Perturbative approach to electrocaloric effects

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We show that the electrocaloric (EC) effect – e.g., the temperature change experienced by an insulator upon application of an electric bias – lends itself to a straightforward interpretation when expressed as a Taylor series in the external field. Our formalism explains in a unified and simple way the most notable small-field effects reported in the literature – e.g., the so-called normal (increase of temperature under bias, as usually found in ferroelectrics) and inverse (decrease of temperature, as e.g. in antiferroelectrics) EC responses – and clarifies their physical interpretation. We also discuss in detail second-principles simulations for prototype ferroelectric PbTiO\textsubscript{3}, explicitly evaluating subtle predictions of the theory, such as the occurrence of competing contributions to the EC response.

Electrocaloric (EC) effects hold the promise of an ecofriendly alternative to refrigeration, one of the most energy-consuming activities today and in the foreseeable future. EC effects are strong in ferroelectric (FE) and antiferroelectric (AFE) materials because of their anomalously large dielectric responses and the field-driven phase transitions that can be easily induced near the Curie point \cite{1}.

The thermodynamic description of the EC cooling cycle is well established \cite{1}. The key step is the adiabatic temperature change, which can be expressed as

$$\Delta T(\alpha) = -\int_{E_0}^{E_0} \frac{T}{C_E} \left( \frac{\partial S}{\partial E_0'} \right)_T dE_0'$$

where the integral runs from zero to a final electric field $E_0$, applied along the $\alpha$ Cartesian direction. $S$, $T$ and $C_E$ are, respectively, the entropy, temperature and constant-field heat capacity. $P_\alpha$ is the polarization component conjugate to the applied field $E_0$, and its $T$-derivative is the pyroelectric coefficient $\pi_\alpha$. Note that we have used the Maxwell relation between the field derivative of the entropy and the pyroelectric vector, which is expected to hold for ergodic materials. (Thus, the formalism introduced here is, in principle, not applicable to relaxor ferroelectrics.) Note also that the repeated $\alpha$ index does not involve an implicit sum; we write this $\alpha$, on both sides of the equation, to emphasize the fact that the EC response can be anisotropic.

Also important is the isothermal entropy change

$$\Delta S(\alpha) = \int_{E_0}^{E_0} \pi_\alpha dE_0'$$

which quantifies the amount of heat the EC material will exchange with the object to be cooled. The product $\Delta T(\alpha)\Delta S(\alpha)$ is usually taken as the figure of merit for EC cooling performance.

These expressions are deceivingly simple, as all the quantities in the integrands depend on both field and temperature (itself field dependent, by virtue of the EC effect). Further, they may present complex behaviors (in particular, discontinuities) across field- and temperature-driven phase transitions.

There are well-known strategies to solve these integrals self-consistently \cite{1}: this will not be our focus here. Rather, we want to examine the ingredient that has the greatest influence in the basic features (magnitude and sign) of the EC temperature and entropy changes, namely, the pyroelectric vector $\pi$. Indeed, $\pi$ fully determines $\Delta S(\alpha)$; further, of the quantities contributing to $\Delta T(\alpha)$, $\pi$ is likely to be the most sensitive to an electric bias and, more importantly, it is the only one whose sign is not defined. (Both $T$ and $C_E$ are always positive.)

Interestingly, we can rewrite Eq. (1) in differential form as

$$\frac{dT(\alpha)}{dE_0'} = -\frac{T}{C_E} \left( \frac{\partial S}{\partial E_0'} \right)_T$$

This expression is the basis for the physical interpretation of EC effects \cite{1}. For example, it is experimentally observed that, in ferroelectrics, the application of an electric field usually results in a positive temperature change, which is attributed to the fact that electric fields create order (reduce the entropy) in such systems \cite{1}. In contrast, negative values of $\Delta T$ have been observed in antiferroelectrics \cite{2-5}, or when a field is applied perpendicular to the polarization of a ferroelectric phase \cite{6}, which is compatible with the intuitive notion that, in such cases, the electric field will destabilize the equilibrium state and cause disorder (increase the entropy). These diverse observations have been reproduced by atomistic simulations \cite{7-13} and explained by the corresponding Landau phenomenological theories \cite{1,2,12,13}, suggesting that we understand EC effects quite well.

However, we think the situation is not fully satisfactory, for one main reason: The theoretical treatments in the literature are case specific, and we lack a unified and simple picture revealing the similarities and differ-
ences among the various known effects. Also, we find that, while intuitively appealing, some frequent assumptions (i.e., that electric fields cause disorder in antiferroelectrics) are somewhat vague, and we miss a formalism that allows us to interpret the observed behaviors (and eventually think about new ones) in a more rigorous manner. Here we address these issues.

Formal considerations. – Let us focus on how $\pi_\alpha$ controls $\Delta T(\alpha)$. For the sake of simplicity, we work with an approximate version of the adiabatic temperature change

$$\Delta T(\alpha) \approx -\frac{T(0)}{C_E} \int_0^{E_\alpha} \pi_\alpha(T(0)) dE_\alpha,$$

where the “0” superscript marks values at zero applied field. This approximate expression captures the EC effect as obtained when we neglect the field and temperature dependences of $T$ and $C_E$, as well as the variation of $\pi_\alpha$ upon EC heating or cooling; these are common approximations in the EC literature. (Unless we work at low temperatures, we can safely assume $|\Delta T(\alpha)| \ll T(0)$, as the largest measured EC effects are typically below 20 K 15. Also, we can expect relatively small variations in $C_E$ except in the close vicinity of phase transitions; more on this below.)

Let us examine Eq. (4) analytically. We start by writing $P$ as a Taylor series in $E$,

$$P_\mu = P^{(0)}_\mu + \epsilon_0 \sum_\beta \chi^{(0)}_{\mu\beta} E_\beta + \epsilon_0 \sum_\beta \chi^{(1)}_{\mu\beta \gamma} E_\beta E_\gamma + ...,$$

where $P^{(0)}$ is the spontaneous polarization, $\chi^{(n)}$ is the $n$th-order dielectric susceptibility tensor, and $\epsilon_0$ is the vacuum permittivity. For convenience, we work with a Cartesian coordinate system with one axis parallel to $\alpha$, the direction of the applied field. Hence, we have $E_\beta = \delta_{\beta\alpha} E_\alpha$, where $\delta_{\beta\alpha}$ is the Kronecker delta; we thus obtain the $\alpha$ component of the polarization as

$$P_\alpha = P^{(0)}_\alpha + \epsilon_0 \sum_\beta \chi^{(0)}_{\alpha\beta} E_\beta + \epsilon_0 \sum_\beta \chi^{(1)}_{\alpha\beta \gamma} E_\beta E_\gamma + ...,$$

where only the $\alpha$-diagonal tensor elements appear. This expression for $P_\alpha$ is general and can be used to describe any phase of an insulating material, be it FE, AFE, paraelectric (PE), or simply dielectric.

By taking the $T$-derivative of Eq. (6) at constant field, we obtain

$$\pi_\alpha = \pi^{(0)}_\alpha + \pi^{(1)}_{\alpha\alpha} E_\alpha + \pi^{(2)}_{\alpha\alpha \alpha} E^2_\alpha + ...,$$

where the $\pi^{(0)}$ vector captures the $T$-dependence of the spontaneous polarization $P^{(0)}$. For $n \geq 1$, the $\pi^{(n)}$ tensors account for the field-induced pyroelectric effect, with

$$\pi^{(n)} = \epsilon_0 \left( \frac{\partial \chi^{(n-1)}}{\partial T} \right)_E,$$

where the pyroelectric tensor of $n$th-order in the field series depends on the susceptibility of $(n-1)$th-order. Using Eq. (7), we resolve Eq. (4) and obtain

$$\Delta T(\alpha) \approx -\frac{T(0)}{C_E} \left( \pi^{(0)}_\alpha E_\alpha + \frac{1}{2} \pi^{(1)}_{\alpha\alpha} E^2_\alpha + \frac{1}{3} \pi^{(2)}_{\alpha\alpha \alpha} E^3_\alpha + ... \right),$$

where we define $\Delta T^{(n)}(\alpha)$ as the $n$th-order contribution to the adiabatic temperature change. Also, here it is implicitly assumed that the pyroelectric coefficients are evaluated at $T(0)$. Let us now see how this expression allows us to understand all the known EC effects in FE and AFE compounds for small applied electric fields. Our conclusions are summarized in Table I.

For the sake of concreteness, here we discuss FE and AFE materials with an isotropic (e.g., cubic) high-temperature PE phase, as is the case of perovskite oxides (e.g., PbTiO$_3$ or PbZrO$_3$), noting that our arguments can be generalized.

Let us begin by discussing the EC response above the Curie temperature ($T_C$) for a material that can be either FE or AFE. In this case we do not have any spontaneous polarization ($P^{(0)} = \pi^{(0)} = 0$); hence, $\Delta T(\alpha) \approx \Delta T^{(2)}(\alpha)$, which is dominated by the lowest-order field-induced pyroelectric effect, $\pi^{(1)}$. As we know from Eq. (8), $\pi^{(1)}$ is just the $T$-derivative of the linear dielectric susceptibility $\chi^{(0)}$.

As it is well-known, both FE and AFE phase transitions are characterized by a dielectric anomaly at zero field, i.e., a maximum of $\chi^{(0)}$ at $T_C$. To fix ideas, we can imagine that all the diagonal components of $\chi^{(0)}$ follow a Curie-Weiss law approximately. (Our simulation results for PbTiO$_3$ – see Fig. 1 – are a representative case.) This maximum controls the $T$-dependence of $\chi^{(0)}$ in a wide range around $T_C$, yielding $\pi^{(1)}_{\alpha\alpha} > 0$ for $T < T_C$.
and $\pi^{(1)}_{\alpha\alpha} < 0$ for $T > T_C$. Hence, in particular, the PE phase of all FEs and AFEs is characterized by $\pi^{(1)}_{\alpha\alpha} < 0$; according to Eq. (9), this should result in $\Delta T(\alpha) > 0$ for all $\alpha$ directions, as it is indeed observed.

Interestingly, the situation is rather similar for an AFE state: we still have $P^{(0)} = \pi^{(0)} = 0$ and $\Delta T(\alpha) \approx \Delta T^{(2)}(\alpha) \propto \pi^{(1)}_{\alpha\alpha}$. However, now we have $T < T_C$ and, as mentioned above, $\pi^{(1)}_{\alpha\alpha} > 0$. Hence, we expect $\Delta T(\alpha) < 0$, in agreement with the experimental observations.

Note that in all the above cases the EC temperature change does not depend on the sign of the applied field, a feature that is expected from the symmetry of PE and AFE states, and which we readily obtain from our formalism.

Suppose now that we are in a FE phase. Without loss of generality, we assume that $P^{(0)} = \pi^{(0)} = 0$ and $\Delta T(\alpha) \approx \Delta T^{(2)}(\alpha) \propto \pi^{(1)}_{\alpha\alpha}$. However, now we have $T < T_C$ and, as mentioned above, $\pi^{(1)}_{\alpha\alpha} > 0$. Hence, we expect $\Delta T(\alpha) < 0$, in agreement with the experimental observations.

Let us imagine we apply a field $E_0$ along the $x$ Cartesian direction, thus perpendicular to $P^{(0)}$. This case is exactly analogous to the AFE state discussed above: according to Eq. (10), the response is controlled by $\pi^{(1)}_{xx} > 0$. Hence, exactly as in the AFE state, we expect an inverse EC response with $\Delta T(x) < 0$, an experimentally-observed behavior that might seem surprising [6, 17, 18], but is readily obtained and explained within our formalism.

Finally, suppose that we apply a field along $z$, the direction of the spontaneous polarization. Here, for the first time in this discussion, we have a non-zero linear contribution to the adiabatic temperature change, and we can write $\Delta T(z) \approx \Delta T^{(1)}(z) + \Delta T^{(2)}(z)$.

Concerning $\Delta T^{(2)}(z)$, the situation is identical to the above cases for $T < T_C$: it is dominated by $\pi^{(1)}_{zz} > 0$, which yields $\Delta T^{(2)}(z) < 0$ regardless of the sign of the applied field $E_z$.

In contrast, the linear contribution does depend on whether $E_z$ is parallel or antiparallel to the spontaneous polarization. Further, $\Delta T^{(1)}(z)$ is proportional to $\pi^{(0)}_{zz}$, which is negative when $E_z > 0$. Hence, we have: $\Delta T^{(1)}(z) > 0$ for a parallel field ($E_z > 0$), and $\Delta T^{(1)}(z) < 0$ when the field goes against $P^{(0)}$.

Thus, we have two qualitatively different cases. If the applied field goes against the polarization, $\Delta T^{(1)}(z)$ and $\Delta T^{(2)}(z)$ are both negative, and we have every reason to expect $\Delta T(z) < 0$. However, for fields parallel to polarization, we have a competition between the linear and quadratic contributions to $\Delta T(z)$, and the net result is in principle undetermined. Interestingly, experimental studies of FE phases show – without exception, as far as we know – that the temperature change is positive for fields parallel to the spontaneous polarization [1], and negative for fields tending to reverse it [6, 17, 18]. This is in agreement with the expectations from our formalism, suggesting that, for the case of parallel fields, the linear effect ($\Delta T^{(1)}(z) \propto \pi^{(0)}_{zz}E_z > 0$) dominates over the quadratic one ($\Delta T^{(2)}(z) \propto \pi^{(1)}_{zz}E_z^2 < 0$).

Hence, as summarized in Table [1], we find that, in all the cases considered, the leading non-zero contribution to $\Delta T(\alpha)$ agrees in sign with the adiabatic temperature change observed experimentally for relatively small applied fields. We should note that the formalism just introduced bears obvious similarities with previously proposed theories to discuss EC effects, e.g. in the context of AFEs [2, 9]. The novelty here relies on the fact that our equations are general and can be applied to any material and phase (FE, AFE, PE or simply dielectric), revealing the way they are connected and evidencing the (somewhat trivial) origin of the so-called inverse effects. Our formalism also emphasizes that the basic EC response (i.e., the sign of the $T$-change) can be understood from simple universal arguments, not relying on specific atomistic or phenomenological models.

Numerical results. – To gain further insight, and to evaluate the accuracy of low-order approximations to $\Delta T(\alpha)$, we now compute explicitly the $\Delta T^{(n)}(\alpha)$ terms in Eq. (11) for prototype compound PbTiO$_3$ (PTO).

We simulate PTO using the second-principles (Refs. [19, 20]; see Supp. Note 1) model potential first introduced in Ref. [19], which has proven its accuracy in reproducing the basic FE behavior of the material as well as many subtle structural features, as e.g. related to its domain walls [21, 22]. Let us stress that, in these simulations, all the degrees of freedom for the lattice (i.e., all atomic positions, all strains) are treated on equal footing; hence, our calculations include all contributions to the EC response, and there is in fact no easy way to differentiate them in the manner is often done in phenomenological Landau approaches (where it is natural to distinguish the “dipole” subsystem from the “phonon” bath [11]). Finally, let us mention that the only noteworthy deficiency of our second-principles model pertains to the predicted $T_C$, which is lower than the experimental one (510 K vs 760 K), but this is not critical for the present purposes.

We solve our PTO model as a function of temperature and applied electric field [19] by running Monte Carlo simulations, using periodically-repeated supercells composed of $10 \times 10 \times 10$ or $12 \times 12 \times 12$ elemental perovskite units. (Larger cells are considered in the proximity of $T_C$.) At a given $T$, we run 10,000 Monte Carlo sweeps for thermalization, followed by 75,000 to 100,000 sweeps to compute averages. We checked that these calculation conditions yield sufficiently accurate results.

The key quantities we monitor are the equilibrium polarization $P$, the dielectric susceptibility $\chi$, the pyroelec-
tric vector $\pi$, and the specific heat $C_E$, which we compute using standard linear-response formulas \cite{23}. (The formulas used here are given in the Supp. Note 2; they closely resemble the ones employed in other studies of EC effects by Monte Carlo simulations, as e.g. in Refs. \cite{12} and \cite{13}) We can thus compute the Taylor series for $\pi$ (Eq. (7)) and for $\Delta T(\alpha)$ (Eq. \(9\)). (In Supp. Note 3 and Supp. Figs. 1, 2 and 3 we give extra details on the calculation of the $\Delta T^{(n)}(\alpha)$ contributions.) Our results are summarized in Fig. \(4\).

We obtain a FE phase transition at $T_C = 510$ K (Fig. \(4\)a), marked by a near divergence of the susceptibility (Fig. \(4\)b); this is characteristic of a weakly first-order transformation, and is in qualitative agreement with the experimental result \cite{24}. Without loss of generality, we choose $P(0) = (0, 0, P_z(0))$, with $P_z(0) > 0$ below $T_C$. Of note is the qualitative change of the phase transition as we apply an electric bias: for small applied field, the susceptibility peak reaches higher values, reflecting the fact that the transition becomes more continuous \cite{24}; for larger fields, the transition becomes diffuse and the related anomalies in the susceptibility (Fig. \(4\)b) and heat capacity (Fig. \(4\)c) tend to disappear.

For clarity, Fig. \(4\)b only shows the temperature and field dependence of one susceptibility component, $\chi_{zz}$. However, note that, by symmetry, the $\chi$ tensor only has diagonal components; further, for $T > T_C$ they are all equal (cubic phase), while for $T < T_C$ we have $\chi_{xx} = \chi_{yy} > \chi_{zz}$ (tetragonal phase). (In the FE phase, the polar direction is electrically stiffer; this is a well-known feature of FE perovskites, related to what is usually called easy polarization rotation \cite{26}.) As can be seen in the Supp. Fig. 4, the three components have an approximate Curie-Weiss behavior, with a maximum at $T_C$ and a monotonic T-dependence on both sides of the transition point.

Figure \(4\)d shows our results for the low-order pyroelectric coefficients. $\pi_{xx}(0)$ is null above the transition point and negative below it, as expected. As for $\pi_{xx}(1)$, we find the expected behavior as well: the tensor has non-zero diagonal components at all temperatures, nearly diverging at $T_C$, and changing sign as the system goes through the transition. Note that our numerical results for $\pi_{xx}(0)$ and $\pi_{xx}(1)$ ratify the competition that occurs when a field is applied parallel to $P_z(0)$, as discussed above. Also, our results for $\pi_{xx}(1)$ reveal an essentially isotropic tensor at all temperatures, even in the tetragonal phase. (The tetragonal symmetry implies $\pi_{xx}^{(1)} = \pi_{yy}^{(1)} \neq \pi_{zz}^{(1)}$; yet, in Fig. \(4\)d, a sizeable difference between the $xx$ and $zz$ components is found only for $T \lesssim T_C$.)

Figure \(4\)e shows the computed $\Delta T(z)$ for various positive fields, with $E_z$ up to 10 MV/m, as a function of temperature. The results are obtained by evaluating the Taylor series in Eq. (9) up to 5th order, which is enough to get a converged $T$-change except in the immediate vicinity of the phase transition. More specifically, Fig. \(4\)f shows that, even for a large field of 10 MV/m, the EC effect at $T < T_C$ is dominated by the leading contribution $\Delta T^{(1)}(z)$, higher-orders becoming significant only very close to $T_C$ (see the result at 490 K). In fact, as shown in Supp. Fig. 2, we find that the leading contribution to the EC response – i.e., $\Delta T^{(1)}(z)$ below $T_C$ and $\Delta T^{(2)}(z)$ above $T_C$, respectively – is usually a very good approximation of the total effect.

Let us stress that in Figs. \(4\)e and \(4\)f we restrict ourselves to fields that are small enough so that no first-order phase transition is induced. This is why we do not show any data very close to $T_C$, and why the fields considered for $T > T_C$ are relatively tiny. (Close to $T_C$, the PE phase is easily transformed into the polar one. See representative results in Supp. Fig. 3.) This is consistent with our perturbative approach to compute $\Delta T(\alpha)$, which is designed to describe the properties of the continuously-deformed zero-field state. To treat a first-order transition, one could split the integral for $\Delta T(\alpha)$ in low- and high-field parts, using different perturbative $P(E)$ expansions for each of them. Additionally, one should account for the latent heat associated to the discontinuous transformation \cite{27,28}. The information to tackle such situations is in principle available from our Monte Carlo calculations. (We can compute latent heats from the thermal-averaged internal energies \cite{30}.) However, we should note that, for treating first-order transitions, direct non-perturbative computational approaches based on microcanonical molecular dynamics \cite{8} or constrained Monte Carlo simulations \cite{31} are better suited.

The values obtained for $\Delta T(z)$ (e.g., a maximum of 0.25 K when $T_C$ is approached from below for a field of 0.5 MV/m) are comparable with EC effects measured for PTO: for example, Ref. \cite{32} reports a temperature change of 0.1 K for $T \lesssim T_C$ and a field of 0.15 MV/m, and a maximum $T$-change of 1.9 K at $T_C$. (We also obtain $\Delta S(z) \approx -2500$ J/Km$^3$ for a field of 0.5 MV/m at $T \lesssim T_C$, while Ref. \cite{32} reports a maximum entropy change of about $-16500$ J/Km$^3$ for a field of 0.15 MV/m applied exactly at $T_C$.) Our results are also consistent with other theoretical estimates of the EC effect for PTO \cite{33}. Finally, in Supp. Fig. 5 we evaluate the approximations made in Eq. (9) – i.e., the use of the zero-field values for $T$ and $C_E$, so they can be taken out of the integral –, and find that their impact is negligible (even for large fields) except very close to $T_C$.

Discussion. – In view of the above, let us comment on the usual interpretation of EC effects in terms of field-induced order or disorder. For illustrative purposes, it is convenient to pay attention to the isothermal entropy
change, which, from Eqs. (2) and (7), can be written as
\[
\Delta S(0) = \pi_{aa}^{(0)} E_a + \frac{1}{2} \pi_{aa}^{(1)} E_a^2 + O(E_a^3) \\
= \Delta S^{(1)}(\alpha) + \Delta S^{(2)}(\alpha) + \ldots \\
= \left( \pi_{aa}^{(0)} + \frac{1}{2} \pi_{aa}^{(1)} E_a + \ldots \right) E_a. \tag{10}
\]

The last line suggests that we can think of $\Delta S(z)$ as depending linearly on $E_z$, the corresponding proportionality constant having spontaneous ($\sim \pi_{aa}^{(0)}$) and field-induced ($\sim \pi_{aa}^{(1)} E_a$) pyroelectric contributions.

Let us consider a FE state with $P_x^{(0)} > 0$, and imagine we apply an electric field $E_z > 0$. For simplicity (and without loss of generality), let us also assume that the dielectric response is dominated by the linear effect $\chi_{zz}^{(0)}$, higher order terms being negligible to a good approximation. In such a situation, it is physically sound to assume that the applied field creates order, as it contributes to further align the local electric dipoles in the FE state and results in a larger order parameter $P_z$. This field-induced ordering is captured by $\chi_{zz}^{(0)}$, and we know that the effect gets stronger as we approach $T \lesssim T_C$. As a result of this ordering, we expect the entropy to decrease in an isothermal process ($\Delta S_z < 0$), and the temperature to rise ($\Delta T_z > 0$) if the process is adiabatic. These are clear expectations that one would hardly question.

Let us inspect how these expected variations of $S$ and $T$ come about in our formalism. Following the simplification mentioned above (linear dielectric response), we can write $\Delta S(z) \approx \Delta S^{(1)}(z) + \Delta S^{(2)}(z)$. (The discussion for $\Delta T(z)$ is analogous.) The first term ($\Delta S^{(1)}(z) = \pi_{zz}^{(0)} E_z$) results in a reduction of the entropy, as we have $\pi_{zz}^{(0)} < 0$ for the spontaneous pyroelectric effect. This seems consistent with the ordering argument given above. However, it is important to stress that this term does not contain any information about the dielectric response to the applied field, or about the order the field may create. (There is no generally expected thermodynamic relationship between $\partial P_z / \partial E_z$ and $\partial P_z / \partial T$.) Instead, the entropy change is fully determined by the $T$-dependence of the spontaneous polarization: $P_z^{(0)} > 0$ decreases as we approach $T_C$, a behavior that is normal.

The response to an applied field does control the quadratic contribution $\Delta S^{(2)}(z)$, where the spontaneous pyroelectric effect in $\Delta S^{(0)}(z)$ is replaced by the field-induced one ($\sim \pi_{zz}^{(1)} E_z$). As mentioned above, it is clear that the applied field strengthens the dipole order of the FE state, as quantified by its order parameter: we have $P_z^{(0)} > 0$ and a field-induced polarization change $\varepsilon_0 \chi_{zz}^{(0)} E_z > 0$. However, the corresponding en-
entropy change is positive, since \( \pi_{zz}(1) \propto \partial \chi_{zz}(0)/\partial T > 0 \) for \( T < T_C \). Thus, the same physical mechanism (captured by \( \chi_{zz}(0) \)) results in field-induced order and a positive contribution to the entropy. Indeed, in what concerns the isothermal entropy change, what matters is not the ordering of the dipoles at a given \( T \). Instead, we have to pay attention to how the field-induced effect changes with temperature. In a FE state, the ordering caused by the field grows as we heat up towards \( T_C \), that is, we have a positive field-induced pyroelectric effect. This somewhat anomalous behavior (the higher the temperature, the greater the – induced – order) is opposite to the spontaneous pyroelectric effect, and is the one causing \( \Delta S(2)(z) > 0 \) (and \( \Delta T(2)(z) < 0 \)).

Hence, the quadratic contribution to the EC effect in a FE state, dominated by the linear susceptibility \( \chi_{zz} \), seems paradoxical: the field creates order (as quantified by the order parameter) but the entropy increases. The key to the puzzle is that polarization (order) created at a given \( T \) is not what controls the entropy; its \( T \)-derivative is. This point is hardly new, as it is quite clear from the well-known equations governing EC effects (Eqs. (1) and (2)); yet, it becomes particularly apparent in our perturbative approach.

Keeping the above in mind, it is easy to interpret the EC effects in PE and AFE states, which are dominated by the quadratic contribution. In the PE case, the field-induced order decreases as \( T \) increases: at \( T > T_C \) we have \( \pi_{zz}(2) < 0 \), which yields \( \Delta S(z) \approx \Delta S(2)(z) < 0 \) and \( \Delta T(z) \approx \Delta T(2)(z) > 0 \). It is tempting to interpret this result by focusing on the response at a given \( T \) (the field creates order, hence the entropy should get reduced), but that would not be correct. Instead, the focus should be on the field-induced pyroelectric effect which, in this case, behaves in the normal way, i.e., we have a weaker – induced – order at higher temperature.

Finally, the inverse EC behaviour of AFE states is also readily explained within this picture. In that case we are at \( T < T_C \), and have \( \Delta S(z) \approx \Delta S(2)(z) \propto (\pi_{zz}(E_z)E_z > 0 \) (and \( \Delta T(z) \approx \Delta T(2)(z) < 0 \)). According to the above discussion, this inverse behavior stems from the fact that the applied field creates polarization more efficiently as \( T \) grows toward \( T_C \). Consequently, this disproves the frequent interpretation that the inverse EC response of AFE states is caused by field-induced disorder at a given \( T \). As a matter of fact, the above analysis shows that arguments focusing on the field-induced (dis)order at a given \( T \) – and overlooking the \( T \)-derivative – are incorrect.

To conclude this part, let us comment on a FE type absent in our discussion: relaxors. As mentioned above (Eq. (1)), ergodicity breaks down in these materials, and the use of the Maxwell relation our formalism relies on is questionable. Nevertheless, some experimental [33] and theoretical [12] reports suggest that, in fact, Eq. (1) approximately captures the EC response of these systems at a quantitative level; further, it seems to yield qualitatively correct results. Hence, we think that, in the future, it may be worth considering whether our formalism, and the kind of rules summarized in Table [1] might be useful in investigations of relaxors.

In summary, we have introduced a perturbative approach to the electrocaloric effect. This formalism can be applied in quantitative simulation studies, in a straightforward way as long as field-induced (first-order) phase transitions are not present. More specifically, our simulations for ferroelectric \( \text{PbTiO}_3 \) show that, except in the vicinity of the phase transition, a low-order approximation captures the electrocaloric response with great quantitative accuracy. Most importantly, our formalism unifies and clarifies the physical interpretation of all the small-field electrocaloric effects (normal and inverse) observed in ferroelectric and antiferroelectric materials.

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