Accuracy of purely classical description of TiO$_2$ nanoparticles

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FOR CHEM396 REPORT: We compare the efficiencies of a classical forcefields and DFT when simulating the potential energy surface of amorphous TiO$_2$ nanoparticles.

INTRODUCTION

Titania (TiO$_2$) has long been the subject of notable research interest due to its high chemical stability and interesting optical, dielectric, mechanical, and photocatalytic properties[1–4]. While most works focus on TiO$_2$ in its most stable and common forms, which are all crystalline, a number of technological uses of this material rely on processing into film or powder form which both tend to be amorphous; further modification of the material is then needed to restore a certain level of crystalline order back to it[5,6]. Dependence on this last step makes titania significantly more difficult and expensive to to use in industrial-scale applications, which has motivated researchers to study amorphous TiO$_2$ ($a-$TiO$_2$) in hope of being able to use in it cheaper, less processed forms[7–9].

One of the defining traits of amorphous materials is their lack of long-range order, which makes their microstructure extremely hard to study experimentally. In spite of this, recent experimental studies have been successful in describing the local atomic structure of $a-$TiO$_2$ under different environments[10–12] by measuring things like the coordination number of bulk and surface Ti atoms and average bond lengths, using various types of X-ray absorption structure spectroscopy. However, the most detailed investigations of amorphous titania's structure have been those combining experimental methods (e.g. X-ray absorbtion spectroscopy) with the computation modeling (notably reverse Monte-Carlo simulations)[13–15]. Our reliance on simulations to properly understand this material is a major research incentive for theoretical chemists to devise the computational tools to perform such simulations adequately.

Seeing as $a-$TiO$_2$ nanoparticles are almost always used for inhomogeneous catalysis purposes, it is often needed to simulate their structure's evolution over time (e.g. the duration of a given reaction or phase transition). This is the purview of molecular dynamics (MD) simulations. There exist two approaches to MD simulations:

- the classical approach, which uses a predetermined potential $U(\mathbf{r}_1, ..., \mathbf{r}_N)$ and Newton's equations of motion to calculate the trajectories and energies of all atoms in the simulation,

- the density functional theory (DFT) approach, which relies on a quantum mechanical description of the system to determine its electronic density

from which all other physical quantities are then derived.

It is generally known that DFT is more accurate than classical simulations, due to the fact that classical mechanics do not apply at the atomic scale. Unfortunately, DFT simulations of large systems ($\sim$1000 atoms) are much more difficult to implement due to the prohibitive amounts of memory needed and long computation times. Researchers have therefore put considerable effort into developing classical potentials that faithfully reproduce experimental measurements which could allow accurate simulations of TiO$_2$ (notably) without resorting to computationally expensive calculations[16–18]. The potential devised by Matsui and Akaogi in 1991[17] has had notable success in describing the structural and mechanical properties of titania's different polytypes[19,20] and is thus the most widely used potential when simulating TiO$_2$ using classical MD. In this work, we focus our attention on nanoparticulate $a-$TiO$_2$ (such as can be found in unprocessed powder form) and on whether this classical potential can accurately predict their structure-energy relationship, or potential energy surface (PES) $V(\mathbf{r}_1, ...\mathbf{r}_N)$. We compare the energies yielded by the classical and quantum descriptions of the system to see how well correlated they are. In this paper, we begin by describing our different calculation methods, then we present and discuss our results, before introducing potential directions for future research.

SIMULATION DETAILS

A. Classical MD

All classical MD simulations described in this work were ran in the NpT ensemble, using the Matsui-Akaogi (MA) potential to model the interactions between pairs of atoms. The MA potential was originally developed for classical MD simulations of the four main polytypes of crystalline TiO$_2$[17] to accurately simulate the structural properties of titania's four main polytypes and the elastic constants of rutile ($r-$TiO$_2$). It is the most widely used potential when classically simulating bulk TiO$_2$ and has been shown by previous studies[19–21] to be the most adequate force field for predicting the structure and properties of its liquid and amorphous phases. The MA potential describes the short-range interaction between atoms with a Buckingham potential and their

TABLE I. Parameters used for evaluating the MA potentials.

Element	Z ($|e|$)	A (Å)	B(Å)	C ($\text{Å}^3\text{kJ}^{1/2}\text{mol}^{-1/2}$)
Ti	+2.196	1.1823	0.077	22.5
O	-1.098	1.6339	0.117	54.0

long-range electrostatic interaction using the traditional Coulomb term:

$$V_{ij}(r) = f_0 \cdot (B_i + B_j) \cdot \exp\Big(\frac{A_i + A_j - r}{B_i + B_j}\Big) - \frac{C_i C_j}{r^6} + \frac{e\, Z_i\, Z_j}{4\pi\epsilon_0 r}, \tag{1}$$

where r denotes the distance between the two interacting ions i and j, e is the elementary charge, Z_i is the dimensionless ionic charge of ion i, f_0 is a standard force of $4.184\,\text{kJmol}^{-1}\text{Å}^{-1}$, and A_i, B_i, and C_i are parameters corresponding to species i. The charges Z_{Ti} and Z_{O} were obtained from Traylor $et\ al.$[22], who derived them from phonon dispersion curves he observed in rutile ($r - \text{TiO}_2$). The numerical values of the other constants listed above where determined by Matsui and Akagi by adjusting them adjusting them to reproduce the the observed elastic constants of rutile and fitting them to reproduce the structures of rutile, brookite, and anatase (the three polytypes of crystalline titania for which precise experimental measurements of lattice parameters were available at the time of their paper). These values are given in table I. The total potential energy of the system is then given by the sum of all pairwise interactions between all of its N atoms:

$$V(\mathbf{r}_1, ..., \mathbf{r}_N) = \sum_{i<j}^{N} V_{ij}(|\mathbf{r}_i - \mathbf{r}_j|). \tag{2}$$

The atomic structures of the various $a - \text{TiO}_2$ nanoparticles described in this work were obtained in multiple steps. We started by melting rutile ($r - \text{TiO}_2$) nanocrystals of 198, 390, and 768 atoms respectively whose structures were previously optimized at the BLYP/DZVP-GTH level of theory (using a plane wave energy cutoff of 2100 Ry) using classical MD in the NpT ensemble with $T = 2000\,\text{K}$ and $p_{\text{ext},0} = 0.0\,\text{Pa}$. We ran this first round of simulations for 40000 timesteps of $\Delta t = 0.5\,\text{fs}$. The resulting melt was then cooled in three steps; classical MD simulations using the same potentials, ensemble, and number of steps were ran using $T = 1500\,\text{K}, 750\,\text{K}$, and $300\,\text{K}$ successively, all with $\Delta t = 2.0\,\text{fs}$. This process simulated the annealing of the melted nanocrystals into a glass which we then studied using Kohn-Sham DFT.

Seeing as the MA potential was originally elaborated to describe the describe the structural and elastic properties of $r - \text{TiO}_2$, we also generated a set of conformations of a rutile lattice comprised of 72 atoms in the NpT ensemble at $T = 300\,\text{K}$, using the same potential as described above. Doing so provided us with energy values which we expect to be well correlated with the ones we obtain with DFT methods, thus giving us a reference data set to which we could compare the rest of our results.

B. DFT calculations

Having obtained equilibriated atomic structures for nanoparticles of different sizes, we sampled 101 conformations from the last 40 ps of the last cooling run, at which point all four nanoparticles were in equilibrium with $T = 300\,\text{K}$ thermal bath. We then ran a single-point energy calculation on each conformation using KS DFT at the PBE/DZVP level of theory, using a plane wave cutoff of 2000 Ry. We also ran similar DFT calculations on the different configurations of the reference rutile lattice which we also sampled from the last 40 ps of the MD simulation we mentioned in the last paragraph of the last section.

RESULTS AND DISCUSSION

For each nanoparticle, we compare the classically evaluated energy of every configuration with the energy obtained through a DFT calculation for that some configuration. We plot our results in figures 1-6; a $y = x$ line was added to every plot to give a better appreciation of the level of correlation between classical and DFT data sets. This allows us to gauge the accuracy of MA forcefield; if the classical and quantum mechanical results are well correlated, then the purely classical representation of the forces in the nanoparticles is sufficiently accurate to discriminate between slight variations in a given system's configuration in a meaningful way and can therefore be used to simulate this system nanoparticles instead of DFT, which is much more computationally expensive.
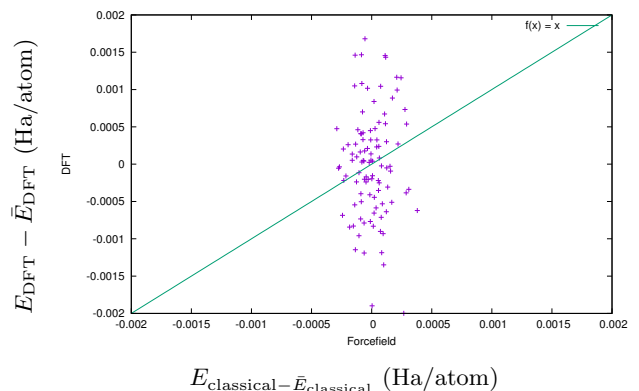

FIG. 1. DFT energy vs. classical energy (both shifted down by their average value) for 101 conformations of an $r - \text{TiO}_2$ lattice with 72 atoms.

Comparing the energies obtained using classical MD and those calculated using DFT reveals that a
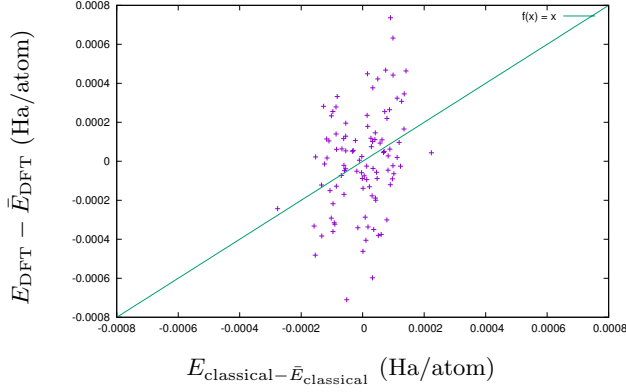
FIG. 2. DFT energy vs. classical energy (both shifted down by their average value) for 101 conformations of an $a - \mathrm{TiO_2}$ nanoparticle with 198 atoms.

description of the forces inside an $a - \mathrm{TiO_2}$ nanoparticle using only the two-body MA potential is not precise enough to yield an accurate representation of its potential energy surface (PES) (with respect to its atoms' positions). Indeed, plotting the energies yielded by both calculation methods reveals that DFT calculation methods are much more sensitive to a change in a given nanoparticle's atomic configuration than classical methods.
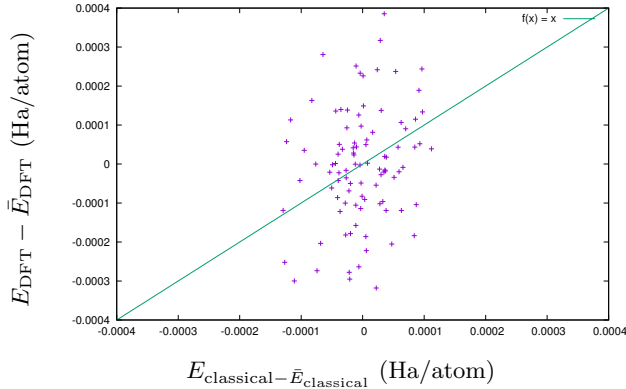

FIG. 3. DFT energy vs. classical energy (both shifted down by their average value) for 101 conformations of an $a - \mathrm{TiO_2}$ nanoparticle with 390 atoms.

The system for which this is the most obvious is the 768 atom nanoparticle, for which all classically evaluated energies lie within $\sim 10^{-4}\,\mathrm{Ha}$ of each other, while the energies obtained usinq quantum mechanical methods vary by $\sim 10^{-1}\,\mathrm{Ha}$. One can get a sense of how dramatic this disparity between the ranges of of both data sets by examining figure 4: when plotting the DFT and classical data on the same scale, the classical energy values almost all lie on the same vertical line and thus appear to all be identical. While this effect is most dramatic for the 768 atom system, every other nanoparticle on which we ran similar calculations exhibit significant

clustering of the energies obtained using the MA potential about their mean value, while their DFT energies spread out over a much larger interval.
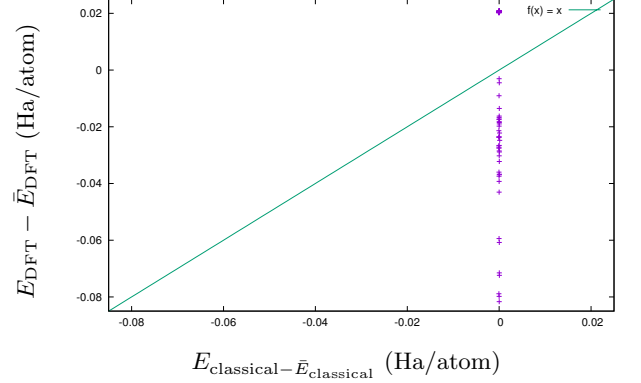

FIG. 4. DFT energy vs. classical energy (both shifted down by their average value) for 101 conformations of an $a - \mathrm{TiO_2}$ nanoparticle with 768 atoms.

All four nanoparticles we ran these calculations exhibit weak correlation between the DFT-calculated energy values and the energies obtained using the MA potential. Even more surprisingly we find that the two sets of energy values of the different conformations of the rutile lattice were even less correlated than the ones obtained from the amorphous nanoparticles. Indeed, as can be seen in table B, our simulated rutile lattice yielded the lowest value of ρ of all the systems we studied.
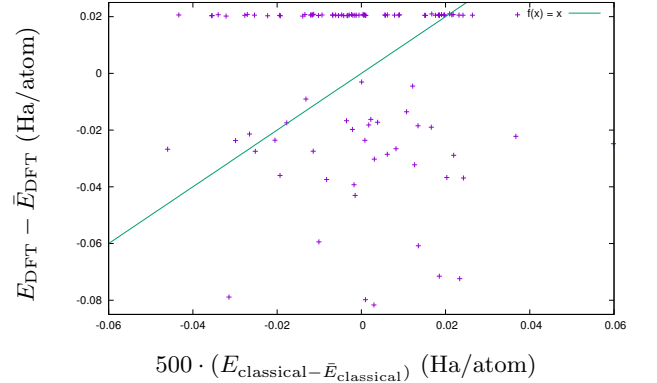

FIG. 5. Rescaled version of figure 4.

In light of this extremely low correlation, we obviously cannot consider our simulated $r - \mathrm{TiO_2}$ lattice a reference system. However this is not overly problematic, it simply suggests that a purely classical two-body description of atomic interactions in $\mathrm{TiO_2}$ in the amorphous or rutile phase is not sufficiently accurate to keep track of small changes in the system's configuration. Moreover the small RMSE values we get for all systems (except the 768-atom nanoparticle) and the fact that all classically obtained energies for a given system are very close

to each other suggest that they are still physically sound at a less precise level of analysis. Indeed, if both sets of energy values for each system varied over intervals of similar sizes and yet remained as uncorrelated as we have observed them to be, then we would be in a position to question the validity of even trying to describe TiO_2 using only the MA potential in the first place. However this is not the case; for every system all energies computed classically differ very little. This is consistent with the fact that the atomic configurations from which such energies are computed were obtained from segments of our MD simulations where the system was already at equilibrium with its environment (i.e. the thermal bath) and thus did not vary greatly either. It is therefore reassuring to see that, within our classical MD simulation, snapshots which have similar structures are also predicted to have close energy values. The contrast between the highly clustered classical values and the much more spread out quantum values could therefore suggest that the quantum description of TiO_2 is much more sensitive to the system's conformational changes while using the MA potential cannot meaningfully register such changes yet still provides an internally consistent and physically viable picture of the system.

[FURTHER DISCUSSION: unshifted DFT values are 500times larger than unshifted classical values rescale shifted energy values by dividing by average E?]

CONCLUSION

Having observed that DFT calculations are necessary to properly sample from an $a - TiO_2$ nanoparticle's PES, we are now faced with the problem posed by the computing power necessary to run such calculations on large systems (i.e. nanoparticles containing more than ~ 1000 atoms). Seeing as computational expense is one of DFT's main drawbacks, a number of optimisation schemes have been proposed over the years to reduce both the amount of memory and the time necessary to run such calculations. Among them, we focus our attention to the absolutely localised molecular orbitals (ALMO) method which partitions the system being simulated into smaller fragments (usually these are the individual atoms or molecules that compose it) and runs traditional DFT on each fragment in parallel. This has the advantage of having a runtime that scales linearly with the number of fragments for large systems. Seeing as ALMO DFT makes a number of large DFT calculations much more feasible, we decide to test its accuracy on our various $a - TiO_2$ nanoparticles. As before, we evaluate the accuracy of the ALMO DFT method by comparing the energy it outputs for a given configuration of a nanoparticle with the energy obtained through classical DFT.

- MA potential not sufficient to

- ALMO needed to study size-dependence of certain properties (structural and electronic)

- Could also make large-nanoparticle simulations using smaller basis set for Ti.

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System	$a - \text{TiO}_2$ (198 atoms)	$a - \text{TiO}_2$ (390 atoms)	$a - \text{TiO}_2$ (768 atoms)	$r - \text{TiO}_2$ (72 atoms)
ρ	0.3066474	0.3497706	-0.0496755	0.0141203
RMSE	0.0486056	0.0628487	22.21090	0.0518275

TABLE II. Pearson correlation coefficient ρ and RMSE between the energy values obtained through DFT and those obtained using the two-body MA potential on various configurations of different systems.

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