## Atomistic study of soft-mode dynamics in PbTiO<sub>3</sub>

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Ferroelectric PbTiO<sub>3</sub> occupies a special place among ferroelectric materials owing to its unique status as a prototype displacive ferroelectric. However, while PbTiO<sub>3</sub> undoubtedly provides one of the best examples of displacive phase transitions, several experimental and theoretical findings seem to suggest a certain degree of order-disorder mechanism associated with the phase transition. While multiple efforts have been undertaken to better understand the nature of the phase transition in this classic ferroelectric, the subject still remains controversial. Here we develop a force field from first principles to study soft mode dynamics in PbTiO<sub>3</sub> from an atomistic viewpoint. Our computations indicate the presence of order-disorder mechanism in the vicinity of the phase transition in this classic displacive ferroelectric.

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PbTiO<sub>3</sub> is regarded as a model ferroelectric perovskite with mostly displacive first-order phase transition associated with softening of the relevant phonons. A microscopic explanation of the mode softening mechanism was proposed by Cochran<sup>1</sup> and derives its origin from the competition between the shortrange interaction which stabilizes the paraelectric phase and a long-range interaction which stabilizes the ferroelectric phase. Near the Curie point the short- and long-range interactions compensate each other in such a way that the frequency of a transverse optical (TO) phonon approaches zero.

Interestingly, while PbTiO<sub>3</sub> indeed provides one of the best example of the displacive phase transition associated with softening of polar mostly underdamped modes, the possibility of an additional excitation associated with order-disorder mechanism has been considered in the literature.<sup>2–7</sup> However, despite considerable efforts towards a better understanding of the soft mode dynamics and nature of the phase transition in this material,<sup>2,7–18</sup> the issue remains controversial. In fact, the most recent experimental study concludes that PbTiO<sub>3</sub> constitutes a clean example of soft-mode-driven ferroelectric system.<sup>18</sup>

The static permittivity of the ferroelectrics with displacive first-order phase transition is expected to follow the Curie-Weiss law  $\varepsilon(0)^{-1} = C(T - T_0)$ . Here C is a constant and  $T_0$  is the temperature associated with the divergence of the static permittivity. Using the Lydanne-Sachs-Teller formula<sup>19</sup> one can relate the static permittivity to the frequency of polar modes which yield the Curie-Weiss law for the frequency of the soft TO mode:  $(\hbar \omega_s)^2 = A_s (T - T_0)$ , where  $A_s$  is a constant. However, in the case of  $PbTiO_3$  the  $T_0$  obtained from the static and dynamical measurements are not the same and could be 10 K apart.<sup>10,15,16,20</sup> Typically,  $T_0$  found from the dynamical measurements are lower than those obtained from the static one.<sup>10,15</sup> It was proposed that this discrepancy between the static and dynamical  $T_0$  could be due to the presence of the so-called "central" mode which is typically associated with the order-disorder mechanism.<sup>15</sup> However, except for Ref. 2 this central mode has not been observed experimentally, and is generally not expected to exist in materials with sharp and underdamped modes such as PbTiO<sub>3</sub>.

As experiments probing mode softening mechanisms are quite challenging<sup>18</sup> the atomistic insight from first-principles calculations becomes critical in providing the answers to

the fundamental questions regarding the nature of the phase transitions and soft mode dynamics in PbTiO<sub>3</sub>. At zero Kelvin, density functional theory based computations have been successfully used to study dynamical properties of PbTiO<sub>3</sub>.<sup>21,22</sup> However, finite temperatures studies of these systems do not exist at present. The purpose of this paper is to fill up this gap and provide an atomistic first-principles view on the nature of the phase transition and the soft mode dynamics in PbTiO<sub>3</sub>. More precisely, in this paper we aim: (i) to develop a first-principles force field that allows simultaneously accurate description of both static and dynamical properties of PbTiO<sub>3</sub>; (ii) use this force field to study the dynamics of the TO modes in a wide range of temperatures; and (iii) provide an atomistic first-principles-based insight into the open questions and controversies regarding this classic ferroelectric.

We begin by developing the first-principles parametrization of a force field for PbTiO<sub>3</sub> on the basis of the effective Hamiltonian.<sup>23–26</sup> The degrees of freedom for the Hamiltonian are local soft modes which are proportional to the dipole moment of a unit cell, homogeneous and inhomogeneous strain variables. The Hamiltonian includes a local mode self energy (harmonic and unharmonic contributions), a long-range dipole-dipole interaction, a short-range interaction between local modes, an elastic energy, and the interaction between the local modes and strains.<sup>23,25,26</sup> The critical differences of our parametrization are the following: (i) The polar distortions are defined as the distortions from the ideal positions in the tetragonal state of PbTiO<sub>3</sub> rather than from the eigenvector of the interatomic force-constant matrix; (ii) the first-principles energies of tetragonal, orthorhombic, and rhombohedral phases are explicitly included in the parametrization through the parameters that couple the local mode and local strain; (iii) all the short-range interaction parameters are computed directly. Furthermore, we center the local mode on the Pb site since the largest polar distortion in the unit cell is associated with the Pb. The local strain is centered on the Ti site. This parametrization accurately reproduces the Born-Oppenheimer first-principles energy landscape associated with the chosen distortions. However, the subspace associated with these distortions does not necessarily provide an accurate description of the dynamical properties which require parametrization based on the eigenvector(s) of the dynamical matrix. The critical question then is: Is it possible to achieve a simultaneously accurate description of the static and dynamical properties of ferroelectric perovskites at a finite temperature? And if yes, what is the route?

To answer these questions we compute zero temperature frequencies of the  $A_1(TO1)$  and E(TO1) modes in the tetragonal state using the force field of the effective Hamiltonian. This is done by solving the equations of motion for the zone-center soft mode analytically. The force acting on the mode is computed from the Taylor expansion of the zonecenter effective Hamiltonian<sup>24</sup>  $E = ku^2 + \alpha' u^4 + \gamma' (u_x^2 u_y^2 + \alpha' u^4 + \alpha'$  $u_{y}^{2}u_{z}^{2} + u_{z}^{2}u_{x}^{2}$ ) up to the harmonic order in the vicinity of the tetragonal minimum. Here  $u_x, u_y$ , and  $u_z$  are the components of the soft mode, while  $u = |\mathbf{u}| \cdot k$ ,  $\alpha'$  and  $\gamma'$  are the first-principles parameters. Prime indicates that parameters are renormalized to include the coupling with strain.<sup>24</sup> We obtain the following frequencies  $\omega_{A_1(TO1)} = \sqrt{-\frac{4\kappa}{m}}$  and  $\omega_{E(TO1)} = \sqrt{-\frac{\kappa\gamma'}{m\alpha'}}$ , where *m* is the mass of the local mode. The mass can now be parametrized using first principles  $\omega_{A_1(TO1)}$ . This completes the set of the first-principles parameters which we will denote as the "static" one. The static parameters, however, underestimate the first principles  $\omega_{E(TO1)}$  by 12%. This is the direct consequence of the aforementioned problem of simultaneous description of static and dynamical properties by the effective Hamiltonian. Interestingly, there exists a way to resolve the issue. It can be shown that it is possible to exactly match the first principles  $\omega_{E(TO1)}$  without affecting the description of any ground state properties by recomputing only two parameters of the effective Hamiltonian. These are the two coupling coefficients between the local mode and local strain. This slightly modified set of parameters will be referred to as "dynamical." The complete set of all parameters is listed in Table I. To obtain the parameters we have used local density approximation to density functional theory (DFT) as implemented in the VASP package.<sup>27,28</sup> The calculations were carried out on 5- and 40-atom cells using the plane-wave basis truncated at 600 eV. For some calculations linear-response density functional perturbation theory computations were used. Table II gives a comparison between the predictions of the effective Hamiltonian, DFT computations, and some available experimental data and demonstrates the accuracy of parametrization.

To study the static and dynamical properties of  $PbTiO_3$  at finite temperatures we used both sets of parameters in the framework of classical molecular dynamics (MD).

TABLE I. First-principles parameters for  $PbTiO_3$  in atomic units using the notations of Ref. 26. Static parameters are given in parenthesis.

On-site	κ <sub>2</sub>	0.01722	α	0.02635	γ	-0.01382
Intersite	$egin{array}{c} j_1 \ j_3 \ j_6 \end{array}$	-0.01290 0.00289 0.00018	j2 j4 j7	0.04077 -0.00235 0.00045	j5	0.00350
Elastic	$B_{11}$	4.74599	$B_{12}$	1.86162	$B_{44}$	1.39531
Coupling	$B_{1xx}$	-0.66101 (-0.68134)	$B_{1yy}$	-0.07801 (-0.13289)	$B_{4yz}$	-0.04681
Other	$Z^*$	9.147	$\epsilon_{\infty}$	8.715	т	58.5

TABLE II. Some ground state properties of PbTiO<sub>3</sub> as obtained from DFT, effective Hamiltonian (Heff), and experiment (Exp). The \* indicates that the energy is estimated from the Curie point. The experimental data are reported for room temperature and taken from Ref. 29 for  $P_s$ , from Ref. 10 for c/a, and from Ref. 13 for frequencies.

	$\Delta E_T$	$\Delta E_{O}$	$\Delta E_R$	c/a	$P_S$	$\omega_{E(TO1)}$	$\omega_{A_1(TO1)}$
	(K)	(K)	(K)		$(\mu C/cm^2)$	$(cm^{-1})$	$(cm^{-1})$
DFT	-668.4	-564.6	-533.1	1.044	75.2	73.9	139.5
Heff	-690.7	-539.5	-502.8	1.041	82.1	73.9	139.5
	(-690.7)	(-567.8)	(-536.0)	(1.039)	(81.9)	(64.9)	(139.5)
Exp	$-760.0^{*}$			1.06	75.0	87.5	148.5

Simulations were done for  $20 \times 20 \times 20$  supercell (40 000 particles) with periodic boundary conditions applied along all three directions to simulate bulk system. Static properties were simulated using the annealing technique with the temperature step of 5 K (0.5 K in the vicinity of the phase transition) within the NPT ensemble. For each temperature step we used 40 000 MD steps. To access the dynamical properties at finite temperatures at a quantitative level we simulated the complex dielectric response of PbTiO<sub>3</sub> in the THz frequency range following the approach of Ref. 30 with one critical difference. In the present simulations the NPT ensemble is used throughout the entire run (2.1 ns) to simulate a free standing sample. We found that, in agreement with experimental studies, the complex dielectric responses are well fitted with the model of damped harmonic oscillator<sup>30</sup> which allows one to obtain the intrinsic mode frequencies  $\omega_i$ , damping parameters  $\gamma_i$ , and the oscillator strength  $\Delta S_i$ . Here index *i* refers to different modes.

Figure 1(a) reports the tetragonality c/a and spontaneous polarization P as a function of temperature as obtained from the simulations. We first notice that both sets of parameters yield similar static properties. Furthermore, the simulations predict first-order-like phase transition with  $T_C = 605 \pm$  $5(625 \pm 5)$  K as determined from static dielectric constant in annealing calculations. Note, that throughout the paper we will quote the data obtained with dynamical set of parameters, while the data from calculations using a static set of parameters will be given in parenthesis. Interestingly, we find that there exists a narrow region of temperatures in the vicinity of the phase transition where the polarization exhibits drastic fluctuations in both magnitude and direction [see Fig. 1(b)]. This region is estimated<sup>31</sup> to be 601–620(625–645) K and associated with polarization rotation, disappearance, and reappearance. Note that the region is inclusive of the temperatures associated with the polarization fluctuations as obtained from both cooling and heating simulations. This behavior seems to suggest that there may exist an order-disorder component to the phase transition as was proposed in Refs. 2-7. Note that the order-disorder character here refers to the *dynamics* of the phase transition. More specifically, it implies that the soft mode has a diffusive, rather than propagating, character which is associated with large thermal hopping motion between multiple states.<sup>32</sup> To gain further insight we have followed the time evolution of the polarization during 2.1 ns for a few temperatures in the vicinity of the phase transition. The computational data



FIG. 1. (Color online) (a) Dependence of the tetragonality c/a (left y axis) and polarization (right y axis) on the temperature for both static and dynamical sets of parameters. (b) Dependence of the Cartesian components of polarization on the temperature in the vicinity of the phase transition as obtained from calculations with the dynamical set of parameters. Arrows indicate the large fluctuations in polarization. (c) The time evolution of the Cartesian components of the polarization at T = 603 K as obtained from a 2.1 ns MD run using the dynamical set of parameters. (d) The probability distribution  $n(\mathbf{P})$  of the Cartesian components of the polarization at T = 603 K as obtained from data given in panel (c).  $n(P_{\beta})$  gives the fraction of the total simulation time spent in a state  $P_{\beta}$ , where  $\beta$  refers to Cartesian coordinates.

for the polarization components are given in Fig. 1(c) and demonstrate large-amplitude thermal hopping between the states associated with different polarizations. The probability distribution for the polarization components computed from such a run is given in Fig. 1(d). The presence of multiple peaks unambiguously demonstrates the order-disorder mechanism associated with this temperature. Similar data were obtained for some other temperatures inside the region associated with large polarization fluctuations and also from an additional set of Monte Carlo simulations.

To gain further insight into the dynamics of the phase transition as well as the soft mode dynamics in general, we computed the complex dielectric response of  $PbTiO_3$  in a wide range of temperatures. An example of our computational data for the real and imaginary parts of the dielectric response is given in Fig. 2. In agreement with Ref. 30, we find that the data in the paraelectric phase can be well fitted with the model of a single damped harmonic oscillator. In the ferroelectric phase two uncoupled oscillators representing the modes of E and A<sub>1</sub> symmetries are sufficient to describe the response. Furthermore, we find that except for a very narrow region in the vicinity of the phase transition the modes are underdamped.

Our data for the dependence of the intrinsic frequency of the soft mode(s) on the temperature are given in Fig. 3(a).

In the paraelectric phase, the frequency of the soft TO mode follows the Curie-Weiss law with  $T_0 = 591 \pm 0.6(620 \pm$ 1.5) K. Interestingly, this "dynamic"  $T_0$  slightly below the "static"  $T_0 = 597 \pm 6(624 \pm 7)$  K obtained from the static dielectric response computations suggesting that in the vicinity of the phase transition the order-disorder mechanism may become sufficiently strong to contribute to the static dielectric constant. More specifically, the frequency of the thermal hopping between different states becomes comparable or higher than the frequency of the soft displacive mode. The possibility of such crossover between displacive and order-disorder mechanisms has been previously suggested in Refs. 2,5, and 7. The difference between the "static" and "dynamic"  $T_0$  is in qualitative agreement with the most recent experimental finding that reported  $12 \pm 15$  K.<sup>18</sup> The orderdisorder mechanism is usually associated with the presence of the central mode. We were unable to directly observe the central mode due to computational limitations. However, the frequency of such a mode can be estimated from the inverse lifetimes associated with different states in Figs. 1(c) and 1(d). We find that at T = 603 K the inverse lifetime is of the order of GHz, consistent with the frequency of the central peak in Ref. 2. It should also be stressed that our data for the soft mode frequencies are in remarkable



FIG. 2. (Color online) The real (a) and imaginary (b) parts of the complex dielectric response in  $PbTiO_3$  for a few temperatures. Symbols represent the computational data, while solid lines provide the fit with a damped harmonic oscillator model.

agreement with the most recent experimental measurements of Ref. 18, which further confirms the accuracy of our model.

In the ferroelectric phase the frequency of the A<sub>1</sub>(TO1) mode follows the Curie-Weiss law  $w^2 = A(T - T_0^f)$  with  $T_0^f = 615 \pm 1.5(644 \pm 3)$  K. We find that in agreement with Ref. 7  $T_0^f$  is higher than  $T_C$ . For the E(TO1) mode we observe that it follows the modified Curie-Weiss law  $w^2 = A(T - T_0^f)^q$  with q = 0.27(0.23). Thus the temperature evolution of the soft mode frequency suggests that in the range of temperatures ( $T_0 : T_0^f$ ) there exist multiple minima in the free energy of PbTiO<sub>3</sub> as consistent with the first-order character of its phase transition. This finding in combination with our direct observation of the thermal hopping between these minima in the range of temperatures 601-620(625-645) K indicates that the phase transition in PbTiO<sub>3</sub> exhibits an order-disorder component.

Figure 3(b) gives computational data for the damping parameter  $\gamma$  associated with the modes investigated as a function of temperature. It should be noted that the temperature evolution of the damping parameter in PbTiO<sub>3</sub> is somewhat controversial. In the seminal works by Burns and Scott<sup>8,9</sup> it was concluded that in the ferroelectric phase the soft TO modes are underdamped with the damping constant diverging as the Curie point approaches. In a later study,<sup>11</sup> it was proposed that the observed divergence of the damping is a consequence of the frequency dependence of the damping parameter. Such frequency dependence of the damping parameter, however, turned out to be controversial as it was demonstrated that the right-angle Raman results can be fit very well using a model of frequency independent damping.<sup>12</sup> In the most recent experimental study the damping parameter has shown only a very small variation with the temperature in the cubic phase.<sup>18</sup> We observe that, in agreement with Refs. 9 and 12,



FIG. 3. (Color online) (a) The soft mode frequency as a function of temperature as obtained using dynamical and static set of parameters. The lines indicate the Curie-Weiss fit discussed in the text. Note, that temperatures taken from Ref. 18 were shifted as  $T = T - \Delta T_C$ , where  $\Delta T_C$  is the difference between the experimental and computational  $T_C$ . (b) Damping parameter as a function of temperature.

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the damping parameter diverges in the vicinity of the phase transition. We find that the frequency independent damping provides an excellent fit to our computational data on the complex dielectric response (see Fig. 2 for an example). To gain further insight into the controversy regrading the frequency dependence of the damping parameter we performed additional calculations in which an ac electric field with a small amplitude and different frequencies is applied to the supercell at a constant temperature T = 800 K. In these simulations we found that within the error of the computational data the damping is independent of the frequency. Therefore, our data suggest that the damping is independent of the frequency and diverges at the Curie point. It is likely that the divergence of the damping parameter is related to the increased or even dominant contribution from relaxational (order-disorder) mode since it occurs in the temperature range associated with this mode.

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In summary, we have proposed a route to first-principles parametrization of force fields for ferroelectric perovskites which yields simultaneously accurate descriptions of both static and dynamical properties of the material. The case of classic ferroelectric PbTiO<sub>3</sub> was considered. The computational data indicated that, while the ferroelectric transition is driven by the soft mode, there exists a narrow temperature region in the vicinity of the Curie point associated with the order-disorder mechanism.

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