Electronic ferroelectricity in carbon-based systems: from reality of organic conductors to promises of polymers and graphene nano-ribbons

Natasha Kirova[1] and Serguei Brazovskii[2]

[1] LPS, CNRS-UMR 8502, Bat. 510,Université Paris-sud, 91405 Orsay cedex, France
[2] LPTMS, CNRS-UMR 8626, Bat. 100,Université Paris-sud, 91405 Orsay cedex, France

E-mail: nathalie.kirova@gmail.com

Abstract. Ferroelectricity is a rising demand in fundamental and applied solid state physics. Ferroelectrics are used in microelectronics as active gate materials, in capacitors, electro-optical-acoustic modulators, etc. There is a particular demand for plastic ferroelectrics, e.g. as a sensor for acoustic imaging in medicine and beyond, in shapeable capacitors, etc. Microscopic mechanisms of ferroelectric polarization in traditional materials are typically ionic. In this talk we discuss the electronic ferroelectrics - carbon-based materials: organic crystals, conducting polymers and graphene nano-ribbons. The motion of walls, separating domains with opposite electric polarisation, can be influenced and manipulated by terahertz and infra-red range optics.

1. Introduction

Phenomenon of the ferroelectricity referrers to an ability of certain materials to develop a spontaneous electric polarization which may have several allowed directions, hence it can be altered by an external electric field. Ferroeletrics have immense range of applications attracting related fundamental studies. The ferroelectric materials are the most universal: beyond their own virtues, they serve as pyroelectrics if treated by poled quenching, or as piesoelectrics if disordered.

The known microscopic mechanisms for the ferroelectric polarization are typically ionic: ions displacements from a centro-symmetric position in displacive ferroelectrics like most known PZT - $Pb(Zr_xTi_{1-x})O_3$, ordering of ions among equivalent potential minima (order-disorder type of the feroelectricity like in $BaTiO_3$), neutral-ionic transition where the charge disproportionation takes place among atoms in non-symmetric positions. There is a particular demand for plastic ferroelectrics, e.g. as a sensor for acoustic imaging in medicine and beyond, in shapeable capacitors, etc. Until now, this demand is satisfied by exploiting composite materials based on powders of ferroelectric oxides in a polymeric matrix. A single example of a purely polymeric FE is the saturated (that means not being active either electronically or optically) polymer Poly(vinylidene flouride) (PVDF). This material shows the ferroelectricity of a conformational origin, i.e. via chain rotation. Polarizabilities of existing plastic ferroelectrics are rather low, providing the dielectric permittivity ε~10, hence resulting in a modest efficiency of devices. A natural attempt is to consider synthetic conductors, like organic crystals or conducting polymers, which π- electronic systems can greatly enhance the dielectric permittivity. In this case, the major polarization comes from redistribution of electronic density,

resulting in amplification of dielectric permittivity ε by a factor of $(\omega_p/\Delta)^2 \sim 10^2$ (ω_p is the plasma frequency, Δ is the gap in the electronic spectrum).

The contemporary discovery of the ferroelectricity in organic conductors [1] has brought to life a new mechanism of the predominantly electronic origin, which opens new scales of the magnitude and the rapidity of the effect. The high dielectric susceptibility, $\varepsilon \sim 10^3$, coexists with an unusually high conductivity, which gives rise to a "ferroelectric narrow-gap semiconductor". The intrinsic conductivity eliminates the usual hysteresis, which may lead to fast repolarization, which can be tuned by terahertz and infra-red optics.

2. Ferroelectricity in π-conjugated systems

The picture of the ferroelectricity implies existence of a doubly degenerate ground state in the system. For quasi one dimensional conductors, the microscopic picture of the ferroelectricity is based on two coexisting symmetry lowering effects: the dimerization of bonds and the dimerization of sites, see figure 1. The important requirement is that one of these two effects should be spontaneous.
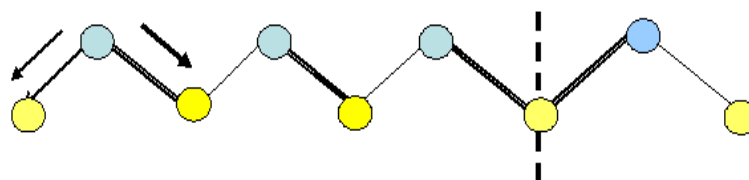

Figure 1. Joint effect of site and bond dimerizations for the ferroelectric ground state. The arrows show dielectric moments of bonds: they do exist because of the site inequivalence and they are different in magnitudes because of inequivalence of bonds. Vertical line indicates the position of the soliton – ferroelectric domain wall.

The combination of the two effects removes the inversion and the mirror symmetry, eliminating the glide plane. Nevertheless, the doubly degenerate ground state is preserved, which immediately gives rise to existence of solitons [1]-[3]. We may consider solitons as ferroelectric domain walls separating domains with opposite electric polarization. A special experimental advantage follows that the ac electric field alternates polarization by moving charged solitons. Through solitons' spectral features in terahertz and infra-red ranges, it opens a special tool of electro-optical interference. In return, the physics of these exotic solitons will serve to describe transient processes in ferroelectric polymers [3].

In perspectives of applications, crystalline organic materials may be too fragile, also their transition temperatures to the ferroelectric state are still in the cryogenic range. So it is tempting to find a similar effect in more robust and technological materials like conjugated polymers.

Major activity in physics and applications of conjugated polymers has been centering on their ability to emit light in the optical range of about 2eV (see e.g. [4] and references therein). These optically active materials are already close to applications and even commercialized. If one succeeds using their fast π-electrons to perform also the ferroelectricity, it will be possible to use the transient ferroelectric processes to monitor the visible range optics and vice versa.

A secure guess is to look for the so called $(AB)_x$ polymer – see figure1, proposed theoretically in early 80s [2]. Indeed, the first member of this potentially vast family of "di-substituted polyacetylenes" has already been synthesized, studied for nonlinear optical properties, but not tested yet for the low frequency response which could have recovered the ferroelectricity.
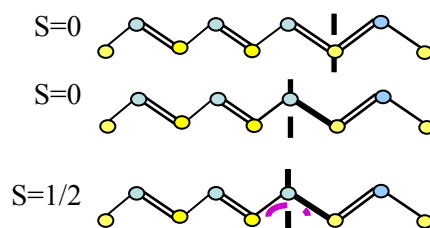
Figure 2. Three types of topological solitons in $(AB)_x$ polymeric chain.

The double degeneracy of the ground state is preserved, giving rise to three different topological solitons - bond dimerization kinks, see figure 2. But unlike the standard polyacetylene chain, all the three types of solitons carry variable, non integer charges [2],[3]. So, for this combined Peierls state, there is no total spin-charge separation, contrary to traditional 1D Peierls and Hubbard models. Thus the earlier neutral spin-carrying soliton, S=1/2, acquires the charge $Q_s=e(2/\pi)\tan^{-1}(\Delta_{ex}/\Delta)$. The spinless solitons (S=0) change their charges according to $Q_\pm=Q_s\pm e$.

The only known existing di-substituted polyacetylene has been synthesized a decade ago. Later on it attracted an attention in view of very promising applications as a light emitting material, even the lasing effect has been demonstrated [5]. The detailed optical characterization [6] provides an indirect proof for presence of the spontaneous bonds dimerization via spectral signatures of solitons. An "accidental" origin of the success to get the Peierls effect comes from a truly weak difference of alternating radicals: they are the phenyl rings which differ only by a side group attached most distantly from the carbon backbone bearing the π-electrons. Then the build-in site dimerization gap is small and the system is provoked to add the bond dimerization contribution to the gap. There was no check for the ferroelectricity yet: it seems plausible to be tried and realistic to be discovered.

We consider also a possibility of ferroelectricity for zigzag edges of graphene ribbons, see Figure 3. The build-in dimerization in this case is originated by different chemical surrounding of edge and bulk carbon atoms. The spontaneous dimerization can be the result of electron-phonon interactions and Peierls transition along the edges.
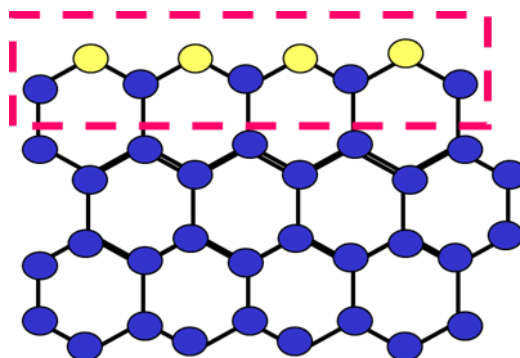

Figure 3. Possible ferroelectricity at the edges of graphene nano-ribbons.

3. Conclusions

π-conjugated systems can support the electronic ferroelectricity. The design is symmetrically defined and can be previewed.

Conductivity and/or terahertz activity of electronic ferroelectrics will add more functionality to their ferroelectric states. Re-polarization ferroelectric walls being influenced by terahertz and infra-red

range optics and their studies will add to reconciliation of applied and fundamental physics of carbon based systems.

References
[1]   Monceau P, Nad F and Brazovskii S 2001 *Phys. Rev. Lett.* **86** 4080
[2]   Brazovskii S, Kirova N 1981 *JETP Lett.* **33** 4
[3]   Kirova N, Brazovskii *Physica B*
[4]   Kirova N 2008 *Polymer Int.* **57** 678
[5]   Gontia I, Frolov S V, Liess M, Ehrenfreund E, Vardeny Z V, Tada K, Kajii H, Hidayat R, Fujii A, Yoshino K, Teraguchi M and Masuda T 1999 *Phys. Rev. Lett.* **82** 4058
[6]   Luer L, Manzoni C, Cerullo G, Lanzani G, Vardeny Z V 2007 *Chem. Phys. Lett.* **444** 61