Ferroelectrics and their possible involvement in biology

N.E. Mavromatos\textsuperscript{1}, D.V. Nanopoulos\textsuperscript{2}, I. Samaras\textsuperscript{3}, K. Zioutas\textsuperscript{3}.

1) P.P.A.R.C. Advanced Fellow, University of Oxford, Department of Physics, Theoretical Physics, 1 Keble Road, OX1 3NP, U.K.
2) Department of Physics, Texas A & M University, College Station, TX 77843-4242, USA, and Astroparticle Physics Group, Houston Advanced Research Center (HARC), The Mitchell Campus, Woodlands, TX 77381, USA, and Academy of Athens, Chair of Theoretical Physics, Division of Natural Sciences, 28 Panepistimiou Avenue, Athens 10679, Greece.
3) Physics Department, University of Thessaloniki, GR54006 Thessaloniki, Greece.

27.2.1998

Abstract

We present the main properties of ferroelectricity, with emphasis given to a specific family of hydrated ferroelectric crystals, which can serve as model systems for corresponding configurations in biology like the microtubules. An experimental method is described, which allows to establish the ferroelectric property of microtubules in suspension.

Presented at the Workshop on the Molecular Biophysics of the Cytoskeleton, August 18-22, 1997, Banff, Alberta, Canada.
1. Introduction

Thales of Miletus (6th century B.C.) made the first observations of electricity by rubbing pieces of amber being biological in origin, thanks to macroscopic charge separation. Spontaneous charge separation appears also with ferroelectric materials, where at the molecular level the positive charge center is shifted relative to the negative charge distribution. The perfect alignment of these individual electric dipoles gives rise to the ferroelectricity. Thus, the ferroelectric state exhibits spontaneously a macroscopic electric dipole moment even in the absence of an external electric field. This occurs below a characteristic temperature, the Curie temperature $T_C$, where the individual electric dipoles of the molecules get spontaneously aligned; for comparison, to polarize a dielectric material to a similar value, one needs electric fields of the order MV/cm to GV/cm, and this distinguishes ferroelectricity.

The consequence of the coherent single dipole alignment is the appearance of unpaired positive and negative bound charges on the two end-faces along the direction of the spontaneous ferroelectric polarization $P_s$. In the ideal case, a piece of ferroelectric material is equivalent to an empty capacitor of the same dimensions, each plate being charged with $Q_\pm = \pm P_s$. Assuming $|P_s|$ values by factor $\sim 1000$ below those encountered often with crystals, the associated surface charge density ($\sigma$) can still be as much as $\sigma \approx 10^{11}$ charges/cm$^2 \equiv 10^3$ charges/µm$^2$. The maximum electric field strength inside matter is given by $E = -P_s/\epsilon$, with $\epsilon$ being the dielectric constant of the medium. For example, for $|P_s| = 1$ mC/m$^2$ only, the associated electric field is of the order of $\epsilon^{-1}$·MV/cm. Such electric fields exist only transiently, and, they can give rise even to the self-emission of energetic electrons ($\sim 100$ keV electrons have been measured (s. Gundel et al., 1989)); depending on the actual conditions those electrons might ionize the surrounding, or, they can cause other related effects.

In this section, we present in short the main properties of ferroelectricity, a phenomenon which is also described in the text books, but we also refer to a few related articles, which can be read actually by non-specialists (Zioutas & Daskaloyannis, 1985, Gundel et al., 1989, Riege, 1994), or, modern theoretical ones (Resta, 1997).

It is worth remembering that ferroelectricity and ferromagnetism have at first sight many common properties. Comparing both types of materials, the main difference comes from the (at least practically) non-existence of magnetic monopoles. The ubiquitous electric charges compensate the large polarization electric fields, and, they determine the transient ferroelectric behaviour during polarization change. Thus, the ferroelectric state is completely described by its widely known static properties as well as its dynamical
behaviour associated with a temperature change, or, applying externally pressure and/or electric pulses. In fact, every ferroelectric material is also piezoelectric and pyroelectric, but not \textit{vice versa}.

Obviously, any change of the intrinsic spontaneous ferroelectric polarization ($\Delta P_s$) is associated with a corresponding surface charge change ($\Delta Q_s$). These bound polarization charges attract (either from the surrounding or from the ferroelectric medium itself) an equal number of charges, but opposite in sign, since no environment can stand those electric fields. In short, a ferroelectric in its static state consists of a polarized crystal or polycrystalline medium, and, quasi free screening surface charges, which partly migrate into the bulk of the ferroelectric. The time period needed, for this charge neutralization to be completed, defines the dynamical behaviour of ferroelectrics. In general, this transient time is much longer than the preceding switching time. Depending on the applying electric field, temperature and the ferroelectric compound itself, transient times can be in the $\sim \mu$sec to sec region. Many ferroelectric properties during polarization change appear much more pronounced compared with those we know in the static case. For example, the dielectric constant takes enormous values around the phase transition temperature.

In fact, a ferroelectric sample in its static state might remain unnoticed at first sight. It is only the change of its spontaneous polarization vector ($P_s$), which makes actually ferroelectricity visible. We mention here a few mostly encountered cases when working with such materials. \textbf{a)} Let the temperature increase from the ferro- to the paraelectric state. During the phase transition, the intrinsic polarization disappears, and, one is left suddenly with the unpaired screening charges on each end-surface, which must be screened so to say, because of the associated strong electric fields. Since those charges are quasi-free, the result will be: either a current flow through the bulk of the ferroelectric material with both charge polarities compensating each other, or, for sufficient high intrinsic resistance of the sample, those almost unbound charges will be removed from each end-surface by their own repulsive Coulomb force (i.e. self-emission). \textbf{b)} In the opposite process, i.e. by lowering the temperature from the paraelectric to the ferroelectric state, the onset of the spontaneous polarization attracts screening charges from the surrounding, because usually those transient electric fields are far above the electrical breakdown limit of any material, including the ferroelectric sample itself, if one should consider this to happen in space. \textbf{c)} Reversal of the spontaneous polarization takes place, for example, by applying an external electric field ($\sim$kV/cm is usually sufficient), being either alternating or pulsed. Thus, during a hysteresis loop measurement two polarization reversals occur per cycle. In a complete reversal of the
intrinsic spontaneous polarization, the new bound polarization charges on each end-face of the sample have the same polarity as the previous screening charges. This makes the associated transient electric fields even stronger than those appearing in the first two cases mentioned before. The result is finally a complete rearrangement of the old screening charges, giving rise to a more pronounced dynamical behaviour, depending on the conductivity of the sample and other factors.

Finally, we mention in short a few other known effects, which occur when changing the polarization vector by $\Delta P_s$, or, much more enhanced during phase transition, which afterall can be of relevance for similar phenomena with the predicted biological ferroelectrics. These are: the flow of pyroelectric current through the sample, which occasionally takes the form of spikes (Barkhausen pulses), similarly to the self-emission of energetic electrons, or, bursts of microwave radiation (Caspers, Riege & Zioutas, 1988). We also like to mention here the antiferroelectric state, which is possibly of not minor importance. This is a peculiar polarized state, since it consists of quasi infinite many 180° domains of opposite alignment each, which does not require screening charges. However, the transition ferroelectric$\leftrightarrow$antiferroelectric gives also rise to a similar dynamical behaviour as for the mentioned paraelectric$\leftrightarrow$ferroelectric phase transition.

2. Hydrated ferroelectric compounds

We like to focus now on a very specific family of hydrated ferroelectric crystals, with the widely investigated potassium ferrocyanide trihydrate ($K_4Fe(CN)_6\cdot3H_2O$), in short KFCT (Helwig, Klöpperpieper, & Müser, 1978), taken to be a representative case. We think that this type of ferroelectricity might serve as a model configuration in biology, with emphasis given to the microtubules, which no doubt play a fundamental rôle in cell’s functioning. In fact, these subcellular constituents have attracted the recent years the particular interest of biophysicists.

Microtubules have been predicted to posses oriented dipoles, assuming ferroelectric phase, which appears to be optimal for microtubule signaling and assembly/disassembly (Sataric et al., 1993, Tuszynski et al., 1995). Such processes are obviously of basic importance. In the light of previous work (Mavromatos and Nanopoulos 1997, 1998), relating the ferroelectric properties to the appearance of mesoscopic quantum-coherent states in internal regions of the microtubule cylinders, playing the rôle of (thermally isolated) electromagnetic cavities, ferroelectricity may also be important for quantum mechanical aspects of microtubular arrangements in the cell. Specifically, it was suggested in [Mavromatos and Nanopoulos 1998] that ferroelectricity in the dimer medium,
strengthens isolation of the ‘cavity regions’, thereby leading to a larger probability for
the coherent states to form and live long enough, so as to transport information and en-
ergy across the microtubular arrangement. The rôle of the surrounding water molecules
for the ferroelectricity in the dimer medium was emphasized.

In this latter respect we now mention that the interesting property of KFCT is the
origin of its ferroelectricity. In fact, the alignment of the water molecules by the surround-
ing crystalline structure (!) causes the measured macroscopic spontaneous polarization
\( |P_s| = 24.6 \text{ mC/m}^2 \), which is compatible with the known microscopic water dipole con-
figuration in KFCT (Helwig, Klöpperpieper, & Müser, 1978). To be more specific, the
onset of ferroelectric behaviour is connected with the ordering of the hydrogen-bonded
water-molecules (Taylor, Müller, Hitterman, 1970). Thus, one is tempting to conclude
from this particular ferroelectric crystal that a similar mechanism might be at work with
the microtubules.

Indeed, a typical microtubular arrangement consists of a quasi solid cylinder of tubu-
lin dimers, which are arranged in 13 arrays (protofilaments). The interior of the micro-
tubules, of cross-section diameter 14 \( \text{nm} \), is filled with water molecules, being ubiquitous
in biology. The dimers (of extent 8 \( \text{nm} \) in the direction of the protofilament axis) are be-
lieved to have unpaired (mobile) electric charges, which lead to electric dipole moments
(Sataric et al., 1993, Tuszynski et al., 1995). In (Mavromatos and Nanopoulos, 1997,
1998) it was further conjectured that there are thin layers in the interior of the cylin-
ders, of a thickness ranging up to few atomic scales (Angströms), fairly isolated from
their environment, which operate as cavities sustaining mesoscopic quantum coherent
modes. In this scenario, the importance of the water molecules lies in the provision
of the necessary coupling with the quantized electromagnetic radiation in the cavity,
via their electric dipole moments, so that: (i) coherent modes appear in the interior of
the cavity (dipole quanta) (Del Giudice et al. 1988), and (ii) a coupling exists between
these coherent modes and the dimer dipole quantum oscillation modes (Mavromatos,
Nanopoulos, 1997). The latter leads to coherent solitonic modes along the protofila-
ment dimer chains, which have been argued to be responsible for dissipationless energy
transfer across the microtubule.

In view of the existence of the afore-mentioned hydrated ferroelectric compounds, we
may now conjecture that such configurations favour an alignment of the water molecules
(actually, not necessarily only those inside the tube). Then, the sofar speculated polar
properties of microtubules, and their connection to quantum physics, might exist in
reality.
3. Suggested experimental method

Because of the importance of such a ferroelectric property for these subcellular constituents, the next step is to establish or exclude it experimentally. A suggested sensitive experimental method to confirm the predicted ferroelectric behaviour of microtubules is via the four probe AC impedance spectroscopy \( (Z(\nu)) \). This technique is based on the measurement of the AC voltage to current ratio using 4-electrodes (Figure 1a) in a quite broad frequency interval (the so called frequency domain technique (Figure 1b)). The experimental set up for the AC impedance measurement of the microtubules in liquid suspension is shown in figure 2. This method has been recognised already as a valuable tool in the study of similar electrochemical systems (MacDonald, 1987). There are practical advantages of this technique compared to the more simple and old one working in the so called time domain, which applies either pulse or step source signals (MacDonald, 1987, Bottelberghs, 1978). In fact, the expected ferroelectric contribution of the suspended microtubules to the measured impedance \( Z(\nu) \) can only be observed in the higher frequency domain (s. Figure 1b). Otherwise, low frequency electrochemical phenomena, being certainly present in such a liquid suspension of microtubules, complicate the whole measuring procedure, which will suppress the appearance of a ferroelectric component inside the sample.

In practice, working with a suspension of microtubules additional experimental modifications might well become necessary. Thus, in addition to a conventional DC polarization for the \( Z(\nu) \) measurement one can also apply a pseudo-DC polarization, in order to avoid quasi-static complex electrochemical phenomena due to the electrode’s polarization coming from slow and heavy ion transport inside the sample. The onset of ferroelectricity can be identified due to a resonance-like response in the phase and the amplitude diagram of the impedance (s. Figure 1b).

Acknowledgements

We thank J. Albers for discussions and for providing us with information on hydrated ferroelectrics. This work is based on presentations by N.E.M. and K. Z. at the Workshop ‘Biophysics of the Cytoskeleton’, Banff, Alberta, Canada, August 18-22 1997. We thank J. Tuszynski for his interest in our work. The work of N.E.M. is supported by P.P.A.R.C. (U.K.), and that of D.V.N. is supported in part by D.O.E. Grant DE-F-G03-95-ER-40917.
REFERENCES

Bottelberghs, P. H. *Solid Electrolytes*, Edits. P. Hagenmüller and W. van Gool, Academic 1978 p 145.

Caspers, F., Riege, H., Zioutas, K., unpublished 1988.

Del Giudice, E.; G. Preparata, G.; Vitiello, G. Phys. Rev. Lett. 61 (1988), 1085.

Gundel, H., Riege, H., Wilson, E. J. N., Handerek, J., Zioutas, K., *Nucl. Instr. and Methods* 1989, A280. 1.

Helwig, J., Klöpperpieper, A. and Müser, H. E., *Ferroelectrics* 1978 18, 257.

MacDonald, J. R. *Impedance Spectroscopy, Emphasizing Solid Materials*, (Ed.), Wiley, New York 1987.

Mavromatos N.E.; Nanopoulos, D.V., [quant-ph/9708003](quant-ph/9708003), Int. J. Mod. Phys. B12, 1997, in press.

Mavromatos, N.E., Nanopoulos, D.V., [quant-ph/9802063](quant-ph/9802063), 1998, contribution to the Proc. of the Workshop Biophysics of the Cytoskeleton (Banff, August 18-22 1997, Canada).

Resta, R., *Europhysics News* 1997, 28(1), 18, and references therein.

Riege, H., *Nucl. Instr. and Methods* 1994, A340, 80.

Satarić, M. V., Tuszynski, J., Zakula, R. B., *Phys. Rev.* 1993 E48, 589.

Taylor, J. C., Müller, Hitterman, *Acta Cryst.* 1970 A26, 559.

Tuszynski, J., Hameroff, S., Satarić, M. V., Trpisová, B., Nip, M. L. A., *J. theor. Biol.* 1995, 174, 371.

Zioutas, K., Daskaloyannis, C. *Nucl. Instr. and Methods* 1985, B12, 200.
Figure captions

**Figure 1.** AC impedance measurement of a suspension of microtubules using: (a) a 4 probe electrode configuration in order to avoid electrode polarization phenomena, and (b) two main experimental regimes in the measured amplitude and phase of the complex impedance $Z(\nu)$.

**Figure 2.** Experimental set-up for the AC impedance measurement of the microtubules in liquid suspension, using evaporated 4 Pt or Au electrical contacts on a glass substrate mounted on a Cu temperature head, allowing measurements at different temperatures (left). The diagram of the experimental set-up with the possibility of a pseudo DC offset is also shown (right).
Figure 1:

4 Pt-electrodes sample holder

Source Pt electrode

V - measurement Pt electrodes

Glass Substrate

Figure 2:

V(t) & i(t)

Z(f) = V/i

Set up

4 probe