

Atomistic simulations of the incipient ferroelectric KTaO_3

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Abstract

A parameterized effective Hamiltonian approach is used to investigate KTaO_3 . We find that the experimentally observed anomalous dielectric response of this incipient ferroelectric is well reproduced by this approach, once quantum effects are accounted for. Quantum fluctuations suppress the paraelectric-to-ferroelectric phase transition; it is unnecessary to introduce defects to explain the dielectric behavior. The resulting quantum-induced local structure exhibits off-center atomic displacements that display *longitudinal, needle-like correlations* extending a few lattice constants

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Numerous experimental and theoretical studies have been carried out on the perovskite KTaO_3 over the last forty years (see, e.g, Refs [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12] and references therein), making this material one of the most-studied “incipient ferroelectrics.” The main reason for this interest is that the dielectric constant of KTaO_3 increases continuously with decreasing temperature down to $\sim 10\text{K}$, but then saturates to a plateau at a large value ($\simeq 4000$) at lower temperatures while remaining paraelectric and cubic all the way down to zero Kelvin [2, 3]. These anomalous low-temperature features are usually thought to be caused by the suppression of a paraelectric-to-ferroelectric phase transition by zero-point quantum fluctuations [2, 3] (hence the name “incipient ferroelectric” or “quantum paraelectric” used to describe KTaO_3 and other materials, such as SrTiO_3 , exhibiting similar unusual dielectric and structural properties). Surprisingly, this generally-accepted picture is apparently *not* supported by various first-principles calculations, using density-functional theory (DFT) either in its local-density approximation (LDA)[13] or generalized-gradient approximation (GGA)[14, 15] form, since these simulations all predict that KTaO_3 should be paraelectric at $T=0$ even when neglecting zero-point motion [4, 5, 6]. This raises the possibility that LDA and GGA are not accurate enough to adequately reproduce the qualitative properties of incipient ferroelectrics. An alternate explanation for this discrepancy between first-principles calculations and experiments is that the simulations assume a perfect material while real samples may contain defects such as oxygen vacancies and Fe^{+3} ions [2, 3, 7, 8] that might lead to the observed anomalous properties of KTaO_3 . In fact, the interpretations of various experiments [9, 10] still remain controversial as to whether they are attributable to extrinsic effects (i.e., defects-induced) or intrinsic off-center atomic displacements. Furthermore, while previous studies invoke the existence of *ferroelectric microregions* inside the *macroscopically-paraelectric* KTaO_3 system to explain some of its properties [9, 11], there has never been any *direct* determination of the size and shape of these proposed polar regions, to the best of our knowledge. For instance, the pioneering work of Ref. [9] made several assumptions in their analysis of low-temperature Raman spectra – such as isotropy of these microregions – to extract a characteristic size $\simeq 16 \text{ \AA}$ for these polar regions.

In this Letter, we use large-scale atomistic simulations to shed light on the aforementioned long-standing problems. We report calculations on KTaO_3 using a parameterized effective Hamiltonian approach. Our main findings are that (i) LDA and GGA are indeed not accurate enough to reproduce the observed anomalous properties of KTaO_3 , even qual-

itatively; (ii) these properties *can* be understood *without the need of introducing defects*, if quantum fluctuations are present to suppress the paraelectric-to-ferroelectric transition; (iii) the low-temperature local structure of KTaO_3 is characterized by off-center atomic displacements that are *longitudinally correlated, in a needle-like (and thus anisotropic) way, with a correlation length spanning a few 5-atom unit cells*.

We use the effective Hamiltonian (H_{eff}) approach developed in Ref. [16] to investigate finite-temperature properties of KTaO_3 . Within this approach, the total energy E_{tot} is a function of three types of local degrees of freedom: (1) the $\mathbf{u}_i$ (B-site centered) local soft-mode amplitude in each i 5-atom cell, describing the local polarization in each cell; (2) the v_i (A-site centered) inhomogeneous strain variables; and (3) the homogeneous strain tensor. E_{tot} contains 18 parameters and 5 different contributions: a local-mode self energy, a long-range dipole-dipole interaction, a short-range interaction between local modes, an elastic energy, and an interaction between the local modes and strains [16]. This effective Hamiltonian approach has been successfully used to model, understand, and design ferroelectric perovskites (see Refs. [16, 17, 18, 19, 20] and references therein). E_{tot} is used in two different kinds of Monte-Carlo (MC) simulations: classical Monte Carlo (CMC) [21], which does not take into account zero-point phonon vibrations, and path-integral quantum Monte Carlo (PI-QMC) [19, 22, 23] which includes purely quantum-mechanical zero-point motion. Consequently, comparing the results of these two different Monte-Carlo techniques allows a precise determination of quantum effects on macroscopic and microscopic properties of perovskites. $12 \times 12 \times 12$ KTaO_3 supercells (corresponding to 8,640 atoms) are used in all Monte-Carlo simulations. We typically perform 30,000 MC sweeps to thermalize the system and 70,000 more to compute averages, except at low temperatures in PI-QMC where more statistics is needed. For example, we use 180,000 MC sweeps for thermalization and 240,000 sweeps at 3K to accurately predict the dielectric response. (Note that we are not aware of any previous work reporting the dielectric response computed using PI-QMC)

In PI-QMC, each 5-atom cell interacts with its images at neighboring imaginary times through a spring-like potential (mimicking the zero-point phonon vibrations), while all the 5-atom cells interact with each other at the same imaginary time through the internal potential associated with E_{tot} . The product TP , where T is the simulated temperature and P is the number of imaginary time slices (Trotter number), controls the accuracy of the PI-QMC calculation. In all our simulations we use $TP=600$, which we find leads to

sufficiently converged results. Outputs of the PI-QMC simulations thus contain local-modes $\mathbf{u}_i(t)$, where i indexes the 5-atom unit cells of the studied supercell while the imaginary time t ranges between 1 and P . Note that CMC simulations can be thought of as corresponding to $P = 1$, so that they do not yield imaginary-time-dependent outputs.

Figure 1(a) shows the χ_{33} dielectric susceptibility – where the index 3 refers to the [001] pseudo-cubic direction – as predicted by the H_{eff} approach, *with all its parameters being derived from LDA calculations on small supercells of KTaO_3 at its experimental lattice constant*. (Technical details of these LDA calculations are similar to those of Ref. [5]). It can be clearly seen that CMC calculations yield a χ_{33} that is continuously increasing as the temperature is decreasing down to nearly zero Kelvin. Turning on quantum effects leads to the appearance of a plateau below $\sim 100\text{K}$ with a value of ~ 100 for the dielectric constant. These CMC and PI-QMC simulations *both* predict a cubic paraelectric ground state. A plateau for the dielectric response has indeed been experimentally observed in KTaO_3 [2, 3], but reaching a much higher dielectric constant ($\simeq 4,000$) and over a much narrower temperature range (i.e., below 10K) than in Fig. 1(a).

In view of these two discrepancies, we have experimented with making minor adjustments in the LDA-fitted parameters in the hope of obtaining better agreement with experimental data. We have found that this can be done by adjusting just one of the 18 parameters, namely, the parameter denoted κ_2 in Ref.[16], which describes the harmonic part of the local-mode self-energy. (In our model, reducing κ_2 favors ferroelectricity with respect to paraelectricity since it leads to a decrease of the zone-center transverse optical frequency by weakening short-range repulsions). Figure 1b shows that decreasing this single κ_2 parameter by $\sim 18\%$ from its LDA value of 0.0866 a.u. (atomic units) leads to reasonable agreement between our PI-QMC simulations and measurements, not only for the value of the dielectric constant plateau, but also at temperatures above 10K.

Furthermore, this modified κ_2 also results in a dramatic difference between the two kinds of Monte-Carlo calculations. CMC simulations yield a *ferroelectric* rhombohedral ground-state. The corresponding Curie temperature is around 30K, as evidenced by the peak in dielectric response displayed in Fig. 1(b). On the other hand, PI-QMC predicts a *paraelectric* ground state. In other words, *quantum effects suppress the paraelectric-to-ferroelectric phase transition*, which is consistent with the accepted picture [2, 3]. Figures 1(a-b) thus (i) reveal that extrinsic defects (such as impurities or vacancies), which have been proposed to be

responsible for the anomalous properties of KTaO_3 [2, 3, 7, 8], are *not* needed to reproduce the experimental behavior of this material; and (ii) strongly suggest that, unlike in *strongly ferroelectric* perovskites [17, 18], the LDA is not accurate enough for simulating KTaO_3 .

As for GGA, Tinte *et al.* [6] report zone-center optical frequencies in cubic KTaO_3 that are all positive and very close to the LDA values. Consequently, according to Fig 1(a-b), we can conclude that a GGA effective Hamiltonian would not provide a significant improvement over our LDA one, and will also fail in reproducing experimental results. This may make KTaO_3 a useful test-case for the development of new functionals within DFT or other *ab-initio* methods.

We now analyze the *microscopic* local structure of KTaO_3 at low temperature. Figure 2 depicts the magnitude of the local modes $\mathbf{u}_i$ inside each i 5-atom cell *versus* the angle that these local modes make with the pseudo-cubic [100] direction, as obtained from a $T=3\text{K}$ snapshot among the thermally equilibrated Monte-Carlo configurations using E_{tot} with the modified κ_2 . (The magnitude of the local mode is directly proportional to the magnitude of the local polarization, e.g., $|\mathbf{u}| = 0.006$ and 0.026 a.u. correspond to a local polarization $\simeq 0.0583$ and 0.253 C/m^2 , respectively). Figure 2(a) displays the CMC results, while Fig. 2(b) corresponds to PI-QMC [25]. Comparing Figs. 2(a) and 2(b) reveals how quantum effects affect the microscopic structure of KTaO_3 : the local polarizations go from all lying close to the [111] direction (corresponding to an angle $\simeq 54^\circ$) and having a relatively large magnitude, to being heavily-scattered in direction and having a much smaller but non-zero magnitude. The fact that KTaO_3 is predicted to exhibit non-zero local dipoles, even when quantum fluctuations are accounted for, is consistent with the first-order lines observed to appear in Raman spectra which are forbidden in the ideal cubic perovskite structure [9, 10]. Furthermore, an inspection of Fig. 2(b) does *not* reveal any obvious polar microregions. For instance, our quantum-statistical results do not show the local-mode distributions breaking up into clusters centered along $\langle 111 \rangle$ directions (i.e., angles of $\simeq 54$ and/or 125°) as would be expected for such polar microregions.

To gain further insight into the local structure of KTaO_3 , we decided to compute an additional set of coefficients defined as

$$\theta_\mu(\mathbf{r}) = \frac{3}{N} \sum_{i=1}^N \frac{u_{i,\mu} u_{i+\mathbf{r},\mu}}{|\mathbf{u}_i| |\mathbf{u}_{i+\mathbf{r}}|} . \quad (1)$$

Here μ denotes the x , y , or z Cartesian axis chosen along the [100], [010] or [001] cubic

directions, respectively. The index i runs over all the N B-sites; $u_{i,\mu}$ and $u_{i+\mathbf{r},\mu}$ are the μ components of the local modes in cell i , and in the cell centered at a distance $\mathbf{r}$ from cell i , respectively. The case in which the local dipoles all have the same (non-zero) magnitude and are all aligned along a given $\langle 111 \rangle$ direction yields a value of 1 for $\theta_\mu(\mathbf{r})$, for any $\mathbf{r}$ and for any μ . This case corresponds to a ferroelectric rhombohedral state having identical local and average structures. On the other hand, the other limiting case — for which neighbors at a distance $\mathbf{r}$ do not exhibit any correlation between the μ -components of their local modes — is associated with a zero value for $\theta_\mu(\mathbf{r})$.

Figure 3 depicts $\theta_x(\mathbf{r})$ (i.e., $\mu = x$) for $\mathbf{r}$ lying in the x - y plane. The results correspond to one snapshot of a thermally equilibrated Monte Carlo configuration at $T=3\text{K}$, using the H_{eff} with the modified κ_2 . Panels (a) and (b) correspond to CMC and PI-QMC simulations respectively. One can see that CMC technique leads to a $\theta_x(\mathbf{r})$ close to unity for any $\mathbf{r}$, and thus generates a macroscopically- and microscopically-ferroelectric rhombohedral structure, as consistent with Fig. 2(a).

On the other hand, PI-QMC simulations give a more complex behavior for $\theta_x(\mathbf{r})$ at low temperature. One can see that the x components of the local modes are *longitudinally* correlated in a *needle-like* fashion: $\theta_x(\mathbf{r})$ adopts large values only when $\mathbf{r}$ is along the $[100]$ direction. These values decreasing as the magnitude of $\mathbf{r}$ increases. (The same result is obtained for all symmetry related cases, e.g., for $\theta_x(\mathbf{r})$ in the x - z plane, etc.) Figure 2(b) further reveals that $\theta_x(\mathbf{r}) \simeq 0.5$ for neighbors at a distance of $\pm 2a$ (where $a \simeq 4 \text{ \AA}$ is the cubic lattice constant) along the x axis. This is in good agreement with the characteristic size of $16 \text{ \AA}$ extracted from low-temperature Raman spectra of KTaO_3 [9]. On the other hand, our simulations go against the hypothesis of isotropic correlation made in ref. [9]. The longitudinal needle-like correlations depicted in Fig. 3(b) have also been predicted to occur in classical ferroelectrics just above the paraelectric-to-ferroelectric transition temperature [26]. In fact, they are pretransitional effects that are probably common to most ferroelectric perovskites, the peculiarity of quantum paraelectric KTaO_3 being that the phase transition does not actually occur. Finally, note that these needle-like correlations are consistent with the peculiar diffuse X-ray scattering observed in Ref. [12].

In summary, we have performed large-scale atomistic simulations to investigate the (defect-free) incipient ferroelectric KTaO_3 system using a parameterized effective-Hamiltonian approach. The effect of quantum-mechanical zero-point motion is investigated

by comparing the results of classical and path-integral Monte Carlo simulations. We find that the fitting of all the H_{eff} parameters within LDA yields a theoretical dielectric constant that is in poor quantitative agreement with experiment, strongly suggesting that LDA is inadequate for this material. Results in the literature also indicate that GGA will not improve the LDA result. On the other hand, a small modification of a single parameter in H_{eff} from its LDA value is enough to obtain reasonable agreement between theory and experiment for the dielectric constant over a wide temperature range. This modified H_{eff} leads to the predictions that (i) KTaO_3 is ferroelectric classically, but becomes paraelectric once zero-point phonon vibrations are included, and (2) the quantum-induced local structure of KTaO_3 is characterized by non-zero local dipoles that have longitudinal, needle-like correlations with a correlation length spanning a few unit cells.

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 - [25] Starting from the path-integral form of the partition function, it can be shown that the local modes $\mathbf{u}_i(t)$ are to be averaged over imaginary time before computing static quantities such as the local mode distributions of Fig. 2(b) or the correlations defined by Eq. (1). Hence, it is not correct to compute these quantities at different imaginary times and then average over t .
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FIG. 1: χ_{33} dielectric susceptibility of KTaO_3 as a function of temperature T . (a) Results for LDA-fitted H_{eff} parameters. (b) Results for modified set of parameters. Solid circles and stars correspond to PI-QMC and CMC results respectively. Dashed and dotted lines represent experimental data from Refs. [2] and [3], respectively. Solid line shows the fit of the PI-QMC results by a Barrett relation $A/[(T_1/2) \coth(T_1/2T) - T_0]$ [24], with $A = 27000$, $T_1 = 72\text{K}$ and $T_0 = 29\text{K}$. Note that our CMC simulations yield a paraelectric-to-ferroelectric transition around 30K, which provides a numerical proof for the concept of classical Curie temperature given to T_0 in the Barrett relation.

FIG. 2: Magnitude of local modes of KTaO_3 at $T=3\text{K}$ *versus* the angle that these modes make with respect to the $[100]$ pseudo-cubic direction. The modified set of H_{eff} parameters is used.

FIG. 3: Correlation function $\theta_x(\mathbf{r})$ of Eq. (1) for KTaO_3 plotted in the x - y plane for a $12 \times 12 \times 12$ simulation at $T=3\text{K}$. (a) CMC results; (b) PI-QMC results. Each small square represents one lattice B site; the origin lies at the center. The modified set of H_{eff} parameters is used. Note that the color scales are different in the two panels.





