## Ab initio elasticity at finite temperature and stress in ferroelectrics

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Computing the temperature and stress dependence of the elastic constants from first principles in noncubic materials remains a challenging problem. Here, we circumvent the aforementioned challenge via the generalized quasiharmonic approximation (gQHA) with the irreducible derivative approach for computing strain-dependent phonons using finite difference, explicitly including dipole-quadrupole contributions. We showcase the gQHA in ferroelectric PbTiO<sub>3</sub>, computing all elastic constants and piezoelectric strain coefficients at finite temperature and stress. The gQHA overestimates the temperature dependence of the lattice parameters and elastic constant tensor, demonstrating the need for an explicit treatment of lattice anharmonicity as a function of strain.

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Ferroelectric materials have been widely studied due to technological importance and interesting physics [1-5]. Many ferroelectric materials are band insulators, which are typically well described by density functional theory (DFT) when using an appropriate exchange-correlation functional. Various studies of ferroelectrics which parametrize an interacting phonon Hamiltonian based on DFT and solve the Hamiltonian within quantum Monte Carlo have produced temperature-dependent structural phase transitions consistent with experiment [6-9]. However, evaluating piezoelectric properties at finite temperatures and stress requires the computation of relevant strain curvatures of the DFT-based vibrational free energy at finite temperatures and stress (i.e., the elastic constants). Computing these elastic constants requires encoding or sampling the vibrational Hamiltonian as a function of strain, evaluating the vibrational free energy in some approximation as a function of strain, and evaluating the second strain derivatives of the free energy. Each of the aforementioned tasks presents substantial theoretical and computational challenges.

The standard approximation for computing finite temperature elastic constants is the quasiharmonic approximation (QHA) [10-13], yielding reasonable agreement with experimental measurements for a variety of cubic systems [14-21]. The computational cost of executing the QHA within DFT is appreciable [22], as evidenced by the sparsity of temperaturedependent elastic constant computations for noncubic systems available in the literature [23-25], and we are not aware of any published results at finite temperature and anisotropic stress. The aforementioned limitations can be mitigated by using the recently developed generalized quasiharmonic approximation (gQHA) [26], which leverages the irreducible derivative approach to computing phonons [27,28]. We define the gQHA as a harmonic truncation of the Born-Oppenheimer potential at a given strain, where no additional approximations are made when evaluating the free energy or any other thermal averages. Here, we showcase the power of the gQHA by studying the displacive ferroelectric PbTiO<sub>3</sub> (space group P4mm) using DFT, computing the lattice parameters, full elastic constant tensor, and piezoelectric strain coefficients at finite temperature and stress. PbTiO<sub>3</sub> is an ideal candidate to study within the gQHA, as the low-symmetry ferroelectric phase persists to approximately T = 760 K [29–31].

DFT calculations were performed using the Vienna ab initio simulation package (VASP) [32-35] with the projector augmented-wave (PAW) method [36,37] unless otherwise stated. The generalized gradient approximation (GGA) revised for solids (PBEsol) [38] and the strongly constrained and appropriately normed (SCAN) [39] exchange-correlation functionals were used. Convergence of the strain-dependent phonons was achieved with a kinetic energy cutoff of 1000 eV and a  $\Gamma$ -centered **k**-point mesh of  $16 \times 16 \times 16$  for the primitive unit cell with corresponding mesh densities being used for supercells. Details of the PAW potentials, computations of the phonons as a function of strain, and Fourier interpolation are provided in Sec. SI of the Supplemental Material (SM) [40]. The Taylor series expansion of the Born-Oppenheimer potential is truncated at fifth order in mixed displacement and strain derivatives unless otherwise stated. The validity of the fifth-order Taylor series expansion is confirmed up to T = 350 K by comparing to the thermal expansion resulting from the evaluation of the second-order irreducible derivatives on a strain grid and then interpolating (see SM for additional details [40]). The relaxed crystal structures using the PBEsol and SCAN functionals are compared with low-temperature experimental measurements in Table I. Due to the significant overestimation of the c lattice parameter by the SCAN functional, our computations use the PBEsol functional unless otherwise stated.

We begin by showcasing the phonons commensurate with the  $4 \times 4 \times 4$  supercell computed at the relaxed lattice parameters [see Fig. 1(a)], achieving reasonable agreement with previous computations [42]. The Fourier interpolated phonons include the dipole-dipole contribution [26,43,44] shown as the red lines, where the dielectric tensor and Born effective charges were calculated from density functional perturbation theory [45,46] within VASP. Along the path from the  $\Gamma$  point to the *R* point, there are interpolated imaginary phonon frequencies caused by a deficiency in the Fourier interpolation. Supplementing the interpolation with the dipole-quadrupole interactions has demonstrated the ability to remove these

TABLE I. Lattice parameters and direct atomic coordinates along the z direction. Top: Results of DFT relaxation using the PBEsol and SCAN functionals. Bottom: Results from the gQHA at T = 1 K compared with experimental measurements at T = 12 K [41].

Method	а	с	z(Ti)	$z(\mathbf{O}_1)$	$z(O_{2,3})$
PBEsol (DFT)	3.872	4.214	0.539	0.118	0.623
SCAN (DFT)	3.865	4.341	0.545	0.139	0.638
PBEsol (gQHA)	3.891	4.164	0.539	0.112	0.618
Mestric et al.	3.891	4.168	0.542	0.124	0.629

spurious imaginary frequencies from the interpolation [47]. Our Fourier interpolation of the phonons including the dipoledipole and the dipole-quadrupole contributions shown as the blue lines does not contain any spurious imaginary



FIG. 1. Phonons and specific Gruneisen parameters computed from DFT (diamonds) and Fourier interpolated (lines), in addition to the corresponding density of states. (a) Computed phonons which are Fourier interpolated with dipole-dipole (red) or dipole-dipole and dipole-quadrupole (blue) contributions. (b), (c) Gruneisen parameters corresponding to strains  $\epsilon_{A_1^\circ}$  and  $\epsilon_{B_1}$ , respectively.

frequencies. Computation of the dipole-quadrupole contribution has been implemented analogously to the dipole-dipole contribution, where dynamical quadrupoles were computed [48] using density functional theory implemented in the ABINIT package [49,50] using the PBEsol optimized normconserving Vanderbilt pseudopotential (ONCVPSP) [51]. Our results illustrate that both dipole-dipole and dipolequadrupole corrections to the Fourier interpolation can straightforwardly be utilized in our irreducible derivative approaches, which are based on the finite-difference method (see Appendix A of Ref. [26] and SM [40] for more information).

We now present generalized Gruneisen parameters  $\gamma_{i,\mathbf{q}\ell} =$  $-\frac{1}{\omega_{\mathbf{q}\ell}}\frac{\partial\omega_{\mathbf{q}\ell}}{\partial\epsilon_i}$  computed at the relaxed lattice parameters, encapsulating the first-order strain dependence of the phonons [see Figs. 1(b) and 1(c). Computation of the full elastic constant tensor within the gQHA requires the strain dependence of the phonons for all strains, whereas the thermal expansion only requires the strain dependence of phonons for strains that do not break point group symmetry (i.e., identity strains). In PbTiO<sub>3</sub>, the identity strains can be defined as  $\epsilon_{A_1^{\square}} = \frac{1}{\sqrt{2}}(\epsilon_{xx} + \epsilon_{yy})$  and  $\epsilon_{A_1^{\circ}} = \epsilon_{zz}$ , and the  $\epsilon_{A_1^{\circ}}$  Gruneisen parameter is shown in Fig. 1(b). Integration of the density of states yields averaged Gruneisen parameters of  $\bar{\gamma}_{A_1^{\square}} = 1.78$  and  $\bar{\gamma}_{A_1^{\circ}} = 0.28$ . The Gruneisen parameter of the nonidentity strain  $\epsilon_{B_1} = \frac{1}{\sqrt{2}} (\epsilon_{xx} - \epsilon_{xx})^2 + \frac{1}{\sqrt{2$  $\epsilon_{yy}$ ) is shown in Fig. 1(c). Symmetry selection rules and firstorder perturbation theory require nonidentity strain Gruneisen parameters to be zero along various directions in reciprocal space [26].

Having computed the strain dependence of the phonons, we apply the gQHA to compute the *a* and *c* lattice parameters at finite temperature and stress. The lattice parameters at a given temperature T and stress  $\sigma$  are computed by evaluating the Biot strain map  $\tilde{\boldsymbol{\epsilon}}(T, \boldsymbol{\sigma})$ , where definitions and notation are equivalent to Ref. [26] [see Eqs. (21)–(26)]. The crystal structure predicted at T = 1 K by the gQHA quantitatively differs from the values obtained from DFT relaxations due to zero point motion, and are compared with experimental measurements at T = 12 K (see Table I). The predicted shift in lattice parameters due to zero-point motion yields remarkable agreement with the values obtained from experiment, however, there are small discrepancies in the predicted basis atom positions for the oxygen atoms. It should be noted that within the gQHA, the Born-Oppenheimer potential is parametrized under the condition where the basis atom positions are always at a minimum energy. Furthermore, the Born-Oppenheimer potential is truncated at second order at a given strain, and therefore the basis atom positions are purely determined by the strain which results from minimizing the free energy. Therefore, the gOHA yields the same result for basis atom positions as QHA methods which employ the zero-staticinternal-stress approximation [52]. The calculation of basis atom positions can be improved by going beyond the QHA using the anharmonic terms (e.g., see Refs. [13,53–55]).

We now compare the computed temperature dependence of the lattice parameters with experimental measurements at various temperatures under unstressed conditions [see Figs. 2(a) and 2(b)]. The most notable difference among the experiments is a relative shift in the a and c lattice parameters, presumably due to imperfections in the measured crystal samples. The



FIG. 2. The (a) a and (b) c lattice parameters as a function of temperature computed with the gQHA (lines) under unstressed (blue) and stressed (red) conditions compared with experimental measurements (diamonds) [41,56,59,60]. The solid green points correspond to samples with 3% Cd, while corresponding open points are extrapolated to 0% Cd. (c) The c lattice parameter as a function of pressure computed with the gQHA at various temperatures compared with experimental measurements [61].

measurements in Ref. [56] were conducted on samples with a composition including 3% and 6% Cd, and we use the roomtemperature measurements to linearly extrapolate to 0% Cd by shifting all measured *a* and *c* lattice parameters by 0.005 and -0.007 Å, respectively (shown as open markers). The gQHA overestimates the change in the lattice parameters with temperature, which has been observed in previous literature studying PbTiO<sub>3</sub> [42] and in various other materials [57,58]. Given that the gQHA allows for anisotropic stress, it is interesting to apply a compressive stress of  $\sigma_{A_1^{\square}} = -0.31$  GPa and a tensile stress of  $\sigma_{A_1^{\circ}} = 0.055$  GPa. The applied stress shifts the *a* and *c* lattice parameters with only minor changes to the temperature dependence.

We present the change in the *c* lattice parameter with respect to pressure at finite temperatures in the range from P = 0 GPa to P = 3 GPa, and compare with experimental measurements at room temperature [see Fig. 2(c)]. The dashed

black line is computed at T = 0 K within the classical QHA, whereby the T = 0 K classical result will be equivalent to the lattice parameter computed in a DFT relaxation at constant pressure, presuming that the strain dependence of the elastic energy is faithfully parametrized. The change in the lattice parameter with pressure at finite temperature is shown at temperatures of T = 1 K and T = 300 K. The computed lattice parameter at zero pressure and room temperature underestimates the measured lattice parameter. There are only small differences in the pressure dependence of the lattice parameter computed at T = 1 K and T = 300 K, and the gQHA overestimates the pressure dependence of the lattice parameter as compared to the experimental measurements [61]. However, it is interesting to note that quantum fluctuations suppress the decrease of the classical gQHA result with pressure, pushing the result towards the experimental measurements.

Having computed the lattice parameters, we now discuss the strain curvature of the free energy at finite temperature and stress. There are three experimentally relevant quantities related to the free-energy curvature at finite stress [62]: the free-energy curvature  $C_{ij}$ , the elastic wave propagation coefficient  $S_{ij}$ , and the stress-strain coefficient  $B_{ij}$ . Additionally, elastic constants in ferroelectrics can be measured under boundary conditions of constant electric field E or constant electric displacement field D. The relation between the two boundary conditions is given by [63]

$$C_{ij}^{D}(T, \boldsymbol{\sigma}) = C_{ij}^{E}(T, \boldsymbol{\sigma}) + \sum_{\alpha\beta} (e_{\alpha i}(T, \boldsymbol{\sigma}) \\ \times e_{\beta j}(T, \boldsymbol{\sigma}) \{ [\hat{\boldsymbol{\epsilon}}^{\infty, S}(T, \boldsymbol{\sigma})]^{-1} \}_{\alpha\beta} \}, \qquad (1)$$

where  $\hat{\epsilon}^{\infty,S}$  is the relaxed-ion dielectric tensor at fixed strain and  $e_{\alpha i}$  is the relaxed-ion piezoelectric stress coefficient [63–66] (see Sec. SI of SM for additional details [40]).

We compute the full elastic constant tensor at finite temperature and stress and compare with experimental values measured under unstressed conditions at room temperature and beyond [67–69] (see Fig. 3). The elastic constants which were only measured at a single temperature are compared to the gQHA in Sec. SI of the SM [40]. There is reasonable agreement between the two sets of experimental values at room temperature, where the largest disagreement is a 4% difference in the measured  $C_{44}^D$  values. At room temperature, the gQHA with PBEsol yields good agreement for  $C_{11}^E$  and  $C_{44}^E$ , however  $C_{33}^D$  and  $C_{44}^D$  are overestimated and  $C_{66}$  is underestimated. The change in the predicted elastic constants with temperature is much greater than the change observed in experiment, likely due to an overestimation of the thermal expansion with temperature (see Fig. 2) and due to the neglect of explicit phonon interactions within the OHA [57,58]. The change in the constant D-field elastic constants with temperature is significantly greater than that of the corresponding constant E-field cases, and Eq. (1) dictates that the origin is the temperature dependence of  $e_{ij}$  and  $\hat{\epsilon}_{ij}^{\infty,S}$ , which depend on the strain-dependent  $\Gamma$ -point dynamical matrix. The strong temperature dependence of the constant D-field elastic constants is in stark disagreement with experiment, likely indicating a deficiency of the gQHA.

We proceed by computing the piezoelectric strain coefficients as a function of temperature and stress, and compare



FIG. 3. (a) Selected axial and (b) shear elastic constants under constant *E* fields or *D* fields computed with the gQHA (lines) under unstressed (solid) and stressed (dashed) conditions compared with previous experimental measurements (markers) [68,69]. See SM for additional elastic constants [40].

with existing experimental values measured under unstressed conditions (see Fig. 4 and SM [40]). The piezoelectric strain coefficients  $d_{ij}$  are constructed using the elastic constant ten-



FIG. 4. Piezoelectric strain coefficient  $-d_{31}$  computed with gQHA (lines) under unstressed (blue) and stressed (red) conditions compared with existing experimental measurements (circles) [68,69,71]. For additional piezoelectric strain coefficients, see SM [40].

sor and the piezoelectric stress coefficients [63,70],

$$d_{\alpha i}(T, \boldsymbol{\sigma}) = \sum_{j} \{ [\hat{B}^{E}(T, \boldsymbol{\sigma})]^{-1} \}_{ij} e_{\alpha j}(T, \boldsymbol{\sigma}), \qquad (2)$$

where  $\hat{B}_{ii}^E$  denotes the stress-strain coefficient under a constant electric field. The graphs of  $d_{33}$  and  $d_{15}$  are shown in the SM [40] as only room-temperature measurements have been performed for these coefficients. The experimentally measured values of the piezoelectric strain coefficients [68,69,71] show quantitative inconsistency, as the values vary as much as 20% for  $d_{31}$  at room temperature. Our quasiharmonic prediction of  $d_{31}$  overestimates the experimental measurements, and the discrepancy can be explained by differences in the  $B_{A_1^{\Box}A_1^{\circ}}^E$  and  $B_{33}^E$  elastic constants. This can be verified at T = 300 K by taking the experimental values of  $e_{\alpha i}$  and  $B_{ij}$  from Ref. [68] and replacing the values of  $B_{A_1^{\Box}A_1^{\circ}}^E$  and  $B_{33}^E$  with our computed values of 108.1 and 56.0 GPa which yields  $d_{31} = -39.9$ pC/N, in good agreement with our pure gQHA result (additional replacements did not have an appreciable effect). The temperature dependence of  $d_{31}$  within the gQHA is in good agreement with experimental measurements up to room temperature [71], though the agreement is likely fortuitous given the discrepancies in the temperature dependence of the elastic constants, thermal expansion, and the relaxed-ion piezoelectric stress coefficients. Therefore, the anomalous temperature dependence of  $d_{31}$  beyond room temperature is not entirely unanticipated.

In summary, we have demonstrated the application of the gQHA to a noncubic crystal, ferroelectric PbTiO<sub>3</sub>, under conditions of finite temperature and stress. The irreducible derivative approach to computing phonons from finite difference yields the strain-dependent phonons, where dipole-quadrupole effects are incorporated in the Fourier interpolation. The thermal expansion, elastic constants, and piezoelectric strain coefficients are computed at finite temperature and stress. The temperature dependence of the thermal expansion and elastic constants at zero stress are over estimated by the gQHA, illustrating the need to solve the vibrational Hamiltonian using a strain-dependent theory which explicitly accounts for phonon interactions. Our observed limitations of the gQHA are not unexpected, as discrepancies of the QHA are well known in various anharmonic materials [57,58]. Advances in the computation of finite-temperature vibrational properties from DFT using more sophisticated approximations than the QHA have been achieved [72-77], however, we are not aware of the application of any of these theories to the computation of the elastic constant tensor at finite temperature. These more advanced theories can be straightforwardly applied as a function of strain to compute thermal expansion and elastic constants at finite temperature and stress using the general formalism outlined previously [26], which will be the subject of future work.

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