Possible Flexoelectric Origin of the Lifshitz Transition in LaAlO$_3$/SrTiO$_3$ Interfaces

Amany Raslan and W. A. Atkinson

Department of Physics & Astronomy, Trent University, Peterborough Ontario, Canada, K9L 0G2

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Multiple experiments have observed a sharp transition in the band structure of LaAlO$_3$/SrTiO$_3$ (001) interfaces as a function of applied gate voltage. This Lifshitz transition, between a single occupied band at low electron density and multiple occupied bands at high density, is remarkable for its abruptness. In this work, we propose a mechanism by which such a transition might happen. We show via numerical modeling that the simultaneous coupling of the dielectric polarization to the interfacial strain (“electrostrictive coupling”) and strain gradient (“flexoelectric coupling”) generates a thin polarized layer whose direction reverses at a critical density. The Lifshitz transition occurs concomitantly with the polarization reversal and is first-order at $T = 0$. A secondary Lifshitz transition, in which electrons spread out into semiclassical tails, occurs at a higher density.

LaAlO$_3$ (LAO) and SrTiO$_3$ (STO) are band insulators; however, when four or more monolayers of LAO are grown on top of a STO substrate, a mobile two-dimensional electron gas (2DEG) forms on the STO side of the interface [1, 2]. One compelling feature of these interfaces is that the character of the 2DEG changes dramatically with the application of a gate voltage. Indeed, for (001) interfaces there is a narrow doping range over which the superconducting transition temperature $T_c$, the superconducting gap and resistive transition for (001) interfaces there is a narrow doping range over which the superconducting transition temperature $T_c$, the superconducting gap and resistive transition $\Delta$ and $\rho$ transition respectively, are sensitive to interfacial strain and raise the question, why is only a single band occupied at low density? In the latter case, the first band actually empties itself into higher energy bands with increasing chemical potential. This cannot be understood within rigid-band models.

Moving beyond rigid bands, intra-atomic Coulomb (Hubbard) interactions [6, 24] have been invoked as a possible explanation for the unusual band filling [14, 16]; however, as we show below, these are too weak to be relevant. We suggest that a purely electronic explanation for the Lifshitz transition is unlikely, and focus instead on STO’s unique dielectric properties. In particular, STO’s proximity to a FE transition allows for a large coupling between the dielectric polarization and lattice strains [34]. This makes STO interfaces qualitatively different from conventional metallic interfaces, and as we show enables a novel switchable state involving the lattice polarization and the 2DEG.

Density functional theory (DFT), while instrumental in establishing fundamental interface properties [25, 28], finds electron densities that are an order of magnitude larger than the Lifshitz transition density $n_L \sim 0.02–0.05$ electrons per 2D unit cell, and cannot easily be tuned through the transition. Schrödinger-Poisson calculations, for which $n_{2D}$ can be continuously tuned, persistently find multiple occupied bands even for $n_{2D} \ll n_L$ [5, 15, 29, 31]. Indeed, we showed previously that, because of STO’s close to a ferroelectric (FE) quantum critical point [32], electrons become deconfined from an ideal interface as $n_{2D} \rightarrow 0$, and form a dilute quasi-three-dimensional (quasi-3D) gas extending far into the STO substrate [33]. This result is incompatible with experimental evidence and raises the question, why is only a single band occupied at low $n_{2D}$?

Furthermore, the evolution of the band structure with $n_{2D}$ is highly unusual. Early work [14] showed that the filling of the lowest band is constant for $n_{2D} > n_L$, and recent experiments have found geometries in which its filling decreases [15, 17]. In the latter case, the first band actually empties itself into higher energy bands with increasing chemical potential. This cannot be understood within rigid-band models.

LaAlO$_3$ (LAO) and SrTiO$_3$ (STO) are band insulators; however, when four or more monolayers of LAO are grown on top of a STO substrate, a mobile two-dimensional electron gas (2DEG) forms on the STO side of the interface. This result is incompatible with experimental evidence and raises the question, why is only a single band occupied at low $n_{2D}$?

While flexoelectric effects are typically negligible in bulk materials, they appear to be a generic feature of nanometer structures in FEs—including domain walls
The quartic terms in Eq. (1), which are parameterized by a coefficient $\gamma$ [53], are generally negligible in the doping range explored here [29, 30], but can be important when flexoelectric effects are included.

Figure 2 illustrates the absence of a Lifshitz transition in an ideal interface. In this case, $\mathbf{D}$ is equal to the matrix $\mathbf{D}$ of stiffness constants for bulk STO, and $E_i = E_i^0$ is the total electric field in layer $i$. Figures 2(a) and 2(b) show the electron potential energy $\phi(z)$ and 3D density $n(z)$ for low and high values of $n_{2D}$. The key point is that the depth of the potential well confining the 2DEG is approximately proportional to $n_{2D}$, and at low density is too shallow to create 2D bound states. Thus, while most of the charge lies within $\sim 20$ unit cells (8 nm) of the interface when $n_{2D} = 0.1$, it spreads far into the substrate when $n_{2D} = 0.01$, with $n(z)$ decaying as a power law [33]. (Densities are per 2D or 3D unit cell, respectively.) The corresponding band structures (without Hubbard interactions) are shown in (c) and (d). Unless otherwise stated, all results in this work are at $T = 1$ K and for $L = 100$ layers.
if strain is included. For a layer-dependent strain $\eta_z$, 

$$\tilde{D}_{ij} = D_{ij} - 2\delta_{ij} g_{11} \eta_z, \quad \tilde{E}_i = E_i + f_{11} \frac{\partial \eta_z}{\partial z}|_{z=z_i}, \quad (2)$$

with $g_{11}$ and $f_{11}$ the coupling constants, and $\delta_{ij}$ the Kronecker delta-function. We adopt an empirical expression that qualitatively fits experimental measurements of the strain profile [41, 42]. $\eta_z = \eta_1 \exp[-(z_i/d)^{11}]$, with $\eta_1 \sim 0.01-0.03$ the strain at the top STO layer and $d = 4a_0$. On general grounds, a piezoelectric term, $-e(z_i)\eta_z$ should also be added to $E_i$, where the coupling constant $e(z_i)$ vanishes away from the interface [43]. Because $e(z_i)$ is unknown, and because it plays the same qualitative role as flexoelectricity, surface piezoelectricity will not be considered explicitly.

Key to Eq. (2) is that, because $\partial \eta_z$ is negative, the effective field $\tilde{E}_i$ can be negative when the electric field $E_i$ is sufficiently small, provided $f_{11} > 0$. In this case, the polarization at the interface will point oppositely to the external field, and towards the interface. This allows for a switchable polarization as a function of gate voltage.

Unless otherwise stated, we adopt the bulk value $g_{11} = 0.1186e_0^{-1}$, with $e_0$ the permittivity of free space. The appropriate value of $f_{11}$ is harder to assess [54–56], first because it is difficult to measure, even in bulk [56], second because surface corrections should be comparable to the bulk value [53], and third because screening by the 2DEG modifies the lattice response to a longitudinal strain gradient. $f_{11}$ is thus the only unknown parameter in our model. One empirical guide is a recent observation that the STO surface polarization in un gated samples points towards the interface [42], implying $f_{11} > 0$. We then take $f_{11}$ of order a few $V$ [54], which is typical for perovskites.

Figure 3(a) shows the filling of the four lowest bands as a function of $n_{2D}$, along with the total filling of the remaining bands making up the tails of the charge distribution. There is a clear Lifshitz transition at $n_{L1} \approx 0.0154$ at which the slope of $n_{1xy}$ (the filling of the 1xy band) is discontinuous: all electrons reside in the 1xy band when $n_{2D} < n_{L1}$, and $n_{1xy}$ is nearly constant over an extended region when $n_{2D} > n_{L1}$. That such a transition emerges naturally from the model without any parameter tuning, and that the predicted transition lies close to the experimental value of $n_{L1}$, is remarkable.

There is a second transition at $n_{L2} \approx 0.025$; this has a small effect on $n_{1xy}$, and is primarily a redistribution of electrons from the 1xz/yz and 2xy bands into the quasi-3D tails. Although no more than 20% of the charge occupies the tails, their 2D density of states is orders-of-magnitude larger than that of the 1xy band, which makes them a highly effective charge reservoir.

The transition at $n_{L1}$ is sharp, suggesting that there are two competing ground states, and indeed the first-order nature of the transition is illustrated by Fig. 3(b), which shows a discontinuity in the inverse isothermal compressibility $k_T^{-1} \propto d\mu/dn_{2D}$. There is, presumably, a second discontinuity at $n_{L2}$; however it is too small to resolve in our data.

To characterize the states on either side of the transition, we show in Fig. 3(c) and Fig. 3(d) the lattice polarization and electron distribution, respectively. The main feature of this figure is that for $n_{2D} < n_{L1}$, there is a thin layer of negative polarization that extends over the region $3a_0 \leq z_i \leq 6a_0$, where the strain gradient is largest. In this region, the polarization points towards the inter-
When \( n \) positive everywhere. In this regime, the electrons move in the electric field is strong enough to overcome flexoelectric effects, and the polarization switches abruptly to be of negative polarization [Fig. 3(c)]. When \( n \) is small enough to cause a conﬁning potential, and pulls electrons into a narrow 2D layer at low density, \( n_{2D} \), the electric field stiffens (i.e. the permittivity decreases), and the spontaneous polarization develops a power-law decay into the substrate. \( \gamma_{ijkl} = 2750 \text{ eVÅ}^4 \) is the estimate for \( \gamma \) in bulk samples reported in [30].

The predictions made here can be directly tested by atomic-resolution probes that can resolve the interface polarization. Notably, Lee et al. [32] observed a “head-to-head” arrangement of LAO and STO polarizations in un gated samples, which they associated with the interfacial doping mechanism. In their measurements, the reversed polarization on the STO side of the interface remains, while the polarized layer near the interface disappears.

Figure 4 shows different factors affecting \( n_{1xy} \). Both the interfacial strain [Fig. 4(a)] and the flexoelectric coupling constant [Fig. 4(c)] have a strong impact on the critical doping, consistent with our earlier assertion that the polarization switches direction at the value of \( n_{L1} \) where the electric field exceeds the flexoelectric term in Eq. (2). That \( n_{L1} \) depends on strain provides a natural explanation for the observed variability between samples of the critical doping.

Conversely, neither the quartic coefficient \( \gamma \) [Fig. 4(b)] nor the electrostrictive coupling constant \( g_{11} \) [Fig. 4(d)] has a signiﬁcant effect on \( n_{L1} \). Rather, they determine the behavior of \( n_{1xy} \) on the high-density side of the transition. The quartic term, which progressively reduces the dielectric screening as \( n_{2D} \) grows, is responsible for an upturn in \( n_{1xy} \) at large \( n_{2D} \), while \( g_{11} \) principally affects the slope on the high-density side of the Lifshitz transition, with large values of \( g_{11} \) actually leading to a decline in \( n_{1xy} \) with increasing \( n_{2D} \).

The slope of \( n_{1xy} \) above the Lifshitz transition is also strongly affected by the doping-dependence of the interfacial strain. In Fig. 4(a), the strain is ﬁxed for each curve; however, the strain is not constant in real interfaces and, for example, shrinks with increasing LAO thickness [42]. The effects of gating have not been reported; however, one may infer from Fig. 4(a) that if the strain were to Relax with increasing \( n_{2D} \), the slope above the transition would be negative, as found in some experiments [15–17].

Figure 4(e) shows that the inclusion of intra-atomic interactions has a small quantitative effect on \( n_{1xy} \), but does not change qualitative features of the transition. This is consistent with our general ﬁnding that electron densities are too small for Hubbard-like interactions to have a signiﬁcant effect.

Figure 4(f) shows the evolution of \( n_{1xy} \) with \( T \). While temperature appears directly in the calculation of the band ﬁllings, the most important effect is in the stiffness coefficients \( D_{ij} \), which reﬂect STO’s strongly \( T \)-dependent dielectric function [53]. In Fig. 4(f), the transition changes very little for \( T < 20 \text{ K} \), over which range \( D_{ij} \) is nearly constant, and then is gradually wiped out as the temperature is further raised. The mechanism for the wipeout is straightforward; as \( T \) increases, the lattice stiffens (i.e. the permittivity decreases), and the spontaneously polarized layer near the interface disappears.
was ultimately shown suppress switchability [28]. The current model differs in two key respects: here, (i) switchability is a consequence of the competition between flexoelectric effects and the external field, and (ii) the switchable region extends over only a few unit cells.

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SUPPLEMENTAL MATERIAL FOR: POSSIBLE FLEXOELECTRIC ORIGIN OF THE LIFSHITZ TRANSITION IN LAALO$_3$/SRTIO$_3$ INTERFACES

Electronic Hamiltonian

The electronic Hamiltonian is

$$\hat{H} = \hat{H}_0 + \hat{H}_V + \hat{H}_U.$$  \hfill (3)

In this expression, $\hat{H}_0$ is the kinetic energy portion of the Hamiltonian, $\hat{H}_V$ describes the potential energy due to the long-range Coulomb interaction, obtained by solving the Poisson equation, while $\hat{H}_U$ contains short-range (intra-atomic) Coulomb contributions of the Hubbard type.

We adopt a layered geometry consistent with the structure of STO interfaces; we assume a (001) interface, such that there is translational invariance in the $x$-$y$ plane, and quantities such as the charge density, lattice polarization, and electrostatic potential depend only on the distance $z$ from the interface. For this geometry,

$$\hat{H}_0 = \sum_{ij \mathbf{k} \alpha \sigma} c^\dagger_{\mathbf{k} \alpha i \sigma} t^{ij}_{\mathbf{k}} c_{\mathbf{k} \alpha j \sigma},$$  \hfill (4)

where $i$ and $j$ label TiO$_2$ layers, and $\mathbf{k} = (k_x, k_y)$ is the 2D wavevector describing the motion of electrons parallel to the interface. The operator $c_{\mathbf{k} \alpha i \sigma}$ annihilates an electron with orbital type $\alpha$, spin $\sigma$, and wavevector $\mathbf{k}$ in layer $j$. The matrix element $t^{ij}_{\mathbf{k}}$ is a hopping matrix element between orbitals of type $\alpha$.

There are two distinct hopping processes: hopping between neighboring orbitals of type $\alpha$ is large if the electron moves in the plane parallel to $\alpha$ (e.g. the $x$-$y$ plane for $d_{xy}$ orbitals), and small if it moves perpendicular to $\alpha$. The matrix elements are denoted by $t^{||}$ and $t^{\perp}$, respectively, and values are given in Table I. We thus have

$$t^{||}_{ij}(\mathbf{k}) = -2(t^{||}c_x + t^{||}c_y)\delta_{ij} - t^{\perp}\delta(i,j),$$  \hfill (5)

$$t^{\perp}_{ij}(\mathbf{k}) = -2(t^{\perp}c_x + t^{\perp}c_y)\delta_{ij} - t^{||}\delta(i,j),$$  \hfill (6)

$$t^{xy}_{ij}(\mathbf{k}) = -2(t^{xy}c_x + t^{xy}c_y)\delta_{ij} - t^{\perp}\delta(i,j),$$  \hfill (7)

where $c_n \equiv \cos(k_n a_0)$ with $a_0$ the lattice constant, and $\delta(i,j)$ is one if $i$ and $j$ are nearest-neighbor planes, and zero otherwise.

Coulomb Potential

The long-range Coulomb term is

$$\hat{H}_V = \sum_{i \alpha \sigma} \phi_i n_{i\alpha \sigma},$$  \hfill (8)

where $n_{i\alpha \sigma} = N_{2D}^{-1} \sum_{\mathbf{k}} c_{\mathbf{k} \alpha i \sigma}^\dagger c_{\mathbf{k} \alpha i \sigma}$ is the electron number operator for orbital type $\alpha$ and spin $\sigma$ in layer $i$, with $N_{2D}$ the number of 2D unit cells. $\hat{H}_V$ contains a potential energy $\phi_i \equiv \phi(z_i)$ with contributions from three distinct interactions: electron-electron interactions between free carriers in the STO, electron-lattice interactions between free carriers and the STO polarization, and interactions between free carriers and the LAO surface charge.

The electrostatic potential energy (in SI units) is obtained by solving Poisson’s equation,

$$\epsilon_\infty \nabla \cdot \mathbf{E}(z) = \rho(z) - \nabla \cdot \mathbf{P}(z),$$  \hfill (9)

where $\mathbf{E}(z)$, $\mathbf{P}(z)$, and $\rho(z)$ are, respectively, the electric field, the lattice polarization, and the charge density, and $\epsilon_\infty$ is the optical dielectric constant. The charge density includes contributions from both the free carriers in the STO substrate and LAO surface charges. In the planar geometry, the polarization and electric field vectors are parallel to the $z$-axis, with $\mathbf{E}(z) = E(z) \mathbf{\hat{z}}$, $\mathbf{P}(z) = P(z) \mathbf{\hat{z}}$.

Then, the potential energy is obtained from

$$\phi(z) = \phi(0) + e \int_0^z dz' E(z').$$  \hfill (10)

Integrating Eq. (9) from a point outside the LAO surface (where $E$ and $P$ vanish) to layer $i$ inside the STO substrate yields

$$\epsilon_\infty E_i = e n_{2D} - \frac{e}{a_0^2} \sum_{j<i} \sum_{\alpha \sigma} n_{\alpha \sigma} - P_i.$$  \hfill (11)

Equation (10) then gives the potential energy,

$$\phi_i = \frac{e^2}{\epsilon_\infty} \left[ n_{2D} z_i - \sum_{j<i} \sum_{\alpha \sigma} \frac{n_{\alpha \sigma}}{a_0^2} (z_i - z_j) \right] - \frac{e a_0}{\epsilon_\infty} \sum_{j \leq i} P_j,$$  \hfill (12)
where \( \phi(0) \) is set to zero.

We solve a discrete version of these equations, in which \( E(z) \to E_i, \ P(z) \to P_i, \) and

\[
\rho(z) = e n_{2D} \delta(z - z_{\text{surf}}) - \frac{e^2}{a_0^2} \sum_{\alpha i} n_{\alpha i} \delta(z - z_i). \tag{13}
\]

Here, \( z_{\text{surf}} \) is the location of the LAO surface, \( z_i = (i - 1)a_0 \) is the location of the \( i \)th layer measured relative to the interface, and

\[
n_{\alpha i} = \langle \hat{n}_{\alpha i} \rangle. \tag{14}
\]

is the occupation of a single orbital \( \langle \alpha, \sigma \rangle \) in layer \( i \).

The short-range Coulomb interaction on the Ti sites takes the form \( [6] \),

\[
\hat{H}_U = \sum_{\alpha i} \left[ U_0 n_{\alpha i} + \sum_{\beta \neq \alpha, \sigma'} (U - J \delta_{\sigma, \sigma'}) n_{\beta i} n_{\sigma' i} \right] \langle \hat{n}_{\alpha i} \rangle,
\]

where \( \sigma = -\sigma \) and with the constraint

\[
U_0 = U + 2J. \tag{16}
\]

In this expression, \( U_0 \) is the intra-orbital Hubbard interaction, \( U \) and \( J \) are inter-orbital Hartree and exchange interactions. We constrain our calculations to eliminate the possibility of ferromagnetism, and require that \( n_{\alpha i} = n_{\alpha i}^\dagger \).

From the form of \( \hat{H}_U \) [Eq. (15)], it is clear that minimization of the intra-orbital Coulomb energy favors a spreading-out of charge between orbitals if \( U_0 \) and \( J \) are large, and the collapse of charge into a single orbital type if \( U \) is large. Indeed, we find that our calculations favor occupation of \( d_{xy} \) orbitals over \( d_{xz} \) and \( d_{yz} \) orbitals when \( J < U_0/5 \), and favor occupation of multiple orbital types when \( J > U_0/5 \). The representative example shown in the manuscript takes \( U_0 = 4 \) eV, and \( J = 0.8 \) eV (so \( J = U_0/5 \)) and from the constraint [16], we obtain \( U = 2.4 \) eV. We have explored other \( J \)-values, and find that while details of the band structure change, our basic conclusions do not.

### Dielectric Model at Zero Temperature

Dielectric screening comes from a soft optical phonon mode with a large dipole moment. The Landau-Devonshire free energy for this mode is

\[
\mathcal{U} = \frac{1}{2} \sum_{i,j} P_i \tilde{D}_{ij} P_j - \sum_i \tilde{E}_i P_i + \text{quartic term} \tag{17}
\]

where \( i \) and \( j \) are layer indices, and \( \tilde{E}_i \) and \( \tilde{D}_{ij} \) are linear and quadratic coefficients of the free energy expansion. The quartic term is discussed below.

In bulk STO, \( \tilde{E}_i \) is equal to the electric field \( E_i \); adjacent to the interface, inversion symmetry is broken and \( \tilde{E}_i \) picks up additive corrections that extend over the first few STO layers. Similarly, the coefficients \( \tilde{D}_{ij} \) equal their bulk values \( D_{ij} \) away from the interface, but may be different near the interface.

Following our earlier work, we take the bulk coefficients

\[
D_{ij} = \begin{cases} D_0, & i = j \\ -D_1 e^{-z_{ij}^2/2a_0^2} - D_2 e^{-z_{ij}^2/2a_0^2}, & i \neq j \end{cases}
\]

where \( z_{ij} = z_i - z_j \). Values for \( D_0, D_1, D_2, \alpha_1, \) and \( \alpha_2 \) that are valid at low \( T \) are given in Table [1].

For a given electric field, the polarization \( P_t \) is obtained by setting \( \partial \mathcal{U} / \partial P_t = 0 \). In a bulk crystal with uniform electric field \( E \) and polarization \( P \), this yields

\[
P = E/D_{q=0} \quad \text{where} \quad D_{q=0} = \sum_j D_{ij}.
\]

The bulk dielectric constant is then

\[
\epsilon = \epsilon_\infty + \frac{\partial P}{\partial E} \approx D_{q=0}^{-1} \tag{19}
\]

The final approximate equality arises because \( \epsilon_\infty = 5.5 \epsilon_0 \) while \( D_{q=0}^{-1} \approx 10^4 \epsilon_0 \) at low \( T \) (\( \epsilon_0 \) is the permittivity of free space). In this dielectric model, the large value of \( \epsilon \) comes from a near cancellation of the local \( (i = j) \) and nonlocal \( (i \neq j) \) contributions to \( D_{q=0} \).

Electrostrictive coupling through the term proportional to \( g_{11} \) modifies the matrix \( \tilde{D} \) such that it has one or two negative eigenvalues, depending on the magnitude of the strain. In this instance, the quartic terms in Eq. (17) are required to stabilize the polarization. We find that the numerics are most easily controlled if we work in a basis in which \( \tilde{D} \) is diagonal. Letting \( \Lambda_n \) and \( S \) be the eigenvalues and the matrix of eigenvectors of \( \tilde{D} \), we make the ansatz

\[
\mathcal{U} = \sum_n \left[ \frac{1}{2} \Lambda_n P_n^2 - \mathcal{E}_n P_n + \gamma \mathcal{P}_n^3 \right]. \tag{20}
\]

where \( \mathcal{E}_n = \sum_i \tilde{E}_i S_{in} \) and \( \mathcal{P}_n = \sum_i P_i S_{in} \). The first two terms in Eq. (20) are formally equivalent to Eq. (17), while the final term is an ansatz. The advantage of Eq (20) is that it is diagonal in the mode index \( n \), and one can minimize each term in the sum analytically. Once \( \mathcal{P}_n \) is known, then \( P_i \) is obtained from \( P_i = \sum_n S_{in} \mathcal{P}_n \).

At low electron densities, \( \mathcal{E}_n \) is sufficiently weak that the quartic term is negligible provided \( \Lambda_n \) is positive and not too small; then, \( \mathcal{P}_n = \mathcal{E}_n/\Lambda_n \), to a good approximation. For the one or two eigenmodes where \( \Lambda_n \) is close to zero or negative, \( \gamma \) cannot be neglected and the cubic equation obtained from setting

\[
\partial \mathcal{U} / \partial \mathcal{P}_n = \Lambda_n \mathcal{P}_n - \mathcal{E}_n + \gamma \mathcal{P}_n^3 = 0 \tag{21}
\]

must be solved, with the solution that minimizes the energy of that eigenmode being selected.
Dielectric Model at Nonzero Temperature

The temperature dependence of the dielectric function comes through the matrix elements $D_{ij}$, and our approach follows Raslan et al. [3]. The $T$-dependence is obtained in two steps. First, the measured dielectric susceptibility \( \chi (T) \) is fitted to an empirical formula

\[
\chi_{q=0}(T) = \left( \frac{T_0}{T_s \coth(T_s/T)} \right) ^\xi ,
\]

(22)

where $T_s = 15 \text{ K}$ is the saturation temperature below which $\chi(T)$ becomes constant, and $T_0 = 1.46 \times 10^4 \text{ K}$ and $\xi = 1.45$ are fitting parameters. Next, using

\[
\chi_{q=0}(T) = \frac{1}{\epsilon_0 D_{q=0}},
\]

(23)

allows us to obtain the temperature dependent parameters in $D_{ij}$. We write

\[
D_{q=0} = \sum_j D_{ij}
\approx D_0 - D_1 \left( 1 - \frac{\sqrt{2\pi} \alpha_1}{a_0} \right) - D_2 \left( 1 - \frac{\sqrt{2\pi} \alpha_2}{a_0} \right).
\]

(24)

Comparing Eq. (24) and Eq. (22) allows us to determine the $T$-dependence of our model parameters. Following Ref. [1], we make the ansatz that $D_2$ is $T$-dependent, while $D_0$ and $D_1$ are constant.

Numerical Solution of the Model

In most cases, the model can be solved using a straightforward iterative procedure to obtain self-consistent values for the polarization $P_i$ and the electron density $n_i$. Given an input potential energy $\phi_i$, we calculate the charge density $n_{\text{oi}}$ by diagonalizing $\hat{H}$ and the polarization $P_i$ by minimizing $U$. The charge density and polarization are then used to generate an updated potential energy. The cycle is repeated until the input and output potentials are the same. This cycle is unstable to charge-sloshing, and we therefore use Anderson mixing to stabilize the iterative process.[7]

In some of the cases, the iterative scheme described above is unstable because the flexoelectric contribution to $\tilde{E}$ can lead to a rapid switching of the polarization direction from one iteration to the next. To stabilize the numerics, we rearrange Eq. (21) such that the depolarizing fields are explicitly grouped with $\Lambda_n$. Thus, from Eq. (11) it is possible to write $E_i = -P_i/\epsilon_\infty + E_{\text{other}}$, from which it follows that Eq. (21) is

\[
(\Lambda_n + \epsilon_\infty^{-1})P_n - \epsilon_n^{\text{other}} + \gamma P_n^3 = 0.
\]

(25)

In our calculations, $\Lambda_n > -\epsilon_\infty^{-1}$ and this rearrangement of terms thus helps stabilize the iterative cycle.

* billatkinson@trentu.ca

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