Hopfions emerge in ferroelectrics

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Paradigmatic knotted solitons, Hopfions, that are characterized by topological Hopf invariant, are widely investigated in the diverse areas ranging from high energy physics, cosmology and astrophysics to biology, magneto- and hydrodynamics and condensed matter physics. Yet, while holding high promise for applications, they remain elusive and under-explored. Here we demonstrate that Hopfions emerge as a basic configuration of polarization field in confined ferroelectric nanoparticles. Our findings establish that Hopfions govern a wealth of novel functionalities in the electromagnetic response of composite nanomaterials opening route to unprecedented technological applications.

Confinement of a ferroelectric material changes radically its electric properties. Termination of the of polarization at the surface leads to the depolarization charges \( \rho = -\text{div} \mathbf{P} \) that produce the depolarization field \( \mathbf{E} \). In turn, the self-consistent interactions result in a nonuniform texture that minimizes electrostatic energy costs associated with these depolarization effects. The corresponding topologically nontrivial textures include regular patterns of Kittel domains1–5, which can be also viewed as the periodic array of vortex-antivortex pairs6 and lattice of skyrmions7 in the films and superlattices, and vortices and skyrmions in the nanords and nanodots8–14. As we show below, a geometrical restriction of a ferroelectric brings about yet another class of the topological formations, Hopfions which appear in a broad variety of nature phenomena15–24.

We consider a spherical nanoparticle. A uniform mono-domain state is not energetically stable because of formation of the surface depolarization charges located at the termination points of polarization lines \( \mathbf{P}(\mathbf{r}) \), see Fig. 1a. To minimize the energy associated with depolarization field \( \mathbf{E} \), the system transforms itself into a structure with the vanishing depolarization charges so that \( \text{div} \mathbf{P} = 0 \). Therefore, the divergenceless of the polarization field is the fundamental condition defining the physics of the spatially nonuniform ferroelectricity. The absence of the depolarization charges at the surface, implies that the polarization vector, \( \mathbf{P} \), is tangent to the surface of the particle.

An instant configuration stemming from the above conditions is the vortex10, see Fig. 1b. For the case of the isotropic spherical nanoparticle, such a solution25 is stable just below the transition from the high-temperature paraelectric phase into the ferroelectric phase. However, in general, far from the transition, the system seeks for the configuration in which the amplitude of the polarization remains close to its equilibrium value everywhere, hence strives to eliminate singularities.

A singularity at the vortex core can be removed by the continuous deformation of the vector field \( \mathbf{P} \) promoting its escape into the third dimension along the vortex axis26, see Fig. 1c. Had this process been occurring in an unrestricted 3D space, it would have resulted in a uniform polarization. However, in the confined spherical geometry, this would have recovered the unfavorable mono-domain configuration shown in Fig. 1a. To avoid that, the polarization flow along the vortex axis spreads into a back-flow over the sphere’s surface, maintaining polarization tangent to the surface hence avoiding the onset of depolarization charges. The resulting \( \mathbf{P} \)-field configuration is a 3D knotted soliton, called ‘Hopfion,’ which is a set of interlinked circles or torus knots, see27 and references therein. A simplest single polarization Hopfion is shown in Fig. 1d.

To unravel the nature of an emergent polarization structure in a nanoparticle, we observe that the lines of the divergenceless polariza-

\[ \mathbf{H} = \int_{\mathcal{M}^3} (\mathbf{P} \cdot \mathbf{A}) d\mathbf{r}, \]

where the gauge field \( \mathbf{A} \) is defined by \( \mathbf{P} = \text{rot} \mathbf{A} \). The definitive property of the polarization lines in a Hopfion is that each field line links through others. This property illustrates an equivalent topological definition of the Hopf invariant \( \mathcal{H} \) as the link index of two loops that are pre-images of two points in \( \mathbb{S}^2 \).
An associated feature that arises in the Hopfion state is the chirality which is the asymmetry with respect to mirror-reflection. The corresponding symmetry group is $C_{∞h}$, and is eventually reduced by the crystal anisotropy. Hopfions can be the “left” and “right” ones, hence spontaneous chiral symmetry breaking upon the formation of the Hopfion state. Chirality marks the Hopfion off from the vortex, endowed with the group $C_{∞v}$, that includes the reflection in the plane, $σ_p$, perpendicular to the vortex axis. We thus use the chirality parameter, $\chi = P \cdot \text{rot} P$, to characterize the Hopfion state. This parameter complements the toroidal moment $T = \text{rot} P$ that is ordinarily used for the description of the state containing topological excitations in ferroelectric nanoparticles, since $T$ cannot expose the difference between the vortex state and the chiral Hopfion state. Note, that the spontaneously arising chirality opens an unprecedented opportunity of manipulating the ferroelectric nanoparticles by circular-polarized laser tweezers, inducing and tuning the optical activity of the media.

To investigate the Hopfions arising in ferroelectric nanoparticle, we perform the relaxation minimization of the Ginzburg-Landau (GL) functional coupled with the electrostatic and elastic equations, see Methods. An insight into the Hopfion emergence is gained by the purposeful initial tuning of the isotropic model functional, simplifying the anisotropy and elasticity effects. We select, however, parameters that are close to those in the realistic oxide materials and that partially account for the elastic interaction. Shown in Fig. 2e-k are the results of computations. Panels (c) and (d) display the Hopf fibration in the isotropic nanoparticle with radius $R = 25 \text{ nm}$ at room temperature realizing the self-linking spiral-like structure of polarization lines. The dense set of lines forming the knots at a single torus is shown in panel (c), whereas the panel (d) exhibits the compactification of entwined tori in the bulk of the nanoparticle. Figure 2e demonstrates the pairwise intra- and inter-tori linking of the polarization lines belonging to the tori shown in panel (d). The nontrivial knotting of the field lines leads to the peculiar spatial distributions of the polarization characteristics of the system. The tendency for the polarization vectors to escape in the third dimension results in the up-stream of the polarization lines near the Hopfion core and to their down-stream at the periphery, as reflected in Fig. 2i showing the $P_z$ component. At the same time, the distribution of amplitudes of polarization vectors, becomes nearly homogeneous, (Fig. 2g), and the residual singularities settle as whorles of the polarization at the points of the termination of the Hopfion axis at the poles of the sphere as shown in Fig. 2h. These residual singularities are essentially non-removable and manifest the Poincaré hairy ball theorem stating that there is no non-vanishing continuous tangent vector field on two-dimensional sphere. Figure 2i demonstrates the distribution of the chirality, $\chi$, inside the particle that concentrates mostly along the Hopfion core.

Panel (j) presents the $T - R$ phase diagram for the spherical particles with the radius $R < 30 \text{ nm}$. Notably, the Hopfion state occupies its major part. The transition temperature $T_0$ from the high-temperature paraelectric state to the low-temperature ferroelectric one, lies only slightly below the bulk temperature $T_0$ in large particles with $R > 20 \text{ nm}$. In small particles with $R < 20 \text{ nm}$, $T_0$ is noticeably suppressed by the size-driven confinement. The polarization texture of the ferroelectric state, which forms just below the transition, has the vortex-like structure. In general, the dependence $T_c(R)$ is well fitted by the formula, following from the dimensional analysis of GL equations, $(T_0 - T_c)/T_0 \approx (\mu_0 \xi_0/R)^2$, where $\xi_0 \approx 0.7 \text{ nm}$ is the coherence lengths and $\mu_0 \approx 2.0$. Vortices start expelling their core singularities into the third dimension below the critical temperature $T_h$, which also scales as $R^{-2}$, with the coefficient $\mu_0 \approx 2.8$. The temperature interval of the vortex phase existence is negligibly small for $R > 10 - 15 \text{ nm}$ and further cooling drives the system into a Hopfion state.
state. The vortex state becomes noticeable only in small enough nanoparticles, where the geometry restriction stabilizes vortices.

The temperature dependence of the principal ferroelectric characteristics, the mean-squared polarization, \((\langle P \rangle)^2\), the absolute value of the mean toroidal moment, \(|\mathbf{T}|\), directed along the Hopfion/vortex axis, and the mean chirality, \(\chi\), chosen negative for concreteness, are shown in the panel (j) for three characteristic sizes of the nanoparticles: \(R = 5, 10\) and 25 nm. The mean squared polarization vanishes as a square root on approach to the ferroelectric transition temperature, \(T_c\), similar to the uniform bulk case. The toroidal moment also vanishes at \(T_c\), whereas the chirality disappears below \(T_c\) at the vortex-Hopfion transition and is used to determine \(T_h\). Note that for the 5 nm nanoparticles \(\chi = 0\) since the system remains in the vortex state.

The inset shows a conceptual setup. The applied closed vortices. The block yellow arrows show the direction of the evolution of the 25 nm nanoparticles of the PZT. The helices with the “upward” and “downward” polarization characteristics, the mean-squared polarization, \(\langle P \rangle\), and average internal field, \(E\), along the \([111]\) direction. The relation between these quantities completely describes the dielectric properties of the system, and is the constitutive relation \(\bar{P}(\bar{E})\). We show that \(\bar{P}(\bar{E})\) dependence is the S-shape curve with slight hysteresis that we describe below.

The state (i) in Fig. 3 corresponds to the zero-field quench of the nanoparticle from the paraelectric state. The polarization lines maintain the torus-winding structure as in the isotropic case. However, the crystal anisotropy drives the polarization towards \([111]\) and \([110]\) (or equivalent) crystallographic directions fixing the orientation of the Hopfion axis along \([111]\) direction. In addition, the pole singularities extend slightly into the bulk, to form two respective vortices coexisting with the bulk Hopfion. Upon the application of the external field (in the negative direction), the virgin curve \(\bar{P}(\bar{E})\) jumps first to the left, across the singular internal field, \(e_0 \bar{E} = 1.4 \times 10^{-5} \text{Cm}^{-2}\) (where \(e_0 = 8.85 \times 10^{-12} \text{C} \cdot \text{V}^{-1} \cdot \text{m}^{-1}\)), related to the topological piercing of the Hopfion by helical polarization lines that will be described further. Then it descends along the left branch of the hysteresis loop forming finally the down-oriented directional helical structure, (state (ii) in Fig. 3). In the emerging polarization structure the open polarization lines thrust the nanoparticle, so that the mean polarization flux gets aligned with the applied field.

Reversing the change in the field, we follow now the right hand side branch of the hysteresis loop from the bottom to the top. The evolution of the system upon the monotonic variation of the field from the negative to the positive value, occurs through first, compression, and then, stretching the helical polarization lines with the change of the mean polarization flux direction from the negative to the positive one. We observe that the system passes through the sequence of topological phases that follow the Arnold’s partitioning of the nanoparticle space into cells where the field lines are entwined around the nested sets of either cylindrical or toroidal surfaces. In the initial helical state (ii) the polarization lines are entwined around the cylindrical surfaces. Upon the decreasing field, the helical structure compresses while broadening its central part (state (iii)) and, finally, a spherical cell containing the toroidal Hopf fibration nucleates at the center of the nanoparticle (state (iv)). The emerging Hopfion grows further ousting the helical states towards the nanoparticle periphery, which bypass Hopfion outside and carry the mean polarization of the nanoparticle along the nanoparticle surface. When the applied field vanishes, the Hopfion fills up the entire nanoparticle asymptotically approaching to the state (i) with \(\bar{P} = 0\).

The change of the sign of the external field from negative to positive leads to the topological phase transition in the course of which the system “turns inside out” and a hyperbolic cell filled up with the nested cylinders sets in along the axis of the nanoparticle. This cell ruptures the Hopfion sphere into a torus (state (v)) and hosts the open polarization helical lines carrying now the mean polarization inside the nanoparticle along its axis. This transition occurs abruptly at some threshold applied field and manifests as a disruption of the smooth behaviour of the internal field \(\bar{E}\) which makes a singular turn in polarization curve. Upon the further field increase, the Hopfion torus rotates towards the equator and eventually disappears there draining out of the nanoparticle, which thus falls into the helical state. Just after the transition the polarization helices maintains the fitted structure (state (vi)), as a legacy of the vanished Hopfion tori, and only at higher applied fields it crosses over to the helical state (vii) equivalent, up to sign \(\bar{P}(\bar{r})\) reversal, to the state (ii). Upon the sequential field reversal and decreasing the field back, the system does not pass through the reverse sequence of the states, but repeats the (ii)→(vii) scenario with the replacement \(\bar{P}(\bar{r}) \rightarrow -\bar{P}(\bar{r})\), demonstrating thus the weakly hysteretic behaviour (left descending branch in Fig. 3). Again, the mean polarization flows, first, along the surface of the nanoparticle and then...
along the nanoparticle axis.

Complexity of the intertwined topological states encoded in the \( \vec{P} \cdot \vec{E} \) characteristic of Fig. 3 stems from the interplay of confinement and depolarizing effects. Most importantly, the system is highly responsive to even weak internal fields, owing to the utmost softness of the helical springs of the polarization lines. In other words, the ease at which the open lines reconnect, ensures an unobstructed redistribution of the field-induced depolarizing charge at the points of their termination, guaranteeing the almost perfect screening of the applied field. This behaviour is similar to that of the ferroelectric with domains, where the easy domain wall motion results in the similar softness.\(^{25}\) Because of that, the absolute value of the effective dielectric permittivity of the nanoparticle, \( \varepsilon = \vec{P}_{\text{eff}}/\vec{E} \), can reach giant values of order 10\(^4\) and even more. Moreover, in the close resemblance of the nanoparticles with domains, the S-shape \( P - E \) characteristic demonstrate segments having the negative slopes, hence negative capacitance effect, which is explained by the advancing reaction of the polarization texture to the applied field.\(^{31}\)

We investigate now the Hopfion-governed physics in a composite material comprising the high-\(\varepsilon\) ferroelectric nanoparticles embedded in the low-\(\varepsilon\) dielectric matrix. Note, that according to the Maxwell Garnett mixing rule \(^{26}\) the dilute high-\(\varepsilon\) nanoparticles, see Fig. 4a, only weakly renormalize the properties of the low-\(\varepsilon\) hosting matrix. This was confirmed by numerical simulation in \(^{35}\). We thus focus on the composite of sintered nanoparticles, where polarization lines can pierce the entire system passing from one grain to another, and model a sintered composite as a rectangular array of contacting nanoparticles as shown in Fig. 4b.

Figure 4c displays the configuration that forms under the conditions of the moderate densification of PZT nanoparticles with \( R = 25 \text{ nm} \), contacted along the [111] direction. The degree of densification is quantified by the thickness of the contacting neck \( 2h = 0.4 \text{ nm} \), see inset, so that the area of the mutual contact of the adjacent particles serves as an aperture for polarization lines. Only a fraction of polarization helical lines passes through the interfacial aperture. Another part of the lines is confined into the Hopfions and does not interact with the applied electric field. They are invisible to the entire dielectric response of the system and can be viewed as an electric realization of the dark matter in the universe. In the case of strongly-densified nanoparticles with \( 2h = 2 \text{ nm} \) all the field lines form helices flowing through the area of the contact (Fig. 4d).

Figure 4e displays the polarization characteristics of the nanocomposite, comprising the sintered 25 nm nanoparticles, as functions of the applied voltage. The chain of the connected particles with the repeating polarization pattern is modeled by a single particle with cut off the skullcaps of the height \( h \), the electrodes covering its top and bottom cuts respectively. The model setup is shown in the inset. As we already mentioned, the particles with the vanishing contact area (\( h \approx 0 \text{ nm} \)) gives almost no contribution to the dielectric properties of the system. The dielectric response grows with the degree of the densification. For the moderate contact \( h = 0.2 \text{ nm} \) the switching between the up- to down-polarized helices, occurs along the gently-sloping hysteresis loop. At each branch, the system quasistatically passes through the sequence of the topological states, similar to those, shown in Fig. 3. For the high degree of the densification, \( h = 1 \text{ nm} \), the sharp hysteresis loop with the polarization jumps is observed. The switching follows through the same sequence of the states, but the system passes through the Hopfion states via dynamic instability, as illustrated in Supplementary Video.

A far reaching implication of our findings is that an array of sintered nanoparticles hosts Hopfion fibrations imprinting in the polarization lines configurations. The emerging topological frustrations are an expected origin of yet mysterious relaxor behaviour of disordered systems. As a marked analogy to a dark matter, the Hopfions store an energy in composite ferroelectrics which opens new routes for design of the ferroelectric-based energy storage devices.

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The functional, $F$, is written as follows

$$
F = \int \left[ \left( a_0(T) P_i^2 + a_0^{(2)} P_i^2 + a_0^{(4)} P_i^2 P_j^2 \right) \delta_{ijk} + \frac{1}{2} G_{ijkl} (\partial_i P_j)(\partial_k P_l) + \frac{1}{2} \epsilon_0 \epsilon_r (\nabla \Phi)^2 + \frac{1}{2} C_{ijk} \left[ a_{ij} \left( \frac{\partial \Phi}{\partial x} \right) \right]^2 \right] d^3r,
$$

(2)

in the insets to the Fig. 3 and Fig. 4e of the article. The internal field was controlled by the voltage $U$, applied to the electrodes. The paraelectric state with the small randomly-distributed polarization was used as the initial condition. To ensure the stability of solution we used the quench from the different initial paraelectric states and the temperature annealing procedure as well as the different finite-element meshes. In order to calculate the $P(E)$ characteristics in the ascending/descending field we used the quasi-station poling when the polarization distribution at previous stage was used as the initial condition. were the summation over the repeated indices $i, j, \ldots = 1, 2, 3$ (or $x, y, z$) was performed. The first square brackets term of (2) stands for the Ginzburg-Landau energy in the form given in [13]. Importantly, the 4th-order coefficients $a_0^{(4)}$ and $a_0^{(4)}$ (and their cubic-symmetry homologues) are taken at zero strain and are calculated by the Legendre transformation from the stress-free coefficients $a_0^{(4)}, a_0^{(4)}$, see also [13]. The second term of (2) with coefficients $G_{ijkl}$ corresponds to the gradient of energy. For the two last terms are the electrostatic and elastic energies, written in terms of the electrostatic potential $\Phi$ and strain tensor $\epsilon_{ij}$, respectively. Here $\epsilon_0 = 8.85 \times 10^{-12} \text{C} \text{V}^{-1} \text{m}^{-1}$ is the vacuum permittivity, $\epsilon_r = 10$ is the background dielectric constant of the non-polar ions, typical for PbTiO$_3$ [29] and $C_{ijkl}$ is the elastic stiffness tensor.

The polarization-induced distribution of the electrostatic potential $\Phi$ and elastic strains $\epsilon_{ij}$ in functional (2) are found at each relaxation step as solutions of equations

$$
\epsilon_0 \nabla^2 \Phi = \partial_i P_i, \quad C_{ijkl} \left( \epsilon_{ij} - Q_{ijkl} P_i \right) = 0,
$$

(3)

implemented in the MOOSE-FERRET package. Here $Q_{ijkl}$ is the electrostriction tensor.

**Material parameters.** For the Pb$_{0.7}$Zr$_{0.3}$TiO$_3$ the coefficients for the uniform part of the functional (2) are as follows, $a_0 = 2.3 (T = 364^\circ \text{C}) \times 10^{-13} \text{C}^2 \text{m}^{-2}$, $a_0^{(2)} = 0.44 \times 10^{-8} \text{C}^4 \text{m}^{-4} \text{N}^2$, $a_0^{(4)} = 0.074 \times 10^{-12} \text{C}^6 \text{m}^{-6} \text{N}^2$, $a_{111} = 0.27 \times 10^{-9} \text{C}^6 \text{m}^{-6} \text{N}$, $a_{12} = 1.21 \times 10^{-9} \text{C}^2 \text{m}^{-2} \text{N}$, and $a_{123} = -5.69 \times 10^{-9} \text{C}^6 \text{m}^{-6} \text{N}$. The electrostriction coefficients are $Q_{1111} = 0.073 \text{C}^{-2} \text{m}^{-2}$, $Q_{1122} = -0.027 \text{C}^{-2} \text{m}^{-2}$, and $Q_{1212} = 0.064 \text{C}^{-2} \text{m}^{-2}$ (with cubic symmetry permutations) were calculated on the base of the expression, given in [38] after transformation from Voigt to tensor notations [39]. The gradient energy coefficients $G_{1111} = 2.77 \times 10^{-10} \text{C}^2 \text{m}^{-2} \text{N}$, $G_{1122} = 0$, and $G_{1212} = 1.38 \times 10^{-10} \text{C}^2 \text{m}^{-2} \text{N}$ selected to be the same as for PbTiO$_3$ [30]. The coefficients $C_{ijkl}$ were taken as $1.68 \times 10^{11} \text{m}^{-2} \text{N}$, $C_{1122} = 0.82 \times 10^{11} \text{m}^{-2} \text{N}$, and $C_{1212} = 0.41 \times 10^{11} \text{m}^{-2} \text{N}$ of the stiffness tensor $C_{ijkl}$, which is given in [38].

To explore the isotropic model we dropped out the elastic part of the functional (2), neglected the 6th-order polarization terms, and imposed $a_0^{(6)} = 2a_0^{(4)} = 2a_0^{(4)} = 0.27 \times 10^{-9} \text{C}^4 \text{m}^{-4} \text{N}$, so that the uniform part of the functional acquired the isotropic form $a_0(T) P_i^2 + a_0^{(2)} P_i^2$. Note that the gradient energy with selected coefficients $G_{ijkl}$ is already invariant with respect to rotation.

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