Abstract

In a theoretical examination of the structures of liquid crystal phases, Robert B. Meyer in 1975 creatively utilized symmetry arguments to predict that tilted, layered liquid crystal phases of chiral molecules are ferroelectric. He then engaged the help of organic chemists to synthesize a compound that might possess such a phase, and once the material was in his hands, Meyer not only verified its ferroelectricity, but also suggested how such a phase could be used for extremely fast displays. This discovery of ferroelectricity in a fluid system with the possibility for unique applications surprised the entire condensed matter research community and quickly paved the way for both increased scientific understanding and significant technological advancement. For this creative synthesis of theory and experiment, Meyer was awarded the 2004 Benjamin Franklin Medal in Physics.

1. Liquid crystals

While everyone is familiar with solids, liquids, and gases as the three common phases of matter, fewer people recognize that certain substances exist in a fourth phase of matter between the solid and liquid phases. This phase of matter is called the liquid crystal phase and is as distinct from the three common phases as they are from each other. In the solid phase, the molecules have a large amount of both
positional and orientational order, in that the molecules maintain specific positions and orientations. In the liquid phase, there is no positional and orientational order, since the molecules diffuse about quite randomly, constantly changing both their positions and orientations. In the liquid crystal phase, the molecules can diffuse about, much as they do in liquids, but as they diffuse they maintain a small amount of orientational order and sometimes a small amount of positional order also. This is illustrated in Fig. 1, where it is clear that the snapshot of the molecules in the liquid crystal phase reveals that there is a slight tendency for the molecules to point up and down. This preferred direction of orientation is called the director, and a liquid crystal with only orientational order as shown in Fig. 1 is called a nematic liquid crystal. Fig. 2 depicts two liquid crystal phases with some positional order in addition to the orientational order. In these smectic liquid crystals, there is a tendency for the molecules to be positioned in layers as opposed to between the layers. The two types of smectic liquid crystal phases shown in Fig. 2 differ in that in the smectic A phase the director is perpendicular to the layers while in the smectic C phase the director is at an angle other than 90° from the layers.

The molecules that form liquid crystal phases tend to be elongated, with a fairly rigid bonding structure in the center of the molecule and more flexible bonding structures toward the ends of the molecule. Fig. 3 shows the structure of a molecule that forms the smectic C, smectic A, and nematic phases, and the temperatures at

![Fig. 1. Some phases of matter.](image1)

![Fig. 2. Two liquid crystal phases.](image2)
which each phase transition takes place. Some substances have only one liquid crystal phase between the solid and liquid phases, but many have several [1].

In order to gain some insight into the properties of these various liquid crystal phases, it is important to understand the concept of symmetry as it is applied to materials. The structure of a material is often such that, if the entire sample is translated in a certain direction by a specific distance, rotated about a specific axis by a certain angle, reflected through a plane oriented in a specific direction, or inverted through a specific point, then the structure of the material is unchanged. For example, in the case of the liquid phase of Fig. 1, the sample can be translated in any way, rotated in any way, reflected through any plane, and inverted through any point and its structure looks exactly the same. A liquid therefore possesses a high degree of symmetry in that many “symmetry operations” can be performed on it and no change occurs. The nematic liquid crystal of Fig. 1 possesses all the possible symmetries of the liquid phase, except that the rotations about an axis perpendicular to the director are restricted to 180° if the structure is to remain unchanged. Thus the transition from the liquid phase to the nematic liquid crystal phase is one in which some rotational symmetry of the liquid phase is “broken.” Likewise, imagine the transition from the nematic liquid crystal phase to the smectic A liquid crystal phase. Whereas translations in any direction by any distance leave the nematic liquid crystal phase unchanged, translations along the director in the smectic A liquid crystal phase are restricted to multiples of the layer spacing if the structure is to be unchanged. This restriction is another example of a symmetry broken at the transition from the nematic liquid crystal phase to the smectic A liquid crystal phase.

Symmetry considerations are important because all the properties of a substance must conform to the symmetry of the structure. For example, since a nematic liquid crystal can be rotated by 180° about an axis perpendicular to the director and remain unchanged, then all properties of the substance associated with a direction parallel to the director must be the same as for a direction anti-parallel to the director. In short, the director can be defined in either of these two directions. Likewise, since rotation by any angle about the director leaves the structure unchanged, properties associated with any direction perpendicular to the director must have the same. This is easily realized by assuming that some property is different along two different directions perpendicular to the director. Rotation about the director by an angle equal to the angle between these two directions points one direction in the direction the other used to point. Since the structure is unchanged by this rotation (by symmetry), properties associated with all directions must remain the same. Therefore the original
assumption of different properties associated with these two directions could not have been true.

Realizing the symmetries present in the smectic C liquid crystal phase is crucial to an understanding of ferroelectricity in liquid crystals. As shown in Fig. 4, neglecting translational symmetries for the time being, the smectic C liquid crystal phase possesses (1) reflection symmetry through the x−z plane (the +y and −y axes are identical), and (2) 180° rotational symmetry about the y-axis (the +x and −x axes are identical and the +z and −z axes are identical). Notice that performing both the reflection and rotation operations one after the other amounts to an inversion of each of the three axes (x becomes −x, y becomes −y, and z becomes −z). Structures that remain unchanged with an inversion of the axes are called centrosymmetric structures [2].

2. Chirality

One of the more subtle forms of symmetry breaking is that of handedness or chirality. A structure is chiral if it does not possess inversion symmetry. Human hands, for example, are chiral. If inverted through a point, a right hand becomes a left hand, and vice versa. The tetrahedral form of bonding of carbon atoms is another example. As Fig. 5 demonstrates, a carbon atom bound to four different atoms, sometimes called an asymmetric carbon atom, cannot be inverted and remain the same, i.e., super-imposable upon itself. Molecular structures with an asymmetric carbon are non-centrosymmetric structures, thus many phases composed of such molecules do not possess inversion symmetry.

3. Ferroelectricity

Although many people are familiar with the fact that some materials are capable of being a ferromagnet and generating a magnetic field, fewer know that materials

![Fig. 4. Symmetries of the smectic C phase.](image)

![Fig. 5. Asymmetric carbon atom.](image)
can also act as a ferroelectret and generate an electric field. Whether it be ferromagnetism or ferroelectricity, the atoms or molecules of the material must act as little magnets (with north and south poles) or little electrets (with positive and negative poles), respectively. If these little magnets or electrets can be made to line up, then a piece of the material will act as a macroscopic magnet with a permanent magnetization or a macroscopic electret with a permanent electric polarization. Both of these situations are depicted in Fig. 6.

If the $z$-axis points along the direction of the electric polarization in a ferroelectric substance, then clearly the $+z$ direction and $-z$ direction are not equivalent. For example, the spot where the $z$-axis leaves the material is the location of one of the electric poles and the spot where the $z$-axis enters the material is the location of the other electric pole. This means that inversion symmetry is not present, or to put it another way, ferroelectric materials must possess non-centrosymmetric structures. This point is illustrated in Fig. 7 with two inorganic solids. Strontium titanate has a centrosymmetric structure with the $x$-, $y$-, and $z$-axes all having the property that the plus direction is equivalent to the minus direction. The structure of barium titanate is different, however, in that the titanium atom is displaced slightly along the $z$-axis,
producing a net displacement of positive charge in the \( +z \) direction and a net displacement of negative charge in the \( -z \) direction. This inequivalence means the structure is non-centrosymmetric just as it clearly shows that barium titanate is a ferroelectric material [3].

4. Ferroelectric liquid crystals

While it is not difficult to imagine how solids such as barium titanate can be ferroelectric, the idea of a fluid, with molecules diffusing quite randomly, being ferroelectric almost sounds preposterous. Such was the conventional wisdom among chemists and physicists around 1970. But Robert Meyer, a young physicist involved in understanding more about liquid crystals, dared to wonder if any liquid crystal phase could be ferroelectric. Certainly liquids could not be ferroelectrics, and, in fact, most liquid crystal phases could not be ferroelectric either because they possess inversion symmetry. But Meyer had worked on the nematic liquid crystal phase of substances composed of chiral molecules and wondered if the fact that chiral molecules lacked inversion symmetry could ever cause a liquid crystal phase to be non-centrosymmetric and therefore ferroelectric. Guided by symmetry considerations, Meyer focused his attention on tilted, layered structures in which the constituent molecules are chiral.

As explained previously, the smectic C liquid crystal phase possesses inversion symmetry and is therefore centrosymmetric. The situation changes dramatically, however, if the molecules are chiral. This is illustrated with the help of Fig. 8, in which the molecules are depicted as fish with one black eye and one white eye. Such fish are chiral, in that inversion changes one kind into the other (just like the human hand). As demonstrated in Fig. 8, inversion seems to leave the structure unchanged until it is noticed that the fish that started out with one handedness have all been changed to fish of the other handedness. Inversion symmetry is not present and the structure is clearly non-centrosymmetric. An even closer look at Fig. 8 reveals that the inverted structure has not been changed along the \( x \)- and \( z \)-axes, only along the \( y \)-axis. To see this, notice that if the eyes are ignored, the structure is unchanged. But
the eyes lie along the $y$-axis, and they all have changed. Therefore, in a smectic liquid crystal phase of chiral molecules, the $+y$ and $-y$ directions are not equivalent. If the molecule possesses a non-zero electric dipole moment along the $y$-axis, then these will add together to produce a macroscopic electric polarization and a ferroelectric material.

But theoretical speculation of this sort is hardly convincing without some proof that substances actually behave in this way. Although smectic C liquid crystal phases had been studied prior to 1975, there were not many examples and none of them involved chiral molecules. Meyer therefore sought the help of a few organic chemists and together they tried to imagine a molecular structure that (1) would be chiral, (2) would possess a smectic C liquid crystal phase, and (3) could actually be synthesized in the laboratory. The result of their work was the molecule, shown in Fig. 9, with a structure similar to molecules known to form the smectic C liquid crystal phase but with one asymmetric carbon atom near one end of the molecule (denoted by an asterisk in Fig. 9). Once synthesized, it did not take Meyer long to convincingly demonstrate through careful experiments that the smectic C phase of these molecules was ferroelectric [4].

Meyer’s theoretical prediction of ferroelectric liquid crystals and experimental confirmation that they did indeed exist caught the interest and imagination of condensed matter scientists by storm. Here was an unanticipated area of material science, with new chemistry and physics just waiting to be discovered. The field of ferroelectric liquid crystals blossomed in no time, literally becoming the dominant area of study among the researchers studying liquid crystals. The list of newly synthesized ferroelectric liquid crystals is now over 50,000. Antiferroelectric liquid crystals and ferrielectric liquid crystals were subsequently discovered. Ferroelectric liquid crystals that spontaneously create defects brought to light an entirely different way that nature orders materials. The investigation of chiral liquid crystals also took on new life, as the power of Meyer’s symmetry arguments led researchers to new phases, new kinds of phase transitions, and unforeseen properties [5].

![Fig. 9. First ferroelectric liquid crystal.](image-url)
5. Ferroelectric liquid crystal displays

At about the time of Meyer’s work, it was becoming clear that liquid crystals had properties that made them very suitable for displays. The fact that they consumed almost no power when used in a reflective mode with ambient light had already been demonstrated. There was also significant optimism that the characteristics of these early liquid crystal displays (LCDs) could be improved in the areas of speed, brightness, and color to the point where they would rival every other display, even the cathode ray tube used in televisions. Because liquid crystal displays rely on the electric properties of liquid crystals, Meyer’s discovery of ferroelectric liquid crystals had important implications for future LCD development, something that he realized as quickly as many other scientists.

Just about all LCDs rely on the same switching mechanism used in the early LCDs. The liquid crystal is contained between two thin pieces of glass, which have been coated with a transparent electrode and a polymer to orient the director of the liquid crystal. With no electrical voltage applied to the electrodes, the liquid crystal allows light to pass through. When a voltage is applied to the electrodes, however, the electric field induces a slight separation of charge in the molecules, which in turn causes all of the molecules, and hence the director, to align with the electric field. With the liquid crystal in this orientation, light does not pass through the display. Thus the basic switching mechanism in nearly all LCDs results from (1) an effect induced on the molecules by an applied electric field, and (2) a relaxation back to the orientation favored by the alignment surfaces when the applied electric field is removed. These two processes, especially the second one, keep the switching times in the millisecond range, making LCDs unsuitable for many applications.

Ferroelectric liquid crystals possess a permanent electric polarization, and therefore no induction of charge separation is necessary in order for them to respond to an electric field. More important is the fact that this permanent electric polarization can be made to orient in two directions simply by reversing the direction of the electric field. Thus the slowest part of the switching mechanism in normal LCDs is avoided, as the ferroelectric LCD is driven both ways by an electric field that simply reverses its direction. This process is much faster than the normal scheme, allowing for switching to occur in microseconds as opposed to milliseconds. Meyer proposed the basic design for a ferroelectric LCD and it did not take workers very long to actually fabricate such a display [6].

Although ferroelectric LCDs were demonstrated in the laboratory over 20 years ago, they are only making a significant impact on the display market now. The reason for this long delay stems from the difficulties associated with aligning a ferroelectric liquid crystal, but finally the problem has been solved. There have been over 2000 patents for ferroelectric LCDs and switching times have grown as short as 50 ns. Small ferroelectric LCDs have found their way into the viewfinders of digital cameras, cell phones, and pocket computers, while larger displays are used for computer monitors and televisions. The speed and resolution of these displays affords many advantages, indicating that ferroelectric LCDs are bound to become an important part of display technology in the future.
6. Other contributions

Robert Meyer has continued to be a leading force in the advancement of knowledge in the area of liquid crystals. He discovered that free standing films of smectic liquid crystals could be made, giving workers in the field a new tool to understand the physics of two-dimensional materials [7]. He also discovered that distorted ferroelectric liquid crystals produce patterns of charge density, a phenomenon called flexoelectricity [8]. This effect is gaining more and more importance as ferroelectric LCDs achieve higher and higher resolution. Meyer has also made significant contributions to the understanding of liquid crystal polymers, liquid crystal elastomers, and the ordered phases of macromolecules [9–11].

Laureate’s biography

Robert Meyer received his B.A. in physics from Harvard University in 1965 and his Ph.D. in physics, also from Harvard University, in 1970. He was on the faculty at Harvard University from 1969 to 1978 as a Lecturer, Assistant Professor, and Associate Professor of Physics. He then moved to Brandeis University, first as an Associate Professor and in 1985 became a Professor of Physics. He has served on the editorial board of two journals, Physical Review and Molecular Crystals and Liquid Crystals, and one book series, the Liquid Crystal Series of World Scientific Publications. He has received an Alfred P. Sloan Foundation Research Fellowship, the Joliot Curie Medal of the City of Paris, a Special Recognition Award from the Society for Information Display, and the Runner-up Award in the LVMH Science in Art prize competition. Meyer is the author of three patents and over 100 scientific publications.

The Benjamin Franklin Medal in physics medal legacy

1915 Heike Kamerlingh Onnes, Franklin Medal, Low Temperature Research and the Discovery of Liquid Helium.
1944 Peter Kapitza, Franklin Medal, Low Temperature Magnetism and Theoretical and Experimental Physics.
1961 Leo Esaki, Ballantine Medal, Quantum-Mechanical Tunneling in Semiconductors and the Tunnel Diode.
1971 Paul J. Flory, Cresson Medal, Physical Chemistry of Polymers.
1972 Brian D. Josephson, Cresson Medal, Low Temperature Theoretical Physics and the Josephson Effect.
1975 John Bardeen, Franklin Medal, Theory and Technology of Superconductivity and Semiconductors.
1993 Alan G. MacDiarmid, Clamer Medal, Conductive Polymers.
1998 Horst L. Stormer, Benjamin Franklin Medal, Experimental Elucidation of the Fractional Quantum Hall Effect.
1998 Daniel C. Tsui, Benjamin Franklin Medal, Experimental Elucidation of the Fractional Quantum Hall Effect.

References


Mr. Peter J. Collings is the Morris L. Clothier Professor of Physics at Swarthmore College. Prior to coming to Swarthmore College, he served on the faculty at Kenyon College as Assistant Professor, Associate Professor, and Professor of Physics. He received his B.A. in physics from Amherst College and his Ph.D. in physics from Yale University. He is a fellow of the American Association for the Advancement of Science and the American Physical Society. Collings won the 1994 Prize for Research in an Undergraduate Institution of the American Physical Society and in 2002 he received the Alan Berman Research Publication Award from the Naval Research Laboratory. Collings is the author of Liquid Crystals: Nature's Delicate Phase of Matter (Princeton University Press) and with Michael Hird Introduction to Liquid Crystals: Chemistry and Physics (Taylor and Francis). He is also the editor with Jay Patel of Handbook of Liquid Crystal Research (Oxford University Press). He has also written three book chapters and over 60 research articles.