

INVITED ARTICLE

Alfred Saupe - 50 Years of Research

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Abstract. In this commemorative article the major scientific achievements of Alfred Saupe are discussed. This comprises those, which are clearly associated with his name and made him famous, and some important issues, where his fundamental involvements are rather less apparent. Emphasis is put on his lasting impact on the liquid crystal field.

Keywords Maier-Saupe theory; liquid crystal NMR; lyotropic liquid crystals; biaxial nematics; lasting impact; Alfred Saupe

1. Introduction

Commemorating Alfred Saupe's scientific work one realizes immediately the enormous breadth and depth of his research maintained on very high levels for a very long time. Trained as a physicist he did not specialize into experimental or theoretical physics, but rather did both. From his Diploma thesis work on polarized ultraviolet (UV) light absorption in the different phases of PAA (4,4-dimethoxyazoxy-benzene) it became obvious that ordinary molecular forces are responsible for the nematic ordering, but there was no theory to explain that. So he devoted his PhD work (with W. Maier as supervisor) to the derivation of the mean-field theory of orientational order due to van der Waals forces – a heavy quantum-mechanical second order perturbation calculation of the angle-dependent mean potential that led to the famous Maier-Saupe expression for the nematic order parameter. This theory made many predictions, which he started to test by several experimental methods. Among the former, the temperature dependence of the Frank elastic coefficients was investigated using director reorientation by magnetic fields well above the well-known Frederiks instability threshold. Again, he supplied the missing parts of the theory for high fields by his own.

As a post-doc (in modern terms) he made contact with a more applied, electro-technical environment. There he grasped very new techniques, like nuclear magnetic resonance (NMR), which were not com-

monly used at that time. He took the opportunity to apply these methods to nematic liquid crystals as well as to non-mesogenic organic molecules dissolved in them. A lot of experimental efforts to make the methods work, together with theoretical work to make them meaningful and useful, followed and established in particular NMR as a valuable and indispensable standard tool for liquid crystal research. Nevertheless, he did not discard previously used methods, but rather combined them with new ones, such as infrared (IR) spectroscopy.

The third step in his scientific career led him, not quite by purpose, to a macromolecular institute, where he was offered the possibility for Habilitation, a necessary prerequisite to make an academic career in Germany at that time. He added polymers and their investigation by NMR to his scientific portfolio - something that certainly played a role many years later, when he spent some time in Mainz as senior Humboldt fellow and when he was asked to head a Max Planck Research Group in Halle after the unification of Germany.

This experience of different scientific environments and the interaction with colleagues of different scientific background and expertise were an ideal preparation for his move to the LCI at Kent State, USA. Here, in a research focussed, multi-disciplined and liquid-crystal oriented place he was able to combine theory with experiment, add new techniques to the already standard ones, look for new materials, new phases and their properties beyond simple uniaxial thermotropic nematics. And this he did to a large extent.

On the occasion of the 70th birthday of Alfred Saupe somewhat 14 years ago, a Festschrift has been produced [1]. Among scientific papers of various col-

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leagues it contains his personal CV (by P. Palffy-Muhoray), a list of his publications (until mid-1997), an English translation of his early papers on what is now called the Maier-Saupe theory originally published in German, and a laudatio "Alfred Saupe – 40 years of Research". There [2] I have tried to discuss the scientific contents and merit of many of his papers, clustering them into topical groups, like 'structure and order', 'defects, dynamics and instabilities', 'new phases and phase transitions', and 'applied research', which gives a glimpse of the broadness of Alfred Saupe's research. Of course, I will not repeat this here and, instead, will focus on the lasting scientific impact on the liquid crystal field that his achievements have gained. As examples I will discuss the Maier-Saupe theory, NMR, tilted smectics, biaxial nematics, and other highlights that will persistently be connected with his name, and a few less known involvements in the early stages of important areas. A discussion of his last 12 research years will finish this homage to Alfred Saupe.

2. Maier-Saupe theory

Without any doubt, Alfred Saupe is best known, not only in the liquid crystal community, but also far beyond, for his share on the Maier-Saupe theory. Based on the assumption that only *induced* dipolar forces are relevant for orientational ordering, this theory is still applied to, or relevant for, quite different kinds of problems given the omnipresence of these van der Waals forces on the molecular level. The number of citations, almost 4000 up to now, for the three publications that developed the theory [3] is an impressive signature for its relevance. Furthermore, the rate of citation has been high over the years (apart from a slow start, probably due the language barrier) and does not yet show a decline. Even for the years of the present decade the averaged rate is 30 citations per year for each of the three papers. The five years with the highest citation number are widely scattered between 1976 and 2001, indicating that the appreciation of the scientific community is a lasting and prevailing one.

Due to its general importance the Maier-Saupe theory is now included in most of the textbooks dealing with statistical and/or condensed matter physics, although often only in a very abbreviated way, for example in [4], or only the results for the self-consistent order parameter are presented and discussed, for example in [5]. A short exposition of the structure of this theory can be found in [2], a more comprehensive treatment in [6], although the real beauty and profoundness of the theory can only be grasped by reading the original publication (or their English translation in [1]). With the assumption of induced dipolar forces many experimental results could be explained, for example the spectra

of benzene π -electrons in PAA and the odd–even effect caused by alkyl chains. But this was not enough for Alfred Saupe. The theory made quantitative predictions regarding the jump of the order parameter at the weakly first-order isotropic to nematic transition, the temperature dependence of the order parameter including pretransitional effects, the density jump at the transition and various thermodynamic quantities like heat of transition, specific heat and compressibility. He successfully tested those predictions experimentally and could corroborate the applicability of the theory to the (thermotropic) liquid crystals known at that time. Clearly, permanent dipolar forces due to special chemical structures, or steric forces due to the elongated form of the molecules are less important for the origin of nematic order. Repulsive steric forces play a role in lyotropics and are nowadays frequently used in computer simulations (even for thermotropics), since they take much less computation time than induced dipolar forces.

This early scientific achievement of Alfred Saupe already demonstrates his working style: to try to tackle a problem from all sides by different means and accept a result only, after having obtained a comprehensive and coherent picture.

3. NMR and order

The use of NMR techniques to investigate liquid crystals is another area that is firmly associated with Alfred Saupe. His first, groundbreaking paper [7] on the application of NMR to nematics and its theoretical interpretation has drawn more than 400 citations, among them 75 in the 21st century. Again this shows the lasting impact his NMR research has had on the liquid crystal field. In the ten years that followed the first publication, NMR was one of his favorite experimental techniques (more than 20 papers). However, also in later years he came back to it, in particular when new types of liquid crystals occurred, since NMR can be used for thermotropic and lyotropic liquid crystals as well as for side-chain and main-chain polymeric and elastomeric mesophases.

Basically, NMR probes the orientation of spins with respect to an applied magnetic field. It makes a difference in the NMR signal, whether a system is disordered (powder or isotropic liquid) or ordered (liquid crystal or crystal). Liquid crystals are thereby in-between the solid case (order) and the liquid one (motional narrowing of the signals) and its NMR need some special theoretical interpretation. Obviously, NMR is suitable to extract information on orientations (e.g., of the director) and the strength of the orientational order. Both aspects have been exploited by Alfred Saupe from the beginning (for further developments of the method in liquid crystals, cf. [8]).

Having an experimental access to the orientational order parameter Alfred Saupe investigated several phase transitions, where often the strength of the order changes. In particular, first order transitions and biphasic regions can be identified. The different orientation of prolate and oblate aggregates in a magnetic field allowed Alfred Saupe to detect a N_C to N_D phase transition in certain lyotropic systems leading ultimately to the discovery of a biaxial nematic phase (see later). NMR measurements on molecules dissolved in a nematic matrix were an important topic right from the beginning (with G. Englert) [9]. Due to the ordered environment that allows to look at definite geometries, on the one hand, and due to the motional narrowing in the liquid phase resulting in sharp spectra, on the other side, a host of valuable information on the dissolved molecules can be so obtained. Of course, Alfred Saupe did not rely on just one technique, but combined NMR with other spectral methods (UV, IR) and with dielectric relaxation to get data on intermolecular forces, quadrupolar interaction, electronic structure, proton distances, anisotropic chemical shifts and more. Such information helps the chemical design of mesogens and the understanding of their liquid crystal phases.

4. Structure and phases

In Kent Alfred Saupe started to carry out much theoretical and experimental work on new phases and their structure as well as on textures and defects that allowed for the identification of those new phases. The origin of these developments can be found in a short publication in 1969 [10], where several new ideas and speculations are laid out. This paper had an enormous immediate impact on the liquid crystal community, although this is not adequately reflected by the relatively low number of 163 citations. In particular, the citations dropped considerably in the 1990s and thereafter. The reason might be that some of the discoveries are nowadays so obvious and well-known that the requirement for a citation is not seen, or the topics were amended afterwards by other researchers and are now not necessarily associated with Alfred Saupe.

The first point is his realization that the tilted smectic C phase has a nematic degree of freedom governed by an elastic free energy analogous to the Frank free energy for nematics. The difference comes from smectic C being biaxial and having only one nematic degree of freedom. He formulated the appropriate non-linear expression and deduced that Schlieren textures are possible and could be used to identify this phase experimentally. And that he did, too.

Secondly, he speculated on possible new smectic phases. Among them he proposed what is now called

the smectic A_2 phase with antiferroelectric double layers. Somewhat later he developed a molecular-field theory of such a phase using the polar order parameter P_1 . After the experimental detection of such polar (and frustrated) smectic phases in 1979, this field of smectic polar polymorphism, and the phase transitions involved, increased immensely in the 1980s and 1990s.

He also predicted the chiral smectic C^* phase (or an achiral smectic C phase with chiral dopants) to show a helical structure of the director similar to cholesterics, albeit tilted (conic helical). Of course, this phase is the prototype of ferroelectric liquid crystals, still today one of the major areas in liquid crystal research and applications (smectic devices). Unfortunately, Alfred Saupe did not realize at that time the ferroelectricity [11] (or more precisely, helielectricity [12]) of that phase.

He was not only interested in static, structural questions. So the third topic of this paper dealt with the possibility of propagating bend/twist waves in nematics. He concluded that for the typical material parameters of nematic liquid crystals the (linear) director dynamics is always overdamped and relaxational. Again, this is common knowledge nowadays.

The fourth highlight concerns the structure of cholesteric blue phases. He gave the first reasonable model involving defect lines that could reconcile the microscopic (molecular) twist structure with the cubic crystalline structure on the mesoscopic length scale (optical wavelength). The field was further developed later and the models refined by others and has seen a revival in recent years due to smectic blue phases, but Alfred Saupe was at the beginning of these developments.

Dealing with the nematic degree of freedom in smectic C liquid crystals, Alfred Saupe built a cell with different surface orientations demonstrating the existence of twist in that phase. At that time J. Ferguson co-invented (the other inventors are W. Helfrich and M. Schadt; for a more detailed discussion of the early development of twisted nematic displays, cf. [13], where Alfred Saupe's involvement is also mentioned), the nematic twist cell in Kent for use as a liquid crystal display. Thus, Alfred Saupe was involved in the early scientific considerations regarding this main application of liquid crystals that still has a colossal commercial impact.

5. Lyotropics and biaxial nematics

In the mid 1970s Alfred Saupe's interest shifted to lyotropic liquid crystals. These mixtures of amphiphilic molecules (surfactants) and a suitable solvent are basically more complex than thermotropic low-molecular-weight liquid crystals, since the additional degree of freedom, the concentration of the amphiphiles (and

that of the cosurfactant), governs the shape of the molecular aggregates. Rod-like and plate-like micelles, lamellar and bicontinuous double-layered structures are frequently found. They order macroscopically to (mostly) liquid crystalline phases. Therefore, they are like conventional liquid crystals with the additional possibility of changing the form and shape of the underlying structural entities making them very interesting at least at the basic scientific level.

NMR is a very versatile method for investigating lyotropic systems. Not only can the structure of the phase be obtained, but also the shape of the micelles. Alfred Saupe did many studies on nematic and cholesteric lyotropic phases. As a possibly unexpected result, it turned out that a nematic phase of calamitic micelles (N_L) has somewhat different physical properties than that made of discotic ones (N_C). In particular, the sign of the dielectric and diamagnetic susceptibility anisotropy differs in the two phases giving rise to a different orientation behavior in external fields. He found a system, where both types of nematics occurred at different temperatures with a N_L to N_C transition in-between. The chiralized system showed an appropriate cholesteric to cholesteric transition.

At least at that point, Alfred Saupe must have got the idea to look for a biaxial nematic phase. After a very delicate fine-tuning of temperature and concentrations of surfactant and co-surfactant he finally succeeded (with L.J. Yu) in detecting the biaxial nematic phase [14] in a (small) temperature range between the two uniaxial phases. Using NMR structure studies, microscopic defect and texture observations and applying external fields, he was able to prove the biaxial nematic structure of that phase. Nevertheless, there were many doubts about this result to start with, because to that date all reports on detecting biaxial nematic phases in thermotropic systems had turned out to be premature. It took the scientific community a considerable amount of time before the experimental results could be corroborated in other laboratories. Lyotropic experiments are notoriously hampered by evaporation effects and a very precise fixing of concentrations is nontrivial.

Of course, he did not stop with the detection of the biaxial phase. He studied systematically the material properties of this and related lyotropic phases, like elastic constants, diffusion coefficients, resistivity, magnetic birefringence, diamagnetic susceptibilities, expansion coefficients, rotational viscosity, relaxation times, electric conductivity and more. While the publication of our manuscript on the hydrodynamics of the biaxial nematic phase [15] was severely hampered in the referee process, Alfred Saupe published almost simultaneously his well-known Leslie-Ericksen-type theory [16] on elasticity and flow (and its stability) of the biaxial nematic phase, which he needed for the interpretation of his measurements. The search for bi-

axial nematic phases outside the lyotropic branch has recently gained much momentum, which is demonstrated by the number of articles in this Volume devoted to that topic. Alfred Saupe will always be remembered as the first to demonstrate its existence experimentally.

6. The late period

In 1992 Alfred Saupe retired from the LCI and Kent State University and took over the duties as head of a Max Planck Research Group in Halle (Amazingly, Alfred Saupe had many direct and indirect relations with Halle well before 1992 as is recounted in G. Pelzl's article in this issue). These and the final years were overshadowed by his progressing illness that severely reduced his scientific output. He was still a sought after discussion partner and informal advisor for many of his colleagues, scholars and friends. He managed to author seven additional publications (in addition to those 127 publications already listed in the Festschrift [1]) – shown here – involving 21 new co-authors (in addition to the 61 already listed in Ref. [1], partly related to his duties in Halle (cf. Table 1).

- *Surface-imaging of frozen blue phases in a discotic liquid crystal with atomic force microscopy* [17]
- *Uniform bookshelf alignment of chiral smectic C films with guided backflow*, [18]
- *Orientalional capillary pressure on a nematic point defect*, [19]
- *Tilted smectic layers of a SmC* liquid crystal between homeotropically treated plates*, [20]
- *Helical filamentary growth in liquid crystals consisting of banana-shaped molecules*, [21]
- *Viscoelastic director rotation of a low molecular mass liquid crystal*, [22]
- *Piezoelectricity of a ferroelectric liquid crystal with a glass transition*, [23]

Table 1: Additional co-authors after 1995.

J. Bajc	X.-H. Chen	S. Diele
M. Giocondo	A. Hauser	G. Heppke
G. Hillig	D. Krüerke	I. Letho
Ch. Lischka	S. Markscheffel	S.-S. Pak
G.G. Peroli	G. Pelzl	M. Schadt
T. Scharf	G. Scherowski	M. Thieme
T. Tóth-Katona	E.G. Virga	W. Weissflog

As always during his whole scientific career, the diversity of topics and the variety of co-authors is remarkable. A new technique, atomic force microscopy (AFM), shows up and a new material, bent-core

molecules, is used. As in his early days Alfred Saupe made use of new possibilities and opportunities at his new place in Halle. Again in the tradition of his kind of research, he came back to previous topics, like defects, tilted smectics, nematic director dynamics and piezoelectricity.

Refusing for a long time to write a book he finally gave in, certainly to convey some of his knowledge to younger students entering the liquid crystal field and he co-authored a book together with A. Jakli:

– *One- and Two-dimensional Fluids: Properties of Smectic, Lamellar and Columnar Liquid Crystals*, [24]

7. Summary

It was not possible in this short article to discuss all areas of Alfred Saupe's research in detail. A few more will be mentioned here. His work on defects and textures, first in nematics and cholesterics and later in tilted smectics, aimed in understanding optical observations, comprises fan textures, focal conics, disclinations, spiral defects in free droplets, reflection bands of Grandjean textures and more. Instabilities, like electrohydrodynamic convection and undulational layer instability in smectic C liquid crystals, were investigated. Electric and/or optical problems played a role during the whole span of his scientific activities, from with selective reflection and absorption in cholesteric fibers to electro-mechanical problems in smectic polymeric liquid crystals and solutions of polymers in low-molecular weight liquid crystals. Again, the enormous breadth of his work is impressive.

Looking at the quantity of his output, one might be astonished by the rather modest number of 134 publications. However, this reflects his careful style of communicating results only when they are verified by different means and fully understood, and not publishing tiny bits of subcritical relevance. Even more significantly, he really did prefer talking to and discussing with people, rather than writing papers. This is the place to apologize to all his many coworkers, whom I could not adequately mention and reference in this manuscript, but who contributed directly and indirectly very much to his successful career.

Alfred Saupe is a striking example that there is scientific impact and influence beyond bibliometric numbers, the Hirsch index and the like. He got several awards highlighting the respect he obtained from his peers, like the Nernst Prize (of the German Bunsen Society), a senior Humboldt award (from the Alexander von Humboldt Foundation) that lead him to Mainz, an invitation as fellow to the Wissenschaftskolleg Berlin, where he spent almost a year, the President's Medal of Kent State University, the Fredericksz Medal (of the

Russian Liquid Crystal Society), and Honored Membership of the International Liquid Crystal Society. Recently, the Alfred Saupe Foundation has been established in his commemoration, which awards the annual Alfred Saupe Prize (through the German Liquid Crystal Society); Helmut Ringsdorf was the first recipient in 2010.

Alfred Saupe will always be remembered by his outstanding achievement known as the Maier-Saupe theory and for his groundbreaking work and very early involvement in liquid crystal NMR, lyotropics and biaxial nematic liquid crystals, tilted smectic and ferroelectric liquid crystals, blue phases and smectic polar polymorphism and twist cell devices. Beyond being a great scientist he made a lasting impression to all who had the privilege of knowing him.

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