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Ferroelectric and Antiferroelectric Liquid Crystals

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Prof. Sven T. Lagerwall
Physics Department
Chalmers University of Technology
S-412 96 Göteborg
Sweden

Cover picture:
Zigzag defects in a smectic C*.
Courtesy of Noel Clark and Tom Rieker.

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Preface

This text has grown out of the chapter *Ferroelectric Liquid Crystals* which I wrote for the *Handbook of Liquid Crystals*, published in 1998. Although this was an unusually large chapter in the *Handbook*, the available space and time could not possibly permit a full coverage of the subject. The editors therefore proposed to extend the material into a monograph, which then also ought to cover antiferroelectric materials. In fact, not to treat the different kinds of polar order from a unified point of view would be to set artificial borders between indissolubly connected phenomena.

The new text is substantially extended in several ways. This does not only concern the discussion of antiferroelectric materials, but foremost the inclusion of two chapters (11 and 12) on the elastic continuum theory of smectics, in particular smectic C and smectic C*. This description, which is indispensible in order to understand the peculiar intrinsic smectic C* properties, of great importance also for the applications of the material, has so far been absent in the literature. (It is not even treated in the *Handbook.*) Much of this discussion concerns the spontaneous bend deformations present in smectic C* and is written in a language – this has been the aim of the whole book – accessible to both experimentalists and theoreticians.

Corresponding to its character of monograph I have tried to have a fair balance in the text between basic physics and applications. I have further attempted the treatment to be self-contained as far as possible, in order to give it likewise the character of textbook. Therefore, priority has also been given to conceptual clarity. Essentially all important equations have been derived from basic principles. In the same spirit, the text contains a quite detailed and in may opinion, necessary, introduction to the Landau formalism in the description of phase transitions. In comparison with the *Handbook* article this part has been further extended by an introductory discussion of order parameters, including many examples, in sections 2.5 and 2.6. The inclusion has necessitated a numbering of equations in those sections which deviates from that of the rest of the book, but otherwise should not affect the reading.

The most important events in the subject-matter of polar liquid crystals can be traced back to 1969, 1975 and 1980. Serious industrial involvement began in 1985 (Canon Inc., Tokyo) after some year of initial testing. The first international conference on ferroelectric liquid crystals (FLCs) was held, on French initiative, in Arcachon (Bordeaux) in 1987 and six more such conferences have since been held: 1989 Göteborg (Sweden), 1991 Boulder/Colorado (USA), 1993 Tokyo, 1995 Cambridge (UK) and 1997 Brest (France). However, outside of these special conferences, the topic has been a dominating one also at the general liquid crystal conferences since the mid 80's, and it still is. The reason lies, no doubt, in its rich physics and chemistry, which continually pours out new surprises. Many of these have been very detrimental for applications and have required extraordinary efforts to cope with. As the industrial pioneer, Canon not only discovered most of those but had to overcome them, which they did in an outstanding combination of academic research and applied display work. However, neither is, by far, the physics and chemistry of these materials exhausted, nor are they sufficiently understood and mastered, theoretically and experimentally.

Liquid crystals are a delight to the condensed matter physicist. Concepts developed to understand magnetism, superfluid helium and superconductivity have shown their unifying power when applied to liquid crystals, as they have when applied to nuclear matter, particle physics and weak and electromagnetic interactions. But liquid crystals are also competing with other technologies for large-area high-resolution displays, which are considered to be the real bottleneck and therefore halting the otherwise very rapid development in information technology. Liquid crystals hold the first position in this area, but the high definition LCD-TV does not seem to be around the corner as has usually been claimed during the last fifteen years. For personal computer screens though, both lap-top and desk-top, the combination nematic-TFT has few rivals. Within liquid crystals a number of different technologies compete. With the exception of antiferroelectric (AFLC) displays it does not seem likely that passively addressed smectic screens will be able to compete in the area of PCs, due to the substantial decrease in cost for transistor arrays. Competing liquid crystal technologies also profit from each other. For instance, the FLC technology has shown that it is feasible to go down to much lower cell thickness (~2–4 μm) and other technologies have followed with a resulting increase in performance. The symmetrically bistable in-plane switching of FLCs has also inspired both the development of nematic in-plane switching (IPS) devices and the present development of fast-switching symmetrically bistable nematics. On the other hand, it is likely that FLC will now in turn profit from the rapid development in TFTs and silicon backplanes, because no nematic-TFT combination can compete in performance with FLC-TFT or "FLT", in particular for the forthcoming market of TV, the biggest flat screen market beyond comparison. The FLT development is the newest aspect of liquid crystal displays.

In this book the discussion of applications has been limited to displays. The main reason is that non-display FLC applications are extensively covered in the *Handbook* article by W. A. Crossland and T. D. Wilkinson. The book does also not discuss the chemistry of FLCs, neither in basic nor applied aspects. These things are covered in the *Handbook* article by S. M. Kelly and in those by J. W. Goodby. Finally, the polymer FLCs are treated very superficially, as illustrative applications and the discotic FLCs not at all. Again, the reader is referred to *Handbook* articles by R. Zentel and by J. C. Dubois, P. Le Barny, M. Mausac and C. Noël, in the first case, in the second case by A. N. Cammidge and R. J. Bushby and by N. Boden and B. Movaghar.

As always however, there are certainly topics I wish I would have discussed, had more space and time been available. To these belong, in particular, the dielectric properties of FLC and AFLC materials, an the non-linear optical properties, but also the very important and physically intriguing phenomena of electro-mechanical properties (pioneered by the Budapest group), in field-induced rotational instabilities (Göteborg) and the newest experimental results with relevance to the Landau description (Clausthal, Minneapolis).

I due a lot of what I have written to my long-time colleagues and collaborators Noël Clark and David Walba at the University of Colorado in Boulder, with whom I always have had the most inspiring and profitable discussions. I likewise due a lot to my colleague Bengt Stebler in Göteborg and to my younger collaborators Joe Maclennan (Boulder), David Hermann and Per Rudquist (Göteborg). With Marek Maruszczyk I have had long discussions about device structures and, in particular, chevron geometries, and he has transferred my handmade sketches of not only those corresponding figures but the majority of the figures in the book, to a shape suitable for publication. The others have been prepared by Tomasz Mastuszczyk and by Jan Lagerwall. My wife has typed this manuscript (as so many others) without complaining, in spite of her own professional activity as an artist. I am also indebted to Dr. Jörn Ritterbusch at Wiley-VCH, who with much patience and encouragement has guided me through this project. Finally, my special thanks go to Dr. H.-R. Dübal of Hoechst, now Clariant, who during many years has been a constant source of support and inspiration.

Sven Torbjörn Lagerwall

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Contents

List of Symbols and Abbreviations

a	general coefficient; Landau expansion coefficient
A	amplification at zero feedback
A	area
A	surface area of pixel
A_{11}, A_{12}, A_{21}	SmC layer torsional constants
$\boldsymbol{A}$	vector potential
b	Burgers vector
b	Landau expansion coefficient
B	Compressional elastic constant for SmA
B	SmC elastic constant in the one-constant approximation
B_1, B_2, B_3, B_{13}	SmC in-layer elastic constants
$\boldsymbol{B}$	bend vector
c	Landau expansion coefficient
c	concentration
c_1, c_2	$\boldsymbol{c}$ director components
c_{ijkl}	elastic constants of solids
$\boldsymbol{c}$	$\boldsymbol{c}$ director (local tilt direction along smectic layer)
C	Curie constant
C_1, C_2	SmC* elastic constants
c^*	chiral coupling coefficient (between tilt and polarization)
d	cell gap thickness, sample thickness, width
d	cross diameter of molecule
d	smectic layer thickness, stereospecific length
d_A	SmA layer periodicity
d_C	SmC layer periodicity
d_{ijk}	piezocoefficients
D	dielectric displacement
D_1, D_3	first order SmC* elastic constants
e	charge of electron
e^*	electroclinic coefficient
$e_\mathrm{b}, e_\mathrm{s}$	flexoelectric constants for bend and splay, respectively
e_{ij}	SmC flexoelectric coefficients
e	flexoelectric coupling coefficient in Landau expansion
e^*	structure coefficient
E	applied electric field
E	external influence symmetry group
E_a	activation energy
E_ac	ac signal
E_o	aligning field
E_th	threshold field

f	probability
f_G	relaxation frequency of Goldstone mode
f_s	relaxation frequency of soft mode
f_l	relaxation frequency for molecular rotation around long axis
f_t	relaxation frequency for molecular rotation around short axis
F	force
G	elastic energy density, free energy density
G_c	free energy density due to c director distortions
G_{cs}	free energy density due to coupling of in-layer and layer distortions
G_n, G_p	nematic-like and polar surface interactions, respectively
G_s	total surface energy from G_n and G_p
G_s	free energy density due to layer strains
$\mathcal{H}$	hamiltonian
H	magnetic field strength
i	electric current
I	intensity of transmitted light
k	Boltzmann constant
k	cholesteric wave vector
$\boldsymbol{k}$	local smectic layer normal
K	elastic constant in the one-constant approximation
$K_{11}, K_{22}, K_{33}, K_{24}$	Oseen elastic constants
l	distance between singularities, penetration length
L	Langevin function
L	Lifshitz invariant
L	sample thickness
$\boldsymbol{m}$	unit vector along chloesteric axis
M	magnetization
n	refractive index
n_1, n_2, n_3	director components
$\boldsymbol{n}$	director
Δn	birefringence
$\boldsymbol{n}(\boldsymbol{r})$	director field
N	molecular density, number of layers, number of spins
$\boldsymbol{N}$	Pikin-Indenbom order-parameter
p	dipole moment
p	secondary order parameter
P	cholesteric pitch
$\boldsymbol{P}$	local polarization direction ($=\boldsymbol{k} \times \boldsymbol{c}$) in a smectic layer
$\boldsymbol{P}$	polarization
P_1, P_2	polarization of sublattices
P_2	second Legendre polynomial
P_f	flexoelectric polarization

P_{i}	induced polarization
P_{ms}	mesoscopic polarization
P_{o}	magnitude of spontaneous polarization per radian of tilt
P_{s}	spontaneous polarization
q	primary order parameter
q	helical wave vector
q_{b}	bend vector
q_{t}	twist wave vector
$\boldsymbol{q}$	wave vector
q	value of helical smectic C* wave vector at the A*–C* transition
Q	total charge
Q_{s}	saturation charge
Q_{ij}	nematic tensor order parameter
r	polar coordinate in three dimensions, rank of tensor
$\boldsymbol{r}$	radius vector (spatial variable)
R	radial distance
R	relative concentration of enantiomer (*R*), resistance
s	strain
s^{e}	electrostrictive strain
s^{p}	piezoelectric strain
S	reduced (scalar) nematic order parameter
S	relative concentration of enantiomer (S)
$\boldsymbol{S}$	splay vector
t	transmission coefficient
t	time
T	temperature
T	transmitted light intensity
T_{c}	Curie temperature, critical temperature, transition temperature
T_{θ}, T_{φ}, T_{δ}	rotation matrices
T_{ij}	second rank tensor
Tr	trace of matrix
u	layer displacement along z direction
u	total energy per unit area
u	distortion
U	field energy
U	potential energy of dipole in electric field
V	voltage
V	volume
w	wall thickness
W	equilibrium width for thick wall
W_{s}	surface anchoring energy
x	distance across cell

x, y, z	axes in Cartesian reference frame
z	layer normal
Z	SmC* helical periodicity
α	angular velocity
α	general coefficient, Landau expansion coefficient
α	polarizability
α_{ij}	thermal expansion coefficient
β	feedback coefficient
β	strength of spontaneous bend
γ	general viscosity
γ_l, γ_t	longitudinal (long axis) and transverse (short axis) rotational viscosities, respectively
γ_1	twist viscosity
$\gamma_1, \gamma_2, \gamma_3$	viscosity components in molecular frame of reference
γ_1, γ_2	surface coupling constants
γ_G, γ_φ	Goldstone mode viscosity
γ_S, γ_θ	electroclinic or soft mode viscosity
$\hat{\gamma}$	viscosity tensor in diagonal form
Γ	total torque
Γ^ε	dielectric torque
Γ^θ	torque acting on director tilt
Γ^v	viscous torque
ε	dielectric constant or permittivity
ε_0	permittivity of free space
$\varepsilon_1, \varepsilon_2, \varepsilon_3$	permittivity principal values in molecular frame of reference
ε_a	dielectric anisotropy
ε_G	dielectric constant contribution from Goldstone mode
ε_{hom}	permittivity of sample in quasi-homeotropic geometry
ε_{helix}	permittivity of QBS sample in presence of helix
ε_p	dielectric constant for planar alignment
ε_r	relative dielectric constant
ε_R	dielectric constant for racemate
ε_s	dielectric constant contribution from soft mode
ε_{unw}	permittivity of QBS sample for unwound helix
$\hat{\varepsilon}$	permittivity tensor in diagonal form
$\Delta\varepsilon$	dielectric anisotropy ($\varepsilon_3 - \varepsilon_1$)
$\partial\varepsilon$	dielectric biaxiality ($\varepsilon_2 - \varepsilon_1$)
ζ	measure of dielectric nonlinearity
η	order parameter
θ	Eulerian nutation angle
θ	angular part of polar coordinates

θ	tilt angle with respect to layer normal
κ	enantiomeric excess
λ	coupling constant
λ	Weiss (molecular field) proportionality constant
λ	surface strength
λ	wavelength of light
μ	magnetic moment
ξ	characteristic length
ξ, ξ_a, ξ_s	tilt vectors
ξ_d	dielectric coherence length
ξ_m	magnetic coherence length
ξ_p	polarization coherence length
ξ	measure of dielectric nonlinearity
ρ	radial part of polar coordinates
ρ_p	polarization charge density
σ	applied stress
σ	surface charge density
σ_{ij}	electrical conductivity
τ	characteristic time
τ	response time
τ_diel	response time due to dielectric torque
τ_φ	response time due to ferroelectric torque
τ_θ	response time for electroclinic effect
ϕ, φ	azimuthal angle
ϕ	tilt angle of optic axis
φ	Eulerian precession angle
χ	dimensionless parameter
χ	susceptibility
χ_a	anisotropy of magnetic susceptibility
ψ	azimuthal angle indicating direction of tilt in layer plane
ψ	complex order parameter
ψ	Eulerian angle of eigen rotation
Ω	biquadratic coupling coefficient
Ω_i	angular rotation araound the i axis
δ	chevron angle

AC, ac	alternating current
AFLC	antiferroelectric liquid crystal
AMLCD	active matrix liquid crystal display
ANNI	axial nearest neighbor Ising
ANNNI	axial next nearest neighbor Ising
8CB	cyanobiphenyl compound

CMOS	complementary metal oxide semiconductor
DC, dc	direct current
DHM	deformed helix mode
DOBAMBC	decyloxybenzylidene amino 2-methyl butyl cinnamate
ED	error diffusion
FLC	ferroelectric liquid crystal
FLCD	ferroelectric liquid crystal display
FLCP	ferroelectric liquid crystal polymer
HDTV	high definition television
HF	high frequency
HOBACPC	hexyloxybenzylidene amino 2-chloro α-propyl-cinnamate
IC	integrated circuit
ITO	indium tin oxyde
KDP	KH_2PO_4
LCD	liquid crystal display
LED	light emitting diode
MHPOBC	methyl heptyloxycarbonyl phenyl octyloxy biphenyl carboxylate
MHTAC	methyl heptyl terephtalylidene-bis-4-amino cinnamate
NLO	nonlinear optics
NMR	nuclear magnetic resonance
NOBAPC	4-nonyloxybenzylidene-4′-aminopentyl cinnamate
o.a.	optic axis
PAR	polyarylate
PC	polycarbonate
PES	polyestersulfonate
PET	poly(ethylene terephthalate)
PI	polyimide
QBS	quasi-bookshelf
RGB	red–green–blue
SmA	smectic A
SmA*	chiral smectic A
SmC	smectic C
SmC*	chiral smectic C
SHG	second-harmonic generation
SSFLC	surface-stabilized ferroelectric liquid crystal
STN	supertwisted nematic
TFT	thin film transistor
TGB	twist grain boundary
TN	twisted nematic
UV	ultraviolet
VGA	virtual graphic adapter
VLSI	very large scale integration
XGA	extended graphic adapter

1 Introduction

Ferroelectric liquid crystals are a novel state of matter, a very recent addition to the science of ferroelectrics which, in itself, is of relatively recent date. The phenomenon which was later called ferroelectricity was discovered in the solid state (on Rochelle salt) in 1920 by Joseph Valasek, then a PhD student at the University of Minnesota. His first paper on the subject [1] had the title *Piezo-Electric and Allied Phenomena in Rochelle Salt.* This was at the time when solid state physics was not a fashionable subject and it took several decades until the importance of the discovery was recognized. Valasek had then left the field. Later, however, the development of this branch of physics contributed considerably to our understanding of the electrical properties of matter, of polar materials in particular and of phase transitions and solid state physics in general. In fact, the science of ferroelectrics is today an intensely active field of research. Even though its technical and commercial importance is substantial, many breakthrough applications may still lie ahead of us. The relative importance of liquid crystals within this broader area is also constantly growing. This is illustrated in Fig. 1, showing how the proportion of the new materials, which are liquid-crystalline, has steadily increased since the 1980s.

The general level of knowledge of ferroelectricity, even among physicists, is far lower than in the older and more classical subjects like ferromagnetism. It might therefore be worthwhile to discuss briefly the most important and characteristic fea-

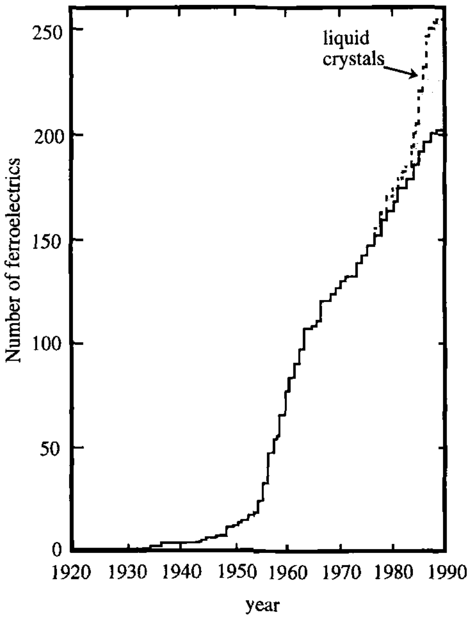


Figure 1. Number of known ferroelectrics. Solid line: solid state ferroelectrics, where each pure compound is counted as one. Dashed line: total number, including liquid crystal ferroelectrics, for which a group of homologs is counted as one. From about 1984, the proportion of liquid crystals has steadily grown which has been even more pronounced after 1990. (After Deguchi [2] as cited by Fousek [3].)

tures of solid ferroelectrics and polar materials, before turning to liquid crystals. This will facilitate the understanding and allow us to appreciate the striking similarities as well as distinctive differences in how polar phenomena appear in solids and how they appear in liquid crystals. One of the aims, of course, is also to make a bridge to existing knowledge. Those not aware of this important knowledge are apt to coin new words and concepts, which are bound to be in contradiction to already established concepts or even contradictory to themselves.

When dealing with ferroelectric liquid crystals, we use the same conceptual framework already developed for solid polar materials. An important part of this is the Landau formalism describing phase transitions (still not incorporated in any textbook on thermodynamics), based on symmetry considerations. It is important to gain some familiarity with the peculiarities of this formalism before applying it to ferroelectric liquid crystals. In this way it will be possible to recognize cause and effect more easily than if both subject matters were introduced simultaneously.

Concepts like piezoelectric, pyroelectric, ferroelectric, ferrielectric, antiferroelectric, paraelectric, electrostrictive, and several more, relate to distinct phenomena and are themselves interrelated. They are bound to appear in the description of liquid crystals and liquid crystal polymers, as they do in normal polymers and crystalline solids. Presently, great confusion is created by the uncritical use of these terms. For example, in the latest edition of the Encyclopedia Britannica [4] it is stated that pyroelectricity was discovered in quartz in 1824. This is remarkable, because quartz is not pyroelectric at all and cannot be for symmetry reasons. To clarify such issues (and the confusion is no less in the area of liquid crystals), we will have to introduce some simple symmetry considerations that generally apply to all kinds of matter. In fact, symmetry considerations will be the basic guidelines and will probably play a more important role here than in any other area of liquid crystals. Chirality is a special property of dissymmetry with an equally special place in these considerations. It certainly plays a fundamental role for ferroelectric liquid crystals at least so far. Therefore we will have to check how exactly the appearance of polar properties in liquid crystals is related to chiral properties, and if chirality is dispensable, at least in principle. Finally, flexoelectricity is also a polar effect, and we will have to ask ourselves if this is included in the other polar effects or, if not, if there is an interrelation.

Can liquids in which the constituents are dipoles be ferroelectric? 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. It is true that such a 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 behavior. An isotropic liquid cannot have polarization in any direction, because every possible rotation is a symmetry operation and this of course is independent of whether the liquid lacks a center of inversion, is chiral, or not. Hence we have at least 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. To search for ferroelectricity in an isotropic liquid would be futile, because a ferroelectric liquid cannot be isotropic. In order to have a bulk polarization, a medium must have a direction, the polarity of which cannot be reversed by any symmetry operation of the medium. On the other hand, 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. However, we would not consider such a liquid ferroelectric or pyroelectric – no more than we would consider a liquid showing flow birefringence to be a birefringent liquid. It is clear that there may be lots of interesting polar effects yet to be explored in flowing liquids, particularly in fluids of biological significance (which are very often chiral). Nevertheless, these effects should not be called "ferroelectric". They should not even be called piezoelectric, even if setting up shear flow in a liquid certainly bears some resemblance to setting up shear strain in a crystal.

Are there magnetic liquids? Yes, there are. We do not mean the just-mentioned "ferrofluids", which are not true magnetic liquids, because the magnetic properties are due to the suspended solid particles (of about 10 nm size). As we know, ferromagnetic materials become paramagnetic at the Curie temperature and this is far below the melting point of the solid. However, in some cases it has been possible (with extreme precautions) to supercool the liquid phase below the Curie temperature. This liquid has magnetic properties, though it is not below its own Curie temperature (the liquid behaves as if there is now a different Curie temperature), but it would be wrong to call the liquid ferromagnetic. The second example is the equally extreme case of the quantum liquid He-3 in the A1 phase. Just like the electrons in a superconductor, the He-3 nuclei are fermions and have to create paired states to undergo Bose–Einstein condensation. However, unlike the electron case, the pairs are created locally, and the axis between two He-3 then corresponds to a local director. Thus He-3 A is a kind of nematic-like liquid crystal, and because of the associated magnetic moment, He-3 A is undeniably a magnetic liquid, but again, it is not called *ferro*magnetic. Thus, in the science of magnetism a little more care is normally taken with terminology, and a more sound and contradiction-free terminology has been developed: a material, solid or liquid, may be designated magnetic, and then what kind of magnetic order is present may be further specified. When it comes to polar phenomena, on the other hand, there is a tendency to call everything "ferroelectric", a usage that leads to tremendous confusion and ambiguity. It would be very fortunate if in future we could reintroduce the more general concepts of "electric materials" and "electric liquids" in analogy with magnetic materials and magnetic liquids. Then, in every specific case, it would be necessary to specify which electric order (paraelectric, dielectric, etc.) is present, just as in the magnetic case (paramagnetic, diamagnetic, etc.).

Coherent and contradiction-free terminology is certainly important, because vagueness and ambiguity are obstacles for clear thinking and comprehension. In the area of liquid crystals, the domain of ferroelectric and antiferroelectric liquid crystals probably suffers from the greatest problems in this respect, because in the implementation of ideas, concepts, and general knowledge from solid state physics, which have been of such outstanding importance in the development of liquid crystal research, the part of ferroelectrics and other polar materials has generally not been very well represented.

Presumed ferroelectric effects in liquid crystals were reported by Williams at RCA in Princeton, U. S. A., as early as 1963, and thus at the very beginning of the modern era of liquid crystal research [5]. By subjecting nematics to rather high dc fields, he provoked domain patterns that resembled those found in solid ferroelectrics. The ferroelectric interpretation seemed to be strengthened by subsequent observations of hysteresis loops by Kapustin and Vistin [6] and by Williams and Heilmeier [7]. However, these patterns turned out to be related to electrohydrodynamic instabilities, which are well understood today (see, for instance, [8], Sec. 4.3 or [9], Sec. 4.2), and it is also well known that certain loops (similar to ferroelectric hysteresis) may be obtained from a nonlinear lossy material (see [10], Sec. 4.2). As we know today, nematics do not show ferroelectric or even polar properties. In order to find such properties we have to lower the symmetry until we come to the tilted smectics, and further lowering their symmetry by making them chiral. The prime example of such a liquid crystal phase is the smectic C*.

In principle, the fascinating properties of the smectic C* phase could have been detected long before their discovery in 1974. Such materials were synthesized by Vorländer [11] and his group in Halle before the first World War. The first one seems to have been an amyloxy terephthal cinnamate with a smectic C* phase from 133 °C to 247 °C and a smectic A* phase from 247 °C to 307 °C, made in 1909 [11] at a time far earlier than the first description of the smectic C phase as such [12] in 1933. At that time it was not, and could not possibly have been realized as ferroelectric. The concept did not even exist.

In a classic review from 1969, Saupe (at Kent State University) discussed a hypothetical ferroelectric liquid crystal for the first time [13]. While a nematic does not have polar order, such order, he pointed out, could possibly be found in the smectic state. The ferroelectric smectic, according to Saupe, is an orthogonal nonchiral smectic in which all molecular dipoles are pointing along the layer normal in one single direction (a longitudinal ferroelectric smectic). He also discussed a possible antiferroelectric arrangement. Among the other numerous topics discussed in this paper (suggesting even the first blue phase structure), Saupe investigated the similarities between nematics and smectics C and introduced the twisted smectic structure as the analog of a cholesteric. In the same year, Gray in Hull [14] synthesized such materials (actually the first members of the DOBAMBC series), but only reported on an orthogonal smectic phase; no attention was paid to smectic polymorphism in those days. Actually, in the year before, Leclerq et al. [15] (in Paris) had reported on a material having two distinct chiral and strongly optically active phases, which they interpreted as two distinct nematic phases. They were thus very close to discovering the helicoidal smectic. (Their material had a first order N*–C* transition.) A helicoidal smectic was then reported for the first time by Helfrich and Oh, at RCA in 1971, who described the first smectic liquid crystal ("spiraling" or "conical" smectic) identified as optically active [16]. Like the substances in the above-mentioned examples, this one belongs to the category that is the topic of this book, but who could have expected them to have special polar properties?

While the smectic C* phase was gradually becoming recognized, the question of ferroelectricity was again brought up by McMillan at the University of Illinois, Urbana, U. S. A. In 1973 he presented a microscopic molecular theory of the smectic C phase [17] based on dipole–dipole interactions, which predicted three different polar phases. McMillan's model molecules have a central dipole and two outboard dipoles perpendicular to the long axis. Either all three can line up or only the outboard ones with the central dipoles random, or the central dipoles can line up with the outboard dipoles random. The transition from the A phase to these polar phases is thought to take place through different rotational transitions where the rotational freedom is lost or frozen out due to the dipole–dipole interaction. The net polarization in the condensed phases lies in the smectic plane and gives rise to a two-dimensional ferroelectric. Actually, whether the order is ferroelectric or antiferroelectric depends on the sign of the interplanar interaction, which cannot be predicted. McMillan's dipolar theory, which does not involve chirality at all, never really applied to liquid crystals and was rapidly superseded by the ideas of Meyer in the following year.

In fact, the discovery and introduction of practically all polar effects in liquid crystals go back to the ideas of Meyer, at that time working at Harvard. In 1969 he published an epoch-making paper entitled *Piezoelectric Effects in Liquid Crystals* [18]. It must be said that the new phenomena described in that paper are beautifully analogous to piezoelectric effects in solids. Nevertheless they are of a different nature. Therefore de Gennes instead proposed the name flexoelectric [19], in order to avoid misunderstanding. Seven years later, together with his student Garoff, Meyer presented a new, original effect which he called the piezoelectric effect in smectic A liquid crystals [20]. The analogies between this effect and the piezoelectric effect in solids are here perhaps even more striking, as we will see. However, it is not the same thing and, after much consideration by the authors, the new phenomenon was finally published under the name electroclinic effect [21], a term which has since been generally adopted. In the following twenty years, there were numerous publications, in which different workers reported measuring a piezoelectric effect in liquid crystals (normally without stating what it meant and why they used this term). Obviously, they meant neither the flexoelectric nor the electroclinic effect, because the meanings of these are by now well established. Therefore the question arises as to whether a third effect exists in liquid crystals, which would finally qualify for the name piezoelectric. Obviously, this state of affairs is not very encouraging. A critical review of the terminology is therefore necessary in this area and should contribute to clarifying the concepts.

Ferroelectric liquid crystals have been a field of research for about twenty years, and have certainly been in the forefront of liquid crystal research, with an increasing number of researchers involved. The first state-of-the-art applications have recently appeared. This account concentrates on the basic physics, but also treats in considerable detail the topics of highest relevance for applications. Literature references have been given, as far as possible, for topics that, for space reasons, could not be treated [8–10, 22–58]. A big help for finding access to previous work is the bibliography of [52], which extends to 1989, as well as the series of conference proceedings published by *Ferroelectrics* [54–58a], covering a great deal of the work from 1987 to 1997. New ferroelectric liquid crystal materials are continually included in the Liqcryst-Database [59] set up by Vill at the University of Hamburg.

2 Polar Materials and Effects

2.1 Polar and Nonpolar Dielectrics

A molecule that has an electric dipole moment in the absence of an external electric field is called a polar (or dipolar) molecule. Such a molecule will tend to orient itself in an electric field. In a material consisting of polar molecules, the induced polarization P due to the average molecular reorientation is typically 10–100 times larger than the contribution from the electronic polarization present in all materials. In contrast, a nonpolar molecule has its distributions of positive and negative charges centered at the same point. A characteristic of materials consisting of nonpolar molecules is that the polarization P induced by a field E is small and independent of temperature, whereas in the first-mentioned case, P is a function $P(T)$ with an easily observable temperature dependence. Hence the same goes for the dielectric constant ε and the susceptibility χ.

If we write the relations between dielectric displacement $\boldsymbol{D}$, induced polarization $\boldsymbol{P}$, and applied electric field $\boldsymbol{E}$, assuming that $\boldsymbol{P}$ is linear in $\boldsymbol{E}$

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P} = \varepsilon_r \varepsilon_0 \boldsymbol{E} = \varepsilon \boldsymbol{E} \tag{1}$$

we get

$$\boldsymbol{P} = (\varepsilon_r - 1)\,\varepsilon_0 \boldsymbol{E} = \chi \varepsilon_0 \boldsymbol{E} \tag{2}$$

with ε_r as the relative, ε as the total dielectric constant or permittivity, and ε_0 the permittivity of free space, where $\varepsilon_0 = 8.85 \times 10^{-12}$ C V^{-1} m^{-1}. It will later be necessary to consider that ε and χ in reality are second rank tensors, and in that context we will write Eqs. (1) and (2) in the corresponding forms

$$\boldsymbol{D}_i = \varepsilon_{ij} \boldsymbol{E}_j \tag{2.2a}$$

and

$$\boldsymbol{P}_i = \varepsilon_0 (\varepsilon_{ij} - 1)\,\boldsymbol{E}_j = \varepsilon_0 \chi_{ij} \boldsymbol{E}_j \tag{2.2b}$$

The scalar dielectric susceptibility χ in Eq. (2) is, like ε_r, a dimensionless number, and lies in the range 0–10 for most materials, although it may attain values higher than 10^4 for certain ferroelectric substances. We will equally use this term, the susceptibility, for its dimensional form $\varepsilon_0 \chi = \partial P / \partial E$.

As examples of nonpolar molecules we may take H_2, O_2, CO_2, CS_2, CH_4, and CCl_4, and as well-known polar molecules CO (0.10), NH_3 (1.47), C_6H_5OH (1.70),

H_2O (1.85), $C_6H_5NO_2$ (4.23), where we have stated the value of the dipole moment in parentheses, expressed in Debye (D), a unit commonly used for molecules. One Debye equals 10^{-18} cgs units and, expressed in SI units, $1\,\mathrm{D} = 3.3 \times 10^{-30}$ C m. For a comparison, let us consider a dipole consisting of two elementary charges $\pm e$ (i.e., with e the charge of the electron, 1.6×10^{-19} C) at a typical atomic distance of 1 Å or 0.1 nm from each other. This gives a dipole moment $p = qd = 1.6 \times 0^{-19} \times 10^{-10} = 1.6 \times 0^{-29}$ C m equal to 4.85 D. Let us assume that we had a gas consisting of molecules with this dipole moment and that we had a field sufficiently strong to align the dipoles with the field. With a density $N = 3 \times 10^{25}$ molecules/m^3 this would correspond to a polarization of $P = 5 \times 10^{-4}$ C m^{-2} = 50 nC cm^{-2}. However, this is a completely unrealistic assumption because the orientational effect of the field is counteracted by the thermal motion. Therefore the distribution of dipolar orientation is given by a Boltzmann factor $e^{-U/kT}$, where $U = -\boldsymbol{p} \cdot \boldsymbol{E}$ is the potential energy of the dipole in the electric field. Integrating over all angles for $\boldsymbol{p}$ relative to $\boldsymbol{E}$ gives the polarization P as a function of E according to the Langevin function L (to be discussed in Sec. 2.5) which expresses the average of $\cos(\boldsymbol{p}, \boldsymbol{E})$,

$$P = NpL\left(\frac{pE}{kT}\right) \tag{3}$$

shown in Fig. 2. For small values of the argument, $L[pE/(kT)] \approx pE/(3kT)$, and thus

$$P = \frac{Np^2 E}{3kT} \tag{4}$$

corresponding to the linear part around the origin. However, even at a field $E = 10^7$ V m^{-1}, corresponding to dielectric breakdown, the value of $pE/(kT)$ is only about 0.03 at room temperature, giving a resulting polarization of 1% of the saturation value. A similar result would be true for the liquid phase of the polar molecules. In liquid crystal phases, it will generally be even harder to polarize the medium in an external field. In the very special polar liquid crystals, on the other hand, the reverse is true: for quite moderate applied fields it is possible to align all dipoles, cor-

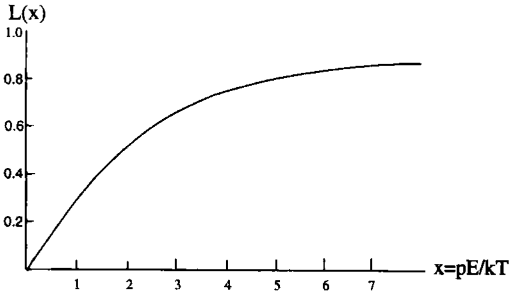


Figure 2. The Langevin function $L(x) = \coth x - 1/x$.

responding to polarization values in the range of 5–500 $\mathrm{nC\,cm^{-2}}$ (depending on the substance).

According to Eq. (4), the polarization, at constant field, grows when we lower the temperature. By forming $\partial P/\partial E$, we may write for the susceptibility

$$\chi = \frac{C}{T} \tag{5}$$

The fact that the susceptibility has a $1/T$ dependence, called the Curie law, is characteristic for gases and liquids, but may also be found in solids. Generally speaking, it indicates that the local dipoles are noninteracting.

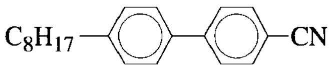
For another comparison, consider a crystal of rock salt, NaCl. It has a χ value of 4.8. If we apply the quite high but still realistic field of $10^6\ \mathrm{V\,m^{-1}}$ ($1\ \mathrm{V\,\mu m^{-1}}$) we will, according to Eq. (2), induce a polarization of $4.25\ \mathrm{nC\,cm^{-2}}$ (or $42.5\ \mathrm{\mu C\,m^{-2}}$; the conversion between these units commonly used for liquid crystals is $1\ \mathrm{nC\,cm^{-2}} = 10\ \mathrm{\mu C\,m^{-2}}$). The mechanism is now the separation of ionic charges and thus quite different from our previous case. It turns out that the displacement of the ions for this polarization is about 10^{-2} nm (0.1 Å), i.e., it represents only a small distortion of the lattice, less than 2%. Small displacements in a lattice may thus have quite strong polar effects. This may be illustrated by the solid ferroelectric barium titanate, which exhibits a spontaneous polarization of $0.2\ \mathrm{C\,m^{-2}} = 20\,000\ \mathrm{nC\,cm^{-2}}$. Responsible for this are ionic displacements of about 10^{-3} nm, corresponding to less than half a percent of the length of the unit cell. Similar small lattice distortions caused by external pressure induce considerable polar effects in piezoelectric crystals.

When atoms or molecules condense to liquids and solids the total charge is zero. In addition, in most cases the centers of gravity for positive and negative charges coincide. The matter itself is therefore nonpolar. For instance, the polar water molecules arrange themselves on freezing to a unit cell with zero dipole moment. Thus ice crystals are nonpolar. However, as already indicated, polar crystals exist. (In contrast, elementary particles have charge, but no dipole moment is permitted by symmetry.) These are then macroscopic dipoles and are said to be pyroelectric materials, of which ferroelectrics are a subclass. Pyroelectric materials thus have a macroscopic polarization in the absence of any applied electric field. Piezoelectric materials can also be polarized in the absence of an electric field (if under strain) and are therefore sometimes also considered as polar materials, though the usage is not general nor consistent. Clearly their polarization is not as "spontaneous" as in the pyroelectric case.

Finally, there seems to be a consensus about the concepts of polar and nonpolar liquids. Water is a polar liquid and mixes readily with other polar liquids, i.e., liquids consisting of polar molecules, like alcohol, at least as long as the sizes of the molecules are not too different, whereas it is insoluble in nonpolar liquids like benzene. If in liquid form, constituent polar molecules interact strongly with other polar molecules and, in particular, are easily oriented in external fields. We will also use this criterion for a liquid crystal. That is, we will call a liquid crystal polar if it contains local dipoles that are easily oriented in an applied electric field.

2.2 The Nonpolarity of Liquid Crystals in General

The vast majority of molecules that build up liquid crystal phases are polar or even strongly polar. As an example we may take the cyanobiphenyl compound 8CB (Merck Ltd) with the formula



which has an isotropic–nematic transition at 40.1 °C and a nematic to smectic A transition at 33.3 °C. Whereas the molecules are strongly polar, the nematic and smectic A phases built up of these molecules are nonpolar. This means that the unit vector $\boldsymbol{n}$, called director, describing the local direction of axial symmetry, does not represent a polar direction but rather one with the property of an optic axis. This means that $\boldsymbol{n}$ and $-\boldsymbol{n}$ describe the same state, such that all physical properties of the phase are invariant under the sign reversal of $\boldsymbol{n}$

$$\boldsymbol{n} \rightarrow -\boldsymbol{n}, \quad \text{symmetry operation} \tag{6}$$

Repeatedly this invariance has, somewhat carelessly, been described as equivalent to the absence of ferroelectricity in the nematic phase, whereas it only expresses the much weaker condition that $\boldsymbol{n}$ is not a polar direction.

How can we understand the nonpolarity expressed by Eq. (6), which up to now seems to be one of the most general and important features of liquid crystals? Let us simplify the 8CB molecules to cylindrical rods with a strong dipole parallel to the molecular long axis. In the isotropic phase these dipoles could not build up a macroscopic dipole moment, because such a moment would be incompatible with the spherical symmetry of the isotropic phase. But in the anisotropic nematic phase such a moment would be conceivable along $\boldsymbol{n}$. However, this would set up a very strong external electrostatic field and such a polar nematic would tend to diminish the electrostatic energy by adjusting the director configuration $\boldsymbol{n}(\boldsymbol{r})$ to some complex configuration for which the total polarization and the external field would be cancelled. Such an adjustment could be done continuously because of the three-dimensional fluidity of the phase. It would lead to appreciably elastic deformations, but these deformations occur easily in liquid crystals and would carry small weight compared to the energy of the polar effects which, as we have seen, are very strong. Thus it is hard to imagine a polar nematic for energetic reasons. Moreover, the dipolar cancellation can, and therefore will, take place more efficiently on a local scale. This is illustrat-