. M. Leslie, *Arch. Rat. Mech. Anal.*, **28**, 265 (1968).
18. C. H. Massen, J. A. Poulis, and R. D. Spence, Ordered Fluids and Liquid Crystals, ACS Monograph No. 63 (American Chemical Society, Washington, D.C., 1967).
19. G. G. Natale and D. E. Commins, *Phys. Rev. Letters*, **28**, 1439–1441 (1972).
20. Orsay Liquid Crystal Group, *J. Chem. Phys.*, **51**, 816 (1969).
21. K. Otnes, R. Pynn, J. A. Janik, and J. M. Janik, *Physics Letters*, **A38**, 335–336 (1972).
22. M. N. Patharker, V. A. V. Rajan, and J. J. C. Picot, *Mol. Cryst. Liquid Cryst.*, **15**, 225 (1971).
23. P. Pieranski, F. Brochard, and E. Guyon, *J. de Phys.* (Paris), **33**, 681–689 (1972).
24. J. Prost. *Phys. Lett.*, **A36**, 245 (1971).
25. V. S. V. Rajan and J. J. C. Picot, *Mol. Cryst. Liquid Cryst.*, **17**, 109–119 (1972).
26. V. S. V. Rajan, M. N. Patharkar, and J. J. C. Picot, *Mol. Cryst. Liquid Cryst.*, **18**, 279–283 (1972).
27. V. S. V. Rajan and J. J. C. Picot, *Mol. Cryst. Liquid Cryst.*, **20**, 55–68 (1973).
28. H. C. Tseng, D. L. Silver, and B. A. Finlayson, *Phys. Fluids*, **15**, 1213 (1971).
29. S. Yano, T. Kasatori, M. Kuwahara, K. Aoki, *J. Chem. Phys.*, **57**, 571 (1972).
30. C. K. Yun, Ph.D. Thesis, Univ. of Minnesota (1970).
31. C. K. Yun and A. G. Fredrickson, *Mol. Cryst. Liquid Cryst.*, **12**, 73 (1970).
32. C. K. Yun, J. J. C. Picot, and A. G. Fredrickson, *J. Appl. Phys.*, **42**, 4764–4767 (1971).