Examination of permittivity for depolarization field of ferroelectric by ab initio calculation, suggesting hidden mechanisms

Yukio Watanabe

Ferroelectrics (FEs) have reversible spontaneous polarization $P_s$ that is useful in various applications, for which high insulativity is desired. Therefore, ideal insulativity of FE is assumed in most studies. In such high insulativity FEs, the depolarization field $E_d$ is universal even in the absence of external electric field $E_{ext}$, owing to the charge $-\nabla \cdot P_s$ originating from inhomogeneity or the existence of surface; For a homogeneous $P_s$, $E_d$ disappears for infinite FE without surface or FE with no surface effect and ideal metal electrodes.

Although analytical formulas of $E_d$ are unnecessary in ab initio calculations, they are indispensable for non ab initio examinations of $P_s$ configurations, stability of domains, and critical thicknesses of FEs. These formulas use the permittivity for $E_d(\varepsilon_d)$, of which difference affects critically the results. No controversy exists for $\varepsilon_d = \varepsilon_f$ used in combination with an initial $P_s$ that is an ideal bulk $P_s$ for no macroscopic field in FE as in Kittel models. Here, $\varepsilon_f$ is static linear permittivity of FE. Otherwise, the choice of $\varepsilon_d$ is controversial.

Because the polarization $P$ under $E_{ext}$ is $P = P_s + (\varepsilon_f - 1)\varepsilon_f E_{ext}$ ({$\varepsilon_0$} vacuum permittivity) and the permittivity of FE under $E_d$ is still $\varepsilon_d \gg 1$ (“Results”), the standard choice of $\varepsilon_d = \varepsilon_f$ is $\varepsilon_d = 1, 10, 16, 17$. We define accurate $P_s$ as $P_s$ obtained by accurate experiments of ideal samples; Accurate $P_s$ can be obtained from ion and electron distribution, e.g. by transmission electron microscopy TEM. When a FE is homogeneous or single-domain, accurate $P_s$ can be obtained by standard electical measurements (“Results”). An alternate description of accurate $P_s$ is $P_s = P_s = 0$.

Examples of $\varepsilon_d = \varepsilon_f$ are followings, which are for single domain homogeneous FEs. In this paragraph, “experimental” $P_s$ refers to $P_s$ of each specific sample, which is obtained by the measurements of that sample or is $P_s$ of similar samples. Mehta et al. studied $E_d$ in capacitors, using experimental $\varepsilon_d = \varepsilon_f = 1000$ and $P_s = 10 \mu C/cm^2$ obtained from the saturated polarization of thin film capacitors. Black et al. studied $E_d$ of thin film capacitors, using experimental $\varepsilon_d = \varepsilon_f = 350$ obtained from the polarization-hysteresis near saturation and $P_s$ obtained from the saturated polarization. Zhao et al. estimated $E_d$ of poly-vinylidenefluoride–trifluoroethyene [PVDF–TrFE]
thin films by using \( E_d = -P_d/\varepsilon_d \varepsilon_0 \) with \( P_d \) from remnant polarization measurements (7 \( \mu \)C/cm\(^2\)) and \( \varepsilon_d = \varepsilon_f = 10 \). In the electrostatic study of Tian et al.\(^7\), \( E_d \) in BiFeO\(_3\) thin films was estimated by using \( \varepsilon_f = 60 \) (in Eq. (1) of Ref.\(^7\)), where this \( P \) is initially a total polarization of a single domain state. Kim et al.\(^8\) estimated \( E_d \) in BaTiO\(_3\) (BTO) ultrathin films through the formula by Mehta\(^9\) with the experimental remnant \( P \) obtained from pulse train methods and \( \varepsilon_d = \varepsilon_f = 80 \) from \( \varepsilon_d = \varepsilon_f \) curves. In the Ginzburg–Landau–Devonshire (GLD) theory of BTO ultrathin films by Jo et al.\(^9\), \( E_d \) was given through the Mehta formula\(^9\) with the same \( P \) as \( P \) in the GLD equation and \( \varepsilon_d = \varepsilon_f = 80 \) of Ref.\(^9\), where \( P \) in GLD theory is the total polarization. Schroeder et al.\(^10\) estimated \( E_d \) in HfO\(_2\) and PZT ultrathin films through the Mehta formula\(^9\) with experimental \( P \) and \( \varepsilon_d = \varepsilon_f = 20–300 \). Similar analyses with \( \varepsilon_d = \varepsilon_f \approx 1 \) are frequently employed.\(^11,12\)

Contrastingly, a primitive considerations show \( \varepsilon_d = 1 \) for \( P \), i.e. a total \( P \) \( \equiv \) \( P(E(E_{d0} = 0)) \)\(^13\), where \( E_d \) is the total macroscopic electric field in FE. For freestanding FEIs, for example, \( E_d(E_{d0} = 0) = E_d(E_{d0} = 0)/\varepsilon_d \) or \( E_d(E_{d0} = 0) = E_d(E_{d0} = 0)/\varepsilon_f \) ("Results"). This implies that \( \varepsilon_d = \varepsilon_f \)\(^14,15,16\) may be double counting, while we note that the electrical measurements of \( P \)\(^4–10,16,17\) are indirect measurements based on induced charge per area in electrodes \( Q \). If \( \varepsilon_d = 1 \) is correct, the successes of the analyses using \( \varepsilon_d = \varepsilon_f \) are attributed to inappropriate parameters or unidentified screening mechanisms.

We think that the existence of this controversy on \( \varepsilon_d \) is due to explanations based on macroscopic quantities. Because macroscopic explanations are abstract, they are unsuitable to bridge the gap between two conflicting views of \( \varepsilon_d \). On the other hand, ab initio estimation of \( \varepsilon_d \) is considered as the clearest method for this problem but is not reported to our knowledge. Hence, we clarify \( \varepsilon_d \) in the formulas of \( E_d \) by ab initio simulations in which ab initio \( P \) is exactly \( P(E(E_{d0} = 0)) \), which is considered as \( P \) obtained by accurate experiments of ideal samples. Here, the standard theoretical assumptions: pure, stoichiometric, clean FEIs are used.

\( E_d \) is related to fundamental issues such as stability of monodomains, critical thicknesses of FE, and the emergence of ferroelectricity in superlattices. Some of these subjects require consideration of other effects such as strain-induced FE and electronic effect at electrodes\(^11\). To avoid the complexity, we concentrate on free-standing insulating FE and its electrostatic identicals, i.e. head-to-head–tail-to-tail (HH–TT) domains. Thus, we estimate the value of \( \varepsilon_d \) in the formula of \( E_d \) in a clear manner.

As expected from the electronic interaction at the electrode\(^11\), it may be argued that the formula of \( E_d \) based on electrostatics is not possible for nm-FEIs. We resolve this by focusing on the formulas of \( E_d \) and using ab initio \( P \) in the formulas. Therefore, \( P \) in these formulas contains the effects of the interactions in slabs or superlattices, whereas the absence of these effects in conventional studies has limited the applicability. The use of nonlinear \( \varepsilon_d \) is often better than linear \( \varepsilon_d \) but can be approximated by an average linear \( \varepsilon_d \).\(^12\) Therefore, the conclusions below are applicable also to the nonlinear \( \varepsilon_d \).

**Model**

For simplicity, we discuss 1-dimensional (1D) cases with \( E_{d0} = 0 \), where FEIs with thickness \( l \) are in periodic slabs (Fig. 1). Here, 1D refers not to the shape of object (Fig. 2) but to the case where all the properties change only along one coordinate; Fig. 1a,b show FE in vacuum with thickness \( l \) and FE/paraelectric \( l_{\text{adj}} \) superlattice, respectively, while the latter mimics an inhomogeneous FE. \( l_{\text{adj}} \) stands for both vacuum and insulator, which is dielectric or paraelectric, while the latter mimics an inhomogeneous FE.

The macroscopic and atomic electrostatic potential (\( \varepsilon_d \)) of these models are represented by Fig. 1c,d, respectively. ab initio \( E_d(E_d_{\text{adj}}) \) \( E_{d_{\text{adj}}} \) was obtained from the envelope of the peak tops of atomic electrostatic potential, of which example is Fig. 1d. All these FE/vacuum and FE/paraelectric exhibited the density of states (DOS) of insulators (Fig. 1f). Additionally, BaTiO\(_3\) (BTO) capacitors are examined, where metal layers are standard electrode materials for FEIs: SrRuO\(_3\) or Pt and ~ 20 Å (Fig. 1g).

**Methods**

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Accurate estimation of \( P \) is indispensable for estimating \( E_d \) correctly and achieved by direct Berry phase calculations. To enable these calculations, we designed special FE slabs and procedures described in "Methods". This is because stable 1D-FEs in vacuum are metallic\(^14,15\) and, hence, direct Berry phase calculations are not possible; Even a two unit-cell thick (~ 8 Å) BTO in vacuum is metallic, when FE is enforced\(^16\) to achieve insulating FE and its electrostatic identicals, i.e. head-to-head–tail-to-tail (HH–TT) domains. Thus, we estimate the value of \( \varepsilon_d \) in the formula of \( E_d \) in a clear manner.

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\[ E_d = -\frac{P_S - P_t}{\varepsilon_0} \left( \frac{\varepsilon_d}{\varepsilon_d + \frac{l}{l_I}} \right), \]

\(\text{for} \theta \neq 0, \theta_I \neq 0, \text{Eq. (1)}\) is \( E_d = -(P_S \cos \theta - P_t \cos \theta_I)/\varepsilon_0(\varepsilon_d + l/l_I) \). In the present study, \( P \) and \( P \) in Eq. (1) are given by ab initio calculations that simultaneously yield \( E_d \) consistent with \( P \). Therefore, the only unknown quantity is \( \varepsilon_d \).

When \( P_I = (\varepsilon_d - 1)\varepsilon_0 P_t \), Eq. (2) for \( \theta = 0 \) is
Figure 1. Atomic model of (a) FE/vacuum and (b) FE/Iadj, where FE is BTO and Iadj is STO. BTO/STO serves also as a mimic of an inhomogeneous FE. (c) Macroscopic model. The minimum and maximum electrostatic potential $\phi$ are 0 and $\phi_{\text{max}}$ respectively. (d) Example of estimation of $E_d$ from the atomic $-e\phi$. The orange line shows the envelope yielding $E_d$. (e) Progressive development of 2D metallic layer: DOS of STO1.005/vacuum, where $l_f$ in unit-cells and $l_V$ in Å are shown on the right. 10-unit-cell-STO with $l_V = 100$ Å is marginally insulating, while 16-unit-cell-STO with $l_V = 30$ Å is metallic. The insulating slabs are used in Fig. 3. $P_S$ in the slab was typically 1 $\mu$C/cm$^2$. (f) DOS of 7 and 10-unit-cell BTO/5-unit-cell-STO calculated with PBEsol and PBE+U. (g) Atomic model of BTO/Pt.
For \( \theta \neq 0 \) and \( \theta _d \neq 0 \), Eq. (2) is \( E_d = -P_d \cos \theta \epsilon_d (\epsilon_f + \epsilon_d l_V / l_I) \).

Equation (2) yields also \( E_d \) in FE capacitors, because equations of continuity of electric flux similar to the above hold; A short-circuited FE capacitor is modelled as a perfect-metal/insulator/(l/2)/FE/insulator/(l/2)/perfect-metal\(^{29}\), where the perfect metal refers to a metal with zero screening length and the thickness of each screening layer \( \lambda \) is \( l/2 \). Assuming \( P_n = \epsilon_f \epsilon_d/\epsilon_I \) in screening layer, Eq. (2) is applicable and yields the Mehta formula\(^3\) with \( \epsilon_d = \epsilon_f \) and \( l/\lambda = 2 \). For FE capacitors with \( \theta \neq 0 \), the formula beneath Eq. (2) is applicable. Because we neglected the electronic interactions at the metal/FE interface of 1–2 unit-cell, e.g. quantum mechanical smearing\(^{30}\), the formula for capacitors may be inaccurate for \( l < \) several unit-cells.

The nominal FE thickness \( l_I \) is the distance between the center position of a top ion and that of a bottom ion, but twice of the atom radius \( \sim 0.5 \text{ Å} \times 2 \) should be added. In case of FE/vacuum, this correction was examined by considering the smear-out of electrons into vacuum\(^{29}\). When \( \lambda_{\text{mean}} \sim 0.8 \text{ Å} \) is the distance between an outermost electron density and a center of ion position (“Methods”), FE thickness appropriate for electrostatics is \( l/\theta = l_I + 2 \lambda_{\text{mean}} \). As seen below, Eqs. (1) and (2) can be valid down to a few nm \( l_I \) in case of FE/vacuum. Additionally, surface buckling layer is electrostatically a dipole layer, and its net charge is zero. Therefore, even in the presence of buckling layer, these formulas for 1D are also valid, by regarding buckling layer as dead layer (“Methods”); The effective thickness is \( l/\theta = 2 \lambda_{\text{buckle}}, \) where \( \lambda_{\text{buckle}} \) is the thickness of a buckling layer \( \sim 1–2 \) unit-cells.

Results

Estimation of \( \epsilon_d \). \( \epsilon_d \) was examined through the comparison of ab initio \( E_d \) with \( E_d \) of Eq. (1) or (2) that uses different values of \( \epsilon_d \). For FE/vacuum (\( P_d = 0 \)), \( E_d \) in Eq. (1) was the rigorously calculated \( P_d \) of the slab by Berry phase. For FE/insulators and FE capacitors, \( P_d \) in Eq. (2) were calculated ab initio. Therefore, all the parameters in Eqs. (1) and (2) except for \( \epsilon_d \) are accurately known.

Figure 3 compares \( E_d \)'s by Eq. (1) with \( E_d \) of ab initio\(^{29}\), where Eq. (1) uses \( \epsilon_d = 1 \), 4. Here, \( \epsilon_d = 4 \) is the lower bound of electronic permittivity of STO\(^{29}\). \( E_d \) of ab initio\(^{29}\) is accurate for a long \( l_I \), and data for \( l_I \gg l_V \) reflects the effect of \( \epsilon_d \) explicitly because of \( E_d = -P_d l_I \epsilon_d \). Large symbols in Fig. 3 show the data points satisfying both conditions and, hence, are important.

In Eq. (3), \( \epsilon_d = 1 \) agrees with \( E_d \) of ab initio\(^{29}\) within 10% always for \( \lambda_{\text{mean}} = 0.8 \text{ Å} \) and mostly for \( \lambda_{\text{mean}} = c/2 \). The difference between \( E_d \) for \( \lambda_{\text{mean}} = 0.8 \text{ Å} \) and \( c/2 \) provides typical error bar and is approximately 10%. Equation (1) with \( \epsilon_d = 4 \) deviates from \( E_d \) of ab initio\(^{29}\) by more than 140%, and the deviations increase monotonically with \( \epsilon_d \). Additionally, Eq. (1) yields the potential difference \( \Phi_{\text{max}} = [E_d l_I / P_d l_I (\epsilon_f + 1/4)] \), which, with \( \epsilon_d = 1 \), quantitatively agrees with bandgap \( \Phi \) that decreases with \( l_I \) and \( l_I \) in Fig. 1e.

Figure 3 compares \( E_d \) of Eq. (1) with \( E_d \) of ab initio\(^{29}\), where Eq. (1) uses ab initio \( P_d \) and ab initio \( P_d \). For \( \epsilon_d = 1 \), Eq. (1) agrees within \( \pm 20\% \) with \( E_d \) of ab initio\(^{29}\). In particular, the agreements are within \( \pm 6\% \) in the results by PBE + \( U \) (a method of ab initio calculation (“Methods”)). Equation (2) with \( \epsilon_d = 20 \) deviated by more than 1000% from \( E_d \) of ab initio\(^{29}\). The deviation increased monotonically with \( \epsilon_d \), whereas \( \lambda_{\text{mean}} > 20 \) is usual for inorganic FEs\(^{15,7–10,16,17}\).

For capacitors, Fig. 5a,b compare \( E_d \) of Eq. (2) with \( E_d \) of ab initio\(^{29}\), where Eq. (2) uses ab initio \( P_d \) and \( l/2 = 0.1 \text{ Å} \), 0.05 Å; \( E_d \) by Eq. (2) with \( \epsilon_d = 1 \) agrees best with \( E_d \) of ab initio\(^{29}\). The disagreements of Eq. (2) with \( E_d \) increases with \( \epsilon_d \). The differences between open and filled symbols provide typical error bar and are 10–20%. Consequently, all the studied cases indicate \( \epsilon_d = 1 \) (Figs. 3, 4, 5).

Bridge between \( \epsilon_d = 1 \) and \( \epsilon_d = 13\). We showed \( \epsilon_d = 1 \) and will use it below. By noting that electrical measurements of \( P_d \) are based on the change of charge per area in electrodes \( \Delta Q \) induced by \( E_{\text{ext}} \), a bridge between \( \epsilon_d = 1 \) and \( \epsilon_d = 13 \) will be shown. Because most studies\(^{1–10,13,17} \) are for FE capacitors, the followings are for 1D FE capacitors with \( \theta = 0 \), which can represent FE/vacuum for \( \epsilon_d = 1 \) and freestanding FE for \( l/\epsilon_d > l_I \).
Figure 3. FE/vacuum. Comparison of $E_d^{\text{ab initio}}$ with Eq. (1) with $\varepsilon_d = 1, 4$ for STO1.005/vacuum and STO0.9999/vacuum. The yellow band shows the range of $1 \pm 0.1$. The filled and open symbols represent data in which $l_f$ in Eq. (2) is estimated with $\lambda_{\text{meas}} = 0.8$ Å and $\lambda_{\text{meas}} = c/2$, respectively. The shape of symbol indicates a slab structure: For STO1.005, orange circles, red triangles, light blue diamonds, and blue inverted triangles correspond to 7-unit-cell-STO with $l_v = 30$ Å, 7-unit-cell-STO with $l_v = 200$ Å, 10-unit-cell-STO with $l_v = 30$ Å, and 10-unit-cell-STO with $l_v = 100$ Å, respectively. For STO0.9999, red squares, green pentagons, and blue 90°-rotated triangles correspond to 5-unit-cell-STO with $l_v = 300$ Å, 6-unit-cell-STO with $l_v = 30$ Å, and 7-unit-cell-STO with $l_v = 30$ Å, respectively.

Figure 4. FE/paraelectric. Comparison of $E_d^{\text{ab initio}}$ with Eq. (1) with $\varepsilon_d = 1, 20$ for BTO/5-unit-cell-STO. The yellow band shows the range of $1 \pm 0.2$, and the dotted lines inside of the band show the range of $1 \pm 0.1$. Inset explains the BTO thickness $l_f$ in unit-cells and ab initio method (PBEsol or PBE + U).
Figure 5. FE capacitor. Comparison of \( E_d^{ab\text{initia}} \) with Eq. (2) with \( \varepsilon_f = 1 \) (orange), 20 (green), and 100 (blue) for (a) BTO/SrRuO\(_3\) and (b) BTO/Pt. The filled and open symbols represent the data for \( l_f = l_{Fe} = u_{BTO} \). 

Using the total electric field in FE \( E_f \) and the total polarization of FE \( P \), \( P_0 \equiv P(E_{ext} = 0) \) and \( E_d \equiv E(E_{ext} = 0) \). When the potential difference between the electrodes is \( V \), Eq. (2) changes to \( E(V) = V(l_f + l_f/\varepsilon_f) - P(E(E_{ext})/l_f(1 + \varepsilon_f/l_f)) \). \( E \), the field in the screening layer of the electrode, is \( E(V) = V(\varepsilon_f(l_f + l_f/\varepsilon_f) + P(E(E_{ext}))l_f(1 + \varepsilon_f/l_f)) \).

\( E(V) \) can be written as \( E(V) = E_{ext} + E_f(E(E_{ext})) \), where \( E_{ext} = V(l_f + l_f/\varepsilon_f) \) and \( E_f(E(E_{ext}))/\varepsilon_f(l_f + l_f/\varepsilon_f) \) similar to Eq. (2).

\( \varepsilon_f \) is defined as \( \varepsilon_f = 1 = P(E(E_{ext})) - P_0(l_f/\varepsilon_f(E(E_{ext}) - E_f)) \), where \( E_f(E(E_{ext}) = 0) = -P_0/\varepsilon_f \) for \( l_f \gg l_f/\varepsilon_f \) and \( \varepsilon_f (\gg 1) \) is linear for \( E_f/) \big| Prepare this sentence for this point: **Discussions**

Here, we discuss only monodomain FE (Fig. 2c).

**Permittivity for non-polarization field (built-in field).** Because the polarization \( P \) in standard GLD theories is \( \varepsilon_f \) is formulated with a single total polarization, \( \varepsilon_f \) should be used in standard GLD theories.

The preceding results have shown that the permittivity that expresses the change of \( P \) in response to \( E_{ext} \) is \( \varepsilon_f \) (\( \gg 1 \)) even for FE under \( E_f \). By the same logic, the change of \( P \) by built-in internal field \( \varepsilon_f \) is also expressed by \( \varepsilon_f (\gg 1) \), where \( \varepsilon_f \) is not due to \( P \) or a dipole that is not expressed by \( P \). \( \varepsilon_f \) exists in FE by various mechanisms such as the diffusion potentials at \( P \) and Schottky junctions and chemical orders, e.g. LaAlO\(_3\) in the polar catastrophe model.

For example, \( P_0 = 0 \) and \( E_d = 0 \) in a bulk cubic BTO. However, \( \varepsilon_f \neq 0 \), when the surfaces of a cubic BTO slab are asymmetrically terminated to form a dipole, e.g. BaO/TiO\(_2\)/BaO/…/TiO\(_2\)/BaO/TiO\(_2\). Hence, to achieve \( \varepsilon_f = 0 \), the present study used chemically symmetric slabs (Fig. 1a,b,g), e.g. BaO/TiO\(_2\)/BaO/…/TiO\(_2\)/BaO.

**Insulator condition.** For 1D-FE to remain insulating without artifactual screening, \( \varepsilon_f |E_d| < \varepsilon_f \) (e: elementary charge), for which Eq. (2) and \( \varepsilon_f = 1 \) yield \( 1/l_f > eP_0 \cos \theta /\varepsilon_f E_g - \varepsilon_f l_f \). Therefore, the condition of insulator is one of the followings

\[
I_f \geq 1.8 \text{Å} E_{fI} \left( \frac{E_g^*}{P_0 (T_c) \cos \theta} \right)^{-1}
\]

where \( E_g^* \) and \( P_0 (T_c) \) are bulk \( E_g \) normalized by 2 eV and \( P_0 \) of bulk FE at \( T_c \) normalized by 10 μC/cm\(^2\), respectively, and the unit of \( I_f \) and \( l_f \) is Å. \( P_0 \) of bulk FE at \( T_c \) approximates the critical \( P_0 \) of FE that is about to become paraelectric by \( E_d \). Equations (3) and (4) explain the insulatority of FE in Fig. 1c-f.

\[
| I_f | > 1.8 \text{Å} \left( \frac{P_0 (T_c) \cos \theta}{E_g^*} - 1.8 \frac{\varepsilon_f}{l_f} \right)
\]
Freestanding insulating FE and HH–TT. The giant permittivity and large piezoelectric coefficients of FE are regarded as an electrical softness due to the tailing-effect of structural instabilities, i.e. phase transitions. This suggests that these properties are incompatible with an extremely stable FE. For freestanding FEs ($l_i = \infty$, $\theta = 0$), Eq. (3) yields $I_\theta < 1.8\, \text{Å}(E_\text{G} / 2\, \text{eV})/(P_s(T_\text{C})/10\, \mu\text{C/cm}^2)$. This suggests that freestanding FEs with normal bulk properties are FEs with metallic layer or insulating paraelectrics[12,15] as explained by the following GLD analysis. This conclusion is valid also for HH–TT domains with $\theta = 0$.

Standard GLD theories are based on a single polarization vector $P$ as the order parameter. We approximate the polarization possibly missed in such GLD theory[46,47] by an extra permittivity $\varepsilon_{\text{NGT}}$, while $\varepsilon_{\text{NG}}$ is speculatively close to electronic permittivity. The GLD energy $F$ of an insulating FE is $F = (T - T_0)P^2 / 2C_\varepsilon + \beta P^4 / 4 + \gamma P^4 / 4 - P E_d / 2$, where $T_0$, $C$, $\beta$, $\gamma$, and $\theta$ are Curie–Weiss temperature, Curie constant, and GLD coefficients, respectively. The effect of strain can be incorporated in $T_0$ and $\beta$[31–33]. Curie temperature $T_\text{C}$ is $T_\theta + \Delta T$, where $\Delta T = 3\beta P^4/16\epsilon C_\varepsilon$. For 2nd order transition, $\gamma = 0$, $\beta > 0$, and $T_\text{C} = T_\theta$. The effect of $E_d = -P_\text{eT}/\varepsilon_{\text{NGT}}$ is the change of $T_\theta$ to $T_\theta - C/\varepsilon_{\text{NGT}}$ in $F$, where Eq. (2) with $\varepsilon_d = \varepsilon_{\text{NG}}$, and $l_i = \infty$ is used.

Hence, the existence of freestanding FE that undergoes 2nd order FE transition is $T_\theta > C/\varepsilon_{\text{NGT}}$. This means $\chi_{\text{GL}} < \varepsilon_{\text{NGT}}^2$ at $T = 0$, because $\chi_{\text{GL}} = C/2T_\theta$ at $T = 0$. The total permittivity $\varepsilon_T = \chi_{\text{GL}} + \varepsilon_{\text{NGT}}$ at $T = 0$ is < $3\varepsilon_{\text{NGT}}/2$ and < 7.5 for $\varepsilon_{\text{NGT}} > 5$.

Similarly, for FE undergoing 1st order FE transition, it is known that $\chi_{\text{GL}} = 1/((T - T_0)/C_\varepsilon + \beta P^2 + 5\gamma P^4)$ at $T < T_\text{C}$. Stable state satisfies $\partial F/\partial P = (T - T_0)/C_\varepsilon + \beta P^2 + \gamma P^4 = 0$. Therefore, $\chi_{\text{GL}} = 1/(4T_\theta/C_\varepsilon - 2\beta P^2)^{1/2} < C/4T_\theta$ at $T = 0$ (we assume $T_\theta > 0$), and $T_\text{C} = T_\theta + \Delta T = T_\theta + 3\beta P^4/16\epsilon C_\varepsilon$. Because $\Delta T \ll T_\theta$ in almost all FEs[31–33], we may assume $T_\theta < 2T_0$. Under this assumption, $\chi_{\text{GL}} < C/2T_\theta$ at $T = 0$, and $C < \varepsilon_{\text{NGT}}T_\text{C}$ means $\chi_{\text{GL}} < \varepsilon_{\text{NGT}}/2$ at $T = 0$. $\varepsilon_T = \chi_{\text{GL}} + \varepsilon_{\text{NGT}} < 3\varepsilon_{\text{NGT}}/2$ at $T = 0$, which is < 7.5 for $\varepsilon_{\text{NGT}} > 5$.

These $\varepsilon_T$'s of FEs undergoing 2nd and 1st transitions appear too small for experimentally observed bulk metal oxide FEs. Therefore, freestanding insulating FE satisfying $C < \varepsilon_{\text{NGT}}T_\text{C}$ are unlikely to exist, unless $\varepsilon_{\text{NGT}}$ is far larger than 5; That is, for freestanding FE materials, there exists virtually one choice between a partial loss of insulativity and a loss of FE.

Design of freestanding insulting FE. For freestanding insulting FE ($\theta = 0$), $C < \varepsilon_{\text{NGT}}T_\text{C}$ was shown, while $\Delta F - P_\text{eT}/E_\text{eT}$. Therefore, FE materials having a very large $\varepsilon_{\text{NGT}}$ ($\gg 5$) can retain FE and remain insulating, when ultrathin. Such FE materials are unlikely to exist. Alternatively, we may consider electrically freestanding FE or FE with clean surface that is not mechanically freestanding. In this case, $T_\theta$ ($\sim T_\text{C}$) of common FEs increases to $T_\theta^\text{ad}$ by inplane strain, while ab initio calculations shows that $T_\theta^\text{ad}$ is much larger than those of standard GLD theories[31]. Therefore, heavily strained FE materials may retain FE and remain insulating, when ultrathin (Formula estimating an effective $T_\theta$ from ab initio $P_\text{e}$ is Ref. [88] of Ref. [46]). The above indicates that $\varepsilon_T$ of such FE is extremely low for $E_d = 0$ but can be large for $E_d \neq 0$, because the coefficient of the first term GLD energy $F$ is $(T - T_\theta^\text{ad} + C/\varepsilon_{\text{NGT}})/2C_\varepsilon$ (freestanding).

LiBeSb. LiBeSb with P6,mc symmetry[48] is reported as a hyper-FE that retains both FE and insulativity in FE/paraelectric superlattices, which may contradict the above conclusion on insulativity and FE stability. Therefore, we ab initio calculated one-unit-cell LiBeSb ($l_i = 6.08$ Å) in vacuum (Fig. 6a). Figure 6b shows a metallic DOS of LiBeSb for $l_i = 31.7$ Å, while metalliclicity increases with $l_i$. This is consistent with the above conclusion and the previous reports[44,45,39–41]. Equations (3) and (4) explain the insulativity of LiBeSb[48] as the effect of adjacent dielectric. Actually, similar to LiBeSb, BTO/STO superlattices are insulating as in Fig. 1f, while BTO/vacuum is partially metallic[45].

Freestanding and free-surface FE: hidden mechanism. Mechanically freestanding FE is customarily referred to as freestanding; Ji et al. reported exceptionally intriguing results of the freestanding insulating BiFeO$_3$ (BFO) that retains FE down to monolayer. This appears to contradict both the reports of metallicity at HH–TT domains of BFO and the present results, esp. the single choice between insulating paraelectric and partially metallic FE.

If $\varepsilon_T = \varepsilon_T = 100$, the potential difference $\Delta F$ across freestanding insulating BFO of 1–4 unit-cell thickness with a moderate $P_\text{e} \sim 20\, \mu\text{C/cm}^2$ is 0.09–0.36 V by Eq. (2) with $l_i = \infty$, which allows this BFO to be insulating in agreement with Ji et al. For $\varepsilon_T = 1$, $\Delta F$ increases by 100 times, by which BFO’s have to be partially metallic.
Hence, we shall look at the measurements of Ji et al.\textsuperscript{42}. For freestanding FE, it was shown that the surface or boundary of 1–2 unit-cell thickness was metal and the rest was insulating FE\textsuperscript{14,15,39,40}. So, the metallicity is detectable only by inplane conductance, which is absent in Ji et al.\textsuperscript{42}. Second, because the crystallographic properties of FE with these metal layers was shown to be those of FE\textsuperscript{14,15,39,40}, the crystallographic measurements of Ji et al.\textsuperscript{42} do not exclude metallic layers. Third, because piezoelectric measurements use bottom and top electrode (or tip) and may move ions\textsuperscript{43}, those by Ji et al.\textsuperscript{42} are not that of freestanding FE. Consequently, all the measurements of Ji et al.\textsuperscript{42} do not contradict the conclusion of the present paper.

More importantly, the interdisciplinarity of nano FE hides true mechanisms. In the present case, “freestanding” is defined by surface science and electrostatics. For example, Fong et al. found monodomain FE of 3 unit-cell thickness as opposed to FE\textsubscript{ad}-limited domain and size effect, which was later attributed to adsorbates\textsuperscript{44}. This agrees with recent ab initio study\textsuperscript{45}. Further, photoemission spectroscopy in UHV showed that SrTiO\textsubscript{3} surface was covered by adsorbates even in ultrahigh vacuum (UHV)\textsuperscript{46}. Actually, the free surface with P\textsubscript{S} \perp surface is insulator-like in air and metallic in UHV when cleaned\textsuperscript{14}. Because the insulating freestanding FE\textsuperscript{42} was exposed to air and water, we suggest adsorbates as its hidden mechanism.

**Conclusion**

We studied the electrostatics of E\textsubscript{d,\textsubscript{b}} especially, the value of permittivity \epsilon\textsubscript{d} in the formula of E\textsubscript{d} by ab initio simulations, where ab initio P\textsubscript{S} corresponded accurately to experimental P\textsubscript{S}. For this, the standard theoretical assumptions: pure, insulating, stoichiometric, and clean FE\textsubscript{S} were used. To validate the analyses of E\textsubscript{d} based on electrostatics, we concentrated on the formulas of E\textsubscript{d} for accurate ab initio total P(E\textsubscript{d,\textsubscript{b}} = 0) that contained various atomic effects and corresponded to experimental P\textsubscript{S}. Further, we focused on the simplest cases of E\textsubscript{d} freestanding 1D-FE, HH–TT domains, and superlattices that mimicked inhomogeneous FE and FE/dielectric.

The present ab initio simulations showed \epsilon\textsubscript{d} = 1 ± 0.06–1 ± 0.2. That is, \epsilon\textsubscript{d} = 1 should be applied to experimental and standard-GLD P\textsubscript{S}'s. A contradiction between \epsilon\textsubscript{d} = 1 and \epsilon\textsubscript{d} = \epsilon\textsubscript{f} was resolved by a bridge: Even under E\textsubscript{d,\textsubscript{b}}, the permittivity for E\textsubscript{d,\textsubscript{b}} \perp d\textsubscript{f} was \epsilon\textsubscript{d}. Therefore, if a study requires \epsilon\textsubscript{d} \gg 1\textsuperscript{4–10,16,17}, the value of P\textsubscript{S} is incorrect, the values of the parameters are inappropriate, or, most likely, hidden screening mechanisms exist\textsuperscript{14,15,43–48}.

For freestanding insulating FE\textsubscript{S} (l\textsubscript{f} \rightarrow \infty), Eq. (2) yields E\textsubscript{d,\textsubscript{b}} = −P\textsubscript{S}/\epsilon\textsubscript{d} (or E\textsubscript{d,\textsubscript{b}} = −P\textsubscript{S} \cos \theta/\epsilon\textsubscript{d}), while, for HH–TT insulating domains, Eq. (1) with P\textsubscript{S} = −P\textsubscript{S} and l\textsubscript{f} = \tilde{l}\textsubscript{f} yields the same E\textsubscript{d,\textsubscript{b}}. Therefore, when the effects at surface of 1–2 unit-cell is unimportant, freestanding FE\textsubscript{S} are electrostatically exactly identical with HH–TT domains.

Consequently, both the electrostatic energy of E\textsubscript{d} and the FE free energy of insulating freestanding and HH–TT FE\textsubscript{S} scale linearly with l\textsubscript{f}. This implies that the stability of 1D-freestanding and HH–TT insulating FE\textsubscript{S} is independent of size\textsuperscript{12,15}, when the energy increase by surface effect and domain walls effect is ignored. A strain effect to overcome this restriction was suggested.

Because l\textsubscript{f}/\epsilon\textsubscript{d} \gg \epsilon\textsubscript{d}/e by \epsilon\textsubscript{d} = 1, the insulativity required an extremely small bulk P\textsubscript{S} \ll 1 \mu C/cm\textsuperscript{2} or paraelectricity (Fig. 7). Alternatively, the stability of 1D-freestanding and HH–TT FE\textsubscript{S} for of (θ = 0) required a partially metallic FE. This conclusion verified the previous results\textsuperscript{14–16,39–41} in a material-independent manner and was confirmed also for hyper-FE LiBeSb that was reported to be insulating in FE/paraelectric\textsuperscript{46}. This conclusion appeared inconsistent with “freestanding” monolayer BFO\textsuperscript{42}. But, the examinations of experimental procedures\textsuperscript{42} suggested adsorbates as a hidden mechanism\textsuperscript{43–49}.

The electrostatic formulas of E\textsubscript{d} (Eqs. 1 and 2) were valid down to a several unit-cell scale (Figs. 3, 4, 5), when atomic-scale surface effects, e.g. interactions with electrodes\textsuperscript{12,28} were unimportant. Even with buckling at FE surfaces, these formulas can be valid by regarding buckling layers as dead layer.
Methods

**Ab initio calculations.** In the examinations of FE/vacuum, the results of SrO-terminated STO slabs are presented, because they have $E_g$ wider than $E_g$ of the TiO$_2$-terminated STO slabs (Fig. 1c). To enforce FE, the ion-positions in the STO/vacuum slabs were not optimized, because, otherwise, FE disappears (Fig. 7). Therefore, the STO unit-cells in the slabs retained the ion positions of bulk STO1.005 or STO.9999. These calculations of STO/vacuum were only for the examination of $E_g$ and $\varepsilon_{\ell}$ and do not correspond to standard experiments. $P_z$ of STO1.005 in the slab was typically 1 $\mu$C/cm$^2$.

The models of FE/paraelectric are BTO/STO superlattices. All the calculated forces were < 1 meV/Å after geometry relaxation, and the $a$-axis lattice constant of STO was expanded by 1.1–1.3%. The bulk STOs that had these $a$-axis lattice constants were paraelectric$^{19}$. The $a$-lattice constant of BTO/SrRuO$_3$ and BTO/Pt capacitor was fixed at the theoretical $a$-axis lattice constant of cubic STO and bulk tetragonal BTO, respectively, and all other ion positions were relaxed (Fig. 1g). The atomic models of BTO/SrRuO$_3$ are similar to BTO/STO (Fig. 1b). The use of the theoretical $a$-lattice constant of cubic STO corresponds to the thin films on STO substrates. The surfaces of the BTO and SrRuO$_3$ were TiO$_2$ and SrO, respectively, and Pt atoms at the interface aligned with O atoms of TiO$_2$ plane.

The present study is about the formulas of $E_g$, for given structure parameters. Here, the change of $P_z$ by the interactions in the slabs is included consistently in these formulas by the use of ab initio $P_z$ in these formulas.

The ab initio calculations with VASP$^{30-32}$ used the projector augmented wave method$^{33}$ with a Monkhorst–Pack$^{34}$ mesh of $8 \times 8 \times 2$ for slabs and an energy cutoff of 650 eV. PBEsol functional$^{25}$ was used, unless otherwise mentioned. Ab initio $P_z$ was calculated through Berry phase$^{26}$. The results of BTO/STO were reexamined with PBE functional$^{27}$ with Hubbard $U$ (PBE + $U$)$^{35}$, which was used also for BTO/Pt. In the slab calculations, graphic processing units acceleration$^{49,50}$ was used. The supercells were produced by VESTA$^{51}$.

**Accurate estimation of $P_z$ under $E_{\ell}$.** For correct $\varepsilon_{\ell}$, accurate estimations of a total polarization $P_z$ under $E_{\ell}$ are essential. Because we compare Eqs. (1) and (2) using ab initio $P_z$ with $E_{\ell}$ for the ion positions same as those of this $P_z$, the accuracy of $P_z$ for given ion positions matters.

Berry phase calculation of $P_z$ for given ion positions is accurate but only possible for insulators. For example, the present Berry phase calculations yields $P_z$ of bulk BaTiO$_3$ that agree with experimental $P_z$ within 4%, when experimental ion positions and lattice constants of at 303 K are used$^{27}$.

Therefore, to obtain accurate $P_z$, the dipole moment of a whole slab was calculated with Berry phase; We treated these slabs as unit-cells to apply Berry phase calculations directly, unlike conventional approaches. $P_z$ was obtained by dividing the dipole moment by the volume of FE part of the slab. These $P_z$'s were referred to “rigorously calculated $P_z$'s of the slab” and obtained for all the FE/vacuum and BTO/STO slabs. Here, STO1.005 and STO.9999 slabs are insulating, allowing accurate Berry phase calculations.

Additionally, $P_z$ of the unit-cell that possessed exactly the same ion positions as those in the slab was calculated with Berry phase and, then, with atomic polarization by $E_{\ell}$ by the procedures in Ref. $^{36}$. These $P_z$'s agree perfectly with “rigorously calculated $P_z$'s of the slab”, which further confirmed the accuracy of the present $P_z$'s of FE/vacuum and BTO/STO. These corrected $P_z$'s$^{36}$ were used for capacitors. Therefore, in the present study, $P_z$'s are accurate total $P_z$'s and self-consistent with $E_{\ell}$. Hence, $P_z$'s in Figs. 3, 4 and 5 are accurate.

**Validity of continuity of electric flux and surface dipoles.** Equations (1) and (2) are applicable to the regions much larger than unit-cell. Here, the peaks of 1.5 Å width at the surface in Fig. 1d may be suspected to invalidate Eqs. (1) and (2). These peaks are due to effective surface dipoles caused by electron tunneling smear-out; Surface electrons smear out in vacuum, making positive charge density inside the surface and negative charge density in vacuum.

The heights and shape of the two peaks from the baseline (yellow line in Fig. 1d) are the same (1.53 V). This means $\sigma_{z=0} = \sigma_{z=1}$ and $\sigma_{z=1} = \sigma_{z=0}$, as expected from their origin, where $\sigma_{z=0}$, $\sigma_{z=1}$, and $\sigma_{z=0}$ are positive and negative charge densities that yield the right and left peak, respectively. Because of the charge neutrality of FE, $\sigma_{z=0} + \sigma_{z=1} + \sigma_{z=1} = 0$, i.e. $\sigma_{z=0} + \sigma_{z=1} = 0$. Therefore, the continuity of the electric fluxes $DFE_{\ell}$ in FE and $DI_{\ell}$ in $I_{adj}$ (Fig. 1b) is $DFE_{\ell} - DI_{\ell} = \sigma_{z=0} + \sigma_{z=1} = 0$, i.e. the continuity of electric flux $DFE_{\ell} = DI_{\ell}$, where $DFE_{\ell} = P_z \cos \theta + \varepsilon_{\ell} \varepsilon_0 E_{\ell}$ and $DI_{\ell} = P_z \cos \theta + \varepsilon_{\ell} \varepsilon_0 E_{\ell}$. A clearer example is shown in Fig. 7, which evidently shows the continuity of electric flux and, hence, validates the use of Eqs. (1) and (2).

Because surface buckling in vacuum is electrostatically dipole due to ion displacements, the arguments exactly the same as the above hold. Therefore, the electric flux of the inside $DFE_{\ell}$ and the outside $DI_{\ell}$ of the buckling layer is continuous ($DFE_{\ell} = DI_{\ell}$).

**Effective $l_z/l_{adj}$.** For FE/vacuum, the effective $l_z/l_{adj}$ was estimated from the planer averaged electron density $\rho$ profiles$^{35}$. Below, $z=0$ corresponds to the position of bottom ion. Because $\rho$ at $z = -0.8$ Å was same as the minimum of $\rho$ in all the $r$-$z$ curves, the region of $z = 0 - 0.8$ Å was considered as a part of FE ($\Lambda_{ Ward} = 0.8$ Å), and $l_z^{WF}$ was $l_z = l_z + 2 \lambda_{ smear}$. In addition, $\Lambda_{ smear} = c/2$ (half unit-cell) was also tested, and $l_z^{WF} = l_z - l_z^{WF}$. For BTO/STO, $l_z$ was defined as the distance between the top and bottom Ti ions of BTO (Fig. 1b), and $l_z = l_z - l_z$. For FE capacitors, $l_z^{WF}$ was $l_z^{WF} - uc_{BTO}$ (outermost ions are Ti, $uc_{BTO}$: length of a BTO unit-cell), for which the quantum mechanical smearing$^{28}$ may be responsible. The estimations with $l_z^{WF} = 1.5uc_{BTO}$ were also tested. The effective thicknesses of the screening layer, i.e. the effective passive layer $l_z/2\varepsilon_{\ell}$ of BTO/SrRuO$_3$ and BTO/Pt were estimated as 0.1 Å and approximately 0.05 Å, respectively$^{29}$. 
Data availability

The data required to reproduce these findings can be provided upon reasonable requests to the corresponding author.

Received: 28 October 2020; Accepted: 1 January 2021

Published online: 25 January 2021

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Acknowledgements
Dr. P. Blöchel and Dr. M. Takashige for discussions, Dr. R. R. Mehta for his questions and discussions about Ref.13, and the support JSPS KAKENHI no. JP19K21853 are acknowledged.

Author contributions
Y.W. did this work.

Competing interests
The author declares no competing interests.

Additional information
Correspondence and requests for materials should be addressed to Y.W.

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