

## The modified interatomic potentials of FeS<sub>2</sub> in atomistic simulations

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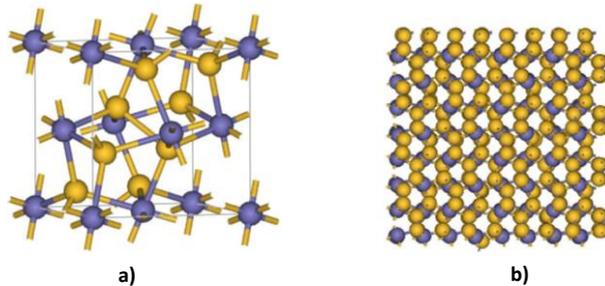
**Abstract.** The modified interatomic potentials were used for both energy minimization and molecular dynamics to study the surfaces and the bulk structure of pyrite. With energy minimization we calculated the surface energies of the surfaces {100}, {110}, {111} and {210}. They revealed that {100} surface is the most stable surface. When we compared the surface energies calculated from the original potentials and the adjusted potentials, it is clear that the adjusted potentials improve the stability of the surfaces. It was also revealed that water stabilizes the surfaces, since the surface energies decreases when hydrated. Molecular dynamics (MD) was used to evaluate the effect of temperature on the bulk structure.

### 1. Introduction

Many properties of materials are found to originate from atomic level physical factors; hence it is necessary to understand the behaviour of these materials at the atomic level. As such, atomistic simulations are breaking through as a helpful tool for analysing and predicting various fundamental static and dynamic properties of materials [1]. Iron sulphide minerals exist in a variety of forms with varying stoichiometries that range from the sulfur deficient mackinawite (FeS<sub>1-x</sub>) through iron deficient pyrrhotites (Fe<sub>1-x</sub>S) to pyrite (FeS<sub>2</sub>) and they are common in nature [2]. Among the iron-based sulphides, FeS<sub>2</sub> is the most abundant natural mineral, and it is available in two closely related polymorphic structures, namely, pyrite and marcasite [3]. The aim of this study is to determine the structure and dynamics of bulk and surfaces of pyrite FeS<sub>2</sub> using the modified interatomic potentials for atomistic simulations (i.e. energy minimization and molecular dynamics). The original potentials were first derived by de Leeuw and co-workers [4]. The modified interatomic potentials of pyrite have been able to improve some of our parameters, e.g. S-S bond length, from the original potentials. They have also improved the stability of the most stable surface, {100} of pyrite. The original potentials gave the surface energy of 1.23 J/m<sup>2</sup> while the modified potentials gave 1.04 J/m<sup>2</sup>, which improves the agreement with density functional theory (DFT) calculations. Energy minimization was used to calculate the surface energies of the low index surfaces. MD was used to identify the melting temperature of the bulk structure. We also study the effect of water molecules on the mineral surfaces. Water on mineral surfaces plays an important role in nature, which include mineral weathering and corrosion. The properties of mineral surfaces, i.e. structure, surface energy and reactivity, change when in contact with water.

### 1.1. FeS<sub>2</sub> (Pyrite) structure

Pyrite has a cubic structure and it belongs to the space group Pa3 [5]. The octahedrally coordinated Fe atoms are at the corners and face centers of the cube unit cell [6], and S atoms are arranged in ‘dumb-bell’ pairs centered at the mid-points of the cube edges and at the cube’s body center, the structure of pyrite shown in Figure 1.



**Figure 1.** Snapshots of a) cubic bulk Pyrite and b) 4x4x4 supercell of bulk pyrite used in the MD calculations, purple atoms represent iron (Fe) and yellow atoms represent sulphur (S).

The four S-S joins are respectively parallel to four non-intersecting body diagonal directions. The cubic pyrite structure can be considered as a derivative of the face-centered rock salt structure, NaCl, where (S<sub>2</sub>)<sup>-2</sup> occupies the Cl sites and Fe<sup>2+</sup> occupies Na sites [7].

## 2. Methodology

This study is based on atomistic simulation of the iron sulphide. We use molecular dynamics (MD), which is coupled with the modified interatomic potentials. The potentials were modified using the GULP [8] code. In our MD calculations we used the MD code called DL\_POLY [9]. The NPT and NVT ensembles were used and we considered cubic supercell consisting of 4x4x4 unit cells, which is equivalent to 768 atoms (shown in Figure 1b). The supercell used gives an approximately cubic simulation box of: 21.75 x 21.75 x 21.75 (in Å). The constant temperature and volume simulations were performed over the temperature range of 300 K to 1500 K with 200 K increments at zero pressure. The structure of the bulk and surfaces will be determined at different temperatures from the radial distribution functions (RDFs), diffusion coefficients. With these parameters we are able to determine the melting temperature of the bulk and the surfaces. The Born ionic model [10] was used and parameters were derived for short range interactions represented by the Buckingham potential, harmonic function and three body terms:

### 2.1. Buckingham Potential

In the Buckingham potential, the repulsive term is replaced by an exponential term and potential takes the form

$$U(r_{ij}) = A_{ij} * \exp^{-r_{ij}/\rho_{ij}} - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

where  $A_{ij}$  and  $\rho_{ij}$  are parameters that represent the ion size and hardness, respectively, while  $C_{ij}$  describe the attractive interaction and  $r_{ij}$  is the distance between ion  $i$  and ion  $j$ . The first term is known as the Born-Mayer potential and the attraction term (second term) was later added to form the Buckingham potential. Very often, for the cation-anion interactions, the attractive term is ignored due to the very small contribution of this term to the short-range potential, or, alternatively, the interaction is subsumed into the  $A$  and  $\rho$  parameters.

### 2.2. Harmonic Potential

The interaction between the sulphur atoms of the S-S pair were described by a simple bond harmonic function:

$$U(r_{ij}) = \frac{1}{2} k_{ij} (r_{ij} - r_0)^2 \quad (2)$$

where  $k_{ij}$  is the bond force constant,  $r_{ij}$  the interionic separation and  $r_0$  the separation at equilibrium.

### 2.3. Three-Body Potential

A further component of the interactions of covalent species is the bond-bending term, which is added to take into account the energy penalty for deviations from the equilibrium value. Hence, this potential describes the directionality of the bonds and has a simple harmonic form:

$$U(\theta_{ijk}) = \frac{1}{2} k_{ijk} (\theta_{ijk} - \theta_0)^2 \quad (3)$$

where  $k_{ijk}$  is the three-body force constant,  $\theta_0$  is equilibrium angle and  $\theta_{ijk}$  is the angle between two interatomic vectors  $i - j$  and  $i - k$ .

## 3. Results and Discussions

The interatomic potentials were modified, so that they can handle other parameters like elastic constants and most importantly the S-S intramolecular distance well. The properties, i.e. lattice parameters and elastic properties to validate the modified potential model of FeS<sub>2</sub> are discussed and also molecular dynamics simulation of bulk FeS<sub>2</sub> and the most stable surface at high temperatures are discussed.

### 3.1. Bulk FeS<sub>2</sub> (Pyrite)

To test our modified potential model we start by showing the calculated properties that were obtained using energy minimisation code GULP i.e., lattice parameters, bond lengths and elastic constants

**Table 1.** The calculated lattice constants, bond lengths and elastic constants in our work, compared with the calculated and experimental data in the given references.

Parameter	Modified Potential	Original Potential <sup>a</sup>	Calculated <sup>b,c,d</sup>	Experimental <sup>e</sup>
$a(\text{\AA})$	5.385	5.357	5.370	5.418
$Vol(\text{\AA}^3)$	156	154	155	159
Distances ( $\text{\AA}$ )				
S – S	2.180	1.838	2.196	2.177
Fe – S	2.290	2.275	2.354	2.262
Fe – Fe	3.870	3.788	-	3.381
Elastic Properties (GPa)				
$C_{11}$	370	352	395	366
$C_{12}$	51	56	30	47
$C_{44}$	99	122	119	105
Bulk Modulus (GPa)	157	155	151	153

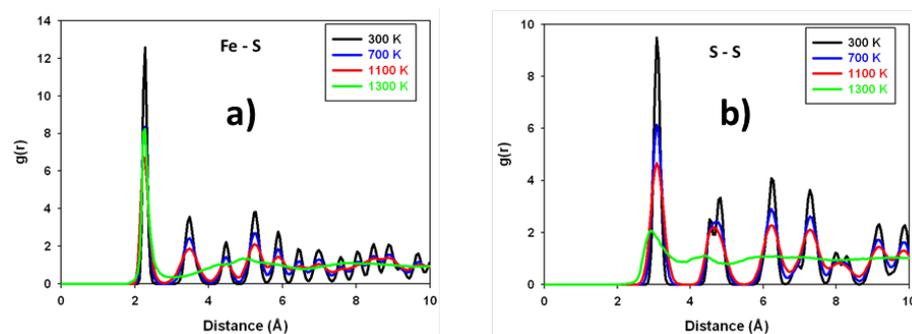
<sup>a</sup>[11], <sup>b</sup>[12], <sup>c</sup>[5], <sup>d</sup>[13], <sup>e</sup>[14]

Table 1 shows the calculated lattice constants, bond lengths and elastic constants of modified potentials compared with those of original potentials, experimental results and theoretical results from

literature. The comparison of the calculated properties with those obtained experimentally shows that the modified potential is better than the original potentials and other theoretical results. Therefore, the modified potential gives more reliable results.

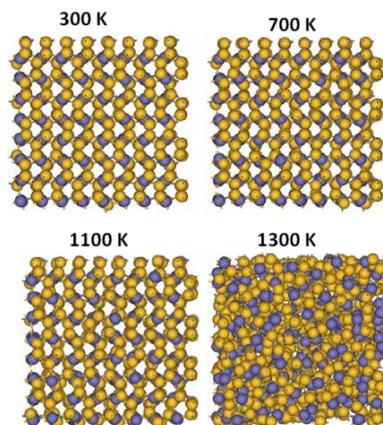
### 3.2. Molecular dynamics simulation of bulk FeS<sub>2</sub> (Pyrite)

The modified interatomic potentials were further tested by predicting the melting temperature of bulk structure using molecular dynamics technique. The melting point of the bulk structure is obtained from the radial distribution functions, structural changes and diffusion coefficients at various temperatures. Figure 2 shows the RDFs of bulk FeS<sub>2</sub> of the interactions Fe-S and S-S at different temperatures. From the radial distribution function plots we observe that at lower temperatures of 300 K, 700 K and 1100 K there are sharp peaks, implying a well-defined structure.



**Figure 2.** Radial distribution functions of pyrite FeS<sub>2</sub> for the a) Fe-S and b) S-S bonds at various temperatures.

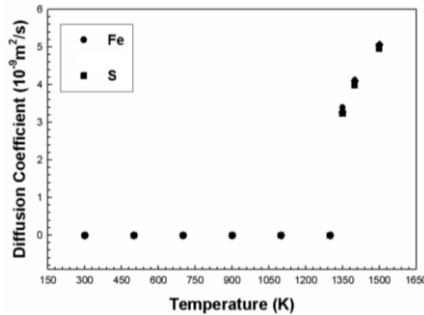
However, as the temperature increased to 1300 K the peaks become broader and their number decreases, showing that the structure is experiencing the phase transition from a solid phase to a liquid phase. This is indicative of the melting temperature of bulk structure at 1300 K, which is not far from the experimental temperature of between 1450 K and 1461 K [15].



**Figure 3.** Snapshots of the 4x4x4 supercell of pyrite at different temperatures, as indicated.

In addition, figure 3 shows the snapshots for the 4x4x4 supercell structure of FeS<sub>2</sub> at different temperatures from MD simulations. From the pictures we observe that there is a phase transition from a lower temperature to a higher temperature. At 300 K, 700 K the structure is still intact and crystalline. However, as we increase the temperature to 1100 K, we observe that the structure loses its crystallinity, as the regular arrangement of atoms disappears. At 1300 K the arrangement of atoms has completely disappeared. This is in further support of the temperature proposition put forward by the

results of the RDFs in figure 2. The melting point of a simulated structure can also be located by increasing the temperature of a crystalline system until ion diffusion appears. In figure 4 we have plotted the diffusion coefficients of Fe and S ions as a function of temperature in the bulk structure. These ions start to diffuse at 1300 K, which is the melting point of the bulk structure deduced from the RDFs in figure 2.



**Figure 4.** Diffusion coefficients of Fe and S ions as function of temperature for bulk structure of pyrite  $\text{FeS}_2$ .

### 3.3. Surface Energies of $\text{FeS}_2$ (Pyrite)

The modified potentials were also used for the calculations of surface energies of pyrite  $\text{FeS}_2$ . We calculated the surface energies from energy minimization. The surface energy is defined as the excess energy, per unit area of the surface compared to the bulk crystal. Thus any calculation of the surface energy also requires that we model a comparable amount of bulk crystal under identical condition.

**Table 2.** Calculated surface energies ( $\text{J/m}^2$ ) compared with the original potentials, and previous DFT calculations.

Pure Surface	Modified Potentials	Original Potentials <sup>a</sup>	DFT <sup>b</sup>	DFT <sup>c</sup>
{100}	1.04	1.23	1.06	1.04
{110}	1.68	2.36	1.68	1.72
{111}	3.38	3.92	1.40	1.43
{210}	1.62	1.99	1.50	1.49

<sup>a</sup>[4] <sup>b</sup>[16] <sup>c</sup>[17]

Table 2 gives the calculated surface energies using modified potential model compared with the original potentials, and previous DFT calculations. The modified potentials improve the stability of the surfaces, since it gives the lowest surface value. Amongst the high symmetry surfaces {100}, {111}, and {110}, {210} atomistic surface energy calculations proposed the {100} surface of  $\text{FeS}_2$  as the most stable in agreement with those from DFT calculations.

**Table 3.** Calculated hydrated surface energies (in  $\text{J/m}^2$ ) compared with those of calculated by original potentials.

Hydrated Surface	Modified Potentials	Original Potentials <sup>a</sup>
{100}	0.96	1.21
{110}	1.06	2.08
{111}	2.91	3.49
{210}	1.49	1.77

<sup>a</sup>[4]

Table 3 shows the hydrated surface energies of low index surfaces of FeS<sub>2</sub>. A comparison with the dry surfaces (Table 2) clearly depicts that hydration lowers surface energies; consequently the surfaces are more stable when hydrated. The {100} surface is still the most stable after hydration.

#### 4. Conclusion

The modified interatomic potentials were used for atomistic simulations to study the surfaces and the bulk structure of pyrite. The simulated results of bulk FeS<sub>2</sub> compared well with experimental observations and other calculations reported in the literature. The surface energies of the miller indexes revealed that {100} is the most stable surface, with a lowest surface value for both pure and hydrated surfaces. When we compared the surface energies calculated from the original potentials and the modified potentials, it is clear that the modified potentials improve the stability of the surfaces by generating the lowest surface values. MD simulation predicted the melting temperature of the bulk structure at 1300 K, which is not far from the experimental. Therefore, the modified potential can be used reliably to investigate bulk properties, surface energies and even to investigate the effect of temperature.

#### Acknowledgements

The computations were performed at the Materials Modelling Centre (MMC), University of Limpopo. We also acknowledge the National Research Foundation (NRF) for funding.

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