Can liquids be macroscopically polar?

Can liquids be macroscopically polar?

S T Lagerwall

Physics Department, Chalmers University of Technology, S-412 96 Göteborg, Sweden

Abstract. We will discuss the meaning of piezo-, pyro-, ferro- and antiferroelectricity (defined for solids) and their possible appearance in the liquid state. We will do this using general symmetry principles as a starting point. The arguments will also be used for the prediction of non-linear optical properties in the liquid state.

1. Introduction

I am going to talk about polar materials and review the phenomena of piezo-, pyro- and ferroelectricity, the latter of which has only recently been found in liquid crystals. The question is whether it could appear in other liquids as well. The three phenomena mentioned are really characteristic for solid crystals, so I will often have to refer to them in that context. Later we will see whether the designations can be meaningfully transferred to liquid matter, and if so, to which categories.

The basic and starting point is how matter behaves in an externally applied field. Insulating (non-conductive) materials are called dielectrics. Almost all of them respond electrically in the same way to external action: they get polarized and the polarization increases linearly, at least at the beginning, with the applied field. This means that the polarization changes sign together with the field and is reduced to zero when the field is taken away. The exceptions to this behaviour are relatively rare, but of such scientific interest and technological importance that they have merited special names. These exceptions are of two kinds, or hierarchies, which in the case of solid crystals can easily be singled out on the basis of symmetry; cf. figure 1. Of the 32 crystal point groups, 20 are piezoelectric, with the meaning that materials belonging to these groups acquire a polarization in the absence of electric field when an external stress (often this means pressure) is applied. The polarization is linear in, and thus changes sign with, the stress. The linearity of the effect furthermore implies that an electric field applied to the crystal will cause the crystal to be strained (the inverse effect). The basic (but not sufficient) requirement for piezoelectricity is that the material lacks a centre of symmetry.

Within the 20 piezoelectric classes there is a higher hierarchy level limited to 10 classes, called pyroelectric, in which a polarization appears *in the absence* of both external electric field and external pressure. Hence these materials have an intrinsic macroscopic polarization. In order to have this their crystal structure must have a direction, the polarity of which cannot be reversed by any symmetry operation of the medium. The same must be valid for a liquid: only if we can intrinsically define such a direction as just mentioned, it might have a macroscopic polarization. The word *macroscopic* should be stressed. There are many examples of simple liquids consisting of polar molecules as well as more complex

Dielectrics   (32 point groups)

Piezoelectrics (20)

Pyroelectrics (10)
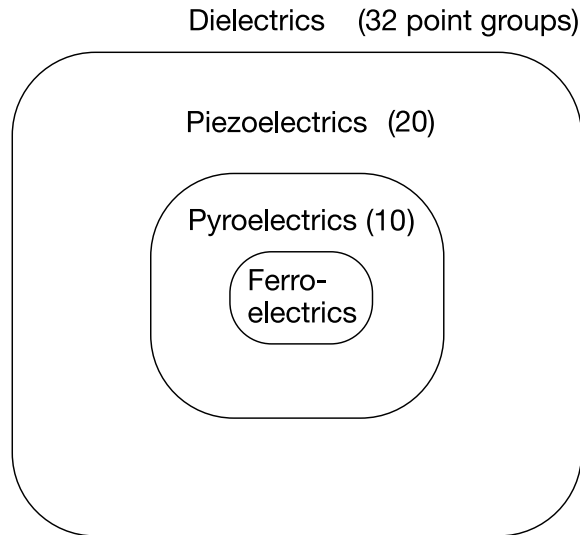
Ferro-
electrics

Figure 1. The hierarchy of dielectric materials. A dielectric without special properties is simply called a dielectric, if it has piezoelectric properties it is called a piezoelectric, if it further has pyroelectric but not ferroelectric properties it is called a pyroelectric etc. A ferroelectric is always pyroelectric and piezoelectric, a pyroelectric always piezoelectric, but the reverse is not true. Knowing the crystal symmetry we can decide whether a material is piezoelectric of pyroelectric but not whether it is ferroelectric.

liquids which may show varying kinds of intrinsic polar order not adding up to a macroscopic polarization. When a macroscopic polarization is present, usually in the form of spontaneous domains, i.e. macroscopic parts characterized by a certain polarization direction, the medium interacts with external fields in a completely different way than otherwise, reminding us about the behaviour of magnets.

While magnetic properties have been known of since ancient times, the recognition that matter can be electrified is of more recent date. Pyroelectricity was discovered in about 1700 by Dutchmen in foreign trade when they brought tourmaline from Ceylon to Europe. They observed how these rodlike crystals acquired a force to attract light objects, like small pieces of paper, when heated. The first scientific description was given by the German F M Hoeck (Aepinus) in 1756, and David Brewster in Scotland, who made a systematic study on a number of minerals, coined the name pyroelectric in 1824. However, one had to wait until our century to really get an understanding of the phenomenon, and the historical name ('pyro' etymologically related to fire) is a very unfortunate one. It is true that a change ΔT in temperature causes the appearance of a polarization P, and pyroelectricity is often defined this way. Still, it is not really the heart of the matter. The basic thing is that a pyroelectric has a spontaneous macroscopic polarization, i.e. is an electric dipole in the absence of an external field. The charged poles normally cannot be observed because they are neutralized in a rather short time by the ubiquitous free charges which are attracted by the poles. (Because there are no free magnetic charges such a screening does not occur in a magnet, which makes magnetic phenomena simpler in many respects than the corresponding electric ones.) However, the magnitude (and in rare cases even the direction) of the polarization is generally a function of temperature, $P = P(T)$. Hence a change ΔT in temperature causes an additional polarization ΔP which is not compensated by the present charges and can be observed (normally in a matter of minutes) until the redistribution

of charges to equilibrium has been completed. This is also one of the standard methods for measuring polarization: the pyroelectric current is integrated through an external circuit after firing a heat pulse from an infrared laser.

Research on pyroelectricity in France led to the discovery of piezoelectricity by the brothers Pierre and Jacques Curie in 1880. Its subsequent strategic importance during the first world war (the development of sonar for submarine detection etc) led to the discovery of ferroelectricity in Rochelle salt by Joseph Valasek at the University of Minnesota in 1920. Modern, powerful ferroelectric materials, like barium titanate, were synthesized mainly in wartime research efforts around the time of the second world war.
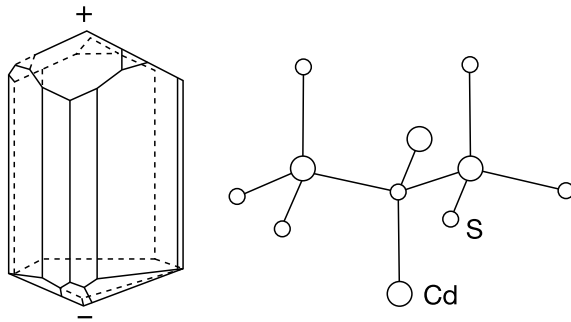
Figure 2. The point group of tourmaline is $3m$ (C_{3v}) with a threefold vertical axis and three vertical mirror planes. Because there is no horizontal mirror plane there is really an 'up' and a 'down' side in these crystals directly observable in the crystal habit. On cooling, the crystal becomes a dipole with a positive charge appearing on the 'up' side. In the much simpler (wurtzite) structure of cadmium sulphide, $6mm$ (C_{6v}), it is easy to see how the centres of gravity of positive charges do not coincide with those of negative charges and, thus, how a dipolar structure is rigidly built into the crystal lattice.
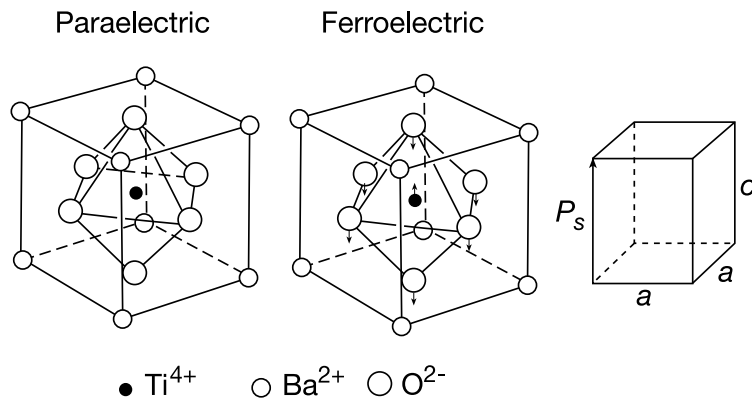
Figure 3. The structure of barium titanate, cubic above 120 °C and tetragonal below that temperature.

In a pyroelectric material like tourmaline or cadmium sulphide the polar dissymmetry is manifest in the crystal lattice, built in rigidly when the crystal is grown. This is even reflected in its crystal habit, which in a well-grown specimen shows a pronounced up side and down side; cf. figure 2. If we apply an electric field along or opposite to the polarization direction it has practically no effect on the polarization which is locked in by the lattice
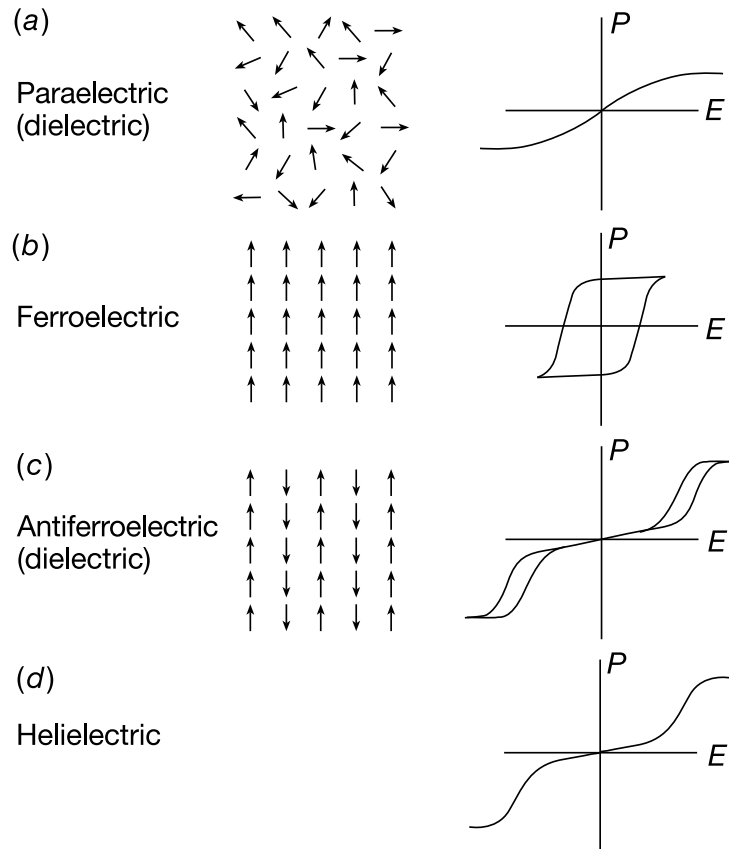
Figure 4. The response characteristics of polar materials in an external electric field.

and, in particular, cannot be reversed. We see here another difference between electric and magnetic phenomena in matter: the spins in a magnetic material are never locked in the same way to the lattice. We may, however, consider a structure which is only a very short distortion along one direction from being cubic, like the example of $BaTiO_3$ in figure 3. This is the equilibrium state at room temperature and the crystal constitutes a dipole along the tetragonal c-direction. (In contrast, a cubic crystal, for symmetry reasons, cannot have a macroscopic polarization—no more than it can have a macroscopic magnetization.) But in this case, if we apply a sufficiently high electric field opposite to the P-direction we can undo the small inner distortion of the atoms and reverse it (the transition state is the cubic one) to the energetically equivalent but opposite distortion. Materials in which the polarization behaves in this way constitute the very special and all-important subclass of pyroelectrics called ferroelectrics. Although several kinds of ferroelectric may be distinguished, their prime distinction from all other materials is that they not only have a macroscopic polarization but also *two stable states* in the absence of a field, and that the polarization can be reversed between these states by application of an electric field. In this they are thus very similar to ferromagnets and their name, given by Erwin Schrödinger in his Habilitation Thesis (1912, eight years before the actual discovery of such materials) certainly reflects this. In analogy to ferromagnetic materials, ferroelectric crystals in the absence of a field generally show domains of homogeneous polarization, arranged in such a

way that the macroscopic polarization of the sample is zero and such that $\nabla \cdot \boldsymbol{P} = 0$ (zero local charge density). In contrast, a pyroelectric crystal has no domains—it is a monodomain as long as the crystal is not crystallographically twinned.

In figure 4 we have illustrated how polar materials may behave in response to an external electric field $\boldsymbol{E}$, by tracing the polarization P as a function of E. By polar materials we mean any kind of matter characterized by local dipoles, for instance a liquid consisting of dipolar molecules or a solid with dipoles distributed randomly or with any kind of specific order, for instance such that we have two sublattices with polarization that is homogeneous but opposite in direction, compensating each other (antiferroelectric). Except for in piezoelectric materials, the P–E trace is the fingerprint of the category that we are dealing with and is also characteristic of the technological potential. In (a) there is the normal dielectric response with P increasing linearly up to a saturation value at high fields. In principle this behaviour is the same whether we have local dipoles or not, except that with local dipoles the saturation value from orientational polarizability will be high (as compared to that from displacement polarizability) and strongly temperature dependent as the thermal agitation counteracts the alignment of the dipoles along the field. If the molecules lack permanent dipoles, the induced local polarization is always along the field and temperature independent. Dipolar molecules may, on the other hand, align spontaneously at a certain temperature (the Curie temperature) to a state of homogeneous polarization. On approaching such a temperature the susceptibility $\partial P/\partial E$ takes on very high values and is strongly temperature dependent. We will describe this state, unpolarized in the absence of a field, but with a high and strongly temperature-dependent value of the dielectric susceptibility, as paraelectric, independently of whether there actually is a transition to an ordered state or not. It should be noted that a piezoelectric material has the same shape of the P–E curve as a normal dielectric (it may show paraelectric behaviour) because an applied electric field causes a linear strain (the converse piezoeffect) which in turn causes a linear polarization.

The contrasting very strong non-linear response of a ferroelectric is shown in figure 4(b). The two stable states $(+\boldsymbol{P}, -\boldsymbol{P})$ at zero field constitute the most characteristic feature of this hysteresis curve which also illustrates the threshold (coercive force) that the external field has to overcome in order to flip over one state into the other. The response of the antiferroelectric state is shown in (c). The initial macroscopic polarization is zero just as in a normal dielectric and the P–E relation is linear, like in (a) at the beginning until, at a certain threshold, one lattice polarization is flipping over into the direction of the other (the external field is supposed to be applied along one of the sublattice directions). The very characteristic double-hysteresis loop reveals the existence of two sublattices as opposed to a random distribution of dipoles as in (a). In the limit where the hysteresis loops shrink to thin lines as in (d) we get a special kind of response on which we will comment later. In the hierarchy of figure 1, and in the logic of what has just been said, antiferroelectric materials belong to the 'undistinguished' dielectrics, outside of the 20 piezoelectric groups. They show, for reasons of symmetry, neither piezoelectric nor pyroelectric response.

There is a certain tendency to just call everything which has some polar character 'ferroelectric'. However understandable this might be, in particular because the word pyroelectric is not very descriptive when we are thinking of a polarization and not of a temperature effect, this habit should be strongly discouraged, as it only leads to confusion. Of course, the words piezo- and pyroelectric must also be used with the same care. It must be underlined that it is the *electric response*—cf figure 4—which decides to which category a material belongs. Indeed, an important function of the name is to give information about the P–E relation.

The presence of two stable states in figure 4(b) indicates that a ferroelectric material
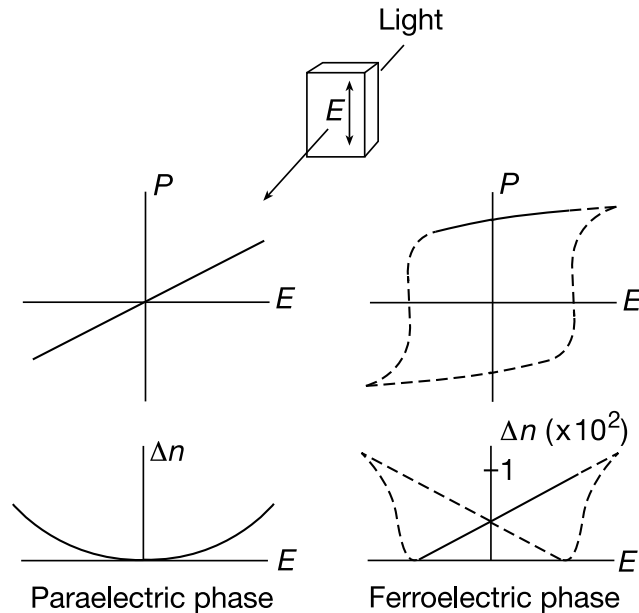
Figure 5. The two electro-optic effects in ferroelectric materials like barium titanate. In the symmetric high-temperature phase the quadratic Kerr effect ($\Delta n \sim E^2$) is observed, while the less symmetric phase ($T < 120\,^\circ$C) always shows a non-zero birefringence, the variations of which are linear in the applied field (the Pockels effect).

basically has memory properties, just like a ferromagnetic material. The fact that it has not yet been possible to develop ferroelectric memory devices is related to the very involved interactions with charge carriers and to the fact that switching between the two states is normally coupled to a change in lattice distortion which may eventually cause a total breakdown of the lattice (crystal fatigue). If the same or an analogous phenomenon could be found for a liquid, this might be an attractive way to solve at least the second problem. Because of these inherent problems, solid-state ferroelectrics have, strangely enough, not found use for their ferroelectric properties, but rather because of their superior pyroelectric (heat detectors), piezoelectric and dielectric (very-high-ε) properties. In addition they are the dominating electro-optic materials as Pockels modulators—cf. figure 5—as well as in non-linear optics, e.g. second-harmonic generation.

2. Liquids

Can liquids in which the constituents are dipoles be ferroelectric or piezoelectric? For instance, if we could make a colloidal solution of small particles of the ferroelectric BaTiO$_3$, would this liquid be ferroelectric? The answer is no, it would not. The response in an electric field would be that pictured by figure 4(a). It is true that the liquid would have a very high value of dielectric susceptibility and we might call it superparaelectric in analogy with the designation often used for a colloidal solution of ferromagnetic particles which likewise does not show any collective behaviour. An isotropic liquid cannot have a polarization in any direction because every possible rotation is a symmetry operation and this of course is independent of whether the liquid lacks a centre of inversion (is chiral) or not. Hence, at least we have to diminish the symmetry and go to anisotropic liquids, that is, to liquid

crystals, in order to examine an eventual appearance of pyroelectricity or ferroelectricity. Naturally, an isotropic liquid consisting of dipoles may show a polarization during flow, because a shear diminishes the symmetry and will partially order the dipoles, thus breaking the randomness. This order will be polar if the liquid is chiral. But we will not consider such a liquid pyroelectric—no more than we would consider a liquid showing flow birefringence a birefringent liquid. Nevertheless, it is clear that there will be lots of interesting polar effects in flowing liquids, particularly in ones of biological significance (which are mostly chiral).


(a) Nematic (N) *(b)* Smectic A (A)
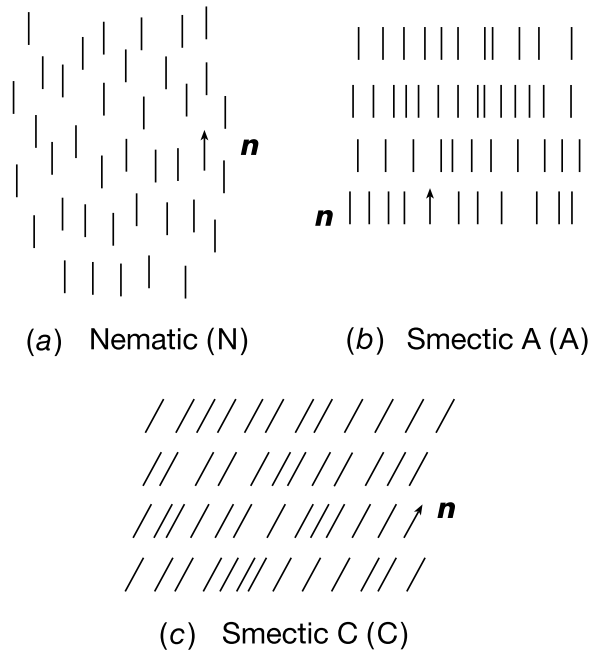
(c) Smectic C (C)

Figure 6. Molecular arrangements characteristic of (*a*) nematic, (*b*) smectic A and (*c*) smectic C liquid crystals. The average local direction is indicated by a unit vector n, called the director.

The most common kind of anisotropic liquid is the nematic liquid crystal shown very schematically in figure 6(*a*). It is a three-dimensional liquid, in which the normally rodlike molecules because of van der Waals and steric interactions tend to be locally parallel. This locally preferred direction is conventionally represented by a unit vector $n(r)$ called the director, which is a sort of local symmetry axis. Even if a single molecule is rather unsymmetric in shape and polarity, such effects are averaged out by the rapid rotation around its long axis and also by heads and tails being equally distributed up and down. Hence the nematic phase has cylindrical symmetry around the director and is invariant under the change of sign in n, i.e. under the condition

$$n \to -n. \tag{1}$$

This invariance also means that a nematic liquid is strictly non-polar. The actual molecules might constitute dipoles (they almost always do) but their long axes are distributed in such a way around the average direction (the director n) that if we describe it in terms of Legendre polynomials $P_n(\theta_i)$ where θ_i is the angle of the ith molecule relative to n, then the first
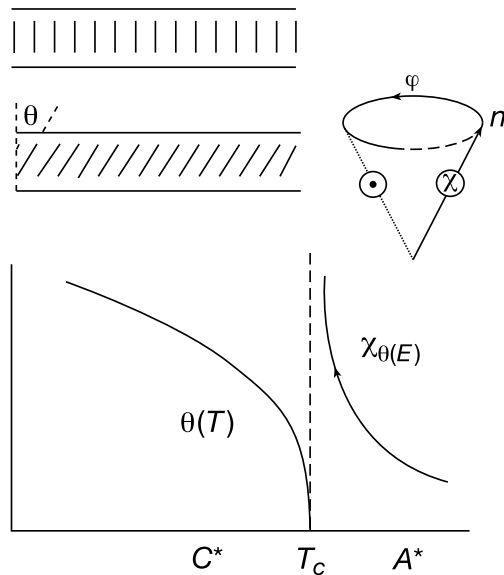
Figure 7. The phase transition A → C and the conical degeneracy of director in the tilted phase. If the substance is chiral (denoted by an asterisk, C*, A*) a tilt can be induced by an electric field above T_c, with the corresponding susceptibility diverging at T_c.

non-zero polynomial is P_2,

$$P_2 \equiv \tfrac{1}{2} \langle 3\cos^2\theta_i - 1 \rangle$$

where the angular brackets denote a local statistical average. For random orientation (isotropic liquid) $P_2 = 0$ and for perfectly parallel alignment $P_2 = 1$. P_2 is therefore commonly used for the scalar part of the nematic order parameter. Typically P_2 varies from around 0.6 at low temperature to around 0.4 at the transition to the isotropic phase where it suddenly goes to zero in a first-order transition, reflecting the fact that the orientation-dependent van der Waals attraction is no longer effective if the molecules are not sufficiently parallel. Even if higher moments like P_4 are sometimes used to more precisely characterize the nematic order, P_2 describes the nematic phase very well and we may say that the nematic has essentially quadrupolar order. The same is true of the smectic phases with P attaining slightly higher values as we go from nematic to smectic A to smectic C. The quadrupolar order along the director of course characterizes all liquid-crystal phases for which the invariance condition (1) is valid. In particular this means that P_1 (and other odd polynomials) are zero. Hence, whereas the molecule itself is a dipole, even the *local* polarization is zero, $\langle P \rangle = 0$, in a nematic. That is what we mean by non-polar. In this case we do not even have to ask whether a nematic could be *macroscopically* polar.

As for an eventual piezoelectric effect in the nematic phase, it can be ruled out immediately as pressure does not distort the director and because a liquid cannot sustain a static shear. We would therefore have to go to the other important class of liquid crystals, the smectics, in which one translational degree of freedom is crystalline. Smectic liquid crystals are layered and come in many different forms; however, in this context we will limit ourselves to the most important ones, labelled smectic A and smectic C, shown in figure 6(*b*) and 6(*c*), respectively. The difference between them is that the director is along the layer normal in the A phase, but inclined to it in the C phase. The layers are perfectly

fluid but confined to two dimensions: these smectics are thus liquids in two dimensions and solids in one. In most substances where these phases appear, a second-order phase transition A → C occurs at a certain temperature T_c, below which the molecules start to tilt, and with an order parameter that can be written as $\psi = \theta e^{i\varphi}$, where θ is the tilt angle with respect to the normal and φ is the azimuthal angle indicating the direction of tilt in the layer plane. The variable φ is a phase variable (the transition is helium-like) with huge fluctuations; the director in the C phase is therefore practically free to move on a cone with half-apex-angle θ around the layer normal. This is illustrated in figure 7.

We will now proceed to the question of whether any of the three liquid-crystal symmetries in figure 6 would be compatible with a macroscopic polarization, i.e. with an intrinsic polar vector in the medium. First of all, the fundamental invariance condition (1) means that if there is a polarization P in the medium, it cannot have a component along n, because the symmetry operation (1) reverses the sign of that component, and thus P must be perpendicular to n [1]:

$$P \perp n. \tag{2}$$

But a polarization P perpendicular to n in the nematic or smectic A state is impossible because these phases have cylindrical symmetry around n. Thus a rotation of 180° around n is a symmetry operation and would cancel any $P \perp n$. In the smectic C the situation is different. Because here the medium exhibits two non-collinear directions, n and z (the layer normal), we can form a vector $z \times n$ which could be a polar direction, except if the tilt plane (the plane of the paper in figure 6(c)) were a mirror plane, in which case the reflection symmetry operation would reverse and thereby cancel any polarization perpendicular to that plane. This means that a chiral smectic C, designated C*, would indeed permit a local polarization perpendicular to the tilt plane.

The symmetry arguments used so far go back more than 150 years. In fact, they have a great historical interest as being the first serious symmetry principles formulated in physics.

3. The Neumann and Curie principles

A student of today might think that elementary-particle physicists introduced the use of symmetry principles in physics. This is not at all the case. It began with Neumann, continued with Curie, and then invaded all of physics. (I thus leave the symmetry principles of Kepler aside, being metaphysical–aesthetic and not developable.) At first it was the symmetry and invariance of objects and properties (Neumann), then that of abstract things like electric and magnetic fields (Curie), and finally that of equations (Einstein, Weyl, Pauli and the whole modern school).

When we are dealing with the question of whether a material can be spontaneously polarized or not, or whether some external action can make it polarized, there are two principles of great generality which are still extremely useful, the Neumann principle and the Curie principle. The first (Neumann, 1833) says that any physical property of a medium must be invariant under the symmetry operations of the point group of the medium.

The second (Curie 1894) says that a medium subjected to an external action changes its point symmetry so as to preserve only the symmetry elements common with those of the influencing action. Symbolically we may write the Neumann principle as

$$\mathcal{K} \subseteq \mathcal{P} \tag{3}$$

i.e. the crystal group either coincides with $\mathcal{P}$, the property group, or is a subgroup of $\mathcal{P}$,

and the Curie principle as

$$\tilde{\mathcal{K}} = \mathcal{K} \cap \mathcal{E} \tag{4}$$

i.e. the point symmetry $\mathcal{K}$ changes to $\tilde{\mathcal{K}}$, the highest common subgroup of $\mathcal{K}$ (the crystal group) and $\mathcal{E}$ (the external-influence symmetry group). This means that, in particular, if

$$\mathcal{K} \subset \mathcal{E} \tag{5}$$

then

$$\tilde{\mathcal{K}} = \mathcal{K} \tag{6}$$

i.e. if $\mathcal{K}$ is a subgroup of $\mathcal{E}$, then the crystal symmetry is not influenced by the external action.

The Neumann and Curie principles are the dominating symmetry principles in condensed-matter physics of today. Both can be formulated in a number of different ways. For instance, the Neumann principle may be stated as follows: 'the symmetry elements of an intrinsic property must include the symmetry elements of the medium'. This formulation stresses that every physical property may and often does have higher symmetry, but never less than the medium. A well-known example of this is that cubic crystals are optically isotropic, which means that the dielectric permittivity has spherical symmetry in a cubic crystal. A more general example is that physical properties characterized by polar second-rank tensors must be centrosymmetric, whether the crystal has a centre of symmetry or not.

How can we know that the Neumann principle is always valid? Consider, for the sake of the argument, that the crystal group $\mathcal{K}$ had a symmetry operation that was not contained in the property group $\mathcal{P}$. Then, under the action of this operation, the crystal would on the one hand coincide with itself, and on the other, change its physical properties. The inherent contradiction proves the validity of the principle. Some persons would tend to find this reasoning circular, in the sense that if there is a contradiction, it only means that the supposed symmetry of the medium was not correct. However, it is hard to deny that there is a predictive power in the principle, because once you *know* the symmetry of a medium you can tell whether a certain property is allowed or not. And if it were to happen that the property was ruled out according to Neumann's principle and at the same time was observed without doubt in the substance, then this falsification (and progress in the sense of Popper) would force us to revise the symmetry of the medium. Thus it is only circular in the same sense as other symmetry principles, and the assumed symmetry may have to be revised as it was when a parity experiment showed that the weak interaction is not invariant under reflection. A much more common case is however that an experiment badly performed or analysed *seems* to reveal a polarization on heating a piezoelectric material when the origin is just temperature gradients and therefore strains in the sample. (To extend pyroelectricity to such cases—equal to allowing a violation of the Neumann principle—would be just as inconvenient as saying that the law of conservation of momentum may be found to be violated 'in practice' in a number of cases.) At any rate Neumann's principle reveals the inherent contradictions of some of the current literature—as for instance in the not-so-rare teaching that quartz, with the point group 32, is pyroelectric [2], which is completely false. The fact that the point group is 32 means that there is a threefold principal axis and three twofold axes perpendicular to that axis. However, it is immediately clear that if a polarization were permitted along any rotation axis, there could not be a second rotation axis making an angle to this first one, without cancelling the polarization.
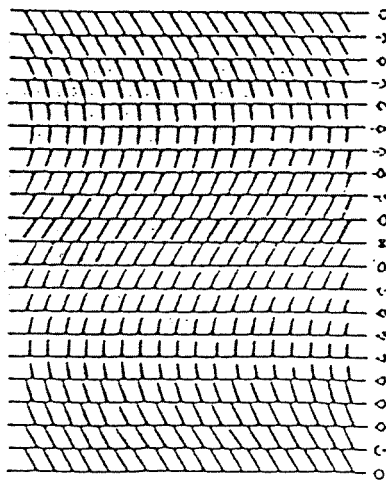
The general application of the Neumann principle in condensed matter is normally much more formalized (for instance involving rotation matrices) than we have had use for in our
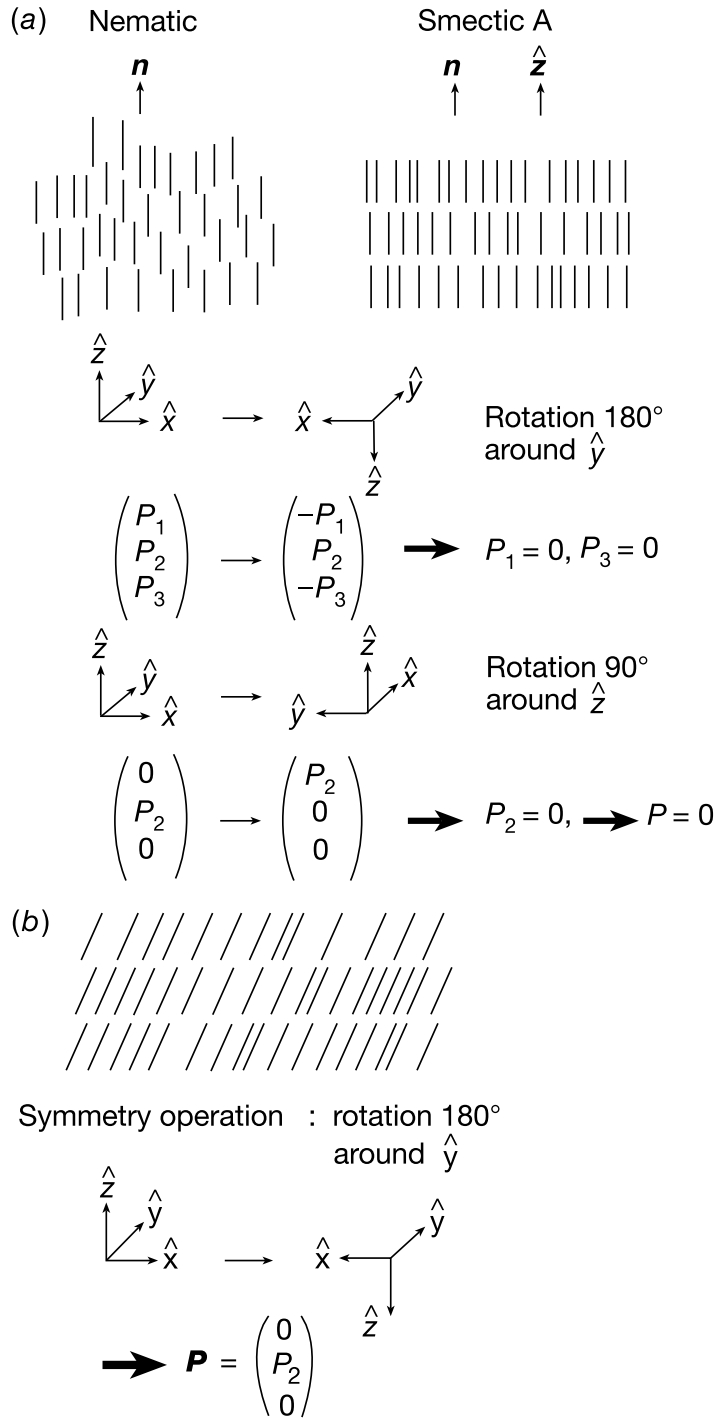
Figure 8. Neumann's principle applied to (*a*) the nematic and smectic A, (*b*) the smectic C and smectic C* phases.
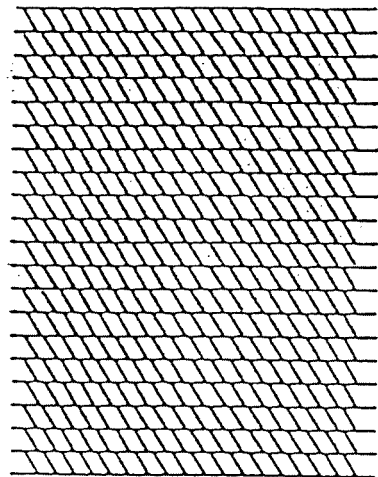
Figure 9. The (a) non-helical and (b) helical bulk director configuration in the smectic C and C* phases, respectively.

brief discussion above. Few textbooks perform such demonstrations on an elementary level, but there are exceptions, for instance the excellent treatise by Nussbaum and Phillips [3]. For a liquid crystal we are illustrating this simple way of using the symmetry operations of the medium in figures 8(*a*), 8(*b*) [4]. We choose the z-direction along the director as shown in (*a*) and assume that there is a non-zero polarization $P = (P_x, P_y, P_z)$ in a nematic or smectic A. Rotation by 180° around the y-axis transforms P_x and P_z into $-P_x$ and $-P_z$, and hence both of these components must be zero because this rotation is a symmetry operation of the medium. Next we rotate by 90° around the z-axis, which transforms the remaining P_y into P_x. We see that the symmetry operations of the medium are not symmetry operations of the property, in violation of Neumann's principle, and P must vanish. In the smectic C

a 180° rotation around the y-axis is still a symmetry operation, so $\boldsymbol{P}$ can have a component in the y-direction, as a 90° rotation around the z-axis is no longer a symmetry operation; cf. figure 8(b). But if the xz-plane is a mirror plane, then P_y must be zero. In order to let P_y survive we can put 'small propellers' on the molecules, i.e. make them chiral. We could for instance synthesize molecules with one or more asymmetric carbon atoms, but it would, in principle, also be sufficient to dissolve some chiral dopant in the medium in order to remove the mirror plane. In both cases the only symmetry element left would be the twofold rotation axis along the y-direction, and a polarization along that direction is thus allowed. The symmetry of the medium is now C_2 which is lower than the symmetry of the property. The polarization $\boldsymbol{P}$, like the electric field, is a polar vector, hence with the symmetry C_∞ (or ∞m in the crystallographic notation.)

It was the Harvard physicist R B Meyer who first recognized that the symmetry properties of a chiral tilted smectic would allow a spontaneous polarization directed perpendicular to the tilt plane, and in collaboration with French chemists he synthesized the first such materials in 1974 [5]. These were the first polar liquid crystals and as such something strikingly new. Of course, substances showing a smectic C* phase had been synthesized accidentally several times before by other groups, but their very special polar character had never been detected. Meyer called these liquid crystals ferroelectric. As it subsequently turned out, this was almost but not quite true. But a most important first step had been taken towards finding a ferroelectric behaviour.

4. Nature strikes back

According to the symmetry argument already given, the local spontaneous polarization $\boldsymbol{P}$ is sterically connected with the molecule, lying along $\pm z \times n$. (The plus-or-minus sign is a characteristic of the material.) But the prerequisite for the existence of $\boldsymbol{P}$ was that the molecules are chiral, and the chiral interactions between them lead to an incommensurate helical superstructure, as shown in figure 9(b). Actually there are two interactions involved in the helix, one chiral leading to a spontaneous twist and one non-chiral (steric) leading to a spontaneous bend deformation in the director field [6]. The phase angle φ describes a right- or left-handed helix with a period of typically some μm whereas the smectic layer periodic length is some nm. The helical arrangement makes the macroscopic polarization zero for the bulk sample at the same time as satisfying $\nabla \cdot \boldsymbol{P} = 0$ everywhere. It therefore is an alternative to the domain formation in a solid ferroelectric. But there is no coercive force in such a structure and if we apply an electric field perpendicular to the helix axis we will wind up the helix and turn more and more of the local polarization into the field direction; cf. figure 10(a). The P–E response is dielectric—in fact it has the shape of figure 4(d), corresponding to an antiferroelectric with an infinitely thin hysteresis loop. This behaviour is also known in the solid state, e.g. in the chiral structure of $NaNO_2$, and the order is called helicoidal antiferroelectric. A shorter useful name is helielectric. The helielectric smectic C* has zero macroscopic polarization (like an antiferroelectric), no hysteresis, no threshold, and no bistability. However, by artifice it can be turned into a structure with very different properties. This is illustrated in figure 10(b). If the smectic layers are made perpendicular to the confining glass plate, there is no boundary condition compatible with the helical arrangement. Let us assume that we can prepare the surface in such a way that the boundary condition imposed on the molecules is that they have to be parallel to the surface but without a specified direction. As we make the distance between the surfaces smaller and smaller, the conflict between the helical order and the surface order will finally elastically unwind the helix via the surface forces, and below a certain sample thickness the
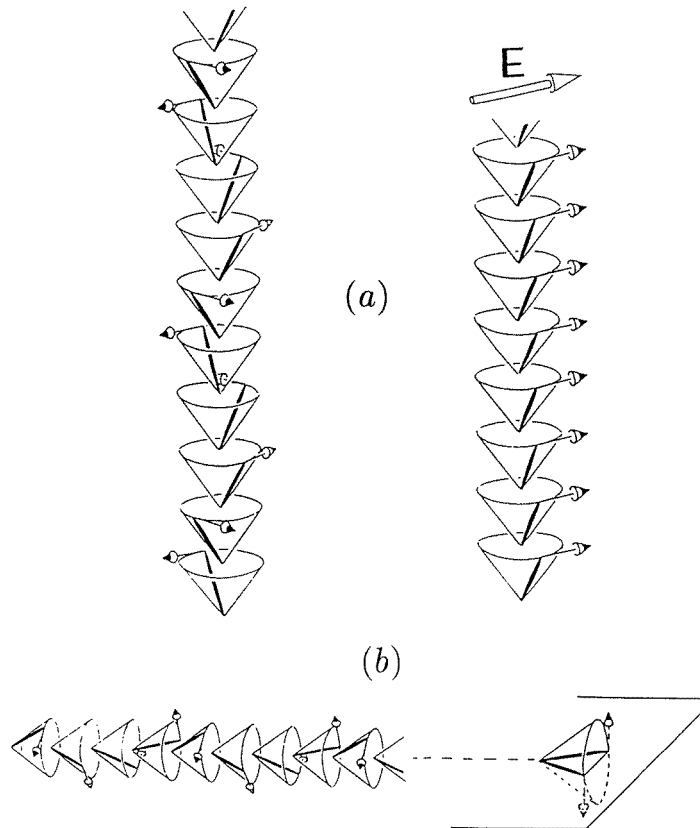
Figure 10. The helical configuration in smectic C* and its unwinding in an external electric field (*a*). The smectic layers are considered to be horizontal in the figure and the directors are confined to a cone around the layer normal. The elastic unwinding is illustrated in (*b*).
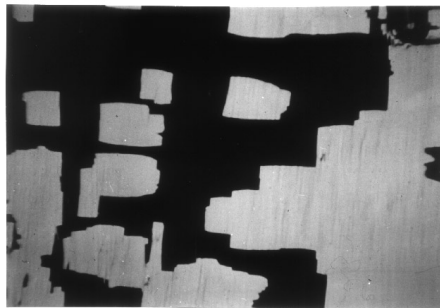
Figure 11. Spontaneous ferroelectric domains appearing in the surface-stabilized state.

helix cannot appear: the non-helical configuration has a lower energy. The physical problem has one characteristic length, which is the helical period p. We can therefore expect that for a sample thickness $d < p$, i.e. of the order of one micrometre, the only allowed director positions will be where the surface cuts the smectic cone, because here both the intrinsic conical constraint and the constraint of the surface are simultaneously satisfied. There are

two such positions, symmetrical around the cone axis and corresponding to polarization up and down, respectively. Energetically these states are equivalent, which leads to a symmetric bistability. Indeed, when very thin samples with $d \approx 1$ μm are made with the appropriate boundary conditions, spontaneous ferroelectric domains all of a sudden appear in the absence of any applied field (figure 11). This second step was realized five years after Meyer's first paper [7]. By applying an external field we can now get one set of domains to grow at the cost of the other and reverse the whole process on reversing the field. There are two stable states and a symmetric bistability; the response is according to figure 4(b). We might therefore call this structure a surface-stabilized ferroelectric liquid crystal (SSFLC). The surface stabilization brings the C* phase out of its natural crystallographic state and transfers macroscopic polarization to the bulk.
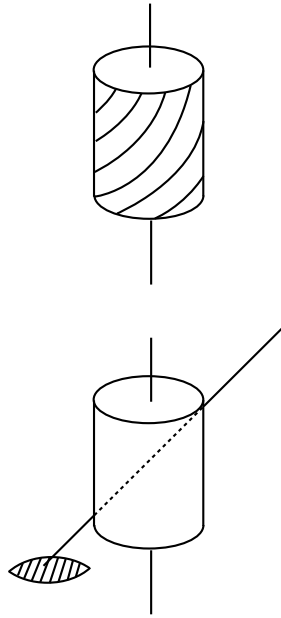
Figure 12. The point symmetry of the helical smectic C* state is D_∞ (∞22) illustrated by a twisted cylinder. The principal rotation axis is along the smectic layer normal and there are an infinite number of twofold rotation axes perpendicular to this axis. The symmetry does not allow pyroelectricity.
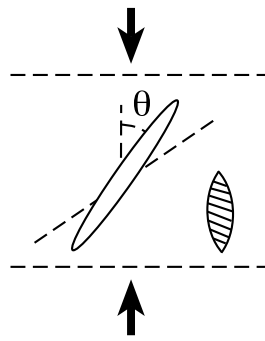
Figure 13. The surface-stabilized smectic C* has C_2 symmetry. A pressure applied across the layers increases the tilt angle and thereby the polarization ($P \sim \theta$) along the twofold axis which is perpendicular to the paper plane.

The helical smectic C* state has the point symmetry D_∞ (∞22), illustrated in figure 12, which does not permit a polar vector. It is therefore neither pyroelectric nor ferroelectric. Nor can it, of course, be piezoelectric, which is easily realized after a glance at figure 10(*a*): if we apply a pressure or tension vertically, i.e. across the smectic layers, in the helical structure shown to the left, no macroscopic polarization can appear. The only effect is that we change the pitch p of the helix. On the other hand, if we do the same to the surface-stabilized structure—cf. figure 13—we change the tilt θ and thereby the local polarization P which is proportional to the tilt; hence in the conformity with the statement that if a structure is ferroelectric it also, by necessity, should be piezoelectric. That this SSFLC structure with symmetry C_2 is also pyroelectric, as it must be, is also evident, because θ and thereby P is a function of temperature T. Because there is now a macroscopic polarization we have

a strong coupling with the external field leading to microsecond response, according to

$$\tau^{-1} \sim \boldsymbol{P} \cdot \boldsymbol{E}/\gamma \tag{7}$$

where γ is a characteristic viscosity for the motion around the cone (a Goldstone mode). The difference 2θ between the two optic axis directions—cf. figure 10(*b*)—leads to an electro-optic effect of high contrast. The high available contrast, the very high speed (about three orders of magnitude faster than in normal liquid crystals), together with the inherent memory, make this a very attractive electro-optic effect for a variety of applications, although very much more involved than conventional liquid-crystal effects and as yet far from developed to a mature stage [8].

As we have seen, smectic C* materials are not automatically ferroelectric but can always acquire this property in certain configurations (SSFLC). It is, however, important to point out that ferroelectricity is not a bulk property in liquid crystals. Thus, this 'ferroelectricity' is not a property of a liquid, not even of a liquid in two dimensions. One might be tempted to unwind the helix using chiral additives having opposite twisting power (and this is easily done) instead of unwinding it elastically using the surfaces and, on doing so, arrive at a structure of the kind depicted in figure 9(a). However, it turns out that even with a compensated helix (infinite pitch) the bulk structure twists in such a way as to cancel the total polarization. This is, after all, not too surprising for matter having liquid properties. In other words, bulk liquid crystals are always antiferroelectric in one way or another. Finally, we should mention that 'regular' antiferroelectric liquid crystals exist, where successive smectic layers (in the simplest case) have their molecules tilting in opposite directions and therefore connected with opposite local polarizations. Thus they really constitute two 'sublattices', which is very similar to the solid-state case. These materials, however, are a vast subject in themselves [9].

5. Piezoelectric properties

If we now want to investigate the conditions for an elastic stress to induce a macroscopic polarization we have to turn to the Curie principle which in a sense is a generalization of Neumann's principle. It cannot be proven in the same way as that principle; in fact it is often the violations (or maybe seeming violations) that are the most interesting to study. Among these cases are the phase transitions (spontaneous symmetry breakings) where the temperature is the 'external force' in Curie's language. As mentioned before, Curie's principle can be stated in different ways and the earliest formulation by Curie himself is that 'when a cause produces an effect, the symmetry elements of the cause must be present in the effect'. This means that the produced effect (the induced property) may have higher symmetry, but never less symmetry than the cause.

Especially in this formulation, the principle has to be used with care. An example of this is related by Hermann Weyl in his book '*Symmetry*' [10]. Weyl here tells about the intellectual shock that the young Ernst Mach received when he learned about the result of the Ørsted experiment—cf. figure 14, taken from the book. The magnetic needle is deflected in a certain sense, to the left or to the right, when a current is sent in a certain direction through the conducting wire. And yet, everything seems to be completely symmetric (magnet, current) with respect to the plane containing the needle and the conductor. If this plane is a mirror plane, the needle cannot swing out in any direction. The solution to this paradox is that this plane is *not* a mirror plane, because of the symmetry properties of the magnetic field. The problem is that while we easily recognize the reflection properties of geometric objects, we do not know *a priori* the corresponding properties for abstract
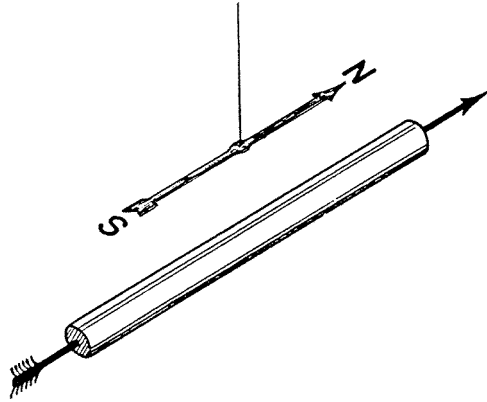
Figure 14. The symmetry paradox of the Ørsted experiment. (From reference [10].)
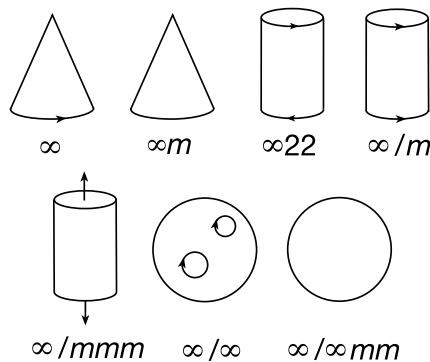
Figure 15. Pierre Curie's seven continuous point groups illustrated by geometric 'objects'. Among them we might distinguish ∞m representing a polar vector (like the electric field), and ∞/m representing an axial vector (like the magnetic field). Three of these symmetries, ∞, $\infty22$ and ∞/∞, can appear in a right-handed as well as in a left-handed form (enantiomorphic). Several equivalent ways of expressing the symmetry are in common use, for instance the one in figure 12. Pyroelectricity (i.e. a macroscopic polarization) is only permitted by the first two groups (∞ and ∞m). If the continuous medium in question can sustain the mechanical strain, piezoelectricity would be allowed by the first three groups (∞, ∞m and $\infty22$).

things like physical quantities. In fact, the magnetic field has reflection properties such that it is rather well illustrated by Magritte's well-known surrealist painting where a man is looking into a mirror and sees his back. A lesson to be learned from this is that we cannot rely on appearances when we judge the symmetry of various fields and physical properties in general. Pierre Curie was the first person to study these symmetries in a systematic way and, in order to describe them, he introduced the seven limiting point symmetry groups (also called infinite or continuous point groups) which he added to the 32 crystallographic groups. By this combination he could classify the symmetry of all possible media and all possible physical properties, illustrating the continuous symmetries with drawings related to simple geometric objects like in figure 15. Obviously, these continuous symmetries have a special relevance for liquids in general.

Let us apply a stress to a general medium and ask under which conditions it could cause an electric displacement. The basic problem that we then have to sort out is the
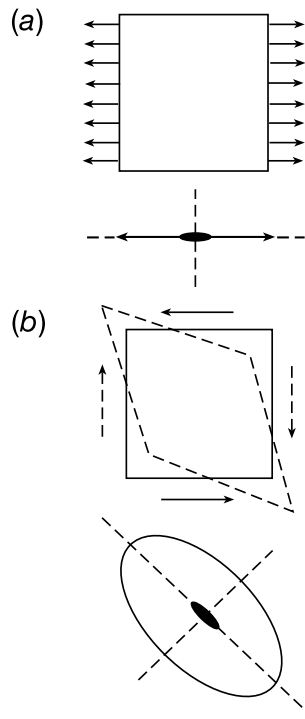
Figure 16. The symmetry of stress. (a) Pure tensile stress. (b) Pure shear stress.

proper description of the symmetry of stress. Clearly a stress cannot be described by a polar vector—there must be at least two. A simple illustration of this is given in figure 16. We see that in two dimensions a homogeneous tensile stress as well as a pure shear stress has two perpendicular mirror planes, one twofold rotation axis and one centre of symmetry (or inversion). In three dimensions we have analogously three mirror planes, three twofold axes and the centre of symmetry which we may enumerate as $m, m, m, 2, 2, 2, Z$. These are the symmetry elements of the point group mmm (or D_{2h}). This is the orthorhombic point group which can be illustrated by a matchbox or a brick [11].

Now apply the stress in the most general way, i.e. such that its three axes of twofold symmetry and its three planes of reflection symmetry do not have the same directions as the axes and planes in the unstrained medium. Curie's principle then says that the stressed medium will retain none of its symmetry axes and planes.

But if the unstressed medium has a centre of symmetry Z, it will retain that centre because the stress also has a centre of symmetry. Therefore, in a medium with inversion symmetry no effect representable by an arrow can be induced by the stress—and hence no electric displacement or polarization—whatever stress is applied. In other words a medium with an inversion symmetry cannot be piezoelectric.

We could also have reasoned formally in the following way. If a property $\mathcal{P}$ (polarization in this case) should appear in the medium $\mathcal{K}$ as a result of the external action $\mathcal{E}$ (stress σ in this case) then $\mathcal{P}$ must be compatible with the symmetry of the strained medium, according to Neumann's principle

$$\mathcal{P} \supseteq \tilde{\mathcal{K}} \tag{8}$$

but, according to Curie's principle

$$\tilde{\mathcal{K}} = \mathcal{K} \cap \sigma. \tag{9}$$

If we now insert ∞m for $\mathcal{P}$ and mmm for σ we get from (8) and (9)

$$\infty m \supseteq \mathcal{K} \cap mmm. \tag{10}$$

The symmetry elements to the right (mmm) contain a centre of inversion, but those to the left (∞m) do not. Therefore, if (10) should be satisfied (i.e. the Neumann and Curie principles together), $\mathcal{K}$ must not have a centre of inversion, i.e.

$$\bar{1} \notin \mathcal{K}. \tag{11}$$

Out of the 32 crystallographic groups, 11 have symmetry elements including a centre of inversion. One should therefore expect piezoelectricity to appear in the other 21, but it appears only in 20. The exception is 432 ($\equiv$O), the octahedral group. But this first example of an exception is sufficient to give the very important insight that the Neumann and Curie principles, and in fact all symmetry principles, only give necessary—never sufficient—conditions, for a certain phenomenon to appear. The principles can only be used in the affirmative when they exclude things from happening.
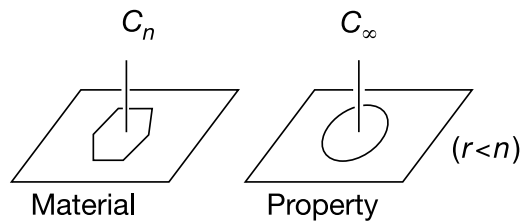

Figure 17. The crystal symmetry compared to the property symmetry around an n-fold rotation axis.

6. The importance of additional symmetries

It is often said that the group 432 is 'too symmetric' to allow piezoelectricity, in spite of the fact that it lacks a centre of inversion. It is instructive to see how this comes about. A powerful symmetry theorem of crystal physics says that if there is a rotation axis C_n (of order n), then every tensor of rank $r < n$ is isotropic in a plane perpendicular to C_n, as shown in figure 17 [11]. For cubic crystals this means that second-rank tensors like the thermal expansion coefficient α_{ij} or the dielectric constant ε_{ij} will be isotropic perpendicular to all four space diagonals which have threefold symmetry. This makes the optical properties (ε_{ij}) isotropic in three dimensions as already mentioned above. Also, if α_{ij} were not isotropic, then heating would cause the crystal to lose the property of being cubic. A centre of symmetry is lacking in three cubic classes, 23 (T), $\bar{4}3m$ (T_d) and 432 (O). The first two are piezoelectric, but the latter has three fourfold rotation axes perpendicular to each other, making the piezoelectric tensor d_{ijk} isotropic in three dimensions. The piezoeffect would then not depend on the sign of the stress, which is only possible for all $d_{ijk} \equiv 0$.

It is clear that similar additional symmetries would occur frequently if we went to liquids, which are generally more symmetric than crystals. As an example we will finally consider whether some of the properties discussed so far would be allowed in the so-called cholesteric liquid crystals, which lack a centre of inversion. A cholesteric is simply a chiral
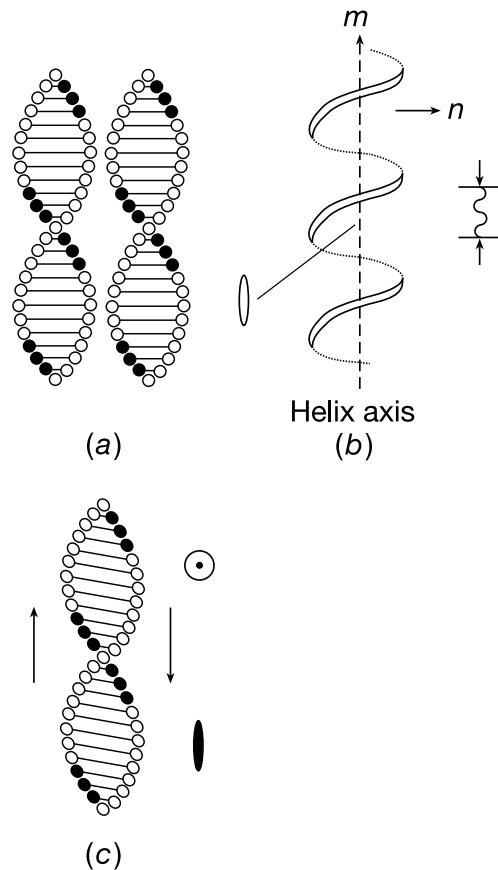
Figure 18. The symmetry of the cholesteric phase, (*a*), (*b*), and the effect of a shear, (*c*).

version of a nematic, abbreviated N*, characterized by the same local order but with a helical superstructure which automatically appears if the molecules are chiral or if a chiral dopant is added; cf. figure 18. Could such a cholesteric phase be spontaneously polarized? If there were a polarization P, it would have to be perpendicular to n, because of the condition (1), and thus along the helical axis direction m. But the helical N* phase has an infinity of twofold rotation axes perpendicular to m and the symmetry operation represented by any of these would invert P. Hence $P = 0$. A weaker requirement would be to ask for piezoelectricity. (Due to the helical configuration the liquid in fact has some small elasticity for compression along m.) But as illustrated in the same figure, a compression does not change the symmetry, and hence a polarization $P \neq 0$ cannot appear due to a compression.

Finally, it is often stated that a medium which lacks a centre of inversion can be used for second-harmonic generation (SHG). This is because the polarizability would have a different value in one direction compared with that in its antiparallel direction. Could this be the case for the cholesteric phase, i.e. could it have a non-linear optical susceptibility $\chi^{(2)} \neq 0$? The answer must be no, as it cannot be in the n-direction and the m-direction is again ruled out by the twofold axis (one of the infinitely many would suffice). The cholesteric example shows that it is not sufficient for a medium to lack a centre of inversion in order to have SHG properties. Questions like these can thus be answered by very simple

symmetry arguments, when we check how additional symmetries may compensate for lack of inversion symmetry. In contrast to the cholesteric phase, the smectic C* phase does have a direction along which a second harmonic can be generated. This is of course the C_2 axis direction in the SSFLC geometry. Even if initially small the existence of this effect was soon confirmed [12, 13] and studied in considerable detail by several groups [14]. The SSFLC structure is the only liquid (if it can be considered as such!) with SHG properties. No other examples—they can only be looked for among anisotropic liquids—are known, the externally poled electret waxes left aside (materials out of thermal equilibrium in which the polar axis is not an intrinsic property). Walba *et al* were the first to synthesize C* molecules with powerful donor and acceptor groups active perpendicular to the director (thus along the C_2 axis) which is a necessity in order to achieve $\chi^{(2)}$-values of interest for practical applications [15, 16]. But in fact there is really no point in having a surface-stabilized ferroelectric liquid crystal as an SHG material. A pyroelectric material would be much better, in which the polar axis is fixed in space, and non-switchable. But this cannot be achieved in the framework of liquids. The first such material was recently presented [17], made by using an SSFLC as a starting material and crosslinking it to a non-liquid-crystalline polymer. It is thus a soft solid.
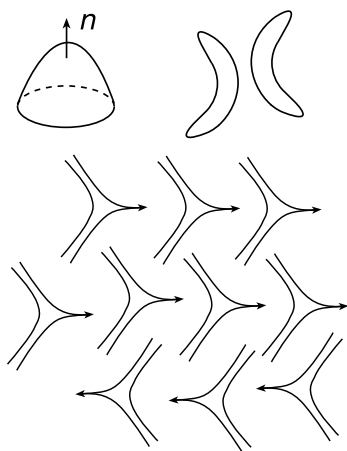
Figure 19. Shapes of some molecular crystals in which an eventual symmetry axis would have a polar character. 'All kinds' of polar material like this could in principle be made, but they also tend to become soft amorphous solids rather than liquids.

7. Can liquids then be macroscopically polar?

As we have seen, most liquid crystals have too high a symmetry to be macroscopically polar if they obey the $n \rightarrow -n$ invariance (which all 'civilized' liquid crystals do—that is, all liquid-crystal phases which are currently studied and well understood). The highest symmetry allowed is C_2 (monoclinic) which may be achieved in materials which are 'liquid-like' at most in two dimensions. And even then external surfaces are required. Generally speaking a polar liquid crystal tends to use its liquid translational degrees of freedom so as to macroscopically cancel its external field, i.e. achieve some kind of antiferroelectric order. For more 'liquid-like' liquids, piezo-, pyro-, ferro- and antiferroelectricity are *a fortiori* ruled out as bulk properties. These phenomena would however be possible in crosslinked

polymers (soft solids). A simple example may illustrate this. If we shear the cholesteric structure as shown in figure 18(*c*), Curie's principle tells us that a polarization is now permitted along the twofold axis shown in the figure. If the liquid crystal would not yield, this would constitute a piezoelectric effect. Now, polymer forms of liquid crystals are well known and, depending on the degree of polymerization and crosslinking a whole no-man's-land of 'fluids' can be created which may have characteristics varying over a broad range from liquid-like to solid-like. With this ambiguity in mind the question in the title of this article may not be straightforward to answer in complete generality. But if we ask 'are there any liquids which are macroscopically polar?', the answer is no. So far there is not a single demonstration of such a liquid, and I would say that this is as good a distinction as any between the solid and the liquid state. When expressions like 'ferroelectric properties' of a liquid appear, they are normally used in a frivolous way. I will explain by making an analogy.

Some of the most sophisticated and beautiful liquid-crystal states of order are called 'blue phases'. They may be considered as extreme cases of a frustrated cholesteric phase where the twisting power is so strong that the nematic order breaks down locally along singular lines (i.e. their cores are isotropic) in exchange for a double twist in the bulk. These phases are spatially strongly inhomogeneous [18] with the director twisting around the three-dimensional disclination network in such a way as to create one of several possible cubic structures. All blue phases are optically isotropic, i.e. they are not birefringent. In complex liquids a dipolar order may appear in a number of different spatially inhomogeneous structures, but with a polarization macroscopically adding up to zero. To name such liquids 'ferroelectric' would be just as nonsensical as to name a blue phase 'locally birefringent'.

The only strongly non-linear dielectric among liquids which may deserve the name ferroelectric so far is the SSFLC structure—and as we have seen it is really questionable whether we are speaking of a liquid because the non-linearity is not a bulk property. This may also remind us that almost all phenomena at surfaces are polar. Thus, whereas a nematic has a quadrupolar order in the bulk, its local order at the confining glass surfaces is certainly polar, i.e. the invariance condition (1) is certainly not valid. This is a common feature at outer boundaries as well as at inner surfaces, for example in lyotropic liquid crystals. By the same logic it is clear that membranes, for instance in biological systems, will generally permit polarized surfaces.

8. Will there be macroscopically polar liquids in the future?

In the last decade efforts have been made to synthesize new mesogenic molecules self-assembling in a polar way so as to create ferroelectric materials which are not necessarily chiral [19–21]. For instance, it must in principle be possible to make smectic or similar phases for which the invariance condition (1) is not valid. Such liquid crystals may be termed longitudinal ferroelectrics and would be more similar to solid ferroelectrics than to ferroelectric liquid crystals of type C^*. The polar order should also be able to be detected by second-harmonic generation for oriented samples. So far these investigations have been highly interesting and promising but not conclusive, probably because of the difficulties of obtaining oriented samples. A different interesting branch of research has started with the recognition [22] that in an antiferroelectric smectic (if we consider the symmetry of a pair of layers instead of one layer) there may be an additional twofold rotational axis *in* the tilt plane, along which we might have a polarization even in the case of a non-chiral medium. This case has recently given the first unambiguous result for a monomer–polymer mixture [23]: it turns out—again, not surprisingly—that the material is antiferroelectric.

The ground state of the bilayer smectic C with a side-group polymer has an alternating tilt with an in-plane antiferroelectric order, which can be switched to a ferroelectric state. The molecules have the general shape of those in the lower part of figure 19.

A different line of research starts with the fact that with a suitable shape of the molecule, the director n (regarded as a direction of symmetry) cannot obey the invariance condition (1), whence we can have polar order along n just as we could have stapled cups of coffee on top of each other (cf. upper left of figure 19). Such mesogenic molecules are called bowlic [24]. They would show both pyroelectricity and second-order non-linear behaviour [25]. They would indeed be ideal for this latter application—if they only can be oriented, which is a non-trivial problem. Anyway, considerable synthetic progress has been made recently in this domain [26]. Knowing the ingenuity of synthetic organic chemists in creating new molecules of almost any shape, we will soon have to take into consideration a whole new domain of complex fluids, the properties of which we can only try to imagine at the present state. It will however be increasingly difficult to regard them as liquids or liquid crystals. If a director n can be defined at all as a symmetry axis, then it will acquire a polar character in some of the clear-cut cases which may now be distinguished, as in the case of bowlic liquid crystals; cf. figure 19. Such matter is intrinsically polar, like some of its precursors, polar discotics. Even more exotic molecules, recently synthesized and sketched in the figure, are so hard to align in the bulk that very little can be said about their spontaneous order. Hence, at the moment, everything seems to be possible (and why not, as we do not know how to classify these materials between solids and liquids?) These new materials are exciting, but no experiments regarding their polar order are as yet conclusive. It is not unlikely that these amorphous or partially ordered media may require stabilizing surfaces to form oriented samples and thus acquire $\langle \chi^2 \rangle \neq 0$ and $\langle P \rangle \neq 0$. But would we then say that they are ordered liquids?

References

[1] Liquid crystals are, very generally, intermediate (mesomorphic) between liquids and crystals. However, the almost boundless variety of organic molecules synthesized in recent decades makes it increasingly difficult to draw a demarcation boundary between these states. An attempt to formulate the necessary (but not sufficient) condition for the liquid-crystalline state may therefore be the assertion that a director n can be defined as (a) a direction of a symmetry axis of the medium, which (b) obeys the invariance condition (1).

[2] Quartz is piezoelectric but cannot be pyroelectric for reasons of symmetry, in spite of many confusing adverse statements, e.g. in
   Ladd M F C 1989 *Symmetry in Molecules and Crystals* (London: Ellis Horwood) p 90
   cf. also the article 'Pyroelectricity' in the latest edition of *Encyclopaedia Britannica*, or the article 'Pyroelectricity' in
   Thewlis J (ed) 1962 *Encyclopaedic Dictionary of Physics* vol 5 (Oxford: Pergamon)

[3] Nussbaum A and Phillips R A 1976 *Contemporary Optics for Scientists and Engineers* (Englewood Cliffs, NJ: Prentice-Hall) pp 379–81

[4] Lagerwall S T and Dahl I 1984 *Mol. Cryst. Liq. Cryst.* **114** 151

[5] Meyer R B, Liébert L, Strzelecki L and Keller P 1975 *J. Physique Lett.* **36** L69

[6] de Gennes P G and Prost J 1993 *The Physics of Liquid Crystals* (Oxford: Clarendon) p 383

[7] Clark N A and Lagerwall S T 1980 *Appl. Phys. Lett.* **36** 899

[8] Nevertheless, 15-inch colour screens of high resolution (1280×1024 picture elements) have recently been commercialized by Canon Inc., Tokyo.

[9] Fukuda A, Takanishi Y, Isozaki T, Ishikawa K and Takezoe H 1994 *J. Mater. Chem.* **4** 997

[10] Weyl H 1952 *Symmetry* (Princeton, NJ: Princeton University Press) p 19

[11] For a treatment in more detail, see
   Lagerwall S T 1997 Ferroelectric liquid crystals *Handbook of Liquid Crystals* ed D Demus *et al* (Weinheim: VCH, Verlag Chemie) at press

[12] Vtyurin A N, Ermakov V P, Ostrovskii B L and Shabanov V F 1981 *Phys. Status Solidi* b **107** 397

[13] Shytkov N M, Barnik M L, Beresnev L A and Blinov L M 1985 *Mol. Cryst. Liq. Cryst.* **124** 379

[14] Taguchi A, Ouchi Y, Takezoe H and Fukuda A 1989 *Japan. J. Appl. Phys.* **28** L997

[15] Walba D M, Keller P, Parmar D S, Clark N A and Wand M D 1989 *J. Am. Chem. Soc.* **111** 8273

[16] Walba D M, Ros M B, Sierra T, Rego J A, Clark N A, Shao R, Wand M D, Vohra R T, Arnett K E and Velsco S P 1991 *Ferroelectrics* **121** 247

[17] Hult A, Sahlén F, Trollsås M, Lagerwall S T, Hermann D, Komitov L, Rudquist P and Stebler B 1996 *Liq. Cryst.* **20** 23

[18] Dubois-Violette E and Pansu B 1988 *Mol. Cryst. Liq. Cryst.* **165** 151

[19] Tournilhac F, Bosio L, Nicoud J F and Simon J 1988 *Chem. Phys. Lett.* **145** 452

[20] Tournilhac F and Simon J 1991 *Ferroelectrics* **114** 283

[21] Tournilhac F, Blinov L M, Simon J and Yablonsky S V 1992 *Nature* **359** 621

[22] Cladis P and Brand H R 1993 *Liq. Cryst.* **14** 1327

[23] Soto Bustamente E A, Yablonsky S V, Ostrovsky B I, Beresnev L A, Blinov L M and Haase W 1996 *Chem. Phys. Lett.* **260** 447

[24] Lam L 1994 Bowlics *Liquid Crystalline and Mesomorphic Polymers* ed V P Shibaev and L Lam (New York: Springer) p 324

[25] Bein T 1993 *Nature* **361** 207

[26] Xu B and Swager T 1995 *J. Am. Chem. Soc.* **117** 5011