Orientation of Liquid Crystals by Heat Conduction

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This is a new phenomenon in heat conduction in which the "liquid crystals" of para-azoxyanisol acquire a preferred orientation under the action of heat conduction in the liquid. A temperature gradient of but 1° or 2°C per cm, at a temperature of approximately 125°C, is sufficient to give a marked effect. The orientation is indicated by the variation in intensity in the x-ray diffraction halo. Both the effect and its magnitude are rather surprising, and it is anticipated that the explanation may rest in the dominance of acoustic waves of inertia and viscosity in heat conduction in liquids, as described by Lucas.

IN a comparison[1] of the x-ray diffraction intensity distributions with para-azoxyanisol in the liquid crystalline and isotropic states, the first author found a new conduction of heat phenomenon. A temperature gradient of 1° or 2°C per cm, the temperature decreasing downward, produced a preferred horizontal orientation of the elongated bundles or swarms of molecules. The direction of "orientation" is taken to be that of the longest axis of a swarm, the axis possessing the greatest induced magnetic moment. The direction of preferred orientation just mentioned was perpendicular to that produced by vertical convection currents.

This new heat conduction effect is somewhat surprising, for in view of the temperature, approximately 400°K, any kind of anticipated effect produced by a gradient a degree or two per cm would be rather small. Herewith is presented briefly the concordant results of three different experimental tests of the phenomenon, with a suggestion of the possible causes of the orientation effect.

Experimental Results

I. The first experiments were those to which reference has already been made. A very thin-walled glass cylindrical tube 1.0 cm in diameter and 9.0 cm in length was surrounded by a loosely-fitting paper jacket and placed in an oven having an internal diameter of 7.3 cm and height of 16.0 cm. This jacket prevented convection currents in the air immediately surrounding the tube. Even the introduction of an air circulating fan into the oven did not produce any alterations in the temperature gradient at the tube as indicated by two thermocouples spaced 1.8 cm apart vertically just outside. A number of tests with different temperature gradients were made, and the x-ray intensity results (obtained by an ionization chamber) and the gradients plotted. These showed that unquestionably any increase in temperature gradient, temperatures decreasing downward, affected the intensity as if by an increase in horizontal preferred orientation. In these experiments the angular diffraction of x-rays in one plane only could be measured.

II. The second set of experiments were made by Donald O. Holland. An oven was constructed so as to provide the passage of a small parallel pencil of x-rays and the diffraction halo was produced on a photographic film. A vertical, thin-walled glass tube was used as before, but now an oven similar to that of Fig. 1 (which was actually used in the third experiment) was constructed. The ends of the tube were surrounded by brass blocks to insure their temperatures as measured by external thermocouples and the tube was surrounded by a brass cylinder to assist in securing a temperature gradient with horizontal isothermal levels. With this type of apparatus the halos completely corroborated the experiments recorded in "I" above. At the nearest attainable uniform temperature throughout, there always remained a slight convection as evidenced by the asymmetry of the circular halo, the alteration in density on the film showing a small preferred vertical orientation of the swarms. With increasing temperature gradient, tempera-

[1] G. W. Stewart, J. Chem. Phys. 4, 231–236 (1936).

ture higher at the top of the tube, the asymmetry in the halo at first disappeared and then appeared again, but as if the halo were rotated through 90°. This indicated the disappearance of one preferred swarm orientation (vertical) and the appearance of another (horizontal). At each selected temperature gradient it was necessary to hold the temperatures constant for several hours to insure a steady condition. A sample of the nature of the change in the diffraction ring with increasing temperature gradient is indicated by the later photographs of Reynolds in Fig. 2.

These experiments were followed by others with the tube in a horizontal position. For a temperature gradient along the tube in either direction, convection currents always existed. Nevertheless the heat conduction phenomenon was in evidence and all the results were interpretable by the combined convection and temperature gradient effects.

III. The third series of experiments was by Leon M. Reynolds. At first an oven was tried where the sample tube was not so completely surrounded by copper blocks at its ends. In this oven, a uniform temperature gradient and strictly horizontal isothermal levels were not successfully secured, convection currents persisted, and the preferred orientation remained dominantly vertical. The conduction of heat phenomenon did not appear. But when the oven in Fig. 1 was substituted, results similar to those of Holland at once appeared. This third set of experiments in which was used the best oven of the three, confirmed the reality of the heat conduction phenomenon and also showed how carefully convection must be reduced if the new phenomenon is to be brought into evidence.

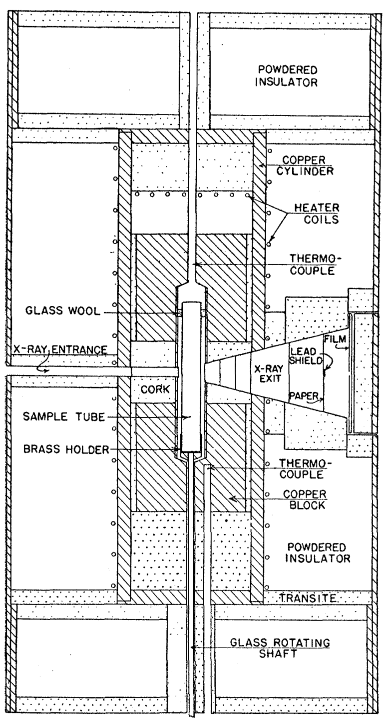


FIG. 1. Oven used by Reynolds in the third group of experiments. Cross section parallel to x-ray path.

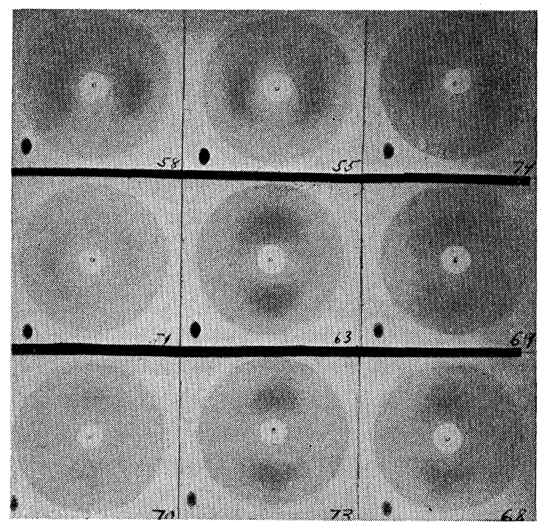


FIG. 2. Diffraction halos, x-ray beam horizontal, photographic film vertical. Sample, para-azoxyanisol at 119° to 130°. Temperature gradients are in degrees C/cm, reading from left to right, top line first, 0°, 0.05°, 0.13°, 0.27°, 0.32°, 0.65°, 0.83°, 1.10°, 1.46°.

Typical results of Reynolds and Holland are shown in Fig. 3. By photometric measurement the ratio of scattered x-ray intensities at the two points of each halo may be obtained. With I_h as the intensity produced by horizontal orientation of the swarms and I_v by vertical orientation, the ratio I_v/I_h is plotted for the two experimenters. If I_v only is plotted, a curve of a similar general shape is obtained but, by using the ratio, the error introduced by variation in development of the film is eliminated.

Reynolds determined the effect of rotation of the sample upon the preferred orientation of the swarms. This is shown in Fig. 4.

Discussion

In Fig. 3 the general course of the curves is similar to the results obtained in x-ray diffraction experiments with a magnetic field.[2] In each case the effect is caused by the orientation of the swarms or bundles of molecules. In Fig. 3, the greater orientation in the Reynolds' experiments is accounted for by the improvement in the horizontality of the isothermal levels. The results of Fig. 4 also confirm the interpretation of the experiments. Rotation of the containing cylinder about a vertical axis would, through irregularities in the tube and in the motion, coupled with viscosity, cause a shear in the horizontal plane perpendicular to the radius of the cylinder. This would produce an effect similar to a horizontal circular convection current, namely, that of a preferred orientation of the bundles in the direction of the velocity stream. Hence one would expect the rotation of the tube to give a preferred orientation in the horizontal plane, or to increase the effect of the temperature gradient. This is shown to be the case of Fig. 4.

Thus all the experiments are consistent with the view that there is a new conduction of heat phenomenon in addition to the well-known magnetic and convection effects in the liquid crystal form of para-azoxyanisol. Although the effect of such a small heat conduction is surprising, yet one must remember that the orientation of these bundles in a magnetic field is relatively easy. A field of 2200 gauss will give practically complete orientation and 1300 gauss but a few percent less. The swarms or bundles are relatively large,[3] containing approximately one million molecules, the size probably having a considerable variation. This accounts for the relative ease of orientation at any ordinary temperature. Orientation by convection is probably produced by the shearing effect of a velocity gradient perpendicular to the convection velocity. Orientation by conduction might be caused by radiation pressure of the acoustic waves. But it seems more simple in accord with the experiments and calculations of Lucas,[4] to regard the important transverse waves of inertia and viscosity in the fluid as effective in producing by their displacements a torque on the bundles. This may cause a preferable orientation in the plane containing these displacements and perpendicular to the direction of flow of heat energy.

At the moment, the possible importance of the new heat conduction effect would seem to be as a tool in the study of liquid crystal bundles or swarms, of the cause of the exerted torque whether momentum or transverse displacement velocity gradient, and of the acoustic waves, both longitudinal and transverse, which are responsible for heat conduction in liquids.

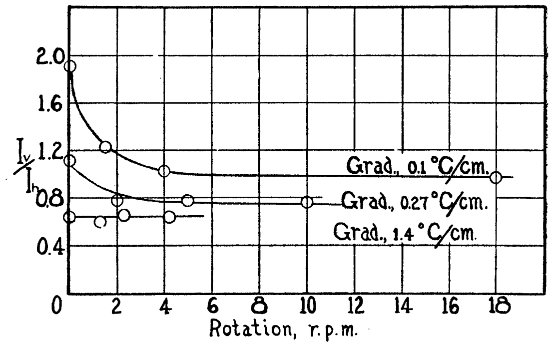


FIG. 4. Rotation increases the effect of heat conduction.

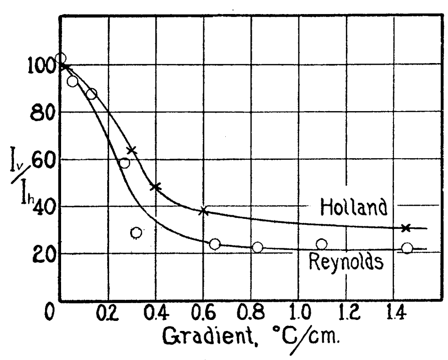
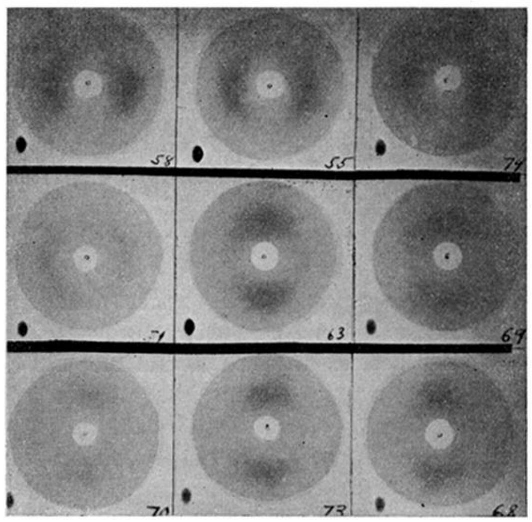


FIG. 3. Alteration in orientation with temperature gradient, temperature decreasing downwards. Circles; Reynolds, corresponding to the nine photographs in Fig. 2. Crosses; Holland. Scale for ordinates modified to give value 100 at zero gradient.

[2] G. W. Stewart, Phys. Rev. **38**, 931 (1931).

[3] Evidence also in Ornstein and Kast, Faraday Society Discussion, 1933, p. 931.

[4] R. Lucas, J. de phys. et rad. **7**, 40 (1937).



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