FERROELECTRICS

Whirls and swirls of polarization

Exotic toroidal polarization textures in a polymer ferroelectric interact with terahertz radiation

By **Lane W. Martin**[1,2]

In Greek mythology, sailors feared the perils of getting near the whirlpool said to be created by the sea monster Charybdis, who created turbulence by swallowing huge amounts of water. Today, researchers are creating whirlpools in materials at the nano- and microscale, not from water but from magnetic spins or electric dipoles. In return, they have observed exotic phenomena and physics. On page 1050 of this issue, Guo *et al.* (*1*) provide another example of how the exacting control of materials is producing effects one thought impossible to achieve. They created self-assembled topological and toroidal polarization textures—that is, a toroidal polarization arrangement in which the polar toroidal dipole configuration corresponds to the field of a solenoid bent into a torus (see the figure, bottom) in ferroelectric polymers. Because of the exotic structure, this material exhibits properties not observed in its native state.

For some time, similar whirling structures were observed in the spins of magnetic materials. Such features include vortex structures that act as domain walls and so-called skyrmions, nanoscale whirls of smoothly evolving spin that are robust because of their topological nature (*2*). Such emergent-spin topologies have been widely studied and are currently being considered for high-density, ultrafast memory applications (*3*). In ferroelectrics (materials that have a spontaneous polarization instead of magnetization), it was not expected that such smoothly evolving, topologically protected structures would be possible because the primary order parameter (polarization) is strongly coupled to the lattice. Thus, continuous evolution of the order parameter would result in a large cost in elastic energy.

Despite this limitation, theoretical predictions provided clues for overcoming these limitations to realize vortex structures (*4*). In turn, as experimental approaches both for synthesizing and characterizing materials and order-parameter structures at the nanoscale matured, such continuous-symmetry structures were realized in the form of polarization vortices and skyrmions in $(PbTiO_3)_m/(SrTiO_3)_n$ superlattices (*5*–*7*), where m and n are the respective number of repeated layers in artificial stacks of different materials created with unit cell–level control. Researchers found that they could create vortices and skyrmions in superlattices by manipulating various energy scales.

By controlling the electric, elastic, and gradient energies, a material could effectively occupy a state in which no single energy dominated. Nanoscale features (with typical length scales of ~10 nm) once thought impossible were observed (see the figure, top) that had merely been hidden until the appropriate energy competitions could be produced. It was quickly realized that emergent properties and function also followed. These effects included emergent chirality (*8*), an exotic capacitive response (*9*, *10*), and an emergent order parameter—a so-called electric toroidal moment (*4*, *11*) that can also give rise to a range of phenomena, such as pyrotoroidic and piezotoroidic effects, in response to thermodynamic stimuli.

Guo *et al.* have now extended this exciting direction in ferroelectrics to a new class of materials based on the ferroelectric polymer poly(vinylidene fluoride-*ran*-trifluoroethylene), or P(VDF-TrFE). Instead of heterostructured complex oxides, they formed exotic polar structures with toroidal-polar topology in a single-layer film of the polymer through self-organized alignment of the polymer chains (see the figure, bottom). This material was purposefully chosen to provide the most robust polarization. The authors used a creative melt-recrystallization process formed ring-shaped bands and a periodically undulating surface topography (which could be described as "wrinkled").

This structure produces substantial strain in a periodic fashion that ultimately provides the appropriate competition between the same electric, elastic, and gradient energies to drive the formation of a concentric, continuously rotating polar structure. It has a net axial moment that makes it toroidal. What is perhaps most unexpected is that whereas the complex-oxide superlattices produce exotic-polar topologies at the ~10-nm length scale, Guo *et al.* created features at the 100- to 1000-nm length scale. This observation suggests that there are multiple length scales across which similar energy competition might produce exotic structures, and alsothat mesoscopic hierarchical-polarization textures (unit cell–level structures inside of domain-level structures) could enable exotic function.

In that regard, when Guo *et al.* probed the properties of the system, they found that it exhibited unexpected responses. Perpendicular to the polymer chains, there is continuous rotation and the formation of a toroidal structure, but parallel to the polymer chains, unexpected relaxor-

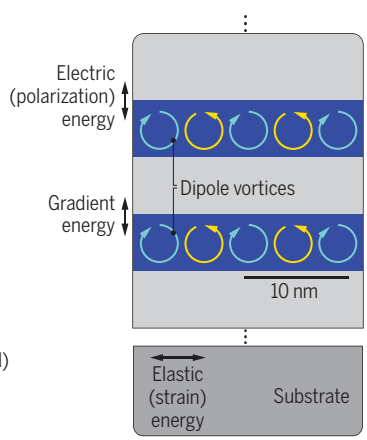
[1]Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, CA 94720, USA. [2]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA. Email: lwmartin@berkeley.edu

Emergent polar textures

In ferroelectrics (materials that have a spontaneous polarization), creating smoothly evolving, topologically protected dipole vortices must overcome large elastic energy costs.

Complex oxides

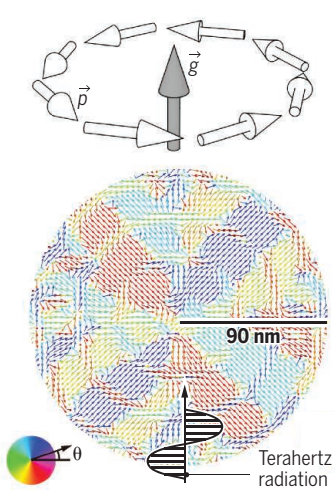
Superlattice heterostructures put electrical polarization, gradient, and strain energies in competition. The emergent and exotic dipole structures form on a 10-nm scale.



$SrTiO_3$ (not polarized)
$PbTiO_3$ (polarized)

Ferroelectric polymers

Guo *et al.* showed that similar structures can form in toroidally structured ferroelectric polymer films (bottom). The circle of electric dipoles p induces an axial toroidal dipole moment g (top). The intrinsic polarization plays off of periodic strain modulations and electrostatic forces to produce similar exotic polarization structures. These structures can interact with terahertz radiation.



Poly(vinylidene fluoride-*ran*-trifluoroethylene)

GRAPHIC: V. ALTOUNIAN/*SCIENCE*

like response is observed. Relaxors are characterized by diffuse-phase transitions and frequency dispersion of dielectric response arising from the complex-polar structure and fluctuations of that structure with applied field and temperature (*12*). Chemical disorder, random electric fields, and coexisting local dynamics are all sources of such fluctuations in complex materials. The periodic strain on the material likely induces this range of responses to applied stimuli and the observed relaxor-like response.

The authors also recognized that strong coupling between ferroelectric polarization and light should occur at the length scale of the emergent toroidal-polar topology, which would be in the terahertz range. They manipulated terahertz radiation with this material in a way that the parent material normally could not. This result could find application in terahertz optics for rastering and light modulation and motivates further design of such mesoscopic polar structures to address important needs in applications.

What this study by Guo *et al.* and other studies in recent years have shown is that advances in our ability to make and probe materials can potentially rewrite what we think is possible. The current work shows the universality of the power of manipulating energy scales—be it in unit cell–sized superlattices or micrometer-sized polymer crystals—to carefully control the pertinent energies that can produce unexpected features. The observation of toroidal order may not only lead to exotic optical responses but could also provide for exotic electric field–induced function and the potential for new types of thermal and electromechanical responses. Also, because of the intrinsically mesoscopic nature of the polymer systems, the study by Guo *et al.* represents just the beginning of what could be a large design landscape in which exotic dielectric, optical, and other properties could be coaxed from these complex materials. ■

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IMMUNOLOGY

Surgical adhesions: A sticky macrophage problem

Body-cavity macrophages superaggregate in a platelet-like response to wounding

By **Sarah E. Herrick** and **Judith E. Allen**

It is estimated that ~66% of patients who have gastrointestinal surgery will develop adhesions (*1*). These bands of scar tissue arise in the abdominal cavity and can lead to small bowel obstruction and infertility in women as well as severe chronic abdominal pain. Unfortunately, there are no satisfactory ways to prevent adhesions, and once formed, surgery is often required to lyse them, which predisposes to further adhesions. Thus, there is an urgent need to develop more effective means to prevent them from forming or to minimize their growth. On page 1013 of this issue, Zindel *et al.* (*2*) demonstrate that macrophages in the peritoneal cavity home to sites of damage, forming an immediate protective wound covering. In response to surgical insult, these macrophages act like platelets to form superaggregates, which then develop into adhesions. A fascinating parallel exists with invertebrates whereby body-cavity macrophages express evolutionarily ancient receptors, which may be potential targets for adhesion prevention.

"...body-cavity macrophages express evolutionarily ancient receptors, which may be potential targets for adhesion prevention."

The peritoneum is a gliding interface that lines the fluid-filled body cavity and internal organs. It comprises a surface monolayer of mesothelial cells adherent to a basement membrane, overlying a submesothelial connective tissue rich in capillaries and lymphatics. Surgical adhesions are proposed to evolve from initial fibrin clots spanning between internal organs and/or the cavity wall (*3*). Critically, reduced fibrinolysis after surgery and subsequent collagen production stabilizes these initial connections and stimulates the formation of mature myofibroblast-rich fibrous bands. Indeed, experimental animal studies and clinical trials investigating the prevention of surgical adhesions have been based on the idea of regulating coagulation and fibrinolytic pathways (*4*).

More recently, attention has shifted to identifying the source of myofibroblasts that stabilize early adhesions. In addition to tissue-resident fibroblasts (*5*), mesothelial cells have been shown to participate in the generation of fibroblasts and adhesion development (*6*, *7*) by undergoing a phenotypic switch, called mesothelial-to-mesenchymal transition (MMT). Anti-adhesion strategies are exploring ways to reduce MMT and hence prevent adhesions from forming (*8*).

Although reduced fibrinolysis and MMT are recognized events in the biology of surgical adhesions, data on the contribution of macrophages are inconclusive. Rigorous exploration of the heterogeneity and functional diversity of serous-cavity macrophage subpopulations during adhesion formation is needed to resolve this uncertainty (*9*). Macrophages that are free-floating in peritoneal fluid include monocyte-derived cells as well as resident macrophages that rely on the transcription factor GATA-binding protein 6 (GATA6) for their differentiation and survival (*10*, *11*). A previous study had demonstrated that GATA6$^+$ cavity macrophages are rapidly recruited, via a nonvascular route, to an injury site on the liver of mice where they assisted tissue repair (*12*).

Building on these observations, Zindel *et al.* showed that within minutes of laser-induced wounding of the cavity wall in mice, GATA6$^+$ macrophages provide a protective wound covering (see the figure). Although it remains unclear exactly how serous-cavity macrophages recognize sites of injury, recruitment was by passive transport, relying on the natural movement of peritoneal fluid. Free-floating macrophages became adherent only after injury. Within several hours, macrophages formed cell-to-cell aggregates with secondary tethers to the initially adherent cells. Notably, GATA6$^+$ mac-

School of Biological Sciences, Faculty of Biology, Medicine and Health, The University of Manchester, Manchester, UK. Email: sarah.herrick@manchester.ac.uk

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