

⁵N. S. Gingrich, Rev. Mod. Phys. **15**, 90 (1943).

⁶ $T=4.2^\circ\text{K}$, $P=0.54$ atm, and $\rho=0.00112$ atom/ \AA^3 .

⁷J. de Boer, Rept. Progr. Phys. **12**, 305 (1949).

⁸The contributions of higher order terms are currently being investigated. Based on the low-density calculations of other gases, it may be safely assumed that the effect of these higher order terms is largely confined to the less important "second-nearest-neighbor" peak. See Ref. 7; I. Z. Fisher, in *Statistical Theory of Liquids*, translated by T. M. Switz (University of Chicago Press, Chicago, Ill., 1964); M. H. Lee, Physica **43**, 132 (1969).

⁹Statistical theory gives the formula

$$\lim_{k \rightarrow 0} S_G(k) = \rho K_B T \chi_T,$$

where ρ is the number density and χ_T the isothermal compressibility of the gas. Hence if χ_T is known, the limit value of $S_G(k)$ may be compared with the usual

assumption [$S_G(k)=1$ for all k] and with our calculation shown in Fig. 1. Using the dilute-gas approximation for $g(r)$ we can easily connect χ_T to the second virial coefficient B [see, for example, P. A. Egelstaff, *An Introduction To the Liquid State* (Academic Press, Inc., New York, 1967), pp. 22-24], and with the second virial coefficient ($B=-78.25$ cm³/mole) obtained by W. E. Keller [Phys. Rev. **97**, 1 (1955)] we have computed the limiting value $S_G(0)=1.39$. Although this value does not closely agree with our value of Fig. 1, $S_G(0)\approx 1.55$, it does support our claim that there is a correction to $S_G(k \rightarrow 0)$ which the experimental workers have apparently overlooked.

¹⁰Feynman and Cohen, Ref. 2.

¹¹For example, at $k=0.5$ \AA^{-1} and $T=1.4^\circ\text{K}$, $x=3.27$, and $\coth x \approx 1.003$. Hence for all practical purposes (5) cannot be distinguished from the Feynman form, $S(k) = \hbar k / 2mC$, at this finite but small value of k .

CAPILLARY FLOW OF CHOLESTERIC AND SMECTIC LIQUID CRYSTALS

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It is shown theoretically that the motion of liquid crystals through capillaries may resemble that of a plug, the velocity profile being flat rather than parabolic.

Capillary viscometry has been done on all three types of liquid crystals.¹⁻³ However, capillary flow is understood only for the nematic mesophase.^{4,5} Apart from the anisotropy of the viscosity and from flow alignment and associated boundary layer effects, nematic fluids were found to flow like isotropic liquids. The viscosities, measured directly⁶ or calculated by means of Poiseuille's law,¹ were always of the same order of magnitude as in the isotropic liquid state.

On the other hand, with cholesteric and smectic liquid crystals Poiseuille's law often yielded viscosities many orders of magnitude above those of the isotropic liquid.¹ In the present note we wish to offer an explanation for these results. We will show that capillary flow of liquid crystals may be controlled by mechanisms other than that underlying Poiseuille's law.

Let us consider a cholesteric material whose helical axis is parallel to the axis of the capillary, as indicated in Fig. 1(a). We assume that the characteristic twisted orientation pattern does not move along the capillary and is not markedly distorted by the flow. Both assumptions will be discussed below. Any translational motion along the capillary is then associated with a rotation of the molecules. According to Erickson and Leslie⁴ the rotation produces shear

stresses resulting in the body couple per cm³

$$\lambda_1 d\varphi/dt$$

around the helical axis. Here φ is the alignment angle, d/dt the material derivative with respect to time, and $\lambda_1 \leq 0$ a constant. With v being the velocity and P the pitch of the helix, one has $d\varphi/dt = 2\pi v/P$. For symmetry reasons one may expect pure forward flow in flat rectangular capillaries if the ratio of the sides of the rectangle is very large, ideally infinite. Then ϵ is the energy dissipated per second per cm³ by the rotation:

$$\epsilon = (-\lambda_1)(2\pi v/P)^2.$$

If Poiseuille shear can be neglected, ϵ must be matched by the energy gain resulting from the motion in the pressure gradient p' along the capil-

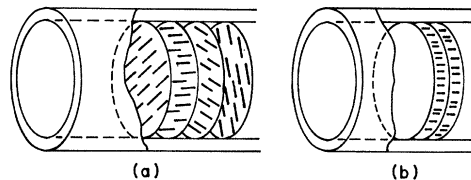


FIG. 1. Envisaged orientation patterns in the (a) cholesteric and (b) smectic case. The dashes represent the rodlike molecules whose long axes are perpendicular (a) and parallel (b) to the capillary axis. Only the molecules on certain areas are shown.

lary. Therefore,

$$p' = \lambda_1(2\pi/P)^2 v.$$

Except for a boundary layer where viscous shear is not negligible, the fluid moves like a plug with uniform velocity. The total flow per second Q is

$$Q = [P^2 A / (-\lambda_1) 4\pi^2] p', \quad (1)$$

where A is the cross section of the capillary.

The motion of the fluid through the fixed orientation pattern may be called "permeation," and the ratio v/p' "permeability."

Because of the strong coupling between flow and molecular rotation in liquid crystals, a circular flow will accompany the forward motion in circular capillaries. However, the effective permeability should be of the same order of magnitude as with pure forward flow.⁷ Poiseuille's law for circular capillaries is

$$Q = (\pi a^4 / 8\eta) p', \quad (2)$$

a being the radius. Equation (1) can be written in the form of Eq. (2) if we replace the viscosity η by the apparent value

$$\eta_{app} = (-\lambda_1) a^2 \pi^2 / 2P^2.$$

The application of (1) to circular capillaries ($A = \pi a^2$) is, of course, an approximation. The largest viscosity derived by Porter, Barrall, and Johnson¹ with Eq. (2) is $\eta \approx 10^5$ P, found on cholesteryl acetate at an apparent shear rate of 10 sec^{-1} . This is 10^6 times the value in the isotropic liquid and unacceptably large for a true viscosity. However, combining $a = 0.0375$ cm from Porter, Barrall, and Johnson with $P = 3000 \text{ \AA}$, an estimated value,⁸ and $(-\lambda_1) = 3 \times 10^{-2}$ P, which is the value for *p*-azoxyanisole,⁹ we obtain $\eta_{app} = 2 \times 10^5$ P which is close to Porter's experimental result.

The concept of permeation should also be useful in the case of smectic liquid crystals. We consider an immobile smectic orientation pattern whose unique axis (normal to the layers) is parallel to the axis of the capillary, as sketched in Fig. 1(b). Flow in this arrangement requires the permeation of molecules through the smectic layers. There should be no circular flow component, independently of the shape of the cross section of the capillary. In a molecular model the permeability is

$$v/p' = \nu_0 \exp(-E/kT) (l^2/kT), \quad (3)$$

where l is the thickness of one monomolecular layer, ν_0 a vibrational frequency (probably $\approx 10^{12}$

sec^{-1}), and E the average activation energy needed by a molecule to jump from one layer to the next. Equation (3) is analogous to that for the drift velocity of charge carriers in the hopping model (with p' replacing the product of carrier charge and electric field strength).

We now turn to the first of our two assumptions. In the case of smectic liquid crystals, we consider a region so close to the capillary wall that the flow is controlled by shear viscosity and comparatively negligible. (At the wall itself the speed of flow is taken to be zero as in isotropic liquids.) Any motion of the orientation pattern in this region would require permeation. However, the energy necessary for this process cannot be gained by the molecules unless there is local material flow along the pressure gradient which is uniform all over the cross section of the capillary. Consequently, the orientation pattern cannot slide along the capillary wall but is immobile. The situation is more complex in the case of cholesteric liquid crystals because of the body couple exerted by the friction. Even at very small flow velocities the torque causes a distortion of the orientation pattern in the planes normal to the helical axis, but this does not affect permeation. The orientation pattern may be held in place by a suitable wall alignment (irregularities might do) absorbing the distortional torque. Otherwise, there could be pluglike flow with some slippage at the walls. Including the distortion just mentioned, the second assumption is also reasonable. The pressure gradient p' , if it is sufficiently small, will be balanced by a slight bending of the cholesteric¹⁰ or smectic layers. The laws governing this elasticity remain to be formulated.⁷

Well-defined measurements of pluglike flow seem feasible, at least if the alignment considered here can be enforced and stabilized by electric or magnetic fields parallel to the capillary. It was observed by Porter *et al.* that at high speeds cholesteric and smectic fluids flow as easily as the isotropic liquids. This seems to indicate an alignment in directions which permit Poiseuille flow, perhaps due to a strong deformation of the orientation pattern at these velocities.

¹R. S. Porter, E. M. Barrall, II, and J. F. Johnson, *J. Chem. Phys.* **45**, 1452 (1966).

²R. S. Porter and J. F. Johnson, *J. Phys. Chem.* **66**, 1826 (1962).

³J. Fisher and A. G. Fredrickson, in *Proceedings of the Second International Conference on Liquid Crystal*,

Kent, Ohio, 12-16 August 1968 (to be published).

⁴For a survey of the continuum theory of liquid crystals, see J. L. Ericksen, *Appl. Mech. Rev.* **20**, 1029 (1967). The basic formulation may also be found in F. M. Leslie, *Proc. Roy. Soc. (London), Ser. A* **307**, 359 (1968).

⁵A theory of boundary layers has been developed by F. M. Leslie, *Arch. Rational Mech. Anal.* **28**, 265 (1968).

⁶M. Miesowicz, *Nature* **158**, 27 (1946).

⁷A detailed study of flow in circular capillaries is

planned to be published elsewhere.

⁸See, e.g., G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals* (Academic Press, Inc., New York, 1962). From the green appearance we estimate $P=3000 \text{ \AA}$, assuming the refractive index to be 2.

⁹W. Helfrich, *J. Chem. Phys.* **50**, 100 (1969). In the notation of that paper $\kappa_1 + \kappa_2$ stands for $-\lambda_1$.

¹⁰The slight bending of the planes of equal alignment does not contradict and is in fact identical with the rather strong distortion of the orientation pattern in the planes normal to the helical axis (Ref. 7).

COUPLING BETWEEN FERRIMAGNETIC INSULATORS THROUGH A SUPERCONDUCTING LAYER

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In agreement with a recent theoretical prediction of de Gennes, the transition temperature of In (or another superconductor) films sandwiched between two magnetic films depends on the relative orientation of the magnetization of these ferrites. The highest transition temperature (nearly the T_c of bulk In, 3.4°K) is obtained when the two ferrites are deposited in antiparallel magnetic fields, while the lowest ($\approx 1^\circ\text{K}$) occurs when the ferrites are deposited in parallel magnetic fields. The depression of the transition temperature of an indium film sputtered or evaporated between two magnetic films magnetized in parallel fields is inversely proportional to the thickness of the In film.

Recently, de Gennes¹ predicted theoretically that two ferromagnetic insulating layers with respective magnetizations M_1 and M_2 are coupled when a superconducting film of thickness smaller than 1 coherence length ξ_0 is placed inbetween. The most striking conclusion was that the transition temperature T_c of the superconducting film would be highest if M_1 and M_2 were antiparallel and lowest if M_1 and M_2 were parallel. In agreement with the theory it is found that a 3000- \AA In film sandwiched between two Fe_3O_4 films with parallel magnetizations has its T_c reduced by 1.5°K while the same film sandwiched between two Fe_3O_4 films deposited in antiparallel magnetic fields displays a reduction of about 0.3°K. Furthermore, a 3000- \AA In film sandwiched between two randomly magnetized Fe_3O_4 films (thus partly antiparallel) showed a reduction of 0.8°K. If a 500- \AA Al_2O_3 layer is deposited between the In and two Fe_3O_4 layers magnetized in parallel fields, the In film displays the bulk T_c of 3.4°K, thus ruling out closure fields as the cause of the depression of T_c . It was also established, in agreement with de Gennes's theory,¹ that the depression of T_c of such triple layers is inversely proportional to the thickness of the superconducting film d . These experiments demonstrate that the reduction in T_c is due to the exchange field produced by the two magnetic layers and not by

the closure field of magnetic domains. Finally, it was estimated from such experiments that the exchange integral Γ was approximately 0.3 eV.

When a superconducting film is in contact with one or two insulating ferrimagnets three effects can be taking place: firstly, a magnetic field effect either from the closure field of domain walls or from the component of magnetization normal to the film surface; secondly, the first-order effect discussed by de Gennes¹ which is caused by the exchange field of the magnetic layers; and thirdly, a second-order effect which can be called an impurity effect and is similar to the one found in dilute alloys.

Most of the experiments described in this study were performed with films of magnetite (Fe_3O_4). The magnetite films were prepared as follows: A powder mixture (8 parts Fe powder to 92 parts Fe_2O_3 powder) was pressed into the form of a button and sintered for 2 h at 700°C in an argon atmosphere; after pressing an iron stem into this button, this target was used in conjunction with the getter sputtering technique² to deposit a film usually 2000 \AA thick. The Fe_3O_4 films had the spinel cubic structure of bulk Fe_3O_4 and a room-temperature resistivity of 0.01 $\Omega \text{ cm}$ which is close to that of bulk magnetite ($7 \times 10^{-3} \Omega \text{ cm}$); the resistivity of the Fe_3O_4 films increased to 100 $\Omega \text{ cm}$ at 77°K which again is in agreement