

Size effect of soft phonon dispersion in nanosized ferroics

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Using Landau-Ginsburg-Devonshire theory, we derive and analyze analytical expressions for the frequency dispersion of soft phonon modes in nanosized ferroics and perform numerical calculations for a thin SrTiO₃ film. We revealed the pronounced “true” size effect in the dependence of soft phonon spatial dispersion on the film thickness and predict that it can lead to the “apparent” or “false” size effect of dynamic flexoelectric coupling constants. Also, we derived analytical expressions describing the influence of finite size effect on the appearance and properties of the incommensurate spatial modulation induced by the static flexoelectric effect in ferroic thin films. To verify the theoretical predictions experimental measurements of the soft phonon dispersion in nanosized ferroics seem urgent.

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I. INTRODUCTION

Microstructural, electrophysical, electromechanical, and magnetoelectric properties of nanosized ferroics (shortly “nanoferroics”), such as thin films and nanoparticles of proper and incipient ferroelectric, quantum paraelectrics, ferroelastics, and ferromagnetics with inherent phase transitions to the long-range ordered phase(s), strongly attract the attention of researchers [1,2]. In particular, experimental and theoretical studies of the lattice dynamics in nanoferroics are an inexhaustible source of versatile valuable information for fundamental physical research and advanced applications [1,2]. Notably, in any phase transition that leads to the instability of the definite phonon vibration modes, the static displacements of atoms at the phase transition correspond to frozen displacements of the soft phonon modes [3,4]. Basic experimental methods, which contain information about the soft phonon modes and spatial modulation of the order parameter in ferroics are dielectric measurements [5], inelastic neutron scattering [3,6–10], x-ray [11–13], Raman [14], and Brillouin [11,12,15–18] scatterings, and the ultrasonic pulse-echo method [15,17], allowing hypersound spectroscopic measurements.

The flexoelectric coupling is of great importance for nanoscale objects [19,20] and especially for nanoferroics [21,22], where the strong strain gradients are inevitably present at the surfaces of thin films [23–25], domain walls, and interfaces [26–28]. The static flexoelectric effect, introduced by Mashkevich, Tolpygo [29], and Kogan [30], manifesting itself in the appearance of electric polarization variation δP_i linearly proportional to the strain gradient $\partial u_{kl}/\partial x_j$, exists in all solids, making the effect universal [31–33]. The proportionality coefficient f_{ijkl} in the linear relation, $\delta P_i = f_{ijkl} \frac{\partial u_{kl}}{\partial x_j}$,

is the component of the flexoelectric coupling tensor. Relatively recently Kvasov and Tagantsev [34] predicted the existence of a dynamic flexoelectric effect contributing to the polarization variation as $\delta P_i = -\frac{M_{ij}}{\alpha} \frac{\partial^2 U_j}{\partial t^2}$, where U_j are the components of elastic displacement, M_{ij} are the components of the dynamic flexoelectric tensor, and α is the dielectric stiffness.

Considering the importance of the flexoelectric coupling (shortly “flexocoupling”) for the physical understanding of the gradient-driven couplings in mesoscale and nanoscale solids, one has to determine its symmetry and numerical values. The available experimental and theoretical data about the flexocoupling tensor symmetry, specifically the amount of independent components allowing for the point group symmetry [35,36] and “hidden” permutation symmetry [37], are contradictory [38]. The upper limits for the values f_{ijkl} established by Yudin *et al.* [39], as well as the values calculated from first principles for bulk ferroics [40–43], can be several orders of magnitude smaller than those measured experimentally in ferroelectric ceramics [44–46] and thin films [47], ferroelectric relaxor polymers [48] and electrets [49], and incipient ferroelectrics [50,51] and biological membranes [52,53]. To explain the paradox, Stengel [54] reasonably argued that a significant difference (e.g., increase) of flexoelectric response can originate from the different electric boundary conditions. Recent papers suggest several probable sources of “giant” flexoelectricity that is measured sometimes. Namely, Abdollahi *et al.* [55] and Rahmati *et al.* [56] revealed that asymmetric distribution of piezoelectric sources in solids [55], as well as nonuniformly distributed electric dipoles and charges in soft electrets [56], can produce a remarkable flexoelectric-like response. Abdollahi *et al.* [55] theoretically predicted that the giant flexoelectric response can originate in a homogeneously poled piezoelectric beam under bending [55]. Rahmati *et al.* [56] proposed a modern theory of soft electrets electromechanical response predicting that nonuniformly distributed dipoles and charges in the

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electrets reveal an apparent electromechanical response that can be ambiguously and interchangeably interpreted as either transverse piezoelectricity or flexoelectricity. They also suggest the routes to engineer high transverse piezoelectric and flexoelectric coefficients in appropriately designed soft electrets, where a homogeneous external electric field can induce curvature enabling the structure application as a bending actuator.

Bersuker argued [57] that the anomalously high flexoelectric coefficients in perovskite ceramics may be related to the manifestation of the pseudo-Jahn-Teller effect. Steaming from a vibronic nature [58], the pseudo-Jahn-Teller effect can affect the dynamic flexoeffect in ferroics, and, indeed, the available information about the numerical values of M_{ij} is completely controversial, because, on one hand, there are microscopic theories in which the effect is absent [54], and, on the other hand, its determination from the soft phonon spectra leads to nonzero M_{ij} [34,59,60], where the impact appeared comparable to that of the static flexoelectric effect in, e.g., bulk SrTiO_3 .

The impact of the static and dynamic flexoelectric effect on the dispersion law $\omega(k)$ of the soft phonon frequency ω in ferroics has been studied recently in Refs. [58,59], where we used Landau-Ginzburg-Devonshire (LGD) approach to model the properties of optic and acoustic phonons in the ferroelectric and paraelectric phases of different ferroics. It appeared that the joint action of static and dynamic flexoelectric effects essentially broadens the k spectrum of generalized susceptibility and leads to the additional “pushing away” of the optical and acoustic soft mode phonons. The degeneration of the transverse optic and acoustic modes disappears in the ferroelectric phase in comparison with the paraelectric phase due to the synergy of flexoelectric coupling and ferroelectric nonlinearity. The soft acoustic modes and spatially modulated phases (SPM) can be induced by the flexoelectric coupling in ferroics [22,61,62] and the surface acoustic waves can propagate in nonpiezoelectric solids due to the static and dynamic flexoelectric effects [63].

Let us underline that the theoretical results [58–62], which can be important for the theoretical analyses of the neutron, Raman, and Brillouin scattering experiments [22], have been obtained for unconfined [58–61] or semi-infinite [62] ferroics. However, to the best of our knowledge, a theoretical description of the phonon dispersion in nanoferroics (e.g., in thin films or nanoparticles) is still absent. Therefore, in this study we derive and analyze the dispersion $\omega(k)$ of soft phonon modes in dependence on the thickness of ferroic film allowing for the static and dynamic flexocoupling, and perform numerical calculations for an incipient ferroelectric SrTiO_3 using LGD theory. The paper is structured in the following way. The problem formulation, used approximations, and an analytical solution for the phonon dispersion in a thin paraelectric film are presented in Sec. II. Obtained analytical expressions for $\omega(k)$ are discussed and illustrated on an example of a SrTiO_3 thin film in Sec. III, where special attention is paid to the “true” size effect of the soft phonon dispersion and to the “apparent” or “false” size effect of the dynamic flexocoupling, as well as to the influence of the film thickness on the SPM appearance and critical values of the static flexocoupling constants. Section IV is a brief summary.

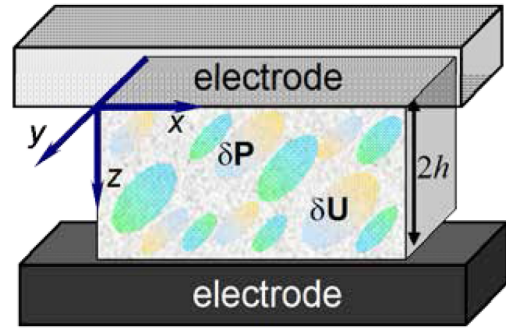


FIG. 1. The geometry of the ferroic film confined in the z direction. The fluctuations of electric polarization and mechanical displacement, $\delta\vec{P}$ and $\delta\vec{U}$, are shown by semitransparent ellipsoids.

The details of calculations are presented in the Supplemental Material [64].

II. ANALYTICAL SOLUTION FOR A THIN FERROELECTRIC FILM

A. Problem formulation

Let us consider a ferroic film of thickness $2h$ confined in the z direction. The film surfaces are covered by two ideally conducting “soft” electrodes, which do not affect its mechanical state. The geometry of the problem is shown in Fig. 1.

Below we calculate the phonon spectra using the well-adopted procedure, when the polarization and displacement variations appear as the response to the fluctuations of applied electric field $\delta\vec{E}$ and elastic force $\delta\vec{N}$ (see, e.g., Refs. [19,58–60]). These fluctuations can be arbitrary, but small enough to allow the linearization of a dynamic equation of state. Also the polarization and displacement variations should satisfy boundary conditions at the film surfaces. Another limitation is the so-called “one-component approximation” [59,60], when the considered fluctuations of the long-range order parameters are one component of electric polarization δP_i and one component of mechanical displacement δU_j . The indexes i, j can be one of 1, 2 or 3 determining the fluctuation direction.

Both in-plane and out-of-plane directions of polarization fluctuations should be considered for a film in a ferroelectric phase, i.e., when the spontaneous polarization is nonzero. Below we consider a paraelectric film without the spontaneous polarization or strain, and so the direction of the polarization and displacement variations are related with the vectors $\delta\vec{E}$ and $\delta\vec{N}$, respectively. The electric field $\delta\vec{E}$ is the sum of depolarization (d) and small external (e) fields, $\delta\vec{E} = \delta\vec{E}^d + \delta\vec{E}^e$. The depolarization field $\delta\vec{E}^d$ is induced by the fluctuations with $\text{div}(\delta\vec{P}) \neq 0$, since it satisfies the Poisson equation $\epsilon_b \epsilon_0 \text{div}(\delta\vec{E}) = \text{div}(\delta\vec{P})$, where ϵ_b is a background permittivity [19] and $\epsilon_0 = 8.85 \times 10^{-12}$ F/m is the universal dielectric constant. It is well known that $\delta\vec{E}^d$ strongly suppresses all “longitudinal” fluctuations, for which $\text{div}(\delta\vec{P}) \neq 0$, and so the longitudinal phonons can be hardly detected experimentally, especially the optic ones [58]. That is why below we performed calculations for the most interesting case

of transverse phonons with $\text{div}(\delta\vec{P}) = 0$ and $\text{div}(\delta\vec{U}) = 0$, which is valid for, e.g., $\delta P_y(x, z)$ and $\delta U_y(x, z)$.

In comparison with the three-component case [58], the one-component approximation for polarization and displacement allows considering only the lowest transverse optic and transverse acoustic soft phonon modes in ferroics [59–61]. As it was shown in Refs. [59,60], the one-component approximation can describe quantitatively the experimental data for the soft phonon dispersion in paraelectric SrTiO_3 [6], uniaxial ferroelectrics $\text{Sn}_2\text{P}_2\text{S}_6$ [65], and $\text{Sn}_2\text{P}_2\text{Se}_6$ [66], and, quite unexpectedly, the dispersion of the lowest modes in the paraelectric phase of ferroelectric PbTiO_3 [3] and organic ferroelectric $(\text{CH}_3)_3\text{NCH}_2\text{COO} \cdot \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ [9]. However, strictly speaking, the one-component approximation cannot describe the soft phonon dispersion in multiaxial ferroelectrics, such as perovskites BaTiO_3 or $(\text{Pb}, \text{Zr})\text{TiO}_3$, wherein three acoustic and several optic phonon modes are observed [58]. This is because the simplified dispersion law, obtained within the approximation, cannot describe the interaction between different transverse and longitudinal optic and three acoustic modes induced by cooperative effects, flexoelectric, and electrostriction couplings in multiaxial ferroelectrics (see e.g., the models by Kappler, Walker [67], and Hlinka *et al.* [68]). Moreover, the one-dimensional approximation cannot describe the behavior of dielectric susceptibility nondiagonal components in a ferroelectric phase, which should originate from, e.g., the flexoelectric component f_{13} in a three-dimensional case [59]. Unfortunately, it appeared impossible for us to derive analytical expressions for a phonon dispersion in thin films in a general three-component case, and, for the sake of clarity, we were limited ourselves by the one-component approximation.

Within the one-component approximation, dynamic equations for the order parameter component $\delta P_i(x, z)$, further denoted as $\eta(x, z)$, and one component of mechanical displacement $\delta U_j(x, z)$, further denoted as $U(x, z)$, can be obtained by the variation of the Lagrange function. The Lagrange function of the ferroic film has the following form:

$$L_V = \int_0^\infty dt \int_{-\infty}^\infty dx \int_{-h}^h dz (F_V - K_V), \quad (1a)$$

$$\begin{aligned} F_V = & \frac{\alpha(T)}{2} \eta^2 + \frac{\beta}{4} \eta^4 + \frac{\gamma}{4} \eta^6 - \eta \delta E \\ & + \frac{g_l}{2} \left(\frac{\partial \eta}{\partial z} \right)^2 + \frac{g_\perp}{2} \left(\frac{\partial \eta}{\partial x} \right)^2 \\ & - q_l \frac{\partial U}{\partial z} \eta^2 - q_\perp \frac{\partial U}{\partial x} \eta^2 - \frac{f_l}{2} \left(\eta \frac{\partial^2 U}{\partial z^2} - \frac{\partial U}{\partial z} \frac{\partial \eta}{\partial z} \right) \\ & - \frac{f_\perp}{2} \left(\eta \frac{\partial^2 U}{\partial x^2} - \frac{\partial U}{\partial x} \frac{\partial \eta}{\partial x} \right) \\ & + \frac{c_l}{2} \left(\frac{\partial U}{\partial z} \right)^2 + \frac{c_\perp}{2} \left(\frac{\partial U}{\partial x} \right)^2 + \frac{v}{2} \left(\frac{\partial^2 U}{\partial z^2} \right)^2 \\ & + \frac{w}{2} \left(\frac{\partial^2 U}{\partial x^2} \right)^2 + \delta N_l \frac{\partial U}{\partial z} + \delta N_\perp \frac{\partial U}{\partial x} \end{aligned} \quad (1b)$$

$$K_V = \left(\frac{\mu}{2} \left(\frac{\partial \eta}{\partial t} \right)^2 + M \frac{\partial \eta}{\partial t} \frac{\partial U}{\partial t} + \frac{\rho}{2} \left(\frac{\partial U}{\partial t} \right)^2 \right). \quad (1c)$$

According to Landau theory [69,70], the coefficient α in Eq. (1b) linearly depends on the temperature T for proper ferroelectrics, $\alpha(T) = \alpha_T(T - T_C)$, where $\alpha_T > 0$ and $T_C > 0$ is the Curie temperature. For incipient ferroelectrics (such as SrTiO_3) α obeys the Barrett-type formula [71], $\alpha(T) = \alpha_T(T_q \coth(T_q/T) - T_C)$, where $T_C \leq 0$ is the “virtual” Curie temperature, $T_q > 0$ is a characteristic temperature. Coefficients q_l and $q_\perp$ are the longitudinal and transverse components of electrostriction tensor in the normal and transverse directions with respect to the film surfaces ($z = \pm h$), respectively, f_l are $f_\perp$ the longitudinal and transverse components of the static flexoelectric tensor, respectively [72]. The higher order coefficient β (that can be positive or negative depending on the ferroic order) and positive coefficient γ are regarded temperature independent; g_l and $g_\perp$ are positive longitudinal and transverse components of the polarization gradient tensor, and c_l and $c_\perp$ are elastic compliances related to the normal and transverse directions, respectively. The longitudinal coefficients v and w of higher elastic gradients are not negative, $v \geq 0$ and $w \geq 0$. M is the dynamic flexocoupling coefficient; ρ is the ferroic mass density at normal conditions, and μ is the kinetic coefficient in kinetic energy (1c).

The surface free energy related with the polar order parameter is

$$F_S = \frac{\zeta}{2} \int_{-\infty}^\infty dx [\eta^2(x, -h) + \eta^2(x, h)]. \quad (2)$$

The coefficient $\zeta \geq 0$ in the surface energy (2) is weakly temperature dependent.

Euler-Lagrange equations for $\eta(x, z)$ and $U(x, z)$, obtained by varying Eq. (1a), are listed in the Supplemental material. The boundary conditions for $\eta(x, z)$ derived by varying Eqs. (1) on η have the form:

$$\begin{aligned} -\zeta \eta - g_l \frac{\partial \eta}{\partial z} - \frac{f_l}{2} \left(\frac{\partial U}{\partial z} \right) \Big|_{z=h} &= 0, \\ \zeta \eta - g_l \frac{\partial \eta}{\partial z} - \frac{f_l}{2} \left(\frac{\partial U}{\partial z} \right) \Big|_{z=-h} &= 0. \end{aligned} \quad (3)$$

Supplementary boundary conditions for $U(x, z)$ make sense only in the case of positive v , and they are listed in the Supplemental Material for the considered geometry. To obtain and analyze relatively simple analytical expressions, one can show that the conditions for $U(x, z)$ can be neglected in the case of small enough v and under the validity of strict equality $f^2 \ll cg$ regarded valid hereinafter (for details see Ref. [59] and the criteria of upper bonds of flexoelectric coefficients in Ref. [39]). The higher gradient terms $\frac{v}{2} \left(\frac{\partial^2 U}{\partial z^2} \right)^2 + \frac{w}{2} \left(\frac{\partial^2 U}{\partial x^2} \right)^2$ are usually omitted, except in several papers, e.g., Eliseev *et al.* [73], Yurkov [74], Mao and Purohit [75], and Stengel [43]. Notably, the supplementary conditions for $U(x, z)$ become redundant in the limit $v = w = 0$ considered hereinafter.

Let us seek for the solution of the problem for the paraelectric phase, where $\alpha(T) > 0$ and the spontaneous polarization is zero. The expansion of the small variations, $\eta(x, z)$ and $U(x, z)$, in Fourier integral in k - ω space have the

form

$$\eta = \int dk_{\perp} dk_l \exp(ik_{\perp}x + ik_l z + i\omega t) \tilde{\eta}(\vec{k}),$$

$$U = \int dk_{\perp} dk_l \exp(ik_{\perp}x + ik_l z + i\omega t) \tilde{U}(\vec{k}). \quad (4)$$

Euler-Lagrange equations [Eqs. (A.1)–(A.2) in the Supplemental Material] linearized with respect to the polarization and displacement fluctuations acquire the following form in k - ω space

$$(-\mu\omega^2 + \alpha + g_{\perp}k_{\perp}^2 + g_l k_l^2) \tilde{\eta} + (f_l k_l^2 + f_{\perp} k_{\perp}^2 - M\omega^2) \tilde{U} = \delta \tilde{E}, \quad (5a)$$

$$(c_{\perp}k_{\perp}^2 + c_l k_l^2 - \rho\omega^2) \tilde{U} + (f_l k_l^2 + f_{\perp} k_{\perp}^2 - M\omega^2) \tilde{\eta} = -ik_l \delta \tilde{N}_l - ik_{\perp} \delta \tilde{N}_{\perp}. \quad (5b)$$

As a result the Fourier images of the order parameter $\tilde{\eta}(\vec{k})$ and elastic displacement $\tilde{U}(\vec{k})$ are linearly proportional to external electric field and mechanical force variations, $\delta \tilde{E}$ and $\delta \tilde{N}$.

Notethat electric field fluctuation δE in Eq. (1c) does not contain contribution related with a depolarization field for considered transverse phonons. However, in the general three-component case $\delta E_i = \delta E_i^d + \delta E_i^e$ is the sum of depolarization $\delta \tilde{E}_i^d(\vec{k}) \approx -\frac{k_i k_j \delta \tilde{P}_j(\vec{k})}{\epsilon_b \epsilon_0 k^2}$ and the small external δE_i^e fields (see supplemental material in Ref. [58]). The field $\delta \tilde{E}_i^d(\vec{k})$ is induced by longitudinal fluctuations with $k_j \delta \tilde{P}_j \neq 0$ and it leads to the substitution $\alpha \rightarrow \alpha \delta_{ij} + \frac{k_i k_j}{\epsilon_b \epsilon_0 k^2}$ in three equations for $\delta \tilde{P}_i$ analogous to Eq. (5a) ($i = 1, 2, 3$). Since almost always $\frac{1}{\epsilon_b \epsilon_0} \gg \alpha$, the longitudinal fluctuations $\delta \tilde{P}_i$ affected by the depolarization field are very small, and their frequency becomes very high in comparison with the frequency of transverse modes [58]. That is why below we analyze results for the transverse phonons only.

The formal solution of Eqs. (5) can be presented in a matrix form and are listed in the Supplemental Material. The condition when the determinant of the system (5) is zero leads to the expression for the phonon frequency dispersion, $\omega(k)$, in a bulk ferroic,

$$\omega_{1,2}^2(\vec{k}) = \frac{C(\vec{k}) \pm \sqrt{C^2(\vec{k}) - 4(\mu\rho - M^2)B(\vec{k})}}{2(\mu\rho - M^2)}, \quad (6)$$

where the functions

$$C(\vec{k}) = \alpha\rho + (\mu c_{\perp} - 2f_{\perp}M + \rho g_{\perp})k_{\perp}^2 + (c_l\mu - 2f_lM + g\rho)k_l^2$$

and

$$B(\vec{k}) = (\alpha + g_l k_l^2 + g_{\perp} k_{\perp}^2)(c_l k_l^2 + c_{\perp} k_{\perp}^2) - (f_l k_l^2 + f_{\perp} k_{\perp}^2)^2,$$

respectively (see the Supplemental Material for details). Dispersion relation (6) contains the transverse optical (O) and acoustic (A) phonon modes, which corresponds to the signs “+” and “−” before the radical, respectively.

B. Approximate analytical solution for thin films

For thin films the boundary conditions (3) makes the k_l -spectra of $\omega(\vec{k})$ discrete, $k_l \rightarrow k_m$, where m are integer numbers. The discrete eigenvalues k_m were determined from the condition of the zero determinant $\|D_m\|$ of the system (5) along with the boundary conditions (3) (see Supplemental Material). It turned out that the condition $\|D_m\| = 0$ is equivalent to the characteristic equation

$$\text{Im}[A(k_m, \omega)] \cos(2k_m h) + \text{Re}[A(k_m, \omega)] \sin(2k_m h) = 0, \quad (7)$$

where

$$A(k_m, \omega) = -\left(\zeta - ik_m g_l - ik_m \frac{f_l}{2} \frac{f_l k_m^2 + f_{\perp} k_{\perp}^2 - M\omega^2}{c_l k_m^2 + c_{\perp} k_{\perp}^2 - \rho\omega^2}\right)^2. \quad (8)$$

The soft phonons dispersion $\omega(k_m, k_{\perp})$ is given by Eq. (6), but with discrete k_m , namely,

$$\omega_{1,2}^2(k_m, k_{\perp}) = \frac{C(k_m, k_{\perp}) \pm \sqrt{C^2(k_m, k_{\perp}) - 4(\mu\rho - M^2)B(k_m, k_{\perp})}}{2(\mu\rho - M^2)}, \quad (9)$$

where the functions $C(k_m, k_{\perp}) = \alpha\rho + (\mu c_{\perp} - 2f_{\perp}M + \rho g_{\perp})k_{\perp}^2 + (c_l\mu - 2f_lM + g\rho)k_m^2$ and $B(k_m, k_{\perp}) = (\alpha + g_l k_m^2 + g_{\perp} k_{\perp}^2)(c_l k_m^2 + c_{\perp} k_{\perp}^2) - (f_l k_m^2 + f_{\perp} k_{\perp}^2)^2$ also depend on the film thickness h and parameter ζ in the boundary conditions (3) due to the dependences of k_m on h and ζ per Eq. (7).

C. Limiting cases of the boundary conditions

The limiting case of zero derivative of the order parameter and displacement at the film surfaces, $\frac{\partial \eta}{\partial z}|_{z=\pm h} = 0$ and $\frac{\partial U}{\partial z}|_{z=\pm h} = 0$, corresponds to $\zeta \rightarrow 0$ and leads to the expression $A(k_m, \omega) = (g_l + \frac{f_l}{2} \frac{f_l k_m^2 + f_{\perp} k_{\perp}^2 - M\omega^2}{c_l k_m^2 + c_{\perp} k_{\perp}^2 - \rho\omega^2})^2 k_m^2$ in Eq. (8). Since $A(k_m, \omega) \geq 0$ for $\zeta \rightarrow 0$ and the variable $k_{\perp}^2$ is independent, Eq. (7) reduces to the equation $\sin(2k_m h) = 0$, where the solution has the form $k_m = \frac{\pi m}{2h}$, where $m = 0, 1, 2, \dots$. However, for this case one should consider the lowest root $m = 0$ corresponding to the constant order parameter, $\eta = \eta_s$, and obtain the bulk expressions (6) for the soft phonon spectra.

For the limiting case of the zero order parameter at the film surfaces, $\eta|_{z=\pm h} = 0$, which is the most favorable case for the observation of finite size effects, the constant $\zeta \rightarrow \infty$ in the boundary conditions (3). Since $A(k_m, \omega) \rightarrow -\zeta^2$ for $\zeta \rightarrow \infty$, the condition $\sin(2k_m h) = 0$ should be valid for the validity of Eq. (7). The equation $\sin(2k_m h) = 0$ gives a well-known solution for eigenwave numbers $k_m = \frac{\pi m}{2h}$, where $m = 0, 1, 2, \dots$. Since $m = 0$ corresponds to identical zero solution for the order parameter, one should consider $m = 1$ corresponding to the lowest root. For this case the first harmonic in the order

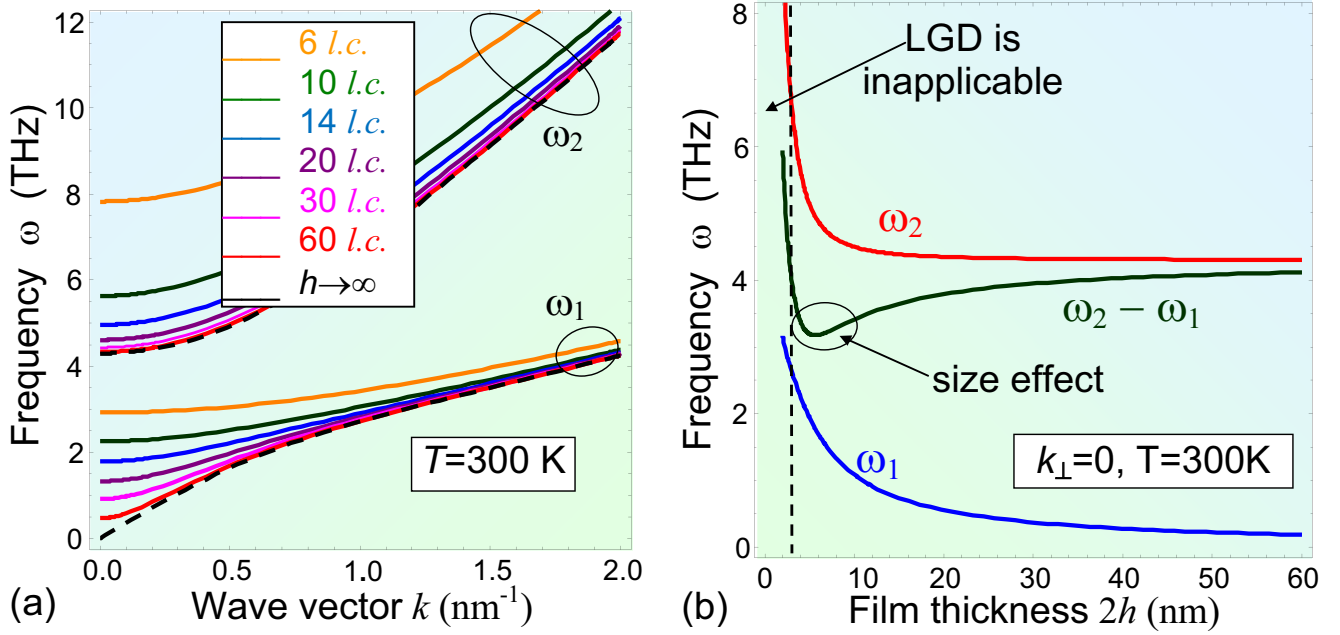


FIG. 2. (a) Dependence of the phonon frequency ω on the wave vector $k_{\perp}$ calculated for SrTiO₃ thin films with different thickness $2h = 6, 10, 14, 20, 30, 60$ l. c. (curves 1–6) and bulk SrTiO₃ (curve 7) at temperature 300 K. (b) Thickness dependences of ω_1 (blue curve), ω_2 (red curve) and $\omega_2 - \omega_1$ (green curve) calculated at $k_{\perp} = 0$ and 300 K. The dashed vertical line indicates the thickness limit (~ 6 lattice constants) of LGD approach applicability. Parameters of SrTiO₃ used in the calculation are listed in Table I.

parameter distribution is

$$\eta = \int dk_{\perp} \exp(ik_{\perp}x + i\omega t) \tilde{\eta}(k_{\perp}, k_l) \cos\left[\frac{\pi z}{2h}\right], \quad k_l = \frac{\pi}{2h}, \quad (10)$$

The soft phonon dispersion $\omega(h, \vec{k})$ given by Eq. (9) acquires the form

$$\omega_{1,2}^2(h, k_{\perp}) = \frac{C(h, k_{\perp}) \pm \sqrt{C^2(h, k_{\perp}) - 4(\mu\rho - M^2)B(h, k_{\perp})}}{2(\mu\rho - M^2)}, \quad (11)$$

where the functions $C(h, k_{\perp}) \approx \alpha(T)\rho + (\mu c_{\perp} - 2f_l M + \rho g_{\perp})k_{\perp}^2 + (c_l\mu - 2f_l M + g_l\rho)(\pi/2h)^2$ and $B(h, k_{\perp}) \approx (\alpha(T) + g_l(\pi/2h)^2 + g_{\perp}k_{\perp}^2)(c_l(\pi/2h)^2 + c_{\perp}k_{\perp}^2) - (f_l(\pi/2h)^2 + f_{\perp}k_{\perp}^2)^2$ depend on the film thickness h . Different signs “−” and “+” correspond to the frequencies $\omega_1(h, k_{\perp})$ and $\omega_2(h, k_{\perp})$, respectively.

III. RESULTS AND DISCUSSION

A. Size effect of the soft phonon dispersion

Figure 2(a) illustrates the dependences of the phonon frequency ω on the wave vector k calculated for SrTiO₃ thin films with different thicknesses $h = (6-60)$ lattice constants (l.c.) (colored solid curves) in comparison with a thick film (black dashed curve) calculated from Eq. (11) at room temperature. Parameters of SrTiO₃ used in the calculation are listed in Table I. All numerical values in the table were obtained from the fitting to experimental spectra of Shirane and Yamada [6] (see Fig. 4(a) and Table I in Ref. [59]).

The frequency $\omega_1(h, k_{\perp})$ monotonically decreases with h increase, but it is nonzero at $k_{\perp} = 0$ for any thickness and tends to the expression (6) for the “bulk” A mode $\omega_1(\infty, k_{\perp} \rightarrow 0) \rightarrow k_{\perp}\sqrt{c/\rho}$ only at $h \rightarrow \infty$. This is a reminiscent of the difference between the phonon spectrum in a thin film with discrete k_z values and the spectrum of a bulk material with continuous k_z values. In particular, for finite thickness h and, $k_{\perp} = 0$ one obtains from Eq. (11) that

$$\omega_1^2(h, 0) \approx \frac{c_l}{\rho} \left(\frac{\pi}{2h}\right)^2 + \frac{g_l c_l - f_l^2}{\alpha \rho} \left(\frac{\pi}{2h}\right)^4. \quad (12a)$$

Approximate equality in Eq. (12) is valid for enough high thicknesses $h \gg a$ (a is a lattice constant) and $\alpha > 0$ [see Eq. (A.29a) in the Supplemental Material]. Therefore, $\omega_1(h \gg a, k_{\perp} \rightarrow 0) \sim \sqrt{\frac{c_{\perp}}{\rho} k_{\perp}^2 + \frac{c_l}{\rho} \left(\frac{\pi}{2h}\right)^2}$ as anticipated.

As is obvious from the figure, the frequency $\omega_2(h, k_{\perp})$ also monotonically decreases with h increase and tends to expression (6) for the “bulk” O mode $\omega_1(\infty, k_{\perp})$ for $h > 30$ l.c. For $k_{\perp} = 0$ the value ω_2 significantly depends on the thickness h until $h < 30$ l.c., namely one obtains from Eq. (11) that

$$\omega_2^2(h, 0) \approx \frac{\alpha}{\mu} + \left(\frac{c_l}{\mu} - \frac{2f_l M}{\mu\rho} + \frac{g_l}{\mu}\right) \left(\frac{\pi}{2h}\right)^2. \quad (12b)$$

Approximate equality in Eq. (12b) is valid in the case $h \gg a$ and $\mu\rho \gg M^2$ that is typical for paraelectrics (e.g., for SrTiO₃).

Figure 2(b) illustrates the thickness dependences of ω_1 (blue curve), ω_2 (red curve) and their difference $\omega_2 - \omega_1$

TABLE I. Description of the symbols in the Lagrange function (1), and their numerical values for SrTiO₃.

Description	Symbol and dimension	Incipient ferroelectric SrTiO ₃ ^a
Coefficient at η^2	$\alpha(T) (\times C^{-2} \text{ mJ})$	$\alpha_T (T_q \coth(T_q/T) - T_C)$
Curie-Weiss constant	$\alpha_T (\times 10^5 C^{-2} \text{ mJ/K})$	15
Curie temperature	$T_C (\text{K})$	$T_C = 30, T_q = 54$
LGD-coefficient at η^4	$\beta (\times 10^8 \text{ J C}^{-4} \text{ m}^5)$	81
LGD-coefficient at η^6	$\gamma (\times 10^9 \text{ J C}^{-6} \text{ m}^9)$	0 (data is absent)
Electrostriction	$q (\times 10^9 \text{ J m/C}^2)$	$q_l = q_{\perp} = q_{44} = 2.4^b$
Elastic stiffness	$c (\times 10^{10} \text{ Pa})$	$c_l = c_{\perp} = c_{44} = 12.7$
Gradient coefficient at $(\nabla\eta)^2$	$g (\times 10^{-10} \text{ C}^{-2} \text{ m}^3 \text{ J})$	$g_l = g_{\perp} = g_{44} = 2$
Strain gradient $(\nabla u)^2$	$v (\times 10^{-9} \text{ V s}^2/\text{m}^2)$	0 (data is absent)
Static flexocoupling	$f (\text{V})$	$f_l = f_{\perp} = f_{44} = 2.2$
Dynamic flexocoupling	$M (\times 10^{-8} \text{ V s}^2/\text{m}^2)$	2
Kinetic coefficient	$\mu (\times 10^{-18} \text{ s}^2 \text{ mJ})$	22
Material density at n. c.	$\rho (\times 10^3 \text{ kg/m}^3)$	4.930
Lattice constant ($l.c.$)	$a (\text{nm})$	0.395

^aAll numerical values in the table were obtained from the fitting to experimental data of Shirane and Yamada [6] (see Fig. 4(a) in Ref. [59]).

^bThis parameter is not used in our calculations.

(black curve) calculated at $k_{\perp} = 0$ and 300 K. A dashed vertical line indicates the estimate for the thickness limit ($\sim 5\text{--}10$ $l.c.$) of the LGD approach applicability. Both ω_1 and ω_2 rapidly increase with a $2h$ decrease below 20 nm and tend to the thickness-independent constants at $2h > 50$ nm. The pronounced size effect (i.e., the minimum) is seen at the dependence of $\omega_2 - \omega_1$ on the film thickness varying in the range (6–20) nm. However, it is questionable whether the prediction can be verified experimentally, because it can be rather difficult to determine experimentally (e.g., by neutron scattering) the phonon dispersion at very small $\mathbf{k}$ in ultrathin SrTiO₃ films. However the Brillouin or Raman scattering of nanoferroics probably can give valuable information about the dispersion law $\omega(h, k)$.

B. “Apparent” or “false” size effect of the dynamic flexoelectric coupling

Let us underline that the available information about numerical values of the static and especially dynamic flexoelectric tensor components is still controversial (since calculations and different experiments give different results) or even unknown [38–49], but the analysis of soft phonon spectra can be one of the most reliable way to define it. Note that expressions (11) allows us to define the relationship between the “true” static (f_l) and “effective” dynamic (M) flexoelectric constants (shortly “flexoconstants”) in thin ferroelectric films from the interpolation of the soft phonon dispersion $\omega_{1,2}(h, k_{\perp})$ in the limit $k_{\perp} \rightarrow 0$. Actually, elementary transformations of Eqs. (11) lead to the expression for the constant M :

$$M_{1,2}[h, \omega] = f_l \left(\frac{\pi}{2h\omega} \right)^2 \pm \sqrt{f_l^2 \left(\frac{\pi}{2h\omega} \right)^4 - \left(\frac{\pi}{2h\omega} \right)^2 (c_l \mu + g_l \rho) + \rho \left(\mu - \frac{\alpha}{\omega^2} \right)}. \quad (13a)$$

Hereafter $\omega^2 \equiv \omega_1^2(h, 0) + \omega_2^2(h, 0)$. Derivation of Eq. (13a) is given at the end of the Supplemental Material. The approximate expressions can be derived from Eq. (13a) in a deep paraelectric phase ($\alpha > 0$) for the case $\mu\rho \gg M^2$ typical for all known incipient and proper ferroelectric perovskites:

$$M_{1,2}[h, \omega] \approx \begin{cases} \frac{1}{2f_l} [\rho(\alpha - \omega^2 \mu) \left(\frac{2h}{\pi} \right)^2 + c_l \mu + g_l \rho], & h \rightarrow 0 \\ \pm \sqrt{\rho \left(\mu - \frac{\alpha}{\omega^2} \right)}, & h \rightarrow \infty \end{cases}. \quad (13b)$$

As it follows from Eq. (13b) the first line contains the evident dependence of M on h , $M \sim \frac{1}{f_l} \left(\frac{2h}{\pi} \right)^2$, the determination of $\omega^2(h, 0)$ from experiments performed for a set of small h may lead to the conclusion about the existence of the “apparent” or “false” size effect of the dynamic flexocoupling at fixed other parameters.

The apparent size effect of dynamic flexocoupling is illustrated in Fig. 3(a) at fixed frequency $\omega^2 = \text{const}$ and room temperature. The flexoconstants M_1 (shown by red curve) and M_2 (shown by blue curve) significantly increase with $2h$ increase from 14 to 30 nm and gradually tend to the “bulk”

values $M_{1,2}[\infty, \omega] = \pm \sqrt{\rho \left(\mu - \frac{\alpha}{\omega^2} \right)}$ at $2h > 35$ nm. At the same time their sum $M_1 + M_2$ (shown by a magenta curve) significantly decreases with $2h$ increase from 14 to 30 nm and then tends to zero at $2h > 35$ nm. The real physical roots $M_{1,2}[h, \omega]$ exist only for $h > h_{cr}$, where the critical thickness h_{cr} depends on the frequency ω and is about 14 $l.c.$ for $\omega = 4.5$ THz.

Figure 3(b) shows the dependences of M_1 , M_2 , and $M_1 + M_2$ on ω at fixed thickness $2h = 8$ nm. The constants M_1 (shown by a red curve) and M_2 (shown by a blue curve) significantly increase with ω increase from 4.9 to 9 THz,

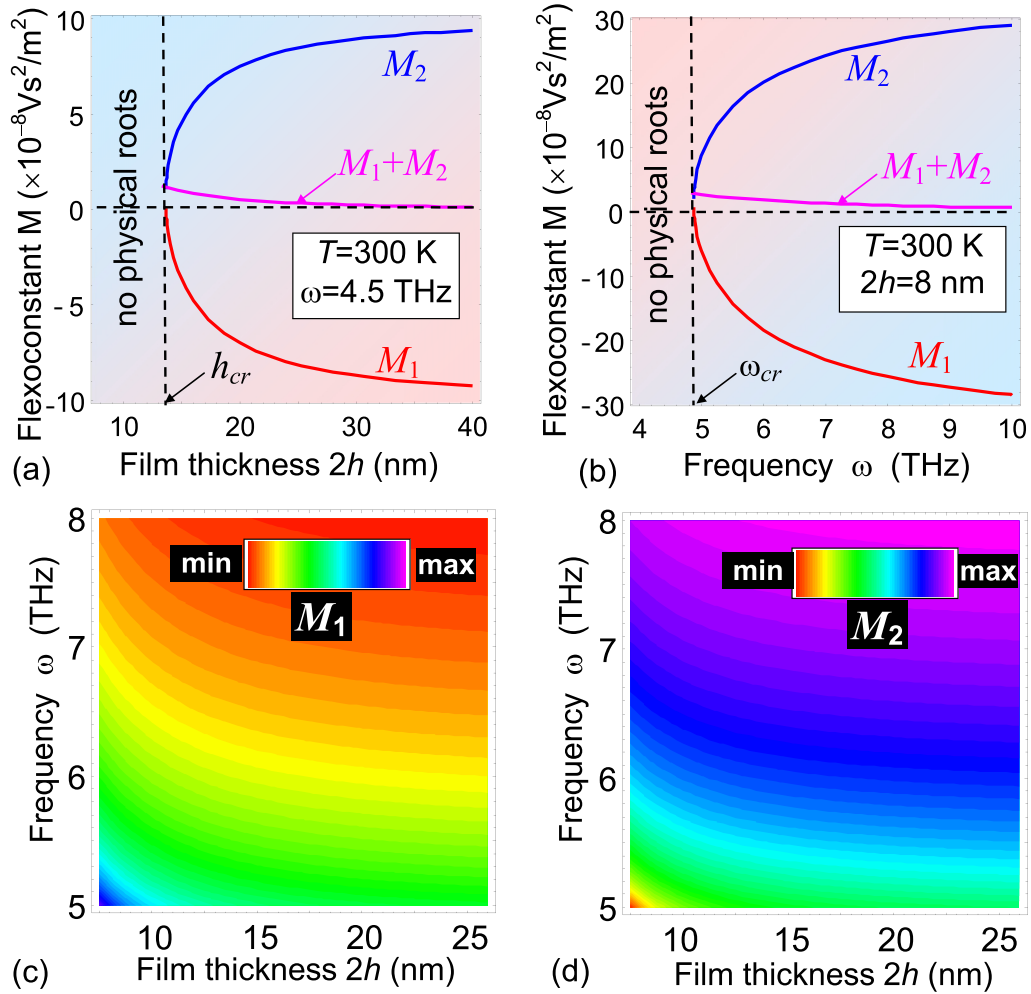


FIG. 3. (a) The “apparent” dependences of the dynamic flexocoupling constants M_1 (red curve), M_2 (blue curve) and their sum $M_1 + M_2$ (magenta curve) on SrTiO₃ film thickness $2h$ calculated from Eq. (13a) at frequency $\omega = 4.5$ THz and $T = 300$ K. (b) The dependences of M_1 (red curve), M_2 (blue curve) and $M_1 + M_2$ (magenta curve) on ω calculated from Eq. (13a) for SrTiO₃ film thickness $2h = 8$ nm. Contour maps of the roots M_1 (c) and M_2 (d) calculated in coordinates ω and h . Other parameters of SrTiO₃ used in the calculation are listed in Table I.

and then gradually tend to the “bulk” values $M_{1,2}[\infty, \omega]$ at $\omega > 9$ THz. At the same time their sum $M_1 + M_2$ (shown by a magenta curve) significantly decreases with ω increase from 4.9 to 9 THz, and then gradually tends to zero at $\omega > 9$ THz. The real physical roots $M_{1,2}[h, \omega]$ exist only for $\omega > \omega_{cr}$, where the critical frequency ω_{cr} depends on h and is about 4.9 THz for $h = 8$ nm.

Contour maps of the roots M_1 and M_2 plotted in coordinates ω and h are shown in Figs. 3(c) and 3(d), respectively. From the maps the apparent size effect exists in the thickness range less than 25 nm. We would like to underline that the “apparent” size effect of dynamic flexocoupling coefficients (shown in Figs. 3) should be clearly distinguished from the “true” size effect of the soft phonon frequency, predicted by us and demonstrated on an example of SrTiO₃ in Figs. 2.

On the other hand, it is not excluded that the origin of the “giant” flexoelectric coefficients extracted by several authors based on experimental results for a spatially confined or strongly inhomogeneous samples is the apparent size effect of a dynamic constant. Qualitatively, the dynamic flexoeffect may arise from pseudo-Jahn-Teller vibrations [56].

C. Size effect of the spatially modulated structures

The spatially modulated structure (SMP) with the modulation period $2\pi/k_{\perp}$ can appear under the condition of the static dielectric susceptibility divergence [58–60]. For a thin film the expression for the static susceptibility $\tilde{\chi}_s(h, k_{\perp})$ is derived in the Supplemental Material and has the form

$$\frac{1}{\tilde{\chi}_s(h, k_{\perp})} = \alpha(T) + g_l \left(\frac{\pi}{2h} \right)^2 + g_{\perp} k_{\perp}^2 - \frac{(f_l(\pi/2h)^2 + f_{\perp} k_{\perp}^2)^2}{c_l(\pi/2h)^2 + c_{\perp} k_{\perp}^2} \rightarrow 0, \quad (14)$$

Equation (14) is equivalent to the conditions $\omega_1(h, k_{\perp}) = 0 \Leftrightarrow B(h, k_{\perp}) = 0$ in Eq. (11). The condition (14) leads to the biquadratic equation for $k_{\perp}$, and the solutions are

$$k_{\perp}^2 = \frac{B - \sqrt{B^2 - 4AC}}{2A} \quad \text{and} \quad k_{\perp}^2 = \frac{B + \sqrt{B^2 - 4AC}}{2A}. \quad (15)$$

Here the parameters $A = c_{\perp}g_{\perp} - f_{\perp}^2$, $B = c_{\perp} + (c_{\perp}g_{\parallel} + c_{\parallel}g_{\perp} - 2f_{\parallel}f_{\perp})(\frac{\pi}{2h})^2$ and $C = (\frac{\pi}{2h})^2(c_{\parallel}\alpha(T) + (g_{\parallel}c_{\parallel} - f_{\parallel}^2)(\frac{\pi}{2h})^2)$ are introduced. The solutions (15) can be essentially simplified in the case $c_{\parallel} = c_{\perp} = c$, $g_{\parallel} = g_{\perp} = g$ and $f_{\parallel} = f_{\perp} = f$ corresponding to cubic m3m paraelectric (see, e.g., Table I for SrTiO₃) allowing for the hidden permutation symmetry of the static flexoelectric coupling [37]. For this case the inverse static dielectric susceptibility

$$\frac{1}{\tilde{\chi}_S(h, k_{\perp})} = \alpha(T) + \left(g - \frac{f^2}{c}\right) \left(\left(\frac{\pi}{2h}\right)^2 + k_{\perp}^2 \right) \quad (16)$$

tends to zero at

$$k_{\perp}^{cr}(T, h) = \frac{1}{R_C(T)} \sqrt{\frac{1}{(f^2/gc) - 1} - \left(\frac{\pi R_C(T)}{2h}\right)^2}. \quad (17)$$

Here the correlation radius $R_C(T) = \sqrt{\frac{g}{\alpha(T)}}$ is introduced. Since we consider the case $\alpha(T) > 0$, the solution (17) exists and so the SMP can occur when the absolute value of the static flexoelectric coupling constant is within the range

$$f_{cr}^{\min} < |f| < f_{cr}^{\max}(T, h). \quad (18a)$$

The ends of the interval (18a) can be considered as the “minimal” and “maximal” critical values of the static flexo-constant, respectively. They are

$$f_{cr}^{\min} = \sqrt{gc}, \quad f_{cr}^{\max}(T, h) = f_{cr}^{\min} \sqrt{1 + \left(\frac{2h}{\pi R_C(T)}\right)^2}. \quad (18b)$$

Note that the value $f_{cr}^{\min}$ obtained by us for $v = 0$ is in agreement with criteria that Yudin *et al.* [39] obtained for the stability of homogeneous bulk material. However, the value $f_{cr}^{\max}(T, h)$ is a temperature and thickness-dependent parameter specific for thin ferroic films; it tends to infinity with the thickness increase.

If the flexoconstant of the film is within the range $f_{cr}^{\min} < |f| < f_{cr}^{\max}$, the SMP with a period $k_{\perp}^{cr}(T, h)$ can occur in the film. The dependence of the dimensionless wave vector $k_{\perp}^{cr}R_C$ on the flexoconstant $|f|/\sqrt{gc}$ was calculated from Eq. (17) for several film thickness $2h = (8-80)R_C$ [see Fig. 4(a)]. The value of $k_{\perp}^{cr}$ diverges at $f \rightarrow f_{cr}^{\min}$, decreases with f increase, and tends to zero at $f = f_{cr}^{\max}$. The dependence of the ratio $f_{cr}^{\max}/\sqrt{gc}$ on the dimensionless thickness $2h/R_C$ is presented in Fig. 4(b). As shown in the figure, the ratio $f_{cr}^{\max}/\sqrt{gc}$ increases monotonically with h increase. The dependence is sublinear at $2h/R_C \leq 1$ and becomes linear ($f_{cr}^{\max} \sim h$) at $2h/R_C \gg 1$. When the flexoelectric coefficient is a known constant the value of $k_{\perp}^{cr}$ depends on the film thickness, as shown in Fig. 4(c). As one can see, the value $k_{\perp}^{cr}$ appears at the critical thickness $2h = H_{cr}^f$, rapidly increases with h increase, and then saturates to the “bulk” value $k_{\perp}^{cr}(T, \infty) = \frac{1}{R_C(T)} \sqrt{\frac{1}{(f^2/gc) - 1}}$. The critical thickness H_{cr}^f can be derived from

Eq. (17) and is equal to

$$H_{cr}^f(T) = \pi R_C(T) \sqrt{\frac{f^2}{gc} - 1}. \quad (19)$$

The dependence of the dimensionless ratio H_{cr}^f/R_C on the flexoconstant $|f|/\sqrt{gc}$ is shown in Fig. 4(d). The ratio critical thickness appears at $f = f_{cr}^{\min}$ and monotonically increases with f increase. In fact, Fig. 4(d) is a 90° rotated version of Fig. 4(c), as it should be

Note that all thickness dependences shown in Figs. 4 can be considered as “true” size effects of the corresponding physical quantities. Figures 4(a)–4(d) are not material specific, because they are plotted in dimensionless variables, $|f|/\sqrt{gc}$, $k_{\perp}^{cr}R_C$ and $2h/R_C$. For the considered case of SrTiO₃ the correlation radius R_C is about 0.7 nm at 300 K, and the experimentally measured flexoelectric coefficient f is about 2 V, much smaller than the minimal critical value $f_{cr}^{\min} = 5.0$ V. Thus, there is no possibility to observe SMPs in SrTiO₃ thin films, since $f \ll f_{cr}^{\min}$, however, it can be induced by flexoelectric effect in other ferroic films with higher flexoconstants (5 – 10) V. Note that the analytical expressions (17)–(19) can describe the influence of finite size effect on the appearance and properties of incommensurate spatial modulation in ferroic thin films.

IV. CONCLUSION

Using Landau-Ginsburg-Devonshire theory and the one-dimensional approximation describing two lowest transverse phonon modes, we derive and analyze analytical expressions for the frequency dispersion $\omega_{1,2}(\mathbf{k})$ of soft phonon modes in nanoferroics and perform numerical calculations for a thin SrTiO₃ film of thickness $2h$.

The frequency $\omega_1(h, k_{\perp})$ monotonically decreases with h increase, but it is nonzero at $k_{\perp} = 0$ for any thickness and tends to the expression [59] for the “bulk” acoustic mode only at $h \rightarrow \infty$. The result illustrates a reminiscent difference between the phonon spectra in thin films with discrete k_z values and the spectra of the bulk material with continuous k_z values. The frequency $\omega_2(h, k_{\perp})$ also monotonically decreases with h increase and tends to the expression [59] for the “bulk” optic mode at $h \rightarrow \infty$.

The pronounced size effect (i.e., the minimum) occurs at the dependence of $\omega_2 - \omega_1$ on the film thickness h , and the minimum are localized in the range (6 – 20) nm for SrTiO₃ film. However, it is questionable whether the prediction can be verified experimentally, because it may be impossible to determine experimentally the phonon dispersion law at very small $\mathbf{k}$ in ultrathin films by inelastic neutron scattering, but probably possible by Raman or Brillouin scattering.

We derived analytical expressions describing the influence of the size effect on the appearance and properties of incommensurate spatial modulation in ferroic thin films. We revealed that a SMP can exist in a thin film when the absolute value of the static flexoelectric coupling constant $|f|$ is within the range $f_{cr}^{\min} < |f| < f_{cr}^{\max}(T, h)$. It turned out that there is no possibility to observe SMPs in SrTiO₃ thin films, since corresponding flexoconstant $|f| \sim 2$ V is significantly smaller than the minimal critical value $f_{cr}^{\min} \sim 5$ V. However a SMP can be induced by flexoelectric effect in other paraelectric

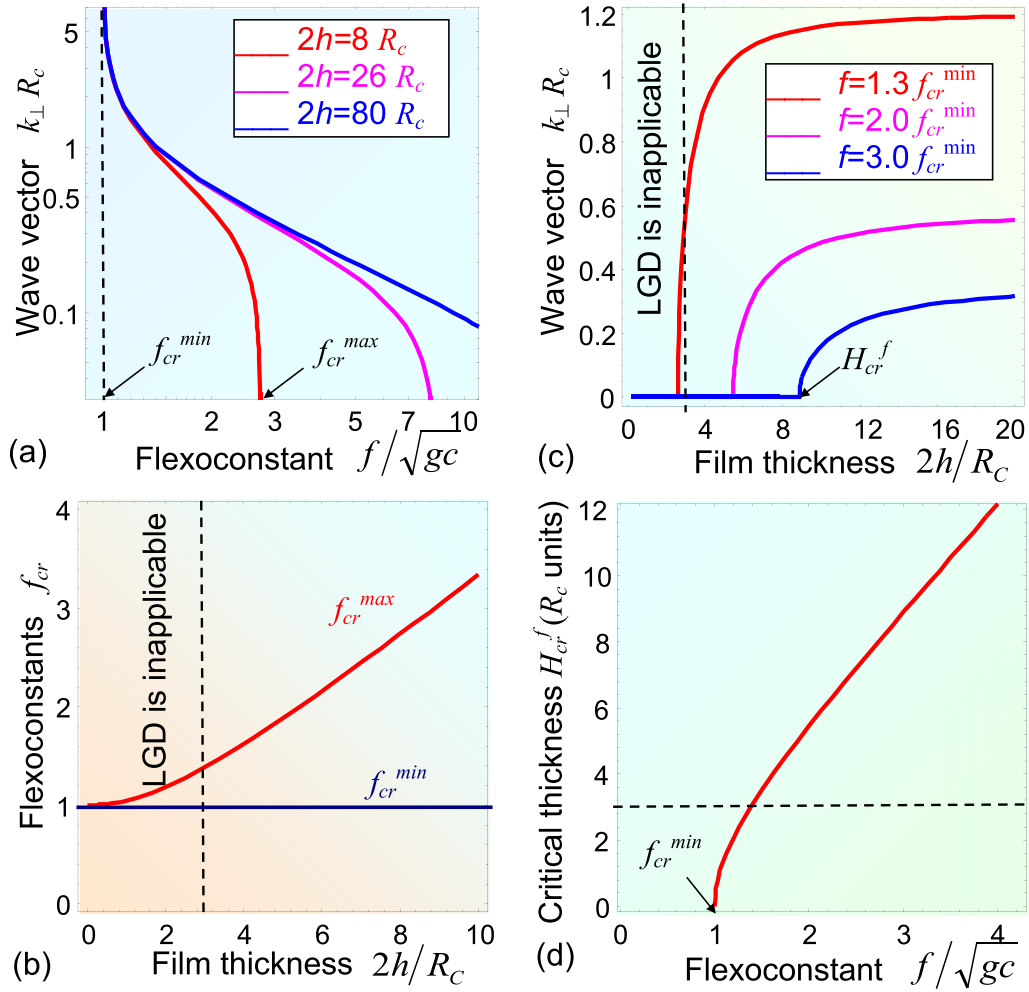


FIG. 4. (a) The dependence of $k_{\perp}^{cr}$ (in R_c units) on the dimensionless flexoconstant $|f|/\sqrt{gc}$ calculated for several film thicknesses $2h = 8, 26$ and $80R_c$ (red, magenta, and blue curves). (b) The dependences of the dimensionless critical flexoconstants $f_{cr}^{max}/\sqrt{gc}$ (red curve) and $f_{cr}^{min}/\sqrt{gc}$ (blue horizontal line) on the dimensionless thickness $2h/R_c$. (c) The dependence of $k_{\perp}^{cr}$ (in R_c units) on the dimensionless ratio $2h/R_c$ calculated for several flexoconstants $|f|/\sqrt{gc} = 1.3, 2$ and 3 (red, magenta, and blue curves). (d) The dependence of the dimensionless critical thickness H_{cr}^f/R_c on the flexoconstant $|f|/\sqrt{gc}$. Dashed vertical lines in plots (b) and (c) indicate the thickness limit of LGD approach applicability.

films with higher flexoconstants, and the prediction can be verified experimentally by dielectric measurements and x-ray diffraction.

We revealed the pronounced “true” size effect in the dependence of soft phonon dispersion on the film thickness that can lead to the “apparent” or “false” size effect of dynamic flexoelectric coupling constants. The true and apparent size effects should be clearly distinguished from each other by experiment. It may be that the origin of the “giant” flexoelectric coefficients extracted by several authors based on experimental results for spatially inhomogeneous samples is the apparent size effect of the dynamic constant. However, the sample must not be necessarily nanosized to reveal the apparent size effect, alternatively, the nanoscale spatial inhomogeneities of polarization or strain should be enough strong. In this sense the apparent size effect of the dynamic flexoelectric constant may effect the flexoelectric-like response of soft electrets and bended piezoelectric bimorphs [56] at

high frequencies. Consequently the dynamic flexoelectric effect may contribute to the giant static flexoelectric response considered in Refs. [55,56]. To verify the predictions made in this paper the measurements of the soft phonon dispersion in nanoferroics seem urgent.

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