pared with Eq. (5), $G=t_0^2(\frac{1}{2}C^2-\omega C)$, and we obtain the following parameters: $t_0\simeq 9$ nsec and $C=14\times10^{-2}$ nsec^{-1}. The value of t_0 agrees well with the number estimated from the time dependence of G [Fig. 1(c)]. The accuracy of C is limited here due to the uncertainty in the absolute frequency scale.

We have measured for $\omega=0$ the dependence of G upon absorption coefficient α between $\alpha=0.03$ and 0.16 cm^{-1}. Good agreement was found with the α^2 dependence predicted from Eq. (5). The parameters t_0 and C obtained from this investigation agree well with the data discussed above.

In conclusion it should be noted that the good agreement between theoretical and experimental transient gain allows a ready determination of material parameters. For instance, the value of c_p can be determined with a single laser pulse. A detailed account of this work will be published elsewhere.

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PIEZOELECTRIC EFFECTS IN LIQUID CRYSTALS*

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A theory of the relationship between curvature strains and electric polarization in liquid crystals is developed in analogy to piezoelectric theory in ordinary crystals. The theory may explain some recently observed phenomena in nematic liquid crystals.

There is currently a great deal of interest in electric field effects in liquid crystals, especially in connection with electro-optical phenomena. Although it has been recognized that an electric field can affect the internal structure of a liquid crystal by acting on the anisotropy of the dielectric constant, many of the observed field effects cannot be explained by this interaction alone. It has been suggested occasionally that nematic liquid crystals may be ferroelectric, which would aid in explaining some of the unusual field effects. However, the generally accepted symmetry properties of nematic and cholesteric liquid crystals are incompatible with ferroelectricity.[1] In this Letter, another kind of interaction between an electric field and liquid-crystal structure is shown to be compatible with the symmetry properties generally attributed to liquid crystals, and it is shown how this interaction can explain some unusual effects observed in nematic liquid crystals.

Frank has demonstrated through symmetry arguments the intrinsic relationship between splay strains and electric polarization in liquid crystals; both splay and polarization are manifestations of polar symmetry.[1] In his curvature elastic theory of liquid-crystal structure, Frank shows that if there is an intrinsic polarity in the molecular ordering of a liquid crystal, then that liquid crystal in its lowest energy structure will tend to be uniformly splayed and ferroelectric. He notes also that since no continuous three-dimensional structure can contain uniform splay, this polar liquid crystal would have a fine domain structure, with approximately optimum splay in each domain, and would be space charged as well as surface charged.

An extension of Frank's ideas is the consideration of cases in which a nonpolar liquid crystal is neither spontaneously splayed nor ferroelectric, but either splay or polarization is externally induced in the structure by mechanical stress or an electric field, respectively. By changing the symmetry of the system from nonpolar to polar, the presence of splay will then induce polarization, or vice versa. The effects should be strongest in systems whose molecules possess a large shape polarity as well as a large permanent dipole moment parallel to their long dimension. In the absence of external influences, such a system can form an ordinary liquid crystal in which the molecules are randomly oriented, end for end, so that the average structural symmetry is nonpolar. However, splay will polarize the substance by acting on the shape polarity, and an electric field will splay the structure by aligning the permanent dipole moments. Such a case is shown schematically in Figs. 1(a) and 1(b).

One can set up a formal theory of these electromechanical effects in liquid crystals in exact analogy to piezoelectric theory in ordinary crystals, although the physical origins of the effects and the strains involved in the two cases are entirely dissimilar.[2] The notation and definitions of curvatures in liquid crystals given here follow those in Frank's detailed discussion of curvature elastic theory.[1]

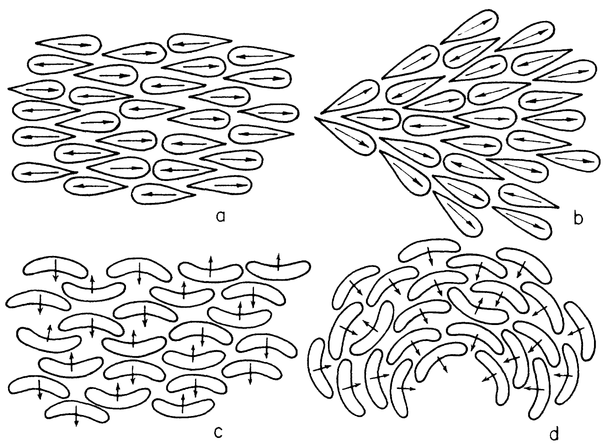

FIG. 1. (a) and (c) Unstrained nematic structures containing polar molecules. (b) Splayed structure in which splay and polarization are coupled by the wedge shape of the molecule. (d) Bent structure in which the bending and polarization are coupled by the crescent shape of the molecule.

The local structure of a liquid crystal is assumed to have uniaxial symmetry, the symmetry axis at a point being parallel to the direction of preferred orientation of the molecules near that point. If the local symmetry axis is denoted by a unit vector $\vec{L}$, then the structure of the liquid crystal is given by specifying $\vec{L}$ as a function of position throughout the liquid crystal. In terms of a local Cartesian coordinate system (x,y,z) in which $\vec{L}=\hat{z}$ at the origin, one can define the curvature strains at the origin as the nonzero spatial first derivatives of $\vec{L}$:

$$\text{splays,}\quad a_1=\partial L_x/\partial x,\quad a_5=\partial L_y/\partial y;$$

$$\text{bends,}\quad a_3=\partial L_x/\partial z,\quad a_6=\partial L_y/\partial z;$$

$$\text{twists,}\quad a_2=\partial L_x/\partial y,\quad a_4=\partial L_y/\partial x.$$

It will be useful to define splay and bending vectors:

$$\vec{S}\equiv(a_1+a_5)\vec{L}=\vec{L}(\nabla\cdot\vec{L}),$$

$$\vec{B}\equiv(a_3\hat{x}+a_6\hat{y})=(\vec{L}\cdot\nabla)\vec{L}.$$

A differential change in the internal energy density at the origin of this local coordinate system, including only curvature and electric effects, is given by

$$dU=t_i da_i+(1/4\pi)E_n dD_n,\quad i=1\text{ to }6,$$
$$n=x,y,z.$$

The t_i are torques conjugate to the curvatures a_i, and $\vec{E}$ and $\vec{D}$ are the electric field and displacement. In terms of these variables alone, one can define three other thermodynamic potentials to derive piezoelectric equations for any pair of independent variables, one electric and one mechanical.

Considering the independent variables a_i and $\vec{E}$, one can use the "electric enthalpy" $H_E=U-\vec{D}\cdot\vec{E}/4\pi$ to derive the equations for a nematic liquid crystal:

$$\partial H_E/\partial a_i=t_i=k_{ij}^{E}a_j-e_{in}E_n,$$

$$-4\pi\partial H_E/\partial E_n=D_n=4\pi e_{in}a_i+\epsilon_{nm}^{a}E_m.$$

The piezoelectric coefficient e_{in} appears twice because of a Maxwell relation.

The k_{ij}^{E} are the curvature elastic constants at constant $\vec{E}$. Ignoring second-order effects, they are the same as the k_{ij} discussed by Frank, who has derived the general form of the nematic k_{ij}

matrix from the symmetry properties of the local nematic structure. These symmetry properties include infinite rotational symmetry about $\vec{L}$, twofold rotational symmetry about all axes perpendicular to $\vec{L}$, and reflection symmetry in planes parallel or perpendicular to $\vec{L}$. This symmetry gives ϵ only two independent nonzero elements, ϵ_{zz} and $\epsilon_{xx}=\epsilon_{yy}$.

The piezoelectric tensor has only four nonzero elements, two of which are independent. The elements $e_{1z}=e_{5z}$ describe the interaction discussed earlier between splay strains and polarization parallel to $\vec{L}$. The elements $e_{3x}=e_{6y}$ describe the interaction between bending and polarization perpendicular to $\vec{L}$, a result not immediately evident from Frank's discussion. This bending effect would be most evident in systems containing bananalike molecules with a permanent dipole moment perpendicular to the long dimension of the molecule, as shown in Figs. 1(c) and 1(d). For many applications it is useful to express $\vec{D}$ in a coordinate-free form, which can be done using the vectors $\vec{S}$ and $\vec{B}$:

$$\vec{D}=4\pi e_{1z}\vec{S}+4\pi e_{3x}\vec{B}+\epsilon_{xx}\vec{L}\times\vec{E}\times\vec{L}+\epsilon_{zz}\vec{L}(\vec{E}\cdot\vec{L}).$$

The local structure of a cholesteric liquid crystal is believed to be the same as that of the nematic except that it lacks reflection symmetry. However, the general form of the piezoelectric tensor is the same for both nematic and cholesteric. In smectic liquid crystals, which may have the point symmetry of either the nematic or the cholesteric crystals, bending is generally unallowed because of the layer structure of these materials. However, the splay effects should still occur.

Because the strains involved in the liquid-crystal piezoelectric effects are curvatures rather than the tensile and shear strains that are involved in the usual homogeneous field crystal piezoelectric effects, the geometric aspects of the liquid-crystal effects are entirely different from the geometry of the usual crystal effects. For instance, a crystal structure with a center of symmetry exhibits no homogeneous-field piezoelectric effects, while a liquid crystal with a center of symmetry is piezoelectric in the sense discussed here. Since the strains are curvatures, $\nabla\cdot\vec{P}$, in which $\vec{P}$ is the polarization, is seldom zero, so that strained structures are usually space charged. This produces internal sources of electric fields which may not be negligible in their effects, and which therefore complicate the calculation of equilibrium structures and polarizations. Also because the strains are curvatures, the field-induced structural changes can be quite complex, and often reach their equilibrium configuration quite slowly compared with crystal piezoelectric strains.

There is one sample geometry in which the effects are very simple, that in which the sample is contained between coaxial cylindrical electrodes, and its internal structure is determined by the boundary conditions on $\vec{L}$ at the electrodes. In piezoelectric parlance, the sample is mechanically clamped. If the boundary condition is that $\vec{L}$ be perpendicular to the surfaces, then $\vec{L}$ will ideally be a radial vector throughout the sample. In cylindrical coordinates (r,θ,z), $\vec{L}=\hat{r}$. Then there is pure splay, $\vec{S}=\hat{r}/r$. In the electrically free case, $\vec{E}=0$ and $\vec{D}=4\pi e_{1z}\vec{S}$. If the boundary conditions can be suitably controlled so that $\vec{L}=\hat{\theta}$, one has a case of pure bend, $\vec{B}=-\hat{r}/r$, and $\vec{D}=4\pi e_{3x}\vec{B}$. Note that in this geometry $\nabla\cdot\vec{P}=0$, so the polarization produces only surface charge, making this case analogous to a plane-parallel capacitor containing a slab of piezoelectric crystal. The total surface charge per unit length of cylinder is independent of the radii of the electrodes, and this charge is given by $2\pi e_{in}$ statcoulomb/cm in the case $E=0$. This offers a direct means for measuring the piezoelectric constants. This total charge can be estimated in the following way. Consider a wedgelike molecule with a wedge angle of a few degrees. Then the total 360° splay of $\vec{L}$ around the cylinder represents a radial polarization of about 100 molecules in any one-molecule-thick ring around the cylinder. If the permanent molecular moment is about 0.1 electron Å and the molecular dimensions are a 5-Å diameter by a 20-Å length, this gives a total surface charge of 10^7 electrons/cm.

There are several experimental observations that may be explained by these effects. At the temperature of the nematic-isotropic transition, one can obtain a number of small (50-μ) droplets of nematic material floating in the isotropic liquid. The structure of these droplets contains two singular points on opposite sides of the droplet. At each singular point there is a large splay, and there is also bending in the structure. We have observed[3] that the droplets tend to stick together in chains, with the singular points in neighboring droplets near their point of contact. The mutual attraction between droplets may be due to the electric field produced by curvature-induced space charge, which is largest near the singular points. The material in which the effect

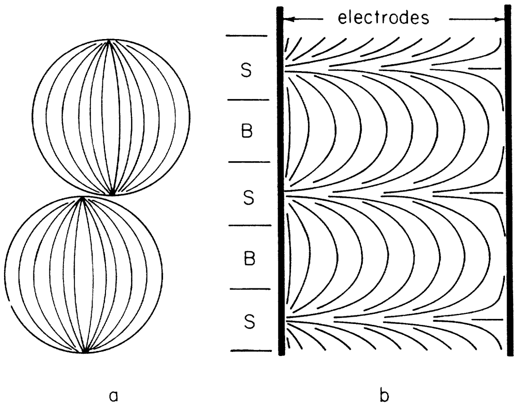

FIG. 2. Nematic structures exhibiting piezoelectric effects. The local symmetry axis is parallel to the lines. (a) Nematic droplets attracting one another because of curvature-induced space charges. (b) Cross section of a field-induced domain pattern between plane-parallel electrodes, containing alternating regions of splay (*S*) and bending (*B*).

has been noticed (*p*-azoxyanisole) does have a permanent molecular moment. One can test this theory by observing the behavior of droplets of various nematic materials, with and without polar molecular structure, to see if mutual attraction takes place only when a permanent moment is present. One difficulty of the experiment is obtaining materials without ionic impurities which would depolarize the droplets. The droplet effect is shown schematically in Fig. 2(a).

Another experimental observation which might be explained by these effects is the domain formation in a nematic material in a moderate electric field.[4] Consider a plane-parallel capacitor containing nematic material which in the absence of an electric field has a structure with $\vec{L}$ parallel to the electrode surfaces. Ignoring current effects, and assuming that the dielectric constant is approximately isotropic, the piezoelectric effects alone will induce curvatures in the structure when a field is present. If e_{1z} and e_{3x} have opposite signs, this can produce a stripelike domain pattern with alternating regions of splay and bending. A cross section of such a pattern for a dc field is shown in Fig. 2(b).

To find the exact form of such a domain pattern, one must find $\vec{L}$ as a function of position in the sample which minimizes $\int H_E d^3r$, at constant $\vec{E}$, using the form

$$H_E = \tfrac{1}{2}k_{11}S^2 + \tfrac{1}{2}k_{22}(\vec{L}\cdot\nabla\times\vec{L})^2 + \tfrac{1}{2}k_{33}B^2 - e_{1z}\vec{E}\cdot\vec{S} - e_{3x}\vec{E}\cdot\vec{B} - (1/8\pi)[\epsilon_{xx}(\vec{E}\times\vec{L})^2 + \epsilon_{zz}(\vec{E}\cdot L)^2].$$

For the stripelike domain pattern, far from the surfaces, this reduces to a one-dimensional problem. If one makes the simplifying assumptions that $\epsilon_{xx} = \epsilon_{zz}$, $k_{11} = k_{33}$, and $e_{1z} = -e_{3x}$, then

$$H_E = \tfrac{1}{2}k_{11}(d\theta/dv)^2 - e_{1z}E(d\theta/dv) - \epsilon_{zz}E^2,$$

in which v is the dimension parallel to the electrodes in Fig. 2(b) and θ is the angle between $\vec{L}$ and $\hat{v}$. H_E is minimized by $\theta = e_{1z}Ev/k_{11}$, which makes the curves in Fig. 2(b) secant curves, far from the surfaces, and the domain width $\pi k_{11}(e_{1z}E)^{-1}$. Because the formation of such a pattern will involve discontinuous structural changes, it will probably exhibit hysteresis in low frequency fields, which may account for the seemingly ferroelectric behavior of this kind of sample.

Another possible application of these effects may be in interpreting some of the potentials and ion distributions observed in liquid-crystalline biological structures.

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