Temperature-dependent dielectric response of $BaTiO_3$ from first principles

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Abstract. Monte Carlo simulations with an effective Hamiltonian parametrized from first principles are performed to study the dielectric response of $BaTiO_3$ as a function of temperature, with particular emphasis on the behavior of the dielectric constant near the transition from the ferroelectric tetragonal phase to the paraelectric cubic phase.

The peculiar dielectric properties of ferroelectric materials stem from the coupling of the electric field to polar distortions of the crystal lattice. In one common scenario, the progressive softening of a lattice vibrational mode in the neighborhood of a phase transition brings about a dramatic rise in the value of the dielectric constant. The resulting very large relative permitivities (in the thousands range) have found important technological applications. From a practical point of view, however, the development of materials with a desired response faces the difficulty of trying to separate experimentally the influences of many effects: composition, structure, domain configuration, etc. There are also open theoretical issues such as whether the relevant phase transitions are indeed associated to the above-mentioned "soft-mode" (and are thus of "displacive" character) or exhibit "order-disorder" characteristics. The use of first-principles calculations can help in both fronts. They allow the study of the response of a system under "controlled" conditions that would be very difficult or impossible to realize in the laboratory. Besides, they provide a microscopic view of the materials which is simply not available experimentally and, unlike simplified models, they are tailored to the detailed chemical composition of the system.

In the last few years much progress has been made in the computational study of ferroelectric materials through the use of effective Hamiltonians which contain the physically relevant degrees of freedom of the structure. The effective Hamiltonians are constructed on the basis of first-principles calculations, and the statistical mechanics of the system is then studied by Monte Carlo simulation. Calculations of the phase transition sequence [1] and ferroelectric domain walls [2] in $BaTiO_3$, and of the ferroelectric transition in $PbTiO_3$ [3], have proved the usefulness of this approach.

In this work we present the first calculations of the temperature-dependent dielectric response of the perovskite $BaTiO_3$ from first principles, with particular emphasis on the behavior of the dielectric tensor in the vicinity of the phase transition from the tetragonal ferroelectric to the cubic paraelectric phase.

The basic ingredient of the Metropolis Monte Carlo algorithm is the generation of a sequence of states which are distributed according to the Boltzmann probability $\mathrm{Prob}_j = \exp(-\beta U^j)$, where U^j is the energy of the state j and $\beta = (kT)^{-1}$. A state j_{n+1} is added to the sequence after state j_n on the basis of a transition probability $\pi(n, n+1) = \min\{1, \exp[\beta(U^{j_n} - U^{j_{n+1}})]\}$. In our method the energy U of the system is represented by means of an effective Hamiltonian $H_{\rm eff}$ which is basically a Taylor expansion of the energy surface around the high-symmetry cubic perovskite structure. $H_{\rm eff}$ is written in terms of the dynamical variables which are relevant to the low-energy distortions: the amplitudes $\{\mathbf{u}\}$ of the local modes (three degrees of freedom per unit cell) which represent the "soft" transverse optical phonon and are directly related to the polarization $\mathbf{P}$ of the crystal [4] [$\mathbf{P} = (Z^*/V)\sum \mathbf{u}$, where Z^* is the mode effective charge and V is the cell volume]; a set $\{\mathbf{v}\}$ of displacement variables representing the acoustic modes; and the six components of the homogeneous strain η. The parameters of the energy expansion, including those for the on-site local-mode self-energy, the interaction between local modes (both short-range and dipole-dipole), the elastic energy, and the local mode-elastic coupling, are computed using highly accurate first-principles LDA calculations with Vanderbilt ultrasoft pseudopotentials [5]. More details about the construction of the effective Hamiltonian can be found in Ref. [1]. The extension of the standard Metropolis Monte Carlo algorithm to include the effects of stress σ and electric field $\mathbf{E}$ involves replacing the Boltzmann probability factor $\exp(-\beta U^j)$ by $\exp[-\beta(U^j - V_0\sigma_\nu\eta^j_\nu - E_i\mathcal{P}^j_i)]$ in the acceptance criterion for state j (here $\mathcal{P}_i = VP_i$ is the ith component of the net dipole moment of the crystal and V_0 is the volume for zero strain). For a given temperature, stress, and field, the strain η and the mode variables are allowed to fluctuate, their average values determining the strain and net polarization of the system. This extended framework has recently been used to study the piezoelectric response of $BaTiO_3$ as a function of temperature, and to illustrate the influence of electric fields on the phase diagram of this material [6].

Here, we use this approach to compute the dielectric response of the cubic and the tetragonal (ferroelectric) phases of $BaTiO_3$. The tetragonal phase is stable from approximately 278K to 403K and exhibits a spontaneous polarization that we take to be along the z axis. The linear dielectric response coefficients (dielectric tensor) are given, in S.I. units, by $\varepsilon_{ij} = \varepsilon_0(1+\chi_{ij})$, where χ_{ij} is the dimensionless dielectric susceptibility defined by

$$\chi_{ij} = \frac{1}{\varepsilon_0}\left(\frac{\partial P_i}{\partial E_j}\right)_{\sigma,T} \simeq \frac{1}{V\varepsilon_0}\left(\frac{\partial \mathcal{P}_i}{\partial E_j}\right)_{\sigma,T} = \frac{1}{V\varepsilon_0}\beta\left(\langle\mathcal{P}_i\mathcal{P}_j\rangle - \langle\mathcal{P}_i\rangle\langle\mathcal{P}_j\rangle\right). \qquad (1)$$

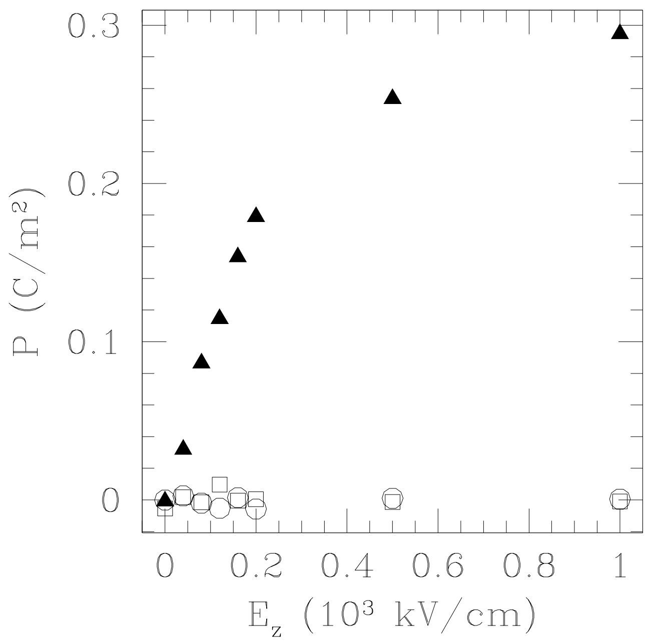

FIGURE 1. Average polarization vs. electric field for the cubic phase of $BaTiO_3$ at a rescaled temperature of 500K. Solid triangles and open circles and squares represent the z, x, and y components of the polarization, respectively.

The approximate equality reflects the neglect of the field derivative of the volume [7]. Here the averages are to be computed using the extended Boltzmann factor defined above [8]. According to these equations, one could either compute the linear dielectric response from direct calculations of the average polarization as a function of electric field ("direct approach"), or from an analysis of the statistical correlation between polarization components ("correlation approach").

As an example of the direct approach, we show in Fig. 1 the results of a series of simulations for the cubic phase in which an electric field of progressively greater magnitude is applied along the z direction. For each field value, the simulation box (a cube with $10 \times 10 \times 10 = 1000$ unit cells) was allowed to equilibrate for 2×10^4 Monte Carlo sweeps (MCS) [9] and polarization averages were taken over another 2×10^4 MCS. A fit to the P_z vs. E_z curve in the linear region corresponding to field strengths up to approximately 150 kV/cm can be used to extract the dielectric susceptibility. For higher fields, nonlinear effects are clearly present. It is important to realize that the nonlinearity is not put in explicitly, as the only extra term in the simulation is $-E_i \Delta \mathcal{P}_i$, which is linear in the field. The nonlinearity appears through the terms of higher order in the local mode variables $\{\mathbf{u}\}$ (and their coupling to the strain) in the effective Hamiltonian. A closer analysis of these effects could form the starting point of an investigation of the nonlinear dielectric response in this material.

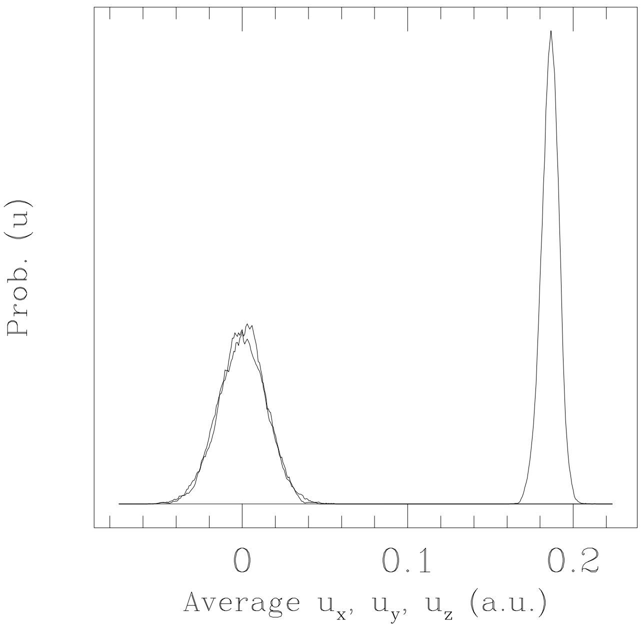

FIGURE 2. Probability histograms for the local mode components in the tetragonal phase, obtained from a run with 3×10^5 MCS and an $L = 14$ simulation box (rescaled temperature: 355 K). The vertical scale is arbitrary.

The computation of linear response coefficients from the correlation approach requires only one simulation at zero field, although relatively long runs (of at least 10^5 MCS) are needed to obtain good statistics. Also, the quality of the calculated correlations should improve with the size of the simulation box (recall that the relations in Eq. 1 are strictly valid only in the thermodynamic limit). We have therefore performed our calculations using larger boxes, with $12 \times 12 \times 12 = 1728$ ($L = 12$) and $14 \times 14 \times 14 = 2744$ ($L = 14$) unit cells. Figure 2 shows histograms for the averages of the three components of the local mode in the tetragonal phase, computed with an $L = 14$ box and 3×10^5 MCS. The profiles are quite clean and gaussian-looking. The diagonal components of χ (which are the relevant ones for the tetragonal and cubic phases) are related to the width of the statistical distribution of the corresponding component of $\mathbf{P}$, and thus to the standard deviation of the system-average of the local mode amplitudes. Wider distributions (such as those for the x and y components in Fig. 2) indicate larger values for the corresponding components of the dielectric tensor.

Note that the correlation method provides information about the whole tensor from a single run, which is particularly economical when dealing with lower-symmetry phases. In these cases the use of the direct method becomes more cumbersome. For example, the determination of χ_{33} and χ_{11} for the tetragonal phase would involve two separate series of direct calculations, for varying E_z and E_x,

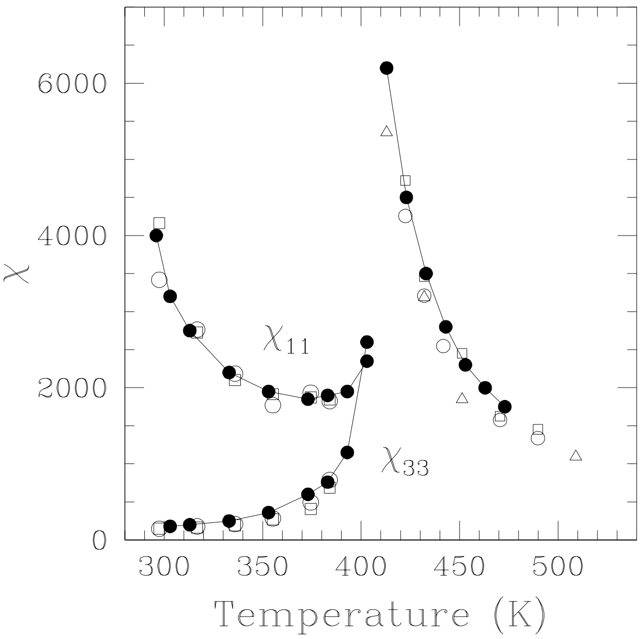

FIGURE 3. Constant-stress dielectric susceptibility for the tetragonal and cubic phases of $BaTiO_3$. Solid circles are experimental data from Ref. [12]. Open symbols represent computed values, plotted vs. rescaled temperature (see text). Triangles are from direct P vs. E simulations, and circles and squares are from correlation analysis with $L = 12$ and $L = 14$ boxes, respectively.

respectively. In the latter, extra care would be needed at temperatures close to the transition to ensure that a transverse field does not cause a switch of the spontaneous polarization from the z to the x direction.

Before presenting our results we must discuss an important point regarding the temperature scale. An effective Hamiltonian based on a *finite* Taylor expansion of the energy should not be expected to reproduce perfectly the behavior of the material at relatively high temperatures. In particular (see Ref. [1]) the theoretical transition temperatures are progressively shifted downwards with respect to the true ones [10], the agreement worsening as the temperature increases. This shift might be related to the neglect of higher order terms in the interaction between local modes in $H_{\rm eff}$, as transition temperatures depend basically on the details of the interaction (as a simple example, recall the Ising model, for which T_c is proportional to the spin-spin coupling J) [11]. In order to provide a better comparison of our results to experiment, we have therefore linearly rescaled the theoretical temperatures so that the end points of the range of stability of the tetragonal phase coincide with the experimental T_c's. The rescaling is also extrapolated into the range of stability of the cubic phase. By fixing the points at which phase transitions occur, we are able to focus on the consequences of lattice instability for the dielectric response. The more important, low-energy regions of the energy surface,

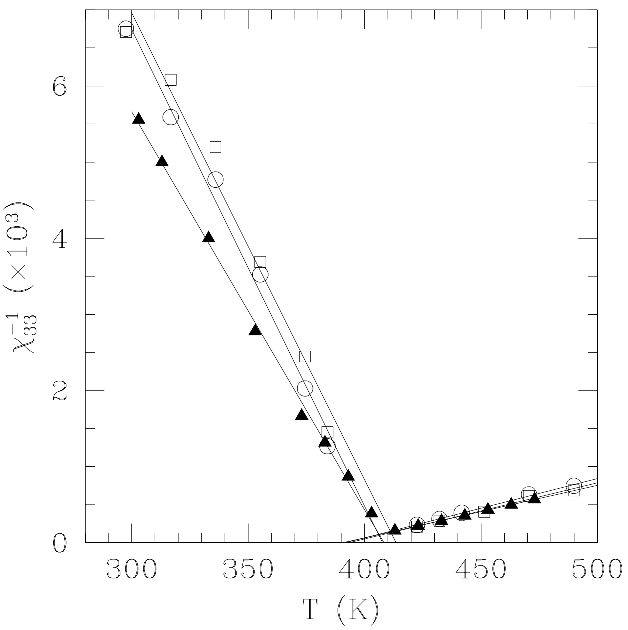

FIGURE 4. Fit of the inverse susceptibility to a Curie-Weiss form. Solid triangles are experimental data from Ref. [12]. Open circles and squares represent values computed from correlation analysis with $L = 12$ and $L = 14$ boxes, respectively.

which are correctly parametrized by our H_{eff}, presumably play the most important role in determining this response.

Figure 3 shows the computed constant-stress dielectric susceptibility for the cubic and tetragonal phases, together with recent experimental data [12] for the low-frequency dielectric response of $BaTiO_3$ [13]. The agreement is excellent, with the simulations reproducing in detail all the features of the observed behavior, including the large anisotropy of the dielectric tensor in the tetragonal phase. Our data from the direct simulation of the **P** vs. **E** curves (cubic phase only) and statistical correlation with various box sizes are comparable within the aforementioned limitations of a finite simulation box. Near the transition temperature T_c the pseudo-divergent behavior of χ_{33} can be approximated to a Curie-Weiss form $\chi_{33}^{-1} = C(T-T_0)$, where T_0 is a temperature close but not identical to T_c (Figure 4). The fitted values of the Curie temperature T_0 extracted from the tetragonal and cubic phases are very similar, reflecting the fact that the transition is only weakly first-order. The values of the Curie-Weiss constants above and below the transition are not related in a simple way in a first-order transition, but are predicted from mean-field arguments (Landau theory [14]) to satisfy $C_{below} = -2C_{above}$ for a second-order transition. Simulations with a three-dimensional ϕ^4 model [15] (which could be seen as a simplified form of our effective Hamiltonian) have shown that this mean-field relationship between the C constants is only valid in the limit of a pure displacive phase transition, and that $|C_{below}|/2C_{above}$ increases with the degree of order-disorder character. Our data (and experiment) show that $|C_{below}|/2C_{above} \simeq 4$. Assuming the deviations from mean-field behavior are similar for our $H_{\rm eff}$ and the ϕ^4 model, this result would be consistent with the analysis in Ref. [1] pointing to a relatively strong order-disorder character of the cubic-tetragonal transition in $BaTiO_3$.

In conclusion, we have shown how the temperature-dependent dielectric response of a system can be computed from first principles using an effective Hamiltonian and Monte Carlo simulations. As an application, we have presented the first calculations of the dielectric response of $BaTiO_3$ as a function of temperature. The analysis of the behavior of the dielectric susceptibility in the vicinity of the cubic-tetragonal transformation gives evidence for a certain degree of order-disorder character in the transition.

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4. To relate the net macroscopic polarization to the soft-mode average, thus excluding the contributions from other polar modes, is equivalent to assuming that there are no anharmonic effects in the dynamics of the other modes, so that their average amplitude is zero.
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8. The relationship between χ and the polarization correlations can be simply obtained by differentiation of the expression $\Lambda\langle X\rangle = \sum_j X^j \mathrm{Prob}_j$, where Prob_j is the extended Boltzmann factor, Λ is the extended partition function, and X is any component of the net polarization.
9. A Monte Carlo sweep is completed after each local variable is considered for a "flip attempt" and each component of the homogeneous strain suffers $2L+1$ attempted changes, where L is the linear size of the simulation box.
10. For the rhombohedral to orthorhombic to tetragonal to cubic transition sequence, the experimental T_c's are respectively 187K, 278K, and 403K, while the theoretical ones are 197K, 230K, and 295K.

11. Another possible source of the error in the computed values of transition temperatures is the underestimation by the LDA of the equilibrium lattice constant. The simulations are run at a negative effective pressure to compensate for this effect (see Ref. [1]).
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