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An Analysis of the Interfacial Effect on the Heat Conduction in a Nematic Mesophase

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Abstract—An analysis of the interfacial effect on the thermal conductivity of a nematic mesophase–liquid crystal *p*-azoxyanisole is given. It is shown that the thermal conductivity data at different gaps in a "parallel plate" cell can be used, in conjunction with a simple theory based on the orientation of "swarms" in nematic mesophases, to estimate some of the properties of the liquid crystal studied. The results show close agreement with those from optical studies. A discussion on the present state of the knowledge on interfacial orientation is also given.

1. Introduction and Analysis

The importance of the study of the transport phenomena in nematic mesophases or liquid crystals such as *p*-azoxyanisole (PAA), *p-n*-decyloxybenzoic acid (DBA) etc., has been extensively discussed by Fisher,[2] Sullivan[9] and Yun.[10] Accepting the "swarm" theory for describing the nematic mesophase structure, they introduced Frenkel's[4] idea of anisotropy tensor to describe the average orientation of the swarms.

$$\mathsf{A} = \langle \mathbf{rr} \rangle - \frac{\mathsf{I}}{3} \tag{1}$$

where

$$\mathbf{r} = \begin{pmatrix} \sin\alpha\cos\beta \\ \sin\alpha\sin\beta \\ \cos\alpha \end{pmatrix} \tag{1a}$$

The swarms are viewed as microscopic units in a macroscopic system when the swarm size is much less than the characteristic dimension of the experimental apparatus. The swarms are treated as rigid ellipsoids whose average orientation about a point varies in a continuous fashion depending on thermal motions, particle interaction effects, surface effects, and external field effects. The internal molecular nature (with parallel molecular orientations) of the swarms is required to explain the above orienting influences. There is still considerable controversy as to the correct method of describing local structure, but the above view of a "swarm continuum" is used herein to describe recent experimental investigations.

The equation of change for A can be written as follows[2,9,10]:

$$\frac{D\mathsf{A}}{Dt} = \lambda \nabla^2 \mathsf{A} - \frac{\mathsf{A}}{\tau} + \mathsf{R}_A \tag{2}$$

$D\mathsf{A}/Dt$ is the convected or substantial derivative of the anisotropy tensor; $\lambda\nabla^2\mathsf{A}$ is the net anisotropy flux due to particle interaction; A/τ is the relaxation term and R_A is the anisotropy generation due to field influences. A discussion of Eq. (2) has been given by Patharkar *et al.*[7] The energy equation under a steady state, non-flow situation is written as follows[1]:

$$\nabla \cdot \mathbf{q} = 0 \tag{3}$$

and

$$\mathbf{q} = -\mathsf{k} \cdot \nabla T \text{ (Fourier's Law)} \tag{4}$$

The conductivity tensor k is expressible[9,10] as a second degree polynomial in A. Assuming that the coefficient in the second degree term is very small and that the coefficients are functions of only the thermodynamic state and not of A, we can write

$$\mathsf{k} = k_o(\mathsf{I} + \lambda_1 \mathsf{A}); \quad \lambda_1 \neq 0 \tag{5}$$

where

k_o = isotropic disoriented or randomly oriented state conductivity —i.e., when $\mathsf{A} = 0$ (5a)

It has been experimentally established that[10]

$$k_o = (k_a + 2k_t)/3 \tag{6}$$

Experimental evidence in the literature indicates that a perfect molecular orientation occurs at a solid surface for liquid crystals in the nematic state. The direction of orientation however, is still a controversial matter. For the infinite parallel plate geometry shown in Fig. 1, with the plates maintained at their respective

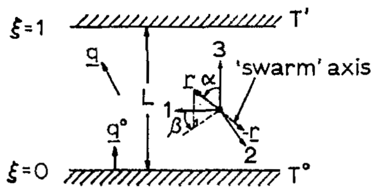

Figure 1. System geometry.

uniform temperatures, A and T are functions of x_3 only. This is because of the homogeneity in the x_1 and x_2 directions—i.e., random orientation in the x_1x_2 plane. In this case, Eqs. (3) and (4) can be written as follows:

$$\left(\frac{\partial q_1}{\partial x_1}+\frac{\partial q_2}{\partial x_2}+\frac{\partial q_3}{\partial x_3}\right) = 0 \tag{7}$$

$$\begin{aligned} q_1 &= -k_{13}\frac{\partial T}{\partial x_3} = -k_o\lambda_1 A_{13}\frac{dT}{dx_3} \\ q_2 &= -k_{23}\frac{\partial T}{\partial x_3} = -k_o\lambda_1 A_{23}\frac{dT}{dx_3} \\ q_3 &= -k_{33}\frac{\partial T}{\partial x_3} = -k_o(1+\lambda_1 A_{33})\frac{dT}{dx_3} \end{aligned} \tag{8}$$

Since the orientation at the surface is perfect and there is no other orienting influence but the interface, the definition of A in Eq. (1) yields A_{13} and A_{23} to be zero at all positions in x_3 direction. This produces zero net flux in x_1 and x_2 directions as follows from Eq. (8). Equation (7) then becomes

$$\frac{\partial q_3}{\partial x_3} = 0 \quad \text{or} \quad q_3 = q^\circ = \text{constant} \tag{9}$$

From Eq. (8),

$$|\mathbf{q}| = q^\circ = -k_o(1+\lambda_1 A_{33})\frac{dT}{dx_3} \tag{10}$$

The effective thermal conductivity as measured in the cell described in Ref. 7 can be defined as:

$$k_e = \frac{q^\circ L}{(T^\circ - T')} \tag{11}$$

Integrating Eq. (10) and using Eq. (11), we get:

$$k_e = \frac{1}{\int_0^1 \frac{d\xi}{k_o(1+\lambda_1 A_{33})}} \tag{12}$$

where

$$\xi = \left\{\frac{x_3}{L}\right\} \tag{12a}$$

With the experimental measurements of k_e, the right-hand side of Eq. (12) can be used to check the mathematical models such as Eq. (2) for describing the orientation phenomenon.

For the present case of a steady state, non-flow, one dimensional situation, Eq. (2) is simplified as:

$$\mathscr{D}\frac{d^2 A_{33}}{d\xi^2} = A_{33} \tag{13}$$

where

$$\mathscr{D} = \left\{\frac{\lambda\tau}{L^2}\right\} \tag{13a}$$

The assumption involved here is that there is no effect of temperature gradient because the heat flux is kept very small and so R_A is neglected. The boundary conditions are as follows:

$$A_{33}|_{\xi=0} = A_{33}|_{\xi=1} = A_{33}^{\circ} \tag{14}$$

The constant A_{33}° at this stage is assumed to be known. This point will be elaborated upon in a subsequent discussion. The solution of Eq. (13) is given as:

$$A_{33}(\xi) = A_{33}^{\circ}\left(\frac{\cosh\frac{(\xi-0.5)}{\sqrt{\mathscr{D}}}}{\cosh\frac{0.5}{\sqrt{\mathscr{D}}}}\right) \tag{15}$$

From Eq. (5), the conductivity at the interface is given as

$$k_e|_{\xi=0\ \&\ \xi=1} = k^{\circ} = k_o(1+\lambda_1 A_{33}^{\circ}) \tag{16}$$

k° is the limiting conductivity as L approaches 0. Hence,

$$\lambda_1 = \left\{\frac{k^{\circ}}{k_o} - 1\right\}\Big/A_{33}^{\circ} \tag{17}$$

Using Eqs. (12), (15) and (17), we get

$$k_e = \frac{k_o}{\displaystyle\int_0^1 \frac{d\xi}{\left\{1 + b\cosh\dfrac{(\xi - 0.5)}{\sqrt{\mathscr{D}}}\right\}}} \tag{18}$$

where

$$b = \left\{\frac{k^\circ}{k_o} - 1\right\} \Big/ \cosh\frac{0.5}{\sqrt{\mathscr{D}}} \tag{18a}$$

The experimental observations[7,8] indicate that $1 < k^\circ/k_o < 2$. Also, $\cosh(0.5/\sqrt{\mathscr{D}}) \geqslant 1$ for all values of $\sqrt{\mathscr{D}}$. It follows that $b \leqslant 1$. Equation (18) can be simplified using the formulas in Ref. 5 as follows:

$$k_e = \frac{k_o\sqrt{1-b^2}}{2\sqrt{\mathscr{D}}}\left[\ln\left(\frac{1 + b + \sqrt{1-b^2}\tanh\dfrac{1}{4\sqrt{\mathscr{D}}}}{1 + b - \sqrt{1-b^2}\tanh\dfrac{1}{4\sqrt{\mathscr{D}}}}\right)\right]^{-1} \tag{19}$$

The unknown parameters in Eq. (19), k_o, k° and $\sqrt{\lambda_T}$ can be estimated by fitting this model to the k_e data given in Table 1, taken

TABLE 1 Experimental Data[7]
$k_e \times 10^4$ cal/cm sec °C

L cm	Purified PAA	Commercial PAA
0.0032	3.59	—
0.0064	3.48	4.57
0.0127	3.40	3.83
0.0254	3.32	3.59
0.0508	3.29	3.38
0.1016	3.27	3.22
0.3175	3.22	3.00

from Ref. 7. The k_e value at the lowest heat flux in each gap size is used for this analysis. The curve fitting for the parameter estimation is done by a nonlinear least-squares technique.

From Eq. (15), when $L \gg \sqrt{\lambda_T}$ (or $\mathscr{D} \ll 1$), we can define an interfacial layer thickness δ_c as the value of ξ where $A_{33} \simeq 0.368\,A_{33}^\circ$.†

† See Appendix.

2. Presentation of Results

Table 2 shows the estimated parameters for commercial and purified PAA around 125–126 °C. The comparison between the estimated and the observed values of k_e at different L is shown in Fig. 2. The agreement between the two for both purified and commercial PAA is encouraging. k_o is the limiting value of k_e as $L \to \infty$ and k° is the limit as $L \to 0$.

TABLE 2 Estimated Parameters

Parameter	Purified PAA	Commercial PAA
$k_o \times 10^4$ cal/cm sec °C	3.24	3.14
$k^\circ \times 10^4$ cal/cm sec °C	3.60	4.94
$\lambda\tau \times 10^5$ cm^2	0.83	1.02
$\delta_c \sim \sqrt{\lambda\tau}$ microns	28.8	31.9
$\left\{\frac{k^\circ}{k_0}\right\}$	1.11	1.58

The significant difference between the conductivities of commercial and purified PAA has been discussed before.[7] The nature and the exact influence of the impurities is still unknown. The estimated value of the interfacial oriented layer thickness is about 30 μ in both samples of PAA and is comparable to the value of 20 μ reported by a different approach.[8] The presence of impurities does not seem to influence δ_c. Fisher[2] has reported the value of the relaxation time constant τ to be about 2.2 seconds. This gives a value of λ of the order of 2×10^{-5} cm^2/sec which is comparable to the value of 10^{-5} cm^2/sec reported by Heilmeier[6] using optical techniques. A collection of the different experimental values is given by Yun.[10]

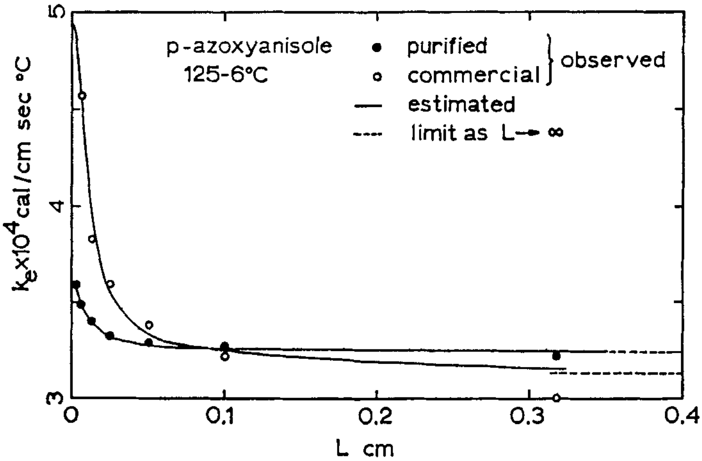

Figure 2. Effective thermal conductivity of PAA versus gap size.

3. Discussions and Conclusions

The use of thermal conductivity data to estimate the properties and the interface influence characteristics seems to be a satisfactory alternate to the optical and other methods. However, it is necessary to use the other techniques to determine the relaxation time which is required in the analysis of field effects. The evaluation of the constant λ_1 in Eq. (17) is possible only if A°_{33} is also known. This brings us to the point of discussion on the nature of interfacial orientation.

In the literature,[7,10] it is found that $k^{\circ} > k_o$. The interfacial orientation is perfect as mentioned before—i.e., the long axis of the transversely isotropic swarms is either perpendicular or parallel to the surface. Picot's[8] measurements of k_e using a hot-wire cell in an electric field is not very conclusive on this question because of the insufficient knowledge of the effect of an electric field on nematic PAA. Fisher[2] measured k_e of PAA in a shear field with heat flux normal to flow direction. It is well known that the spheroidal swarms orient their long axes along the direction of flow at high shear rates. Thus, the value of k_e at high shear rates would be close to k_t. Fisher found that $k_t > k_o > k_a$. If we assume that the interface orientation is normal to the surface as indicated by Yun[10] in his magnetic field studies on DBA, the present observations indicate that $k_a > k_o > k_t$.

This logically concludes that Fisher should have found a decreasing k_e with increasing shear rates. On the other hand, if the interface orientation is parallel to the surface, it follows that $k_t > k_o > k_a$. This would mean that the conductivity should increase with increasing shear rate as observed by Fisher. Recent communications with Fredrickson and Yun[3] raise the possibility of convection due to secondary flows caused by eccentricity in Fisher's concentric annulus cell. This convective effect gives a higher value of k_e. However, we will retain the conclusion of parallel orientation[2] at the surface ($k_t > k_o > k_a$) until definitive experimental proof appears to the contrary.

Since the anisotropy tensor A° has been shown[9] to be given by the following:

$$\mathsf{A}^\circ = \begin{pmatrix} \frac{1}{6} & 0 & 0 \\ 0 & \frac{1}{6} & 0 \\ 0 & 0 & -\frac{1}{3} \end{pmatrix} \quad \text{[random orientation in } x_1 x_2 \text{ plane]} \tag{20}$$

then, from Eq. (17)

$$\begin{aligned} \lambda_1 &= \left\{\frac{k_t}{k_o} - 1\right\} \Big/ A^\circ_{33} \\ &\simeq -0.334 \text{ (purified PAA)} \\ &\quad\ -1.73 \text{ (commercial PAA)} \end{aligned} \tag{21}$$

In summary, we have made an attempt to estimate the properties of a liquid crystal using the experimental data on the thermal conductivity measured by a parallel plate cell. Further work to analyze the temperature gradient effect reported in the literature[7] is under way.

4. Nomenclature

Dimensions are given in terms of force (F), heat (H), length (L), mass (M), temperature (T) and time (θ).

A_{ij} = ij component of anisotropy tensor, dimensionless
b = defined in Eq. (18a), dimensionless
$\mathscr{D}$ = diffusion number for swarm interaction, dimensionless
D_r = rotational diffusion coefficient, $(1/\theta)$
e_i = base vector in x_i direction, (L)

I = identity tensor, dimensionless
k = thermal conductivity, $(H/L\theta T)$
L = gap between the parallel plates, (L)
q_i = component of heat flux vector along x_i, $(H/L^2\theta)$
R_A = field effect tensor, $(1/\theta)$
r_i = i component of the vector along the long or major axis of spheroidal swarms, (L)
T = temperature, (T)
t = time, (θ)
V = velocity, (L/θ)
x_i = Cartesian coordinate in i direction, (L)

$\mathbf{r}$, $\mathbf{q}$, etc. = vector
A, k, etc. = tensor of second order

SUBSCRIPTS

a = axial direction of swarms
e = effective value
o = disoriented or randomly oriented value
t = transverse directions of swarms

SUPERSCRIPTS

$'$ = value at $\xi = 1$
$^\circ$ = interface condition

GREEK SYMBOLS

α, β = orientation space coordinates (Fig. 1)
δ_c = interfacial oriented layer thickness, (L)
λ = swarm interaction diffusion coefficient for orientation, (L^2/θ)
λ_1 = constant, dimensionless
ξ = distance from surface, dimensionless
τ = relaxation time constant for swarm orientation, (θ); $[\tau = 1/6D_r]$

MATHEMATICAL OPERATORS, SPECIAL FUNCTIONS, SYMBOLS, ETC.

$$\frac{D(\cdot)}{Dt} = \text{convected derivative} = \frac{\partial(\cdot)}{\partial t} + \mathbf{V}\cdot\nabla(\cdot)$$

$\mathbf{rr}$ = dyadic product

$<(\cdot)>$ = ensemble average over a distribution of swarm orientations $f(\alpha, \beta)$

$$= \int_0^{2\pi} \int_0^{\pi} (\cdot) f(\alpha, \beta) \sin\alpha \, d\alpha \, d\beta$$

Appendix

From Eq. (15):

$$\frac{A_{33}|_{\xi \sim \delta_c}}{A_{33}^{\circ}} = \cosh \frac{\delta_c}{\sqrt{\mathscr{D}}} - \sinh \frac{\delta_c}{\sqrt{\mathscr{D}}} \tanh \frac{0.5}{\sqrt{\mathscr{D}}}$$

When $\mathscr{D} \ll 1$ and $\delta_c \sim \sqrt{\mathscr{D}}$

$$\frac{A_{33}}{A_{33}^{\circ}} \simeq \cosh(1) - \sinh(1)$$

$$= 1.543 - 1.175$$

$$= 0.368$$

Hence,

$$A_{33}|_{\xi \sim \sqrt{\mathscr{D}}} \simeq 0.368 \, A_{33}^{\circ} \; (\mathscr{D} \ll 1)$$

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