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Electrodynamics of ferroelectric films with negative capacitance

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We construct a theory of the electrodynamic response of ferroelectric thin films containing periodic domain textures (PDT) with 180° polarization-oriented domains. We demonstrate that depolarization field induced by PDT gives rise to the negative capacitance of the ferroelectric film. We derive frequency-dependent dielectric permittivity related to the PDT dynamics across the entire frequency range. We find the resonance mode of domain oscillations in the THz spectral band and the singular points in the phase of the reflected THz beam that are intimately related to the negative capacitance. Our findings provide a material platform for the THz negative capacitance-based optics of ferroelectric films and for epsilon-near-zero plasmonic THz metamaterials.

INTRODUCTION

Functional properties of ferroelectric films and superlattices are drastically different from those of the bulk materials. Extensive experimental [1–7] and theoretical [8–14] studies revealed new physics that emerges from the periodic domain textures (PDT) stabilized by the strains and the depolarization fields. One of the most striking features of the PDT is the manifest of the negative capacitance [15], the phenomenon that has been a subject of an intense recent attention [16–22]. The interest is motivated by both, its fundamental importance, and by its high potential for technological applications, in particular, as a platform for novel low-dissipation field-effect transistors.

Another facet of emergent functionalities of ferroelectric films arises due to the strain-tunability of their multiscale spontaneous polarization dynamics that provides a wide range of operational frequencies from a few kilohertz to tens terahertz ($1 \text{ THz} = 10^{12} \text{ Hz}$). The spectral band $10^4 \text{ Hz} - 0.3 \text{ THz}$ is covered by the relaxation dynamics of the domain walls (DWs) and polar clusters. The far-infrared spectral region of $3 - 30 \text{ THz}$ is governed by the soft-mode vibrations of the polar ions. Recent studies suggested that oscillations of domain walls (DW) in PDT occur in the frequency window of $0.3 - 3 \text{ THz}$ [23–25], i.e. within the least studied frequency range, referred to as a THz gap.

Our work steps into the breach and demonstrates that the resonant behavior of oscillations of PDT is the collective effect similar to the plasmonic excitations in metals. We find that this effect is governed by the stiffness of PDT promoted by the depolarization field and is a consequence of the negative capacitance. Namely, the negative low-frequency effective permittivity associated with the negative capacitance crosses the zero value within the THz spectrum band leading to a resonance behavior in complete analogy with the plasmon resonance. We investigate the THz optics of the PDT structure and demonstrate the existence of the topologically protected phase-singular points of the absolute darkness in the Fresnel reflection coefficient. These points are a fingerprint of the negative capacitance phenomenon.

Formation of the PDT lowers the energy of the depolar-

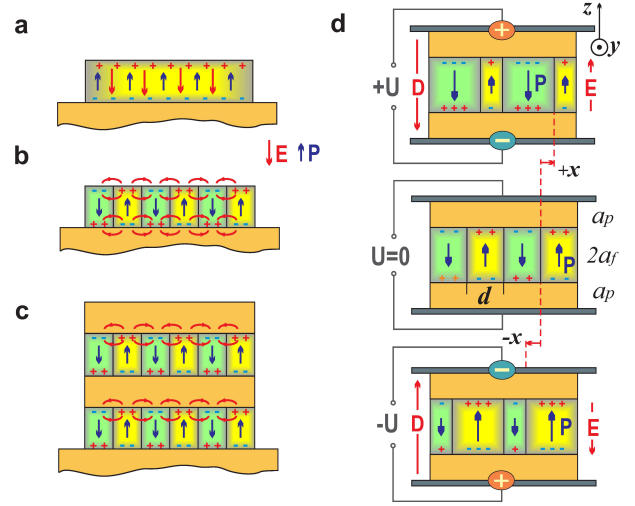


FIG. 1. Formation and dynamics of the periodic domain texture (PDT). (a) A single-domain state, the ferroelectric polarization and the depolarization field are shown by the blue and red arrows, respectively. The depolarization field traverses across the film. (b) The PDT with the alternating 180° polarization domains. The depolarization field is confined to the surface of the film. (c) A sketch of the ferroelectric-paraelectric superlattice with PDT. (d) The response of the PDT structure to variations of the voltage U applied to the ferroelectric-paraelectric system. The applied voltage induces the electric displacement D satisfying continuity condition across the entire system. The average electric field E within the ferroelectric film is directed opposite to the induced average polarization P and displacement D . This manifests the effect of the negative capacitance. Stray fields are not shown in order to avoid an overcrowded picture.

ization field induced by surface depolarization charges that appear at polarization termination points. Had the polarization maintained the same direction throughout a slab, see Fig. 1a, the electrostatic energy stored by the depolarization field would be proportional to the volume of the whole system hence huge. Splitting the system into the PDT implies that the surface depolarization charges form stripes of alternating signs. As a result, the depolarization field becomes restricted to the near-surface shell, see Fig. 1b, hence drastically diminishing the related electrostatic energy. Although predicted already in earlier works by Landau [26, 27] and Kittel [28] in

the context of ferromagnetic systems, the PDT in ferroelectric films has long been viewed as unlikely until the recent direct experimental evidences for equilibrium 180° stripe domains in strained ferroelectric thin films of PbTiO₃ (PTO) deposited on the SrTiO₃ (STO) substrate [1, 6] (as sketched in Fig. 1b) and in PTO/STO superlattices [3, 5] (Fig. 1c). The observed PDT behaviors appeared to well follow the theoretical predictions [8–14]. In particular, it was found that the mono-domain *z*-oriented state in the unscreened films is always unstable with respect the PDT formation.

Imagine, however, that surfaces of the slab get short-circuited, for example, by the metallic electrodes. Then charges would acquire the capability of arbitrary sliding along the surfaces and flowing between the electrodes, thus compensating the depolarization field inside the ferroelectric. As a result, the depolarization energy is nullified, the domain walls would creep away, and the mono-domain state stabilizes. This tendency of a ferroelectric with the PDT to self-generating the charge at its surfaces can be expressed via attributing to the ferroelectric slab a *negative* capacitance. One should bear in mind, however, that in reality, the slab that is not linked to the electrodes, maintains the PDT since charges cannot propagate across the dielectric and the charge redistribution described above would not occur.

The origin of the negative capacitance is as follows, see Fig. 1d. In the absence of the applied electric field, the up- and down-directed domains are of the equal size, hence both the average polarization and the average depolarization field are zero. The applied electric field displaces DWs unbalancing the sizes of domains, which results in the onset of the average polarization, oriented along the applied field. This, in turn, generates the depolarization field penetrating the bulk of the ferroelectric slab from the surface. The direction of the depolarization field is opposite to the polarization, hence to the applied field, and exceeds the latter by the absolute value. As a result, the total field inside the slab is counter-directed to the induced polarization, which is a hallmark of the negative permittivity, hence the negative capacitance of the ferroelectric layer.

We calculate the permittivity of the PDT and explicitly demonstrate that it assumes the negative value in the static limit. Then, writing down the coupled PDT equations of motion and Maxwell equations, we derive the frequency dependence of the permittivity of the PDT in the entire frequency range and find the corresponding resonance mode. We show that this mode arises in the frequency band where the negative permittivity changes its sign. Finally, basing on the calculated frequency dependence of the permittivity we derive the THz optical properties of the ferroelectric layer.

RESULTS

Negative capacitance

We start the description of the domain electrostatics with the static limit, and show that PDT in response to the applied field develops the fascinating negative dielectric permittivity ε_f and, accordingly, the effective negative capacitance, $C = \varepsilon_0 \varepsilon_f S / (2a_f)$, of the ferroelectric layer of surface area S and thickness $2a_f$.

The applied field is characterized by the electric displacement vector \mathbf{D} that conserves all across the system, see Fig. 1d, and generates the net polarization of the ferroelectric layer, $\mathbf{P} \parallel \mathbf{z}$ (the electrostatic fields in the ferroelectric slab with domains are macroscopically averaged). In our ferroelectric film the electric displacement is related to the electric field through

$$\mathbf{D} = \varepsilon_0 \varepsilon_{\parallel} \mathbf{E} + \mathbf{P}_{\text{dw}}. \quad (1)$$

Note that in the absence of the applied field, both terms in rhs of Eq. (1) are zero. The contribution \mathbf{P}_{dw} stems from the motion of the domain walls. In the absence of the motion, Eq. (1) reduces to standard electrostatic relation between the electric field and electric displacement. The dielectric constant ε_{\parallel} is the intrinsic permittivity of the ferroelectric material along the polarization direction. The \mathbf{P}_{dw} term reflects the change in the overall polarization due to the displacement of the DWs altering thus the relative contribution from the “up” and “down”-oriented domains. This implies the imbalance of the related depolarization charges of the opposite sign leading to the nonzero average charge density $\sigma = P_{\text{dw}}$. Thus the depolarization field $\mathbf{E}_{\text{dep}} = -(\varepsilon_0 \varepsilon_{\parallel})^{-1} \mathbf{P}_{\text{dw}}$ penetrates the bulk of the slab and is directed opposite to the applied field \mathbf{D} . This field, together with the driving field $\mathbf{E}_{\text{D}} = (\varepsilon_0 \varepsilon_{\parallel})^{-1} \mathbf{D}$ which would have settled down if DWs were immobile, contributes to the total field, $\mathbf{E} = \mathbf{E}_{\text{D}} + \mathbf{E}_{\text{dep}}$. Hence the sign of the system’s dielectric permittivity, which is defined as

$$\varepsilon_f = \frac{D}{\varepsilon_0 E}, \quad (2)$$

depends on the relative magnitude of the oppositely oriented \mathbf{E}_{D} and \mathbf{E}_{dep} .

Making use of the relation (1), one obtains

$$\varepsilon_f = \frac{\varepsilon_{\parallel} D}{D - P_{\text{dw}}}. \quad (3)$$

To derive ε_f , we have to know how the polarization related to the DW displacement depends on the applied field D . The calculations presented in the Appendix result in

$$\varepsilon_f = \varepsilon_{\parallel} - \frac{\pi \zeta}{4 \ln 2} \left(\frac{\varepsilon_{\perp}}{\varepsilon_{\parallel}} \right)^{1/2} \frac{2a_f}{d} \varepsilon_{\parallel}, \quad (4)$$

where the first term stems from the positive intrinsic contribution of \mathbf{E}_{D} , whereas the second, the negative one, is generated by the depolarizing field \mathbf{E}_{dep} , reflecting the effect of the moving DW. The depolarizing term outweighs the intrinsic term,

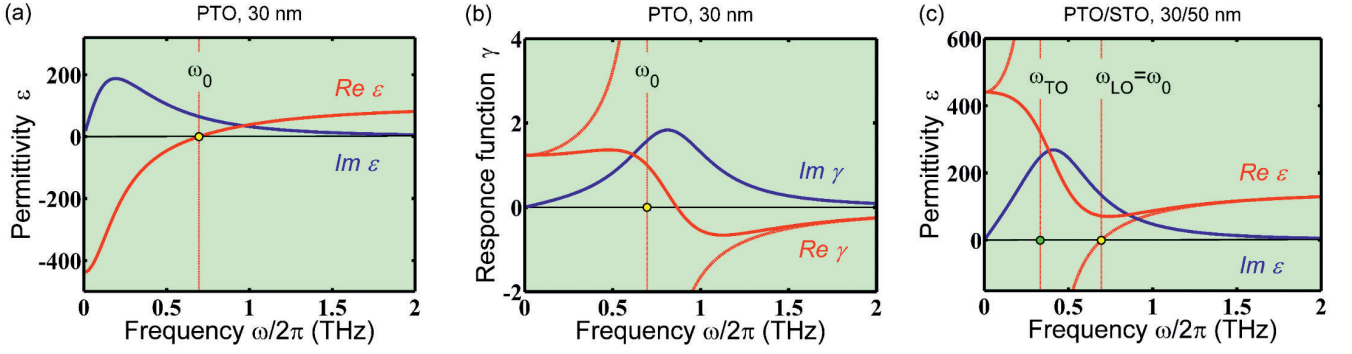


FIG. 2. Dynamical properties of the PDT. Real and imaginary parts of the frequency-dependent response are shown by red and blue colors respectively. Dashed lines depict the behavior of the system in the absence of dissipation. (a) Dielectric permittivity of the 30 nm thick film of the PTO. (b) Response function, defined as $\mathbf{P}_{dw\omega} = \gamma(\omega)\mathbf{D}_\omega$, for the same film. (c) Dielectric permittivity for either the 30/50 nm sandwich of the PTO/STO layers, or for the equivalent superlattice.

hence the negative dielectric permittivity settles, provided the film thickness, $2a_f$ exceeds the domain width, d . The equilibrium value of d can be either taken from the experiment [1, 5] or estimated by the Landau-Kittel square root law [26–28] specifically adapted for ferroelectrics in [8, 12, 29],

$$d \simeq \sqrt{3.53 (\epsilon_\perp/\epsilon_\parallel)^{1/2} \zeta \delta \cdot 2a_f}. \quad (5)$$

The resulting typical domain configuration for PTO films is shown in Fig. 1b. The DW thickness, δ , is about 1 nm [30]. In the above formulas $\zeta = 1 + \epsilon_p / (\epsilon_\parallel \epsilon_\perp)^{1/2}$, and the values of intrinsic permittivities along and across the polarization direction, ϵ_\parallel , ϵ_\perp , and of paraelectric layer, ϵ_p , are specified below; in the experimental range $1 \leq \zeta \leq 4$. If the sandwiching paraelectric layers possess different permittivities, ϵ_p^+ and ϵ_p^- , the effective parameter ζ_{eff} is defined by the relation $\zeta_{\text{eff}}^{-1} = \frac{1}{2} [\zeta^{-1}(\epsilon_p^+) + \zeta^{-1}(\epsilon_p^-)]$. In particular, if the ferroelectric film is deposited on the metallic substrate so that $\epsilon_p^- = 1$ and $\epsilon_p^+ = \infty$, one has $\zeta_{\text{eff}} \simeq 2$. The polarization profile in this case can be obtained by the image method.

DW oscillations

To quantify the electromagnetic behavior of PDT, we derive the dynamic response function $\gamma(\omega)$, defined by the relation $\mathbf{P}_{dw\omega} = \gamma(\omega)\mathbf{D}_\omega$, for the periodic structure of the domain stripes aligned along the y -axis which forms in the ferroelectric layer. The polarization axis \mathbf{z} is perpendicular to the film plane, while the in-plane DW motion occurs along the \mathbf{x} -axis, the index ω indicates the Fourier transforms of the respective quantities. We neglect the longitudinal DW fluctuations which can broaden the resonance peak [31].

In the harmonic oscillator approximation [32] the driven dynamics of DWs is given by

$$\mu \ddot{x}(t) + \eta \dot{x}(t) + kx(t) = 2P_s E_D(t), \quad (6)$$

where x is the coordinate of alternating DW displacements (Fig. 1d), the coefficients k , μ and η are calculated per unit

of DW area, and $2P_s E_D(t)$ is the pressure due to the electric displacement-induced driving field forcing DW to move to flip the surrounding spontaneous polarization from $-P_s$ to $+P_s$.

We calculate k as a coefficient at the restoring force that pushes the domain walls back in order to reduce the depolarization field, $E_{\text{dep}} = -\Delta P_s / \epsilon_0 = -2(x/d)P_s$, arising upon the displacement of DW from the equilibrium. This field is induced by the extra depolarization surface charges, $\sigma = \pm \Delta P_s$, appearing due to the spontaneous polarization excess, $\Delta P_s = 2(x/d)P_s$, and is directed antiparallel to ΔP_s . We evaluate the depolarization energy of the system as the electrostatic energy of the dielectric slab with permittivity ϵ_\parallel and with surface charges $\sigma = 2(x/d)P_s$ as $W = (2a_f \sigma^2 / 2\epsilon_0 \epsilon_\parallel) S$, where S is the surface area. The corresponding energy per unit area of the displaced DW is $w = (d/2S a_f) W$. Relating it with the harmonic oscillator stiffness energy $kx^2/2$, we find

$$k = \frac{4P_s^2}{\epsilon_0 \epsilon_\parallel d} g, \quad g \simeq 1 - \frac{4 \ln 2}{\pi \zeta} \left(\frac{\epsilon_\parallel}{\epsilon_\perp} \right)^{1/2} \frac{d}{2a_f}. \quad (7)$$

The factor g , calculated in the Appendix and confined in the interval $0 < g \lesssim 1$, takes into account the non-uniform part of the depolarization field near the surface caused by the stepwise distribution of the depolarization surface charges. In realistic cases that we considered here, namely, the PTO films with $2a_f \simeq 10 - 30$ nm, it varies from 0.4 to 0.9.

Equation (6) presumes that the DW is rigid and atomically narrow. However, in the tens-nanometer-thin films the DW broadens significantly, especially, on approach to the film surface, due to depolarization effects in the broad range of temperatures (yet the effective thickness of the DWs remains smaller than the distance between them as long and the model holds) [12, 14, 33, 34]. Upon the DW displacement, the polarization reverses first at the surface and then propagates into the interior of the film [23]. As a result of the DW broadening, the underlying pinning potential for the DW due to the periodic atomic structure gets essentially reduced and becomes relevant only at low temperatures.

In general, the PDT can be viewed as a meandering two-

dimensional crystal with the spatially nearly random in-plane orientation of stripes [4]. The elasticity of such a structure is described by the Landau-Peierls elastic free energy similar to that of the layered liquid crystal, Smectic A [35]. This implies that the compression deformations (corresponding to THz oscillations in our case) are much more rigid than the bending deformations. The latter is a generic property of layered systems following from their symmetry. As a result, the longitudinal dispersion of the PDT stiffness, $k(q)$, q being a wave vector along the DW, is small in the long-wave limit. Therefore, k is not too sensitive to the possible roughness of the DW on the scales much less than the domain size, and the THz PDT oscillations can be described by the 1D model given by Eq. (6). Moreover, a purely electrostatic origin of the stiffness k makes oscillations weakly sensitive to the orientation of the PDT with respect to crystallographic axes.

The effective DW mass, μ , and the viscosity, η , in Eq. (6) are related to the motion of the material-constituent polar ions during the displacement of the DWs [36] and with the piezoelectric effect of the time-varying depolarization field [32]. The magnitude of μ was calculated in *ab-initio* simulations of DW dynamics in the sub-THz range [23]. We propose an interpolation formula μ [kg/m²] $\approx 1.3 \sqrt{2a_f}$ [nm] $\times 10^{-9}$, which matches well the numerical result. Viscosity, η , is expressed through the damping factor of the DW motion, $\Gamma = \eta/\mu$. Since the consistent theory for Γ is not available, we chose the value of Γ that comes out from the measurements of the soft-mode relaxation of polar ions which has the characteristics damping time of order of few picoseconds. This time is much shorter than the typical switching time of the PDT [4] of hundred nanoseconds, and serves therefore, as a characteristic time restricting the damping of oscillatory dynamics from below.

THZ resonance

In what follows we calculate the complex dynamic permittivity of PDT, $\varepsilon_f(\omega)$. The resulting plots of the real, $\Re \varepsilon_f(\omega)$, and imaginary, $\Im \varepsilon_f(\omega)$, parts of the dispersion $\varepsilon_f(\omega)$ for 30 nm thick film of PTO are shown in Fig. 2a.

The reaction of the ferroelectric layer to the time-dependent applied field $\mathbf{D}(t) = \int d\omega \mathbf{D}_\omega e^{-i\omega t}$ is characterized by the linear response function, $\gamma(\omega)$. Solving Eq. (6) by Fourier transformation, we find:

$$\gamma(\omega) = \frac{g^{-1} \omega_0^2}{\omega_0^2 - \omega^2 - i\Gamma\omega}, \quad \omega_0 = \left(\frac{4P_s^2 g}{\mu d \varepsilon_0 \varepsilon_{\parallel}} \right)^{1/2}, \quad (8)$$

where the characteristic oscillation frequency is the usual $\omega_0 = (k/\mu)^{1/2}$ with k and μ related to the system parameters as discussed above. When deriving Eq. (8), we took into account that $\mathbf{P}_{\text{dw}\omega} = 2P_s (x_\omega/d) \mathbf{z}$ and $\mathbf{D}_\omega = \varepsilon_0 \varepsilon_{\parallel} \mathbf{E}_{\text{D}\omega}$.

Shown in Fig. 2b are the real and imaginary parts of $\gamma(\omega)$ for our sample exhibiting a characteristic Lorentzian-type form. The latter is a legacy of a singularity at ω_0 , which

would have been exhibited by a system without the dissipation, illustrated by the dashed lines. The emergence of the resonance response to the applied field is clearly demonstrated by the frequency dependencies of the absolute value of the response function, $|\gamma(\omega)|$, for different film thicknesses, see Fig. 3a, and reaching its maximum at the resonance frequency $\omega_r^2 = \omega_0^2 - \Gamma^2/2$. The dependence of ω_r upon the film thickness, $2a_f$, is shown in Fig. 3b. Shown by the blue line in the same panel is the Landau-Kittel dependence of the domain width, d , on the film thickness given by Eq. (5).

Equation (8) enables optimization of the materials parameters and the film thickness to make sure that ω_r falls within the desired THz frequency range. In particular, for the strained films of the PTO with the high spontaneous polarization, $P_s \approx 0.65 \text{ C m}^{-2}$, see [37], relatively low permittivities $\varepsilon_{\parallel} \approx 100$, $\varepsilon_{\perp} \approx 30$, soft mode damping factor $\Gamma \approx 20 \text{ cm}^{-1}$ (0.6 THz) [38] and μ defined as above, the resonance frequency ω_r decreases and spans the range from 1.5 to 0.75 THz when $2a_f$ increases from 10 to 40 nm. We find the damping frequency, $\omega_d^2 = \omega_0^2 - \Gamma^2/4$, of the attenuated oscillations of domains in PTO, $x(t) = x_0 e^{-(\Gamma/2)t} \sin \omega_d t$, which is slightly larger than ω_r , see Fig. 3b. Remarkably, our formulas perfectly describe the results of *ab-initio* simulations of DWs oscillations in PZT free-standing ultrathin films [23]. The calculated damping frequency, ω_d , is shown by the dashed line in the Fig. 3b, the symbols display the results of simulations. Here we used the following parameters for PZT: $P_s \approx 0.40 \text{ C m}^{-2}$ [37], $\varepsilon_{\parallel}, \varepsilon_{\perp} \approx 350$, $\Gamma \approx 27 \text{ cm}^{-1}$ (0.8 THz) [39] and the same value for DW mass, μ . At the same time, the resonance frequency of PZT, ω_r , drops rapidly with the thickness and vanishes above 4 nm. The data in this paragraph are given for ceramic samples. The values for strained films can be slightly different.

Making use of the relation $\gamma(\omega) = 1 - \varepsilon_{\parallel}/\varepsilon_f(\omega)$ that follows

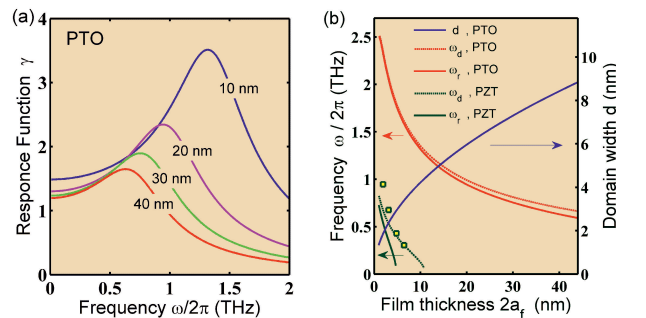


FIG. 3. Resonance in the PDT. (a) Resonance behavior of the amplitude of the response function $|\gamma(\omega)|$ for different film thickness of the PTO. (b) Dependencies of the domain resonance frequency, ω_r , of the damping frequency, ω_d , and of the domain width, d , upon the film thickness. The solid red line stands for ω_r of the PTO, the dashed red line shows ω_d of the PTO. The solid and dashed green lines show ω_r and ω_d , respectively, for PZT. Green square symbols display the results of the *ab-initio* simulations for the PZT [23]. The blue solid line displays the behavior of the domain width, d .

directly from Eq. (1), we obtain the dynamic permittivity of a ferroelectric layer

$$\varepsilon_f(\omega) = \frac{\varepsilon_{\parallel}}{1 - \gamma(\omega)} = \varepsilon_{\parallel} \frac{\omega_0^2 - \omega^2 - i\Gamma\omega}{(1 - g^{-1})\omega_0^2 - \omega^2 - i\Gamma\omega}, \quad (9)$$

with $1 - g^{-1} < 0$. At small ω this yields the negative static permittivity described by Eq. (4). We plot the real, $\Re\varepsilon_f(\omega)$, and imaginary, $\Im\varepsilon_f(\omega)$, parts of complex dispersion, $\varepsilon_f(\omega)$, calculated for 30 nm thick film of PTO in paraelectric environment, see Fig. 2a. At low frequencies $\Re\varepsilon_f(\omega)$ remains negative. At high frequencies the oscillations of DWs freeze out, and therefore $\varepsilon_f(\omega)$ should become positive and equal to intrinsic permittivity, $\Re\varepsilon_f(\infty) = \varepsilon_{\parallel} > 0$. At frequency $\omega = \omega_0$, the real part of permittivity turns zero, $\Re\varepsilon_f(\omega_0) = 0$. This behavior of PDT permittivity resembles that of a metal, having the negative real part of permittivity below the *plasma frequency* at which it becomes equal to zero. Accordingly, this will lead to the plasma resonance at $\omega = \omega_0$ in a PDT as a response to the driving field \mathbf{D} .

The discovered resonance mode gives rise to the Drude-Lorentz frequency response of a biased capacitor consisting of the ferroelectric layer (of thickness $2a_f$) sandwiched between paraelectric buffer layers (of thickness a_p and permittivity ε_p each). The same response appears in $2a_f/2a_p$ ferroelectric-paraelectric superlattice. The effective permittivity, calculated for the system of in-series capacitors, $\varepsilon_{\text{tot}}^{-1}(\omega) = \alpha_p\varepsilon_p^{-1} + \alpha_f\varepsilon_f^{-1}(\omega)$, results from the interplay of the positive, paraelectric, and negative, ferroelectric, contributions and remains positive in the static limit in a compliance with the energy conservation law. Here $\alpha_p = a_p/(a_p + a_f)$ and $\alpha_f = a_f/(a_p + a_f)$ are the relative weights of the respective layers. The adopted in-series decomposition of the total permittivity into the paraelectric and ferroelectric contributions is possible provided the thickness of the paraelectric buffer layer, a_p , is larger than the domain width, d , so that the depolarization stray fields of domains would not interact with the electrodes [40], see also [41].

The frequency dependence of the $\varepsilon_{\text{tot}}(\omega)$ for PTO/STO 30/50 nm system is shown in Fig. 2c. One sees (the detail of calculations are given further) that $\Re\varepsilon_{\text{tot}}(\omega)$ maintains a positive value for low frequencies and reflects the presence of the oscillatory mode at ω slightly less than ω_0 . As before, the dashed line depicts the behavior of $\Re\varepsilon_{\text{tot}}(\omega)$ in the absence of dissipation. We thus introduce a new metamaterial operating in the THz frequency-range $\varepsilon_{\text{tot}}(\omega)$ tunable by the variation of ratio $2a_f/2a_p$.

Optics

The effective permittivity of a ferroelectric/paraelectric layered system is calculated as $\varepsilon_{\text{tot}}^{-1}(\omega) = \alpha_p\varepsilon_p^{-1} + \alpha_f\varepsilon_f^{-1}(\omega)$ and can be conveniently written in a standard form:

$$\varepsilon_{\text{tot}}(\omega) = \frac{\omega_{\text{Lo}}^2 - \omega^2 - i\Gamma\omega}{\omega_{\text{To}}^2 - \omega^2 - i\Gamma\omega} \varepsilon_{\text{tot}}(\infty), \quad (10)$$

where the characteristic frequencies ω_{Lo} , ω_{To} are the analogues of the longitudinal and transversal oscillation frequencies in the polar mode spectroscopy. The former one, is the DW oscillation frequency, $\omega_{\text{Lo}} = \omega_0$. The latter frequency can be obtained from the relation $\omega_{\text{To}}^2/\omega_{\text{Lo}}^2 = \varepsilon_{\text{tot}}(\infty)/\varepsilon_{\text{tot}}(0)$ that is the analog of the Lyddane-Sachs-Teller relation. Here $\varepsilon_{\text{tot}}^{-1}(0) = \alpha_p\varepsilon_p^{-1} + \alpha_f\varepsilon_f^{-1}$ and $\varepsilon_{\text{tot}}^{-1}(\infty) = \alpha_p\varepsilon_p^{-1} + \alpha_f\varepsilon_{\parallel}^{-1}$. Equation (10) describes the dispersion curve in Fig. 2c. It clearly shows that the obtained PDT resonance mode freezes out when the frequency exceeds ω_0 and what is left are the molecular vibrations including the polar soft mode oscillations.

The derived dispersion relation for the dielectric permittivity provides a foundation for the description of the THz optical properties of a ferroelectric film with PDT, in particular, for finding its complex refraction index, $n(\omega) = \sqrt{\varepsilon(\omega)}$. This enables to devise an approach for inferring the resonance properties and negative permittivity effects from the optical measurements in the sub(THz) frequency band. Importantly, in the systems that we address, the typical thicknesses of the ferroelectric layer, $2a_f \approx 10 \div 40$ nm and the PDT period, $2d$, are both less than the wavelength of THz radiation, $\lambda \approx 1 \div 0.15$ mm for $0.3 \div 2$ THz. Hence the THz wave will interact with the system hosting the PDT as with an ultra-thin dielectric film endowed with the anisotropic dielectric permittivity, the latter having the in- and out of plane components ε_{\perp} and $\varepsilon_f(\omega)$ respectively.

Reflection

We consider the situation where the incident THz beam gets reflected from the dielectric substrate, STO, with dielectric permittivity $\varepsilon_p = 300 + 10i$ in the sub-THz frequency range, passing twice through the PTO ferroelectric film with PDT. To ensure the interaction of the beam with the PDT polarization, the electric field of the light should be confined to the plane of incidence, hence the p-wave polarization geometry should be used. The experimental setup is shown in the inset in Fig. 4a. The calculated reflectance, R , of such a system is shown in the main panel of Fig. 4a as function of the angle of incidence, θ , by the solid blue line. The plot illustrates a typical p-wave reflectance with the amplitude that nearly vanishes in the vicinity of the Brewster angle of the substrate, $\theta_B \approx \arctan(\Re\varepsilon_p)^{1/2} \approx 86.7^\circ$. For comparison, shown in Fig. 4a by the blue dashed line is also the net contribution of the substrate. Note that because of the very small thickness of the film, it is practically indistinguishable from the reflectance of the whole system. The difference between them, $\Delta R = R_0 - R \approx 10^{-3}$, is seen only under a magnification. Thus, to ensure the efficient filtering of the resonance PDT signal from the background substrate contribution, one has to focus instead on the relative variance of the signals difference, $\Delta R/R_0$, usually referred to as to reflectively and used to detect the tiny molecular mono-layers adsorbed on the substrate [42], see Fig. 4.

An advantage of using the reflectivity is that the value of

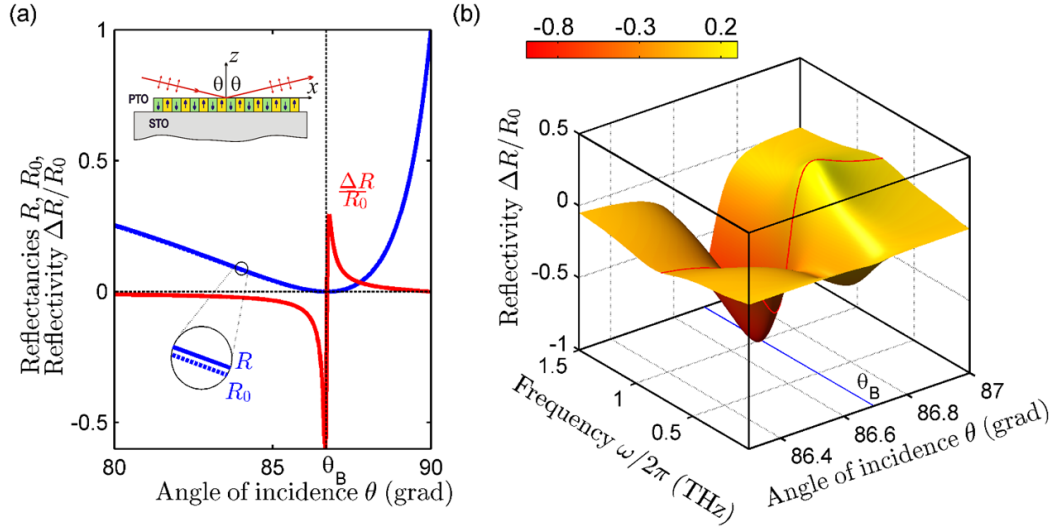


FIG. 4. Reflection characteristics of the PDT. The p -polarized THz beam reflects from the $2a_f \approx 30$ nm-thick PTO film deposited on the STO dielectric substrate. (a) The dependence of the reflectance of the film on the substrate, R , and the dependence of the net reflectance of the substrate, R_0 , on the incidence angle, θ , calculated at the PDT oscillation frequency $\omega_0/2\pi \approx 0.75$ THz are shown by the blue solid and dashed lines correspondingly. The difference between the both is tiny, $|\Delta R| = |R_0 - R| \lesssim 10^{-3}$, and in the figure scale is seen only under magnification. At variance, the reflectivity, $\Delta R/R_0$, experiences the drastic variation of about unity and clearly displays the Lorentz-like spike at the Brewster angle $\theta_B \approx 86.7^\circ$ where R_0 almost vanishes. This spike is a fingerprint of the PDT resonance and can be used for its experimental identification. The inset shows the geometry of the experiment. (b) The 3D color plot of the reflectivity, $\Delta R/R_0$, as function of the frequency and the incident angle in the immediate vicinity of the Brewster angle, θ_B , marked by thin blue line. The red line corresponds to the Lorentz-spike-like reflectivity behaviour at the PDT oscillation frequency, ω_0 . This spike smoothens upon the deviation from ω_0 .

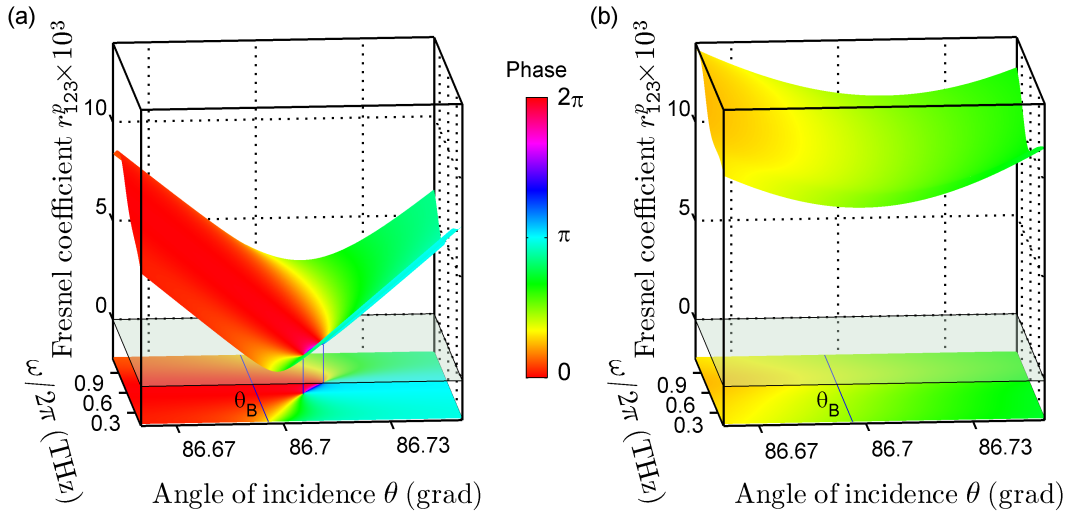


FIG. 5. The complex Fresnel reflection coefficient, r_{123}^p , of the PDT. (a) The 3D color plot of the phase and the amplitude of r_{123}^p as function of the frequency, ω , and the angle of incidence, θ , for the $2a_f \approx 30$ nm-thick PTO film deposited on the transparent substrate. The substrate permittivity $\epsilon_p = 300$ is real with the vanishingly small imaginary part. Two topologically protected phase singularity dark points, at which $|r_{123}^p| = 0$, appear in the vicinity of the Brewster angle θ_B at frequencies where $\epsilon_f = 0$ and where $\epsilon_f \approx -\sqrt{\epsilon_p \epsilon_\perp}$. These singular points and the inversion of the phase rotation between them that came out in blue is the fingerprint of the negative permittivity in the low-frequency region at $\omega < \omega_0$. (b) The same as (a) but for the finite transparency STO substrate with $\epsilon_p = 300 + 10i$. The singular phase dark points merge and annihilate. The color legend refers to both panels (a) and (b). The color maps of the phase distribution are shifted down from $|r_{123}^p| = 0$ plain for convenience.

the substrate reflectance, R_0 , almost vanishes at θ_b and the use of the ratio $\Delta R/R_0$ unravels the net contribution of the ultra-thin film *per se*. Shown by the solid red line, the reflectivity of our system does experience the drastic variation of about unity and clearly displays the Lorentz-like spike in vicinity of θ_b . This spike is a fingerprint of the PDT resonance and can be used for its experimental identification. The complete qualitative behavior of the resonance feature is illuminated by the three-dimensional color plot of $\Delta R/R_0$, as function of the frequency and the angle of incidence (Fig. 4b). The Lorentz-spike sharp behaviour gets smoothed upon the deviation from the resonance frequency.

The reflectancies R and R_0 are calculated as a square of the magnitude of the corresponding Fresnel reflection coefficients, $R = |r_{123}^p|^2$ and $R_0 = |r_{13}^p|^2$. Here index p refers to the beam polarization and indices 1, 2, and 3 correspond to the ordering of the media: the air, the film, and the substrate, respectively.

The Fresnel reflection coefficient of the substrate-deposited film is given by the expression [42]

$$r_{123}^p = \frac{r_{12}^p + r_{23}^p e^{2i\beta}}{1 + r_{12}^p r_{23}^p e^{2i\beta}}, \quad (11)$$

where

$$r_{ij}^p = \frac{\varepsilon_j \xi_i - \varepsilon_i \xi_j}{\varepsilon_j \xi_i + \varepsilon_i \xi_j}, \quad i, j = 1, 2, 3 \quad (12)$$

are the generalized Fresnel reflection coefficients between two adjacent media and $\beta = 2\pi(2a_f/\lambda)\xi_2$ is the phase shift of the electromagnetic wave after a single pass through the film. The generalized indices of refraction, ξ_i , are defined via the angle of incidence, θ_1 , and dielectric permittivities of the media, ε_i , as

$$\xi_1 = \sqrt{\varepsilon_1} \cos \theta_1, \quad \xi_2 = \left(\varepsilon_{\perp} - \frac{\varepsilon_{\perp}}{\varepsilon_2} \varepsilon_1 \sin^2 \theta_1 \right)^{1/2} \quad (13)$$

$$\xi_3 = \left(\varepsilon_3 - \varepsilon_1 \sin^2 \theta_1 \right)^{1/2}. \quad (14)$$

While the refraction indices ξ_1 and ξ_3 represent the customary properties of the air, $\varepsilon_1 = 1$, and substrate, $\varepsilon_3 = \varepsilon_p$ endowed with the isotropic permittivities, the targeted electrodynamic response of PDT with negative capacitance is encoded in the anisotropic refraction index ξ_2 that is deduced from [43]. The latter grasps both the transversal permittivity of the film, ε_{\perp} , and the effective longitudinal permittivity of PDS, $\varepsilon_2 = \varepsilon_f(\omega)$.

The described approach identifies the PDT resonance behavior via detecting the characteristic Lorentz-like spike features in the angular and frequency dependencies of the reflectance. However, the developed theory of the electromagnetic response equips us with the extraordinary more advanced technique. Namely, the resonance point ω_0 where $\varepsilon_f(\omega)$ changes the sign, is found, with the great precision from the phase map of the Fresnel coefficient r_{123}^p . The latter (unlike the real-value reflectance $R = |r_{123}^p|^2$, where the phase information is lost) is a complex quantity which is measured, for example, by the phase-resolved ellipsometry technique [44].

To develop a feasible protocol for observation of the frequency domain endowed with negative ε_f let us describe the dependence $r_{123}^p(\theta)$ near the Brewster angle in the system with the ideally transparent substrate with $\Im\varepsilon_p = 0$. If the film were absent, the Fresnel coefficient would have been real and changed the sign upon passing zero at $\theta = \theta_b$. Placing the film on the substrate, gives the contribution, albeit very small, that pulls r_{123}^p into a complex plane, where the trajectory $r_{123}^p(\theta)$ circumflexes the zero from the positive- to negative semi-axis acquiring the phase $\pm\pi$. Equations (11)-(14) offering a full description of the electromagnetic response show that the direction (clock- vs. anticlock-wise) of the phase rotation is determined by the sign of ε_f . The frequency ω_0 at which ε_f changes the sign corresponds, therefore, to a particular point in the (θ, ω) -plane where phase acquires a factor of 2π when making a close loop around it, and the Fresnel coefficient, r_{123}^p , vanishes. These zeros of the complex function, $r_{123}^p(\theta, \omega)$, where the intensity of the reflected light is zero are often called ‘points of absolute darkness’ [45]. They are stable with respect to small variations of parameters hence topologically protected, and we refer to them as to topological darkness points.

Figure 5a displays the 3D color plot of the phase and amplitude of the Fresnel reflection coefficient, r_{123}^p , of the PDT in the 30nm PTO film as a function of an incident angle and frequency for the case of transparent substrate with $\varepsilon_p = 300$, derived from Eqs. (11)-(14). Two topological dark points resulting from the negative permittivity are clearly visible at the manifold depicting $r_{123}^p(\theta, \omega)$. The higher-frequency point corresponds to the discussed above sign change of ε_f . The second, lower-frequency one, appears when $\varepsilon_f \approx -\sqrt{\varepsilon_p \varepsilon_{\perp}}$. This manifestly illustrates the topological protection effect: the topological darkness points are not smoothed but merely shifted by dissipation. Figure 5b shows the the same phase plot for the PTO on a real substrate STO with $\varepsilon_p = 300 + 10i$. One sees that if the dissipation is sufficiently large, the darkness points merge and cease to exist, i.e. the sharp Brewster-angle singularities in the phase plot get smoothened.

The obtained results and recent measurements of the negative capacitance in PDT [15] open a new area of research in the field of the THz optics in ferroelectric materials. Exciting opportunities open in the area of the plasmonic epsilon-near-zero (ENZ) metamaterials having the unique property that the electromagnetic wave propagates with almost no phase advance. Although such materials have been made artificially in the microwave, visible and far-infrared spectral ranges [46], the engineered ENZ structures in the THz spectral range have not been explored so far.

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APPENDIX

Calculations of the electrostatic properties of PDT in the applied field \mathbf{D} generalize the zero-field Landau-Kittel calculations of PDT given in the textbook [27] in application to magnetic domains. The geometry of the system is shown in Fig. 6. The x -axis is directed along the PDT texture, the y -axis is parallel to the domains and the z -axis is directed across the film. Since the polarization distribution does not change along the y -axis, the problem is reduced to the 2D one in the xz -plane. In the external field the up- and down-oriented polarization domains have different widths, d_+ and d_- , the field-induced polarization due to DW motion being expressed via the field dependence of the asymmetry factor $\kappa = (d_+ - d_-)/2d$ as $P_{\text{dw}} = \kappa(D)P_s$, with $2d = d_+ + d_-$ being the period of the structure. Following the relation (3) we express the dielectric permittivity of the PDT as:

$$\varepsilon_f = \frac{\varepsilon_{\parallel}}{1 - (\kappa(D)/D)P_s}. \quad (15)$$

The linear dependence κ on D is found by minimization of the electrostatic energy of the system, considering κ as variation parameter.

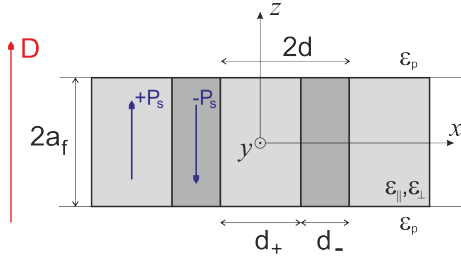


FIG. 6. The geometry of the system.

We start with the derivation of the spacial distribution of the electric fields inside the ferroelectric (f) and paraelectric (p) layers, $\mathbf{E}^{(p,f)} = (E_x^{(p,f)}, E_z^{(p,f)})$, induced by the depolarization surface charges arising at the interfaces between f - and p -layers at $z = \pm a_f$. These charges, appearing due to termination of the alternating polarization in PDT, are conventionally presented as $\sigma_{\pm}(x) = \pm\vartheta(x)P_s$ where the sign-alternating function, ϑ , is defined as $\vartheta(x) = \pm 1$ if $x \in d_{\pm}$. The corresponding electrostatic potentials in the f - and p -layers $\nabla\varphi^{(p,f)} = -\mathbf{E}^{(p,f)}$

satisfy the Laplace equations:

$$\begin{aligned} (\varepsilon_{\parallel}\partial_z^2 + \varepsilon_{\perp}\partial_x^2)\varphi^{(f)} &= 0, \\ \varepsilon_p(\partial_z^2 + \partial_x^2)\varphi^{(p)} &= 0. \end{aligned} \quad (16)$$

The boundary conditions for the potential at the interfaces are fixed by the charges $\sigma_{\pm}(x)$:

$$\begin{aligned} \varepsilon_0\varepsilon_{\parallel}\partial_z\varphi^{(f)} - \varepsilon_0\varepsilon_p\partial_z\varphi^{(p)} &= \pm\sigma_{\pm}(x), \\ \varphi^{(f)} &= \varphi^{(p)}. \end{aligned} \quad (17)$$

System (16) with boundary conditions (17) is solved by the Fourier-series expansion method, taking into account that

$$\sigma_{\pm}(x) = \pm\vartheta(x)P_s = \pm\left(\kappa + \sum_{n=1}^{\infty} p_n \cos q_n x\right)P_s \quad (18)$$

with $q_n = \pi n/d$ and

$$p_n = \frac{4}{\pi n} \sin \frac{1+\kappa}{2}\pi n \quad (19)$$

After straightforward calculations we obtain:

$$\begin{aligned} \varphi^{(f)} &= \frac{z}{a_f}\varphi_0 + P_s \sum_{n=1}^{\infty} \psi_n \frac{\sinh\left(\sqrt{\varepsilon_{\perp}/\varepsilon_{\parallel}}q_n z\right)}{\sinh\left(\sqrt{\varepsilon_{\perp}/\varepsilon_{\parallel}}q_n a_f\right)} \cos q_n x, \\ \varphi^{(p)} &= \pm\varphi_0 - (z - a_f) \frac{D}{\varepsilon_0\varepsilon_p} \\ &\quad \pm P_s \sum_{n=1}^{\infty} \psi_n \exp q_n(a_f - |z|) \cos q_n x \end{aligned} \quad (20)$$

where $\varphi_0 = \mp(\varepsilon_0\varepsilon_{\parallel})^{-1}(D - \kappa P_s)a_f$ is the average value of the potential at the upper/lower surface of the ferroelectric slab, and

$$\psi_n = \frac{p_n}{q_n \varepsilon_0 \sqrt{\varepsilon_{\perp}/\varepsilon_{\parallel}} \coth\left(\sqrt{\varepsilon_{\perp}/\varepsilon_{\parallel}}q_n a_f\right) + q_n \varepsilon_0 \varepsilon_p}. \quad (21)$$

The electrostatic energy of the system can be calculated as the integral $\sum_{\pm} \int dx \int [\varphi(x)]_{z=\pm a_f} d\sigma_{\pm}(x)$ over the surfaces of the ferroelectric layer. The integration over σ_{\pm} reflects the self-consistent adiabatic charging of the surfaces, driven by the self-polarization of the system from the paraelectric state, until the state with the equilibrium spontaneous polarization, $\pm P_s$, is achieved inside domains.

Taking into account the dependencies given by (20) of $\varphi(x)$ and $\sigma_{\pm}(x)$ on P_s we calculate the energy per unit length of PDT (here the factor 2 is because of the two 2 sides of the slab):

$$\begin{aligned} F_{\text{el}} &= 2 \frac{1}{2d} \int_0^{2d} dx \int_0^{P_s} [\varphi(x, P'_s)]_{z=a_f} \vartheta(x) dP'_s = 2 \int_0^{P_s} dP'_s \left(\varphi_0(P'_s)\kappa + \frac{1}{2} P'_s \sum_{n=1}^{\infty} p_n \psi_n \right) \\ &= \frac{2a_f}{\varepsilon_0\varepsilon_{\parallel}} \left(\frac{1}{2} P_s^2 \kappa^2 - D P_s \kappa \right) + P_s^2 \sum_{n=1}^{\infty} \frac{8d}{\pi^3 n^3} \frac{\sin^2(1+\kappa)\pi n/2}{\varepsilon_0 \sqrt{\varepsilon_{\perp}/\varepsilon_{\parallel}} \coth\left(\pi n \sqrt{\varepsilon_{\perp}/\varepsilon_{\parallel}} a_f/d\right) + \varepsilon_0 \varepsilon_p}, \end{aligned} \quad (22)$$

In the experimentally relevant limit $\sqrt{\varepsilon_{\perp}/\varepsilon_{\parallel}} a_f/d \gg 1$, Eq. (22) is simplified as:

$$F_{el} = \frac{2a_f}{\varepsilon_0 \varepsilon_{\parallel}} \left(\frac{1}{2} P_s^2 \kappa^2 - DP_s \kappa \right) + \frac{8}{\pi^3 \varepsilon_0 \zeta \sqrt{\varepsilon_{\perp} \varepsilon_{\parallel}}} df(\kappa) P_s^2, \quad (23)$$

where

$$f(\kappa) = \sum_{n=1}^{\infty} n^{-3} \sin^2(1 + \kappa) \frac{\pi n}{2} \stackrel{\kappa \rightarrow 0}{\approx} \frac{7}{8} \zeta(3) - \frac{\ln 2}{4} (\pi \kappa)^2. \quad (24)$$

Minimization of (23) with respect κ gives:

$$\kappa = \frac{D}{P_s} \left(1 - \frac{4 \ln 2}{\pi \zeta} \left(\frac{\varepsilon_{\parallel}}{\varepsilon_{\perp}} \right)^{1/2} \frac{d}{2a_f} \right)^{-1}. \quad (25)$$

Finally, making use of (15), we obtain the dielectric permittivity of the PDT (4). Note that the expression (4) can also be derived from the general expression for the permittivity of a paraelectric-ferroelectric system given in [47] and also from the calculations presented in [9], see SI.

The DW displacements in PDT shown in Fig. 1d are given by $\pm x = \pm \kappa d/2$. Equating the stiffness energy of the DW displacement, $2a_f \cdot kx^2/2$, to (23) (taken in harmonic approximation at $D = 0$ and multiplying by d , i.e. using the energy per a single DW), we obtain the expression for the stiffness coefficient, k , (7). The Landau-Kittel formula (5) for the domain width, d , is obtained by minimization of $F_{el} + F_{dw}$ energy with respect d at $\kappa = 0$. Here $F_{dw} = (a_f/d)w_{dw}$ is the domain wall energy, calculated per unit length of PDT and w_{dw} is the surface energy of DW. The spatial distribution of the electric and polarization fields in the p - and f -slabs are found from (20) as: $\mathbf{E}^{(p,f)} = (E_x^{(f)}, E_z^{(f)}) = -\nabla \varphi^{(p,f)}$, $\mathbf{P}^{(p)} = \varepsilon_0 (\varepsilon_p - 1) \mathbf{E}^{(p)}$, $\mathbf{P}^{(f)} = (P_x^{(f)}, P_z^{(f)})$ where $P_x^{(f)} = \varepsilon_0 (\varepsilon_{\perp} - 1) E_x^{(f)}$, $P_z^{(f)} = \varepsilon_0 (\varepsilon_{\parallel} - 1) E_z^{(f)} + \vartheta(x) P_s$.

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