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Heat Transport in Liquid Crystals†‡

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Abstract—Several reports have appeared during the past half century describing temperature changes of nematic liquid crystals, in particular *p*-azoxyanisole, upon exposure to a magnetic field. Although all the experiments were conducted with the sample in good thermal contact with the oven or bath, the temperature changes persisted until the field was removed. It is proposed here that the thermal changes were a result of anisotropy of the thermal conductivity and heat leakage through the temperature measuring device. A new experiment supporting this view is discussed.

Since nematic liquid crystals have been discussed in detail elsewhere,[1] only those characteristics that are relevant to this article will be reviewed. Because liquid crystal molecules are somewhat elongated, one can specify a direction of orientation. In the liquid crystalline, or mesomorphic, state, there exists a long range ordering of this molecular orientation. It is well-known that the range and the directional anisotropy of this orientation can be enhanced by a magnetic field, an electric field, a shear force, or proximity to an interface. For *p*-azoxyanisole (PAA), a constant electric or magnetic field tends to align the long molecular axes parallel to the field direction; a high-frequency electric field, perpendicular.[2] A shear force tends to align molecules parallel to the direction of shear.[3] Finally, the direction of orientation near an interface is usually parallel to the interface.[4] It will be assumed here that molecular orientation is parallel to silver, gold, and brass surfaces. This assumption is not unreasonable as explained later.

The literature contains several reports of changes in the tempera-

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ture of nematic liquid crystals, associated with the application of a magnetic field. Moll and Ornstein[5] noted that the temperature of a thin, vertical silver plate inside a gold beaker of PAA slowly rose 0.1 °C when a magnetic field was applied perpendicular to the plate. The effect lasted until the field was removed, whereupon the temperature gradually returned to its original value. If a magnetic field was applied parallel to the silver plate during the latter temperature transient, the return of the plate's temperature to the no-field value was more rapid. Miesowicz and Jezewski[6] observed the temperature of the middle brass plate in a brass-PAA-brass-PAA-brass sandwich. The PAA layers were 2 mm thick. When a 2.3 kilogauss magnetic field was applied perpendicular to the middle brass plate, its temperature rose 1.05 °C; when applied parallel, there was no change. Observations were also made of temperature changes resulting from application of a magnetic field when various electric fields were applied continuously between the brass plates. The results of these compound experiments are consistent with our interpretation presented below. Finally, Yun and Fredrickson[7] found that the temperature within a test tube of PAA immersed in a wax bath increased up to 0.14 °C when a magnetic field was applied perpendicular to the axis of the test tube. The actual temperature increase was found to be dependent on the strength of the magnetic field, the ambient temperature, and the thermal history of the sample. Another nematic liquid crystal, *p*-n-decycloxy benzoic acid, was found to produce similar results. All six investigators found the temperature changes to last until the magnetic field was removed. Also, in each case, only the temperature in the middle of the sample was measured.

There is no obvious, consistent explanation for these experiments. Frictional heating due to realignment will only give a transient effect, and it is not possible to take energy from a constant magnetic field. Even if one ignores the " isothermal " nature of the above experiments, the classical adiabatic magnetocaloric effect[8] for diamagnetic molecules does not explain the observed temperature changes: the temperature derivative of the magnetic susceptibility is too small. Finally, the existence of any significant magnetocaloric effect would cause a density change because of thermal expansion. However, since the density remained constant[9] when a magnetic field was applied to PAA, it can be inferred from the volume-change sensitivity of the experiment that the temperature changed less than 0.0004 °C.

The paradoxical situation reviewed above led to the development of a new type of experimental arrangement to study the temperature changes in PAA caused by magnetic fields. The results of this experiment show that by aligning the liquid crystal, the magnetic field changed the net thermal conductance between the oven and the temperature-sensing probe within the liquid crystal. Thus, the thermal conductance to room temperature provided by the probe's lead together with the field-induced change in the liquid crystal conductance produced the observed temperature change at the measurement point.

In order to gain some knowledge of the thermal gradients in our experiment, the oven and the liquid crystal temperatures, and their difference, were measured concurrently† to a sensitivity of 0.0001 °C. Our oven was an electrically-heated, vertical copper rod ($6\frac{3}{4}''$ long by $\frac{3}{4}''$ diameter with about $\frac{1}{2}''$ asbestos insulation). A hole ($3\frac{1}{4}''$ deep) was bored in each end along the rod's axis. The bottom hole ($\frac{3}{8}''$ diameter) held one of the temperature probes; the top hole ($\frac{1}{2}''$ diameter) held a $\frac{1}{2}$ dram vial. This vial contained about $\frac{1}{2}$ gram of PAA and the second temperature probe (about $\frac{1}{8}''$ above the bottom of the vial). Horizontal magnetic fields to about 5 kilogauss could be applied to the sample. Normally, the temperature probe immersed in the liquid crystal was cooler then the probe in contact with the oven. Typically this difference was 1 °C, and, upon application of a magnetic field, the temperature recorded by the liquid crystal probe increased 0.02 °C. No change was noticeable in the temperature of the oven probe. When the thermal gradient in the PAA was reduced by providing better thermal contact between the upper (liquid crystal) probe's lead and the oven, the temperature rise was smaller. It was found that the temperature gradient could be reversed temporarily by slowly cooling the oven. In that circumstance, application of the magnetic field caused the temperature of the liquid crystal probe to *fall* relative to the oven temperature. These results are explained consistently by an increase in the thermal conductance through the liquid crystal when a magnetic field sufficient to align

† Hewlett-Packard Model 2801A Quartz Crystal Thermometer.

the liquid crystal is applied. In addition three aspects of the temperature change were verified: it saturated with high fields[7] as an alignment effect should; it existed only when the liquid crystal was in its nematic state;[6,7] it decreased in magnitude as the ambient temperature was increased.[6,7]

In light of this new interpretation, the earlier experiments can be analyzed, assuming the temperature sensor acts as a heat sink. In an anisotropic medium, the thermal conductivity in Fourier's equation for heat conduction becomes a second rank tensor. It is necessary to define k_l and k_t as the thermal conductivities parallel to and perpendicular to, respectively, the direction of molecular orientation (long molecular axis) of PAA. Let k_0 be the (possibly history-dependent) bulk conductivity of non-aligned PAA. The experiments of Moll and Ornstein[5] and Miesowicz and Jezewski[6] require k_l to be greater than k_t. The experiments of Yun and Fredrickson[7] require k_0 to be less than $\frac{1}{2}(k_l + k_t)$. Our experiments indicate k_0 is less than k_t.

For PAA, k_0 is known[10–12] to within a few percent. It can be inferred[13,14] that k_l is about $1.25k_0$; k_t has been measured[12] as $1.06k_0$ using a shear alignment experimental arrangement. Also, the conductivity[15] near and perpendicular to a platinum surface is $1.11k_0$. The proximity of this value to k_t suggests parallel alignment with a platinum interface. This gives credence to our earlier assumption that a similar parallel alignment occurs with gold, silver, and brass interfaces.

An experiment to measure k_0, k_l, and k_t is in progress. The results should be of sufficient accuracy to test quantitatively our theory that the observed temperature changes result from an alteration of the thermal conductance.

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