

A new twist in ferroelectric liquids

Spontaneous chirality emerges in a highly polar liquid of achiral molecules

By **Liana Lucchetti**

Liquid crystals are of scientific interest because of their many potential applications in soft matter-based technologies. The most studied liquid crystal phase is the nematic (N), in which molecules possess orientational but not positional order. The recent discovery of the ferroelectric nematic (N_F) phase, the polar variant of the N phase, demonstrated that liquid systems can have spontaneous polarization comparable to that of ferroelectric solid crystals. On page 1096 of this issue, Karcz *et al.* (1) report a ferroelectric nematic liquid crystal composed of achiral molecules in which strong dipolar interactions drive the spontaneous formation of a chiral phase. This demonstrates that chirality can emerge in achiral systems as a result of electrostatic interactions and that N_F systems can exhibit spontaneous twist of molecular dipoles that minimizes electrostatic energy. Kumari *et al.* (2) also recently showed that, under proper conditions, the energetically favored ground state configuration of N_F liquid crystals is chiral.

Chirality—a geometric property in which a system cannot be superimposed on its mirror image—is usually built into molecular structure by synthesis. The emergence of chirality from achiral building blocks is still a fundamental challenge in soft matter and material science. Spontaneous chirality reported in nematic liquid crystals has been attributed to the specific molecular shape (3), geometrical constraints (4), or elastic constants anisotropy (5). In ferromagnetic ferrofluids exhibiting nematic order, spontaneous chirality was observed under an oscillating magnetic field (6). In the recently described polar nematic N_F phase (7), molecular arrangement breaks mirror symmetry of the director (a unit vector that specifies the average molecular

orientation) (2). This leads to unusual properties such as the dominance of electrostatic interactions over fluid elasticity. Karcz *et al.* report that the mirror symmetry breaking of the N_F phase extends to the spontaneous emergence of chirality driven by noncollinear orientation of electric dipoles. Both Karcz *et al.* and Kumari *et al.* observed that spontaneous chiral symmetry breaking is induced by the tendency of the N_F phase to adopt configurations that minimize the electrostatic energy. Contrary to conventional nematics, in which the equilibrium configuration is mainly dictated by elasticity, electrostatic interactions dominate over elastic energy in the N_F phase so that the shape of the polarization field, which is locally collinear to the average molecular orientation, is mainly determined by long-range electrostatic forces and topological constraints.

The possibility of polarity-driven chirality in three-dimensional N_F liquid crystals was

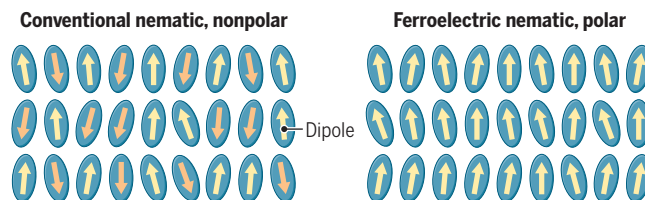
suggested by the emergence of a spontaneous twist in quasi-two-dimensional N_F domains (8). Now, Karcz *et al.* describe the spontaneous formation of a heliconical molecular arrangement in a N_F system formed by molecules with an elongated core. The authors call this new polar phase a ferroelectric nematic twist-bend phase, N_{TB} . Because the pitch of the helical structure is in the submicrometer to micrometer range, this phase resembles a heliconical cholesteric, a peculiar class of chiral nematics where the molecular director rotates in a helical fashion, forming an angle $\theta < \pi/2$ with the helix axis (9). Heliconical cholesterics are stabilized by an external electric field parallel to the helix axis and require the bend elastic constant to be much smaller than the twist constant, a condition not satisfied in typical nematics formed by rodlike molecules. The heliconical polar phase observed by Karcz *et al.* is instead stabilized by intrinsic electrical interactions that induce a

noncollinear orientation of electric dipoles, without any requirements of the elastic constants or the need for an external electric field. This structure exhibits an effective polarization along the helix axis, and the handedness of the twist is most probably related to the polarization direction (see the figure).

The observed spontaneous twist of electric dipoles reported by Karcz *et al.* is an additional peculiarity of N_F . This phase is stabilized by strong dipolar interactions, which would suggest an equally strong tendency to collinearity; therefore, spontaneous emergence of noncollinear orientation of dipoles is in some sense unexpected. Evidence that the ground state of polar nematic liquid crystals is not necessarily unidirectionally polar was also reported by Kumari *et al.* In properly designed samples with asymmetric boundary conditions, the liquid crystal prefers to split into periodic right and left twisted domains, even when confinement would allow the bulk structure to be uniformly aligned. This indicates that although the chosen configuration increases the elas-

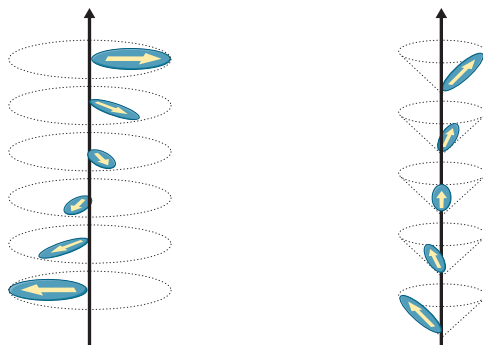
Polarity and chirality in liquid crystals

Molecular arrangement in a liquid crystal determines the polarity and chirality.



In a conventional nematic, the mixed organization of dipole moments of achiral molecules results in a nonpolar phase, whereas in a ferroelectric nematic, collinear organization of the dipoles gives rise to macroscopic polarization.

Ferroelectric chiral nematic Ferroelectric heliconical nematic



Intrinsic electrical interaction of achiral molecules in the polar phase breaks mirror symmetry, resulting in noncollinear orientation of dipoles and the emergence of chirality. In the helical configuration (left), the molecular director and spontaneous polarization rotate at a right angle with the helical axis. In the heliconical configuration (right), the angle is less than $\pi/2$.

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tic energy (which would be undesirable in conventional N), it is preferred because it reduces the electrostatic energy associated with a unidirectionally polar orientation of the spontaneous polarization. Because it is generated by the polarity of the N_F phase, chirality disappears upon heating to the N phase and can be switched on and off under the action of an electric field.

The emergence of a twisted orientation of electric dipoles reinforces the similarity between ferroelectric nematic liquid crystals and magnetic systems (10, 11). Indeed, N_F phases have a low viscosity that is typical of liquids and exhibit an easily deformable polarization field similar to that of magnetic systems, where the spins easily reorient in the crystal lattice and give rise to a spontaneous twist arrangement. In the N_F systems of Karcz *et al.* and Kumari *et al.*, left- and right-handed helices are formed with equal probability, indicating that electric dipolar interactions maintain degeneracy of the chiral sense.

Electrostatically induced chirality represents a new twist in ferroelectric nematic liquid crystals and may pave the way to a class of new effects. The combination of polarity and chirality is expected to produce unusual polar textures where flexoelectricity and bound charges may play dominant roles in creating and controlling complex topological configurations. These should be fertile ground for exploring new phenomena and possibly other exotic polar phases, such as the N_{TB} reported by Karcz *et al.* Additionally, spontaneously chiral N_F might be used to design new devices on the basis of their alternate chiral domain structure or the self-stabilized polar heliconics. For example, all-optical tuning—partly demonstrated for nonpolar heliconics (12)—could be achieved in the polar version of this phase, which does not require a stabilizing electric field. Investigating how the polar nature of N_{TB} affects the shear thinning observed in some nonpolar twist-bend nematic phases will also be of great interest. ■

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CLIMATE CHANGE

Greenhouse gas mitigation requires caution

Strategies to mitigate emissions must consider methane and nitrous oxide together

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Methane (CH_4) and nitrous oxide (N_2O) are greenhouse gases that rank second and third behind carbon dioxide (CO_2) as primary contributors to global warming and climate change. Outside of fossil sources, these gases are emitted by microorganisms as they interact with their environment. Many strategies have targeted reduction of methane emissions. Although such efforts are well meaning, the microbial communities that live in these settings can respond to mitigation efforts by producing more N_2O , which reduces or even negates the positive climate impact (1, 2). Mitigation approaches too often have not accounted for these trade-offs, and doing so requires additional monitoring to make sure any specific strategy achieves a net climate benefit.

Compared to CO_2 , N_2O is 300 times more potent in holding heat on a 100-year timescale. Methane is over 80 times more potent on a 20-year timescale. Outside of fossil sources, CH_4 and N_2O emissions from soils, wetlands, agriculture, thawing permafrost and Arctic lakes, wastewater, and land-use change are largely controlled by microorganisms and their activities in concert with chemical and physical properties of the environment. A portion of these emissions is exacerbated by human activities (1).

The interactions between the CH_4 and N cycles that underlie the relationship between CH_4 and N_2O emissions are complex (see the figure). Aerobic bacteria that live on CH_4 (methanotrophs) rely on nitrogen as an essential macronutrient. Some organisms can use NO_3^- and/or NO_2^- as terminal electron acceptors to form N_2O when O_2 availability becomes limited (2). In addition, some methanotrophs produce a copper-chelating chalkaphore (methanobactin) that effectively outcompetes copper from denitrifying microorganisms, preventing them from synthesizing the enzyme that consumes N_2O (3).

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In these circumstances, the copper competition can result in increased N_2O emission by preventing its conversion and return to atmospheric N_2 (3). Synthetic or biological amendments aimed at inhibiting microbial communities that convert ammonia to nitrate (nitrifying communities) can reduce N_2O emissions (4). However, many classes of nitrification inhibitors (NIs) will also inhibit methanotrophs, potentially increasing CH_4 emissions. Conversely, in the anoxic zone, methanogens produce CH_4 , but some anaerobic methanotrophs consume CH_4 and reduce NO_3^- or NO_2^- without N_2O release.

Promising biology-based CH_4 mitigation technologies under development include CH_4 biofilters both as open treatment systems and closed bioreactors, bioconversion of CH_4 into protein and bioplastics, and development of biocontrol treatments to reduce CH_4 production in rice paddy and landfill soils and in ruminants (5). Each strategy has an impact on the N cycle, including the possibility of increasing N_2O emissions. Using porous biocovers such as compost, for example, to decrease CH_4 emissions by enhancing aerobic methanotroph-mediated CH_4 consumption unfortunately resulted in increased N_2O emissions (6). Instead, biocovers enriched in iron and copper might simultaneously reduce N_2O and CH_4 emissions by relieving essential nutrient limitations. A similar situation can be expected if aerobic or anaerobic CH_4 consumption is enhanced in rice paddies by nutrient addition to stimulate the natural methanotrophic populations owing to nitrogen excess. In these cases, amendments that include an N source to increase methanotroph biomass may lead to N_2O production when the C:N balance of the system is lowered. Because the combination of landfills and rice paddies generates about 100 to 150 million tonnes per year of CH_4 (7), the potential impact for mitigating gas release from these two sources is substantial.

Beyond these specific examples, monitoring both CH_4 and N_2O across other emissions reduction scenarios is important to make sure excess NO_3^- is not present. Further, the amount of CO_2 fixation needs to also be determined to ensure a net climate benefit. Capped or inactive gas wells, coal mines, and