

# Using DFT to model $\text{TiO}_2$ nanoparticles

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## Abstract

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TABLE I: Parameters used for evaluating the MA potentials.

Element	$Z$ ( $ e $ )	$A$ (Å)	$B$ (Å)	$C$ (Å <sup>3</sup> kJ <sup>1/2</sup> mol <sup>-1/2</sup> )
Ti	+2.196	1.1823	0.077	22.5
O	-1.098	1.6339	0.117	54.0

## Introduction

### Outline

### Simulation details

#### 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<sub>2</sub> and has been shown by previous studies 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 long-range electrostatic interaction using the traditional Coulomb term:

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

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 kJmol<sup>-1</sup>Å<sup>-1</sup>, and  $A_i$ ,  $B_i$ , and  $C_i$  are parameters corresponding to  $i$ . The numerical values of the constants listed above are given in table I.

The atomic structures of the various  $a$  – TiO<sub>2</sub> nanoparticles described in this work were obtained in multiple steps. We started by melting rutile ( $r$  – TiO<sub>2</sub>) nanocrystals of 198, 390, 768, and 1842 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  $T = 2000$  K and  $P_{\text{ext},0} = 0.0$  Pa. We ran this first round of simulations for 40000 timesteps of  $\Delta t = 0.5$  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  $T = 1500$  K, 750 K, and 300 K successively, all with  $\Delta t = 2.0$  fs. This process simulated the annealing of the melted nanocrystals into a glass which we then studied using Kohn-Sham DFT.

[MAYBE PART W RDFs]

### A. DFT calculations

Having obtained equilibrated atomic structures for nanoparticles of different sizes, we sampled 100 conformations from the last 40 ps of the last cooling run, at which point all four nanoparticles had already reached their equilibrium configuration. We then ran single-point energy calculation using KS DFT at the PBE/DZVP level of theory, using a plane wave cutoff of 2000 Ry. Our results are plotted in figures 1-5, in which we plot the DFT energies of every configuration of a given nanoparticle vs the classically computed energies of those same configurations. We also added a  $y = x$  line to help the reader any kind of correlation between both data sets.

Comparing the energies obtained using the classical MD and those calculated using DFT reveals that while the MA potential adequately describes the structural features of  $\alpha$ -TiO<sub>2</sub>, it does not allow for an accurate evaluation of the system's energy. 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. The system for which this is the most obvious is the 768 atom nanoparticle, for which all classically evaluated energies lie within  $\approx 10^{-4}$  Ha of each other, while the energies obtained using quantum mechanical methods vary by  $\approx 10^{-1}$  Ha. 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.

We followed the same procedure for a lattice of  $r - \text{TiO}_2$

## **Results and discussion**

## **Conclusions**

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