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Evaluation of TiO_2 Force Fields

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Evaluation of TiO₂ Force Fields

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Abstract

A total of nine force fields for TiO₂ have been compared and evaluated using bulk lattice and surface energy minimization procedures. Calculated crystal properties of four polymorphs of TiO₂ (rutile, anatase, brookite and a high pressure phase TiO₂(ii)) are presented, together with details of the energetics of the (100), (110) and (001) surfaces of rutile.

1 Introduction

The primary motivation for this work is to attempt to identify or derive a force field suitable for Molecular Dynamics (MD) simulations using the package DL_POLY [1]. A number of force fields for TiO_2 , including rigid ion and shell models, have appeared in the literature. The performance of the seven most promising force fields [2-7] (as judged from details published in the original papers), together with two determined by empirical fitting in the course of this work, are evaluated using bulk lattice and surface energy minimization procedures. Bulk lattice energy minimization calculations have been performed using THBREL [8] and GULP [9] and surface energy minimization calculations using MIDAS [10].

2 The Force Fields

A brief summary of the force fields evaluated in this work is given in Table 1. Further details are presented below for each force field in turn beginning with the seven literature force fields.

2.1 Force Fields Appearing in the Literature

(i) Catlow, Freeman & Royal [2] - (CFR)

This formal charged shell model force field was produced by fitting to the structure, elastic and dielectric properties of rutile. When used in bulk lattice energy minimization simulations it is reported to give reasonable dielectric properties; however, the structure is poor, resulting in a c axis that is too long by 8%. In their paper the authors suggested that this model was probably the best that could be achieved with pair potentials and a simple shell model.

(ii) Catlow & James [3] - (CJ)

Originally used in defect calculations, this formal charged shell model force field was derived by empirical fitting to the structure, elastic and dielectric properties of rutile.

The model was later criticized [4] on the grounds that full relaxation of the non-defective rutile structure leads to both poor structural and dielectric properties.

(iii) *Matsui & Akaogi* [5] - (MA)

A rigid ion force field employing partial charges was parameterized by fitting to the structures of rutile, anatase and brookite, together with the elastic constants of rutile. The authors went on to use this force field to study structural and physical properties of the four polymorphs of TiO_2 using molecular dynamics.

(iv) *Mostoller & Wang* [4] - (MW3)

This parameterization employed partial charges and an anisotropic shell model (consisting three directional dependent spring constants) for oxygen. It was fitted empirically so as to reproduce accurately the phonon spectra and give reasonable lattice constants. Reproduction of the lattice energy was sacrificed in the derivation.

Note the original anisotropic shell model of Mostoller & Wang is unsuitable for use in THBREL, GULP and MIDAS, consequently an isotropic model possessing an averaged spring constant has been used in this work.

(v) *Mostoller & Wang* [4] - (MW4)

This model uses almost formal charges ($\text{Ti}=+3.9$) and anisotropic shell model parameters (consisting three directional dependent spring constants) for oxygen. It was fitted so as to reproduce the lattice constants of rutile exactly and the lattice energy reasonably; however, the phonon spectra were not reproduced well.

Mostoller & Wang stated that they were unable to parameterize a force field containing an isotropic shell model that gave good agreement with the phonon spectra, lattice energy and the structure of rutile. They went on to suggest that a simple isotropic shell model can not reproduce the dielectric properties of rutile, as the electron distributions around the oxygen atoms are distorted and an account of quadrupolar moments must be included in the model.

As for MW3, a single averaged value oxygen shell constant was used in MW4 in this work.

(vi) *Post & Burnham* [6] - (PB)

An electron gas procedure was used to produce a simple formal charged rigid ion model. The model was then used by the authors to simulate in reasonable agreement with experiment the structures of rutile, anatase and brookite.

(vii) *Sawatari, Iguchi & Tilley* [7] - (SIT)

The model was parameterized so as to reproduce the structure, elastic and dielectric properties of rutile. The authors employed formal charges and a point polarizable shell model in order to study point defects in rutile. The model was subsequently criticized [4] as it was found to contain instabilities in the phonon spectra and elastic constants. Owing to ambiguities in the original paper, regarding the shell model parameters, the force field was used in a rigid ion form in this study.

2.2 Force Fields Fitted Empirically in the Course of This Work

Empirical determination of force field parameters requires the least-squares fitting of calculated to experimental observables. Conventional fitting involves calculating the gradients and properties at the experimental crystal structure and adjusting the potential parameters so as to minimize the error in the calculated quantities, assuming the experimental gradients are zero at the observed atom positions. However, unless the calculated gradients are minimized to be zero (and hence the strains are removed completely), there is no guarantee that the potential will give the correct structure and reproduce the crystal properties during an energy minimization calculation. The main criterion to determine the accuracy of a potential model is normally not the forces at the observed geometry but rather the atomic displacements (the strains) of the optimized configuration with respect to the observed geometry. There is also a further problem with conventional fitting. The elastic and dielectric constants are strictly calculable only from the second derivative matrix when the gradients are zero. Thus calculating such

properties at the experimental structure when it is not in its equilibrium geometry can often be misleading. Both of these difficulties can be removed by performing a new fitting technique referred to as relaxed fitting [11]. After each fitting cycle, the structure is relaxed to zero strain (energy minimized) with a subsequent property calculation (now at the equilibrium geometry). The differences between the observed and calculated structural parameters (the strains) are then minimized instead of the derivatives.

Relaxed fitting is believed to be of particular importance for materials that exhibit unusual dielectric properties such as rutile where the small changes in atom positions can alter drastically the calculated dielectric constants.

New force fields for TiO_2 have been derived in the course of this work using the least-squares fitting capabilities in GULP [9], which can perform both conventional and relaxed fitting.

In attempting to fit new force fields parameters for TiO_2 a number of philosophies were pursued. Details of two force fields derived in this manner (C1 & C2) are given below, this is followed for the sake of completeness by a brief discussion of fitting procedures that did not lead to parameterizations suitable for testing.

(i) Collins Model 1 (C1)

This formal charged shell model force field was derived by the slight adjustment of parameters reported in the CFR model, using relaxed fitting to the structure, elastic and dielectric constants of rutile. The original CFR model was derived by conventional fitting.

Despite varying different combinations of parameters during the relaxed fitting procedure, it was not possible to generate a set of new parameters that reproduced accurately the structure, elastic and dielectric constants. C1 does, however, represent a slight improvement over CFR, as it correctly reproduces the static dielectric constants in energy minimization calculations, despite the disagreement with the observed structure being similar to that produced by CFR. It should be emphasized that the improvement in the dielectric properties probably arises from the fine tuning of the Ti shell model parameters. The symmetry of the Ti atom is such that the core and shell reside at

the same position. Hence the Ti shell model parameters can be varied in order to reproduce the dielectric properties while having no effect on the crystal structure or the elastic constants. In effect the Ti shell model parameters are simply 'mop up' terms used to reproduce the dielectric constants of rutile at the perfect 0K configuration. The reliability of a force field employing such parameterization in MD studies, where the structure is not confined to the perfect 0K configuration, is open to question, particularly as the core and shell of the Ti atom are both positive and hence do not represent the physical meaning intended for the shell model.

(ii) Collins Model 2 (C2)

C2 is a formal charged rigid ion model that was derived using simultaneous relaxed fitting to the structures of the four TiO₂ polymorphs (rutile, anatase, brookite and TiO₂(ii)). The superiority of relaxed fitting over conventional fitting is demonstrated here, the sum of squares for the best fits being 6 and 7200, respectively.

(iii) Unsuccessful Fitting Attempts

A compilation of force field parameters for oxides, that includes a single set of oxygen parameters common to all the oxides, has been derived recently using simultaneous relaxed fitting [11]. Parameters for TiO₂ determined by fitting to anatase are included in the compilation. The authors report their parameterization for TiO₂ could not reproduce the structural properties of rutile. Various attempts to include rutile as observables in the simultaneous fitting failed. This led the authors to state that due to the high polarizing power of titanium it is likely that each phase of TiO₂ will require a specific set of oxygen parameters containing optimized polarizabilities.

In the course of this work, a number of attempts were made at fitting a new TiO₂ force field using the 'common oxygen' parameterization of Bush et al. [11]. These attempts included both fixing and allowing the oxygen parameters to vary while fitting to (i) the structure of rutile only; (ii) the structure, elastic and dielectric constants of rutile; and (iii) the structures of all four polymorphs simultaneously. All these attempts failed to produce a set of parameters suitable for testing.

Further attempts at fitting to rutile (structure, elastic and dielectric constants) using both rigid ion and shell models from a range of starting parameters also failed to produce parameters suitable for testing.

3 Results & Discussion

Details of bulk and surface energy minimization calculations carried out in the course of this evaluation using the force fields described previously are now presented in three parts. First, perfect lattice properties including structure, elastic and dielectric constants for rutile are calculated for all nine force fields. Second, the (100), (110) and (001) surface energies of rutile are determined using six force fields (three force fields are discarded after the first stage). Third, structural and energetic properties of the four polymorphs of TiO_2 are calculated using four force fields (a further two force fields are discarded after the second stage).

3.1 Perfect Lattice Properties of Rutile

Lattice energies, elastic constants and dielectric constants of rutile determined using all nine force fields are compared to experimental data in Table 2. The important features of Table 2 are summarized below.

(a) The results reported in the original papers have generally been reproduced here, except for MW4 where a minimum energy configuration could not be generated. MW4 was discarded at this stage. The failure of MW4 maybe due to the omission of the anisotropic polarizability employed in the original model; however, it is noted that a similar omission in MW3 has little effect on the properties reported in Table 2.

(b) All the formal charged models reproduce the lattice energy to within 10% of that determined experimentally [12]. The partial charged models (MA & MW3) both underestimate significantly the lattice energy.

(c) The formal charged shell models of CFR, CJ and C1 all overestimate the c lattice constant by over 8%. SIT underestimates the a lattice constant by 9%. All the other models reproduce the observed rutile structure [13] reasonably well.

(d) The elastic constants for the three formal charged rigid ions models (PB, SIT & C2) are all predicted to be too stiff. The remaining partial charged rigid ion model of MA and the formal charged shell models of CFR, CJ and C1 all give a reasonable description of the observed elastic tensor [14].

(e) The static and high frequency dielectric constants for rutile have been measured experimentally [15, 16]. Only CFR and C1 predict the static dielectric constants to be large and anisotropic, although this may be an artefact of non-physical Ti shell model parameters (as discussed in section 2.2). Both however, underestimate the high frequency dielectric constants. CJ contains an instability as it predicts large negative static dielectric constants and is therefore rejected at this stage. SIT is also rejected as it fails to reproduce the structure, elastic constants and dielectric constants.

3.2 Surface Energies of Rutile

The (100), (110) and (001) surfaces energies determined using CFR, MA, MW3, PB, C1 and C2 are shown together with data determined by *ab initio* HF [17] and LDA [18] procedures in Table 3. At present there are no experimental data available for the surface energies of rutile.

The important features of Table 3 are summarized below.

(a) All sets of calculations suggest (110) is more stable than (100), which in turn is more stable than (001).

(b) C1 failed to produce relaxed configurations for (110) and (100), while MW3 failed for all three surfaces. Both models are discarded at this stage. Again it is emphasized that originally MW3 was parameterized using an anisotropic description for the oxygen polarizability and was simplified in the current work to an isotropic shell model. It is possible that the failure of MW3 to generate relaxed low miller index surfaces for rutile may be due to the simplification in the treatment of oxygen polarizability.

(c) Despite MA incorrectly predicting the bulk lattice energy, the surface energies are in reasonable agreement with the *ab initio* data.

(d) CFR is also in reasonable agreement with the *ab initio* data despite overestimating the c lattice parameter and therefore overestimating the (100) and (110) surface

areas.

(e) Both the formal charged rigid ion models (PB & C2) predict very large energies for all three surfaces. This may be attributed to the hardness of the potential functions in both models. As shown in Table 2 both predict the elastic constants to be far too stiff.

3.3 Relative Stabilities of TiO₂ Polymorphs

TiO₂ occurs naturally in three polymorphs (rutile, brookite & anatase). All three can also be prepared synthetically. Rutile is the most abundant and generally believed to be the most stable [19]. Although there have been a number of studies on synthesis and phase changes of TiO₂ [20-22], a definitive phase diagram has not been produced because most published data are believed to reflect kinetic rather than equilibrium phenomena.

Ti is in octahedral coordination in each polymorph, however, the number of shared edges increases from two (out of twelve) in rutile, to three in brookite, to four in anatase. It has been suggested [23] that the relative stabilities of the three phases might be related inversely to the number of shared edges, i.e. rutile is more stable than brookite, which in turn is more stable than anatase. Brookite and anatase form under low temperature hydrothermal conditions, transforming irreversibly and exothermically to rutile above 900K [22]. However, the rates of transformation are influenced greatly by the particle size, together with the nature and amount of impurities present.

A fourth phase TiO₂(ii) possessing the α -Pb structure has been synthesized at high pressures (60 ± 20 Kb at 294K and 40-120Kb at 700-1800K) and shown to exist metastably at ambient conditions [24]. At extremely high pressures it has been suggested a fifth phase possessing a fluorite or distorted fluorite structure may exist [24,25].

The relative stabilities with respect to rutile of TiO₂(ii), brookite and anatase calculated using CFR, MA, PB and C2, together with the limited experimental data [20-22,26] are shown in Table 4.

A complete set of experimental data relating the stabilities of all four polymorphs at the same temperature is unavailable. Instead two sub-series have been reported. First, calorimetric experiments at room temperature [20,21] have suggested rutile is more stable

than $\text{TiO}_2(\text{ii})$ with in turn is more stable than anatase. Second, solution calorimetry measurements at 971K [22] have suggested rutile is more stable than brookite which in turn is more stable than anatase. Since differences in specific heats between polymorphs are usually small, the enthalpy trend at 971K is expected to be the same as that at room temperature. Thus the only uncertainty in the experimental data is whether $\text{TiO}_2(\text{ii})$ comes before or after brookite.

After relaxation only MA and C2 predict an order that is compatible with experimental observation, both giving the order: rutile is more stable than $\text{TiO}_2(\text{ii})$ is more stable than brookite is more stable than anatase. However, the agreement is only qualitative, the relative differences calculated by MA and C2 are much larger than those determined experimentally. Although PB predicted rutile to be the most stable polymorph after relaxation, it predicted anatase to be more stable than both brookite and $\text{TiO}_2(\text{ii})$. After relaxation CFR predicted anatase to be the most stable, followed by $\text{TiO}_2(\text{ii})$, followed by rutile, followed by brookite.

The unit cell dimensions, together with the volume per TiO_2 unit and the density of the four polymorphs determined using CFR, MA, PB & C2 are compared to experimental data in Table 5. Significant discrepancies exist for the structures of all four polymorphs using CFR. PB reproduces rutile, $\text{TiO}_2(\text{ii})$ and brookite reasonably well; however, the c axis of anatase is overestimated by 6%. Both MA and C2 reproduce the structures of all four polymorphs in reasonable agreement with the experimental data.

4 Conclusion

Of the nine force fields tested in this study, not one was able to reproduce, in good agreement with experiment, all of the following properties (lattice energy, structure, elastic & dielectric constants). When the relative stabilities of the low miller index surfaces of rutile and the relative stabilities of the TiO_2 polymorphs are considered, only two force fields (MA & C2) give results in qualitative agreement with *ab initio* calculations and experimental observation.

Since MA and C2 do not predict correctly all the perfect lattice bulk properties,

there remains scope for improvement. Clearly both models fail to describe all the fundamental physics of rutile. Of particular concern is the poor prediction of the lattice energy and dielectric properties by MA and elastic and dielectric properties by C2. The inclusion of a description of electronic polarizability in both models may yield significant improvements. However, it has been shown that obtaining suitable parameters by fitting to the structure, elastic and dielectric properties of rutile is unlikely to succeed. The parameterization of the short range oxygen–oxygen interaction by fitting to bulk properties is a major problem since it is relatively insensitive to the forementioned observables. Unfortunately the general oxygen–oxygen interaction derived for a range of oxides [11] is not appropriate for rutile. Further advances could be achieved by fitting to data from *ab initio* calculations or the observed phonon spectra, however, both procedures are non-trivial.

This work has also shown that for the case of TiO_2 relaxed fitting methods are superior to conventional fitting. It seems likely that a simple central force rigid ion model will not be able to provide a complete solution, and a description of electronic polarizability must be included. However, the required complexity of electronic polarizability remains uncertain. There are several comments in the literature indicating that a simple isotropic shell model maybe insufficient and that a breathing and/or deformable shell model is needed. In addition to the difficulties in parameterizing such models it should be stressed that their implementation in MD simulations of TiO_2 could lead to an increase of an order of magnitude in computational expense.

It is suggested that both MA and C2 (and possibly PB) be used in initial MD studies. The derivation of a new force field for rutile (and more generally TiO_2) may become necessary at a later date. As the project progresses it may be necessary to use several force fields, where the nature of the calculation determines the choice of force field.

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Table 1. Summary of Force Fields Used.

Author	Label	Method	Charges	Polarizability
Catlow, Freeman & Royal [2]	CFR	empirical	formal	shell model
Catlow & James [3]	CJ	empirical	formal	shell model
Matsui & Akaogi [5]	MA	empirical	partial	rigid ion
Mostoller & Wang [4]	MW3	empirical	partial	an. shell model [†]
Mostoller & Wang [4]	MW4	empirical	partial	an. shell model [†]
Post & Burnham [6]	PB	electron gas	formal	rigid ion
Sawatari, Iguchi & Tilley [7]	SIT	empirical	formal	shell model [†]
Collins (This work)	C1	empirical	formal	rigid ion
Collins (This work)	C2	empirical	formal	rigid ion

[†] isotropic shell model used in this work

[‡] rigid ion model used in this work

Table 2. Perfect lattice properties of rutile.

Property	EXPT [†]	CFR	CJ	MA	MW3	MW4	PB	SIT	C1	C2
Lattice Energy										
unrelaxed	-126.	-112.0736	-109.7818	-39.7305	-93.0800	-122.4450	-122.7825	-122.6067	-111.5590	-129.4747
relaxed		-112.5066	-110.2542	-39.7770	-93.2366		-122.9185	-123.7949	-112.0393	-129.5095
Structure										
a	4.59373	4.50955	4.58962	4.49380	4.47889		4.50063	4.18342	4.53300	4.58028
c	2.95812	3.20354	3.22878	3.01027	3.07644		3.06621	2.96143	3.21574	2.96340
u	0.3053	0.3100	0.3100	0.3033	0.3061		0.3054	0.3075	0.3102	0.3012
Elastic Constants										
c ₁₁	26.60	26.88	22.61	32.14	33.97		62.83	47.72	26.02	124.78
c ₃₃	46.99	55.36	47.43	44.42	59.45		99.96	91.38	53.76	148.45
c ₄₄	12.39	10.08	4.13	12.25	12.31		27.76	22.73	9.34	47.77
c ₆₆	18.86	21.28	18.36	22.58	23.13		39.51	36.51	20.74	58.29
c ₁₂	17.33	19.87	14.93	22.90	19.26		38.52	36.07	19.14	57.36
c ₁₃	13.62	19.81	20.97	14.68	23.80		27.78	25.00	20.04	50.06
Static Dielectric Constants										
ε ₁₁	86.	83.12	-96.13	3.22	49.23		5.30	8.76	85.68	3.88
ε ₃₃	170.	257.12	-609.83	2.48	37.04		5.03	9.28	169.14	3.96
High Frequency Dielectric Constants										
ε ₁₁	6.843	2.54	5.41	NA	2.19		NA	NA	2.62	NA
ε ₃₃	8.427	2.46	5.89	NA	2.23		NA	NA	2.54	NA

Units: Lattice energy in eV, cell dimensions in Å and elastic constants in 10¹⁰Nm⁻².

† (a) Lattice Energy [12], (b) Structure [13], (c) Elastic Constants [14] and (d) Dielectric Constants [15,16]

Table 3. Surface energies of rutile.

Surface	HAR [†]	RVK [‡]	CFR	MA	MW3	PB	C1	C2
(110)								
unrelaxed	2.63	1.76	3.05	2.05	2.94	4.45	3.00	5.50
relaxed	1.37	0.89	0.95	1.77	—	2.76	—	3.49
(100)								
unrelaxed	2.97	1.93	3.39	2.34	3.32	5.11	3.33	6.35
relaxed		1.12	1.24	2.07	—	3.21	—	3.95
(011)								
unrelaxed		2.11		2.06				
relaxed		1.40		1.85				
(001)								
unrelaxed	4.04	2.94	4.87	2.80	4.99	6.69	4.83	7.64
relaxed	2.84	1.65	2.20	2.40	—	4.45	1.57	4.78

Units: Surface energy in Jm^{-2} .

[†] Harrison [17] - HF calculation

[‡] Ramamoorthy, Vanderbilt & King-Smith [18] - LDA calculation

Table 4. Relative stabilities of TiO₂ polymorphs with respect to rutile.

	CRC [†]	NCW [†]	MK [×]	CFR		MA		PB		C2	
				unrelaxed	relaxed	unrelaxed	relaxed	unrelaxed	relaxed	unrelaxed	relaxed
TiO ₂ (ii)		3.2		-12.9	-1.2	6.1	3.4	7.7	14.0	39.5	30.0
Brookite	2.1		0.7	18.1	5.4	30.9	17.1	26.7	22.5	40.8	34.1
Anatase	5.0	5.2	3.3	9.8	-25.4	25.0	29.1	15.3	9.8	54.1	41.5

Units: Energy in KJ mol⁻¹.

[†] CRC Handbook of Chemistry and Physics [26] – differences enthalpies of formation at 298.15K

[†] Navrotsky and co-workers [20,21] – transformation enthalpies from calorimetric experiments at room temperature

[×] Mitsuhashi & Kleppa [22] – transformation enthalpies from solution calorimetry at 971K

Table 5. Unit cell properties of TiO₂ polymorphs.

	EXPT [†]	CFR	MA	PB	C2
Rutile					
a	4.5937	4.5095	4.4938	4.5006	4.5803
c	2.9581	3.2035	3.0102	3.0662	2.9634
Volume (TiO ₂ unit)	31.2116	32.5789	30.3950	31.0541	31.0846
Density	4.2499	4.0715	4.3641	4.2714	4.2673
TiO₂(ii)					
a	4.5318	4.7184	4.5236	4.5623	4.5603
b	5.5019	5.6552	5.3807	5.4300	5.5153
c	4.9063	4.9322	4.9377	4.9746	4.9204
Volume (TiO ₂ unit)	30.5828	32.9023	30.0459	30.8096	30.9389
Density	4.3373	4.0315	4.4148	4.3053	4.2873
Brookite					
a	9.1740	9.3859	9.1499	9.1926	9.1529
b	5.4490	5.3933	5.3907	5.3885	5.4425
c	5.1380	5.3501	5.1474	5.2419	5.1596
Volume (TiO ₂ unit)	32.1055	33.8539	31.7366	32.4569	32.1283
Density	4.1316	3.9182	4.1796	4.0868	4.1286
Anatase					
a	3.7845	3.5972	3.7707	3.7059	3.7794
c	9.5145	11.2197	9.5794	10.1334	9.5136
Volume (TiO ₂ unit)	34.0670	36.2958	34.0506	34.7927	33.9719
Density	3.8937	3.6546	3.8955	3.8125	3.9046

Units: Unit cell axes in Å, volume in Å³ & density in g cm⁻³

[†] (a) Rutile [13], (b) TiO₂(ii) [27], (c) Brookite [28] and (d) Anatase [29].