ASSESSMENT OF MECHANICAL, THERMAL AND SURFACE PROPERTIES OF MONOCLINIC $M_1$ AND $M_3$ $C_3S$ BY MOLECULAR DYNAMICS

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Abstract

Monoclinic $M_1$ and $M_3$ $C_3S$, which are the two main forms of industrial alite, were characterized at the molecular scale. Several methods were used to compute their mechanical and thermal properties. These methods were discussed and results in good agreement with experimental measurements were found. The cleavage energies were computed and the (100) and (001) showed the lowest energies for both polymorphs. Using the Wulff construction method, equilibrium shapes were proposed, and discussed with base on previous crystallographic studies.

Keywords Tricalcium silicate. Mechanical properties. Thermal properties. Cleavage energy. Crystal shape. Molecular dynamics.

1 INTRODUCTION

The research in cementitious materials is experiencing new challenges mainly due to the need to preserve the environment and save energy. To reduce CO$_2$ emissions and energy cost of production, alternative binders are under study [1]. However, Original Portland Cement (OPC) should continue to be employed for a long time and understanding of its principal constituent, alite, is primordial for its improvement.

As a matter of fact, even at high water/cement ratio ($w/c$), the total hydration of OPC is quite never achieved. Previous quantitative X-ray diffraction analyses estimated at about 85 % the amount of hydrated alite after 65 days for $w/c = 0.45$ [2]. The hydration degree of cement paste obtained by deconvolution technique applied to nanoindentation experiments reached 90 % at $w/c = 0.4$ [3]. Computation of thermal and mechanical properties at the molecular scale can provide important information on the behaviour of OPC clinker and hydrated product. Furthermore, from the computation of surface energies, the shape of $C_3S$ grains can be theoretically constructed for different polymorphs [4]. Determination of such properties by experimental methods are most of the time limited, especially in the case of surface energies [5]. In all cases, a proper synthesis procedure of pure $C_3S$ is necessary, and the determination of the amount of each polymorph in a sample is neither trivial nor accurate.

In this work, the mechanical, thermal and surface properties of $M_1$ and $M_3$ $C_3S$ (the main phase of alite in industrial OPC [6]) were characterized by molecular dynamics (MD) simulations. The atomistic systems investigated herein were built from the pure $M_1$ [6] and $M_3$ [7] crystal structures [Fig. 1]. While the latter has already been used [8-10], this is the first time that a $M_1$ $C_3S$ model has been employed with such computational techniques, despite of its predominance in alite of Portland clinker with high SO$_3$ content [11]. Regarding atomic structural organization along the (010) direction, and b parameters, the two cells are very closed. However, the two models are shifted by 1/4 in cell units in the (010) direction, meaning that the (010), Ca-rich, plane of the $M_1$ model corresponds to the (001) plane of $M_3$ model. The atomic organization along (001) axis in the $M_1$ model is close to $M_3$ model in the (100), and the c and a parameters in $M_1$ and $M_3$ respectively are almost equals. Conversely, the a parameter of the $M_1$ unit cell is approximately 3 times larger than the c parameter for $M_3$, and the major structural difference is expected in the (100) direction for $M_1$ and (001) direction for $M_3$.

The present article is thus divided into three sections, namely: elastic properties, thermal properties, and cleavage energies and equilibrium shapes. Each section has an introduction, a description of the method employed and a presentation and discussion of results. To finish, a conclusion resume the different findings.

2 ELASTIC PROPERTIES

Understanding the mechanical properties of $C_3S$ is important for two reasons: 1) as mentioned above, the total hydration of a cement paste is never achieved, so clinker components are to some extent, involved in the final microstructure of hydrated cement and 2) to optimize the grinding of clinker during cement manufacturing. The investigation of elastic properties of cementitious materials are most of the time related to hydrated products and very few data can be found in the literature concern-
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Figure 1: Unit cells of M\textsubscript{1} C\textsubscript{3}S (cell parameters: a = 27.874 Å, b = 7.059 Å, c = 12.257 Å, β = 116.03°) \[6\] and M\textsubscript{3} C\textsubscript{3}S (cell parameters: a = 12.235 Å, b = 7.073 Å, c = 9.298 Å, β = 116.31°) \[7\]. Color code: calcium cations in green, oxygen anions and silicate oxygen in red, silicon atoms in yellow, and silicate polyhedra in blue.

ing elastic properties of clinker components. Synthetic alite can be made by solid state sintering of decarbonated calcium oxide and fine silica, with possible addition of impurities (alumina, magnesium, sulfates), depending on the polymorph to be reached \[12\]. The elastic properties are typically determined by nanoindentation experiments and at the macroscale by resonance frequency measurements \[13, 14\]. Nanoindentation experiments are most of the time performed on hydrated mortar or cement paste \[3, 15, 16\], and more rarely on pure and doped clinker phases \[13\]. Unhydrated clinker phases are known to exhibit stiffnesses by 3–5 times larger and hardnesses by one order of magnitude larger than hydrated phases \[3, 13, 17\]. According to the generalized Hooke’s law, the elastic properties of anisotropic materials can be derived by the relation between the components of the stress and strain tensors \(\sigma_{ij}\) and \(\varepsilon_{kl}\):

\[
\sigma_{ij} = \sum_{k=1}^{3} \sum_{t=1}^{3} C_{ijkl} \varepsilon_{kl}
\]

(1)

where \(C_{ijkl}\) are the 81 components of the stiffness tensor. These components can be expressed as the derivative of the stress components \(\sigma_{ij}\) with respect to the strain components \(\varepsilon_{ij}\) and related to the strain energy \(U\):

\[
C_{ijkl} = \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} = \frac{\partial^2 U}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}}
\]

(2)

The elastic moduli \(E_i\) along the different directions can be derived from the compliance tensor, defined as \(S_{ij} = C_{ij}^{-1}\), and \(E_i = S_{ii}^{-1}\).

Considering the minor and major symmetries of the stiffness tensor it is possible to reduce the number of stiffness constants to 21 for a general anisotropic material. The more suitable Voigt notation divides the number of indices of stiffness constants by two and the number of components is reduced to 13 for a monoclinic crystal:

\[
\begin{bmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} & 0 & C_{15} & 0 \\
\sigma_{21} & \sigma_{22} & \sigma_{23} & 0 & C_{25} & 0 \\
\sigma_{31} & \sigma_{32} & \sigma_{33} & 0 & C_{35} & 0 \\
0 & 0 & 0 & C_{44} & 0 & C_{46} \\
0 & 0 & 0 & C_{55} & 0 & C_{56} \\
0 & 0 & 0 & C_{65} & 0 & C_{66}
\end{bmatrix}
= \begin{bmatrix}
\varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} & 0 & \varepsilon_{15} & 0 \\
\varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} & 0 & \varepsilon_{25} & 0 \\
\varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} & 0 & \varepsilon_{35} & 0 \\
\varepsilon_{44} & \varepsilon_{45} & \varepsilon_{46} & 0 & \varepsilon_{46} & 0 \\
\varepsilon_{54} & \varepsilon_{55} & \varepsilon_{56} & 0 & \varepsilon_{56} & 0 \\
\varepsilon_{64} & \varepsilon_{65} & \varepsilon_{66} & 0 & \varepsilon_{66} & 0
\end{bmatrix}
\]

(3)

Elastic properties of solids are generally computed by applying a strain or a stress in the desired directions and by determining the strain-stress or strain-energy relations. Two type of methods are used and discussed in this work: static optimization methods and time integration methods.

Static optimization methods are typically applied at 0K, or where anharmonical vibrations can be neglected, although lattice vibration frequency can be included through quasi-harmonic approximation techniques \[18\]. In the so-called static method, a small strain \(\Delta \varepsilon_j\) is applied positively and negatively in each direction \(j\):

\[
C^+_{ij} = \frac{-\sigma_i(\Delta \varepsilon_j) - \sigma_i(0)}{\Delta \varepsilon_j}
\]

\[
C^-_{ij} = \frac{\sigma_i(-\Delta \varepsilon_j) - \sigma_i(0)}{\Delta \varepsilon_j}
\]

(4)
The stiffness constants can be obtained by averaging $C_{ij}^+$ and $C_{ij}^-$ and the symmetric constants:

$$C_{ij} = \frac{C_{ij}^+ + C_{ij}^- + C_{ji}^+ + C_{ji}^-}{4} \quad (5)$$

This method performs quick calculation, minimizing the energy of the system before and after application of a small strain $\Delta \varepsilon$. However, it does not provide the stress-strain behavior nor give a prediction of the failure point. This computational scheme can be extended by applying a strain on several steps followed by an energy minimization after each step. The stiffness constant are therefore obtained by linear regression on the desired strain range.

For a system of particles with a volume $V$, the stress components can be computed as the sum of the kinetic and virial terms over the $N$ particles:

$$\sigma_{ij} = \frac{\sum_{k} N m_k v_{ki} v_{kj}}{V} + \frac{\sum_{k} N r_{ki} f_{kj}}{V} \quad (6)$$

where $i$ and $j$ are the directions $x$, $y$ and $z$, $m_k$, $r_{ki}$, $v_{ki}$ are the mass, position and velocity respectively, and $f_{kj}$ is the force applied on the particle $k$. In the case of a molecular mechanics (MM) optimization, the kinetic term is zero.

Time integration methods use equilibrium MD (EMD) or non-equilibrium (NEMD) to compute the deformation of the simulation box while controlling the stress or vice versa. In EMD, the equilibrium is made before each production run, resulting in a one point averaged result. In NEMD, the strain, or the stress, is changed continuously during the run. This is convenient because only a single run is needed, however the strain/stress rate may influence the result. The simulation can be either strain or stress controlled. In the first case, a strain rate is applied on the desired direction and with a fix stress (usually 0 GPa) on the other directions. In the second case, a stress rate is applied in one direction while keeping the others at 0 GPa. The box is thus allowed to relax in the other directions.

2.1 Methods

2.2 Force fields

In this study, two force fields (FF) were employed to describe atomic interactions in $\text{C}_3\text{S}$: INTERFACE FF (IFF) and ClayFF. The PCFF implementation of IFF, used here, include quadratic bonded terms for covalent bonds in silicates, an electrostatic term and a 9-6 Lennard-Jones (LJ) potential for short-range interactions:

$$U = \sum_{ij}^4 K_{ij}(r_{ij} - r_{0,ij})^6 + \sum_{ij}^4 K_{ij}(\theta_{ij} - \theta_{0,ij})^8$$

$$+ \frac{1}{4\pi \varepsilon_0 \varepsilon_r} \sum_{ij} \frac{q_i q_j}{r_{ij}} + \sum_{ij} \varepsilon_{0,ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^9 - 3 \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (7)$$

Conversely, the ClayFF does not account explicitly for covalent bonding in silicates, but larger charges are used for silicon atoms (2.1e), compared with the IFF (1.0e). Its interaction potential is thus the sum of a 12-6 LJ potential and electrostatic interactions. A 12 Å cutoff, and an Ewald summation with precision of $10^{-5}$ were adopted for short-range and long-range interaction, respectively.

2.2.1 Static calculations by MM

The elastic properties of M1 and M3 $\text{C}_3\text{S}$ were computed from the static MM calculation method on unit cells using the LAMMPS simulation code [19]. The enthalpy of the cell was minimized at 0 GPa, thus allowing the cell parameters and the atoms to move freely. Then a deformation was applied in the desired direction, the energy of the system was minimized, allowing the atoms to move while fixing the cell parameters. The process was repeated negatively and positively in each direction, to calculate the 21 components of the stiffness matrix according to the Eq. (5). The unit cells experienced maximal deformations of ±0.2, with increments of $1 \times 10^{-4}$, but the values $C_{ij}^\pm$ were obtained by linear fitting on values from zero to ±0.02 deformation.

Homogeneous values of bulk and shear moduli for large crystals randomly dispersed were obtained by calculating Reuss and Voigt bounds (respectively subscripted $R$ and $V$). The Voigt-Reuss-Hill (or VRH) estimation for monoclinic crystals is obtained as the arithmetic average of Voigt and Reuss bounds on bulk ($G_V$, $G_R$) and shear modulus ($G_V$, $G_R$) [20,21].

2.2.2 MD calculations

In order to determine elastic properties at finite temperature, supercells of 1296 atoms ($1 \times 4 \times 2$ and $2 \times 4 \times 3$ for M1 and M3 $\text{C}_3\text{S}$ respectively) were created from the unit cells presented in Fig. 1. For each polymorph, three replicas were created by using different seeds for the initial velocities of atoms. Equilibration runs were performed during 500 ps at 300 K in the NpT ensemble at hydrostatic pressure $\sigma$ varying between 0 and 15 GPa, followed by a production run of 1 ns. Nose-Hoover thermostat and barostat were employed and the Newton equation of motion was integrated with the Verlet algorithm. Long-range interaction were computed with an Ewald summation with precision of $10^{-5}$ and a cutoff of 10 Å was applied for van der Waals interactions.

The bulk modulus was calculated from the EMD simulation in the NpT ensemble with incremental equilibrium pressure. It is, by definition, the factor ratio between the variation of the hydrostatic pressure, and the volume variation rate, at constant temperature:

$$K = -V_0 \left( \frac{\partial P}{\partial V} \right)_T \quad (8)$$

In the NEMD calculation scheme, the supercells underwent 1 ns runs of compression and traction at a strain rate of $1 \times 10^8 \text{ s}^{-1}$ up to 20 %, the stress components were computed from Eq. (6). No noticeable influence was reported for rates of one order of magnitude above and below $1 \times 10^8 \text{ s}^{-1}$. This is predictable because the resulting
dislocation velocity is \( \sim 0.28 \text{ m s}^{-1} \) for the largest dimension. This dislocation velocity is large when compared to macroscale tests, but is negligible compared to the velocity of acoustic waves in C\(_3\)S. Based on the values of bulk modulus \( K \), Poisson’s ratio \( \nu \) and density \( \rho \) from previous acoustic measurements, compressive and shear waves are calculated as 7200 and 3700 \text{ m s}^{-1} \) respectively \[\text{[23]}\]. This ensures that atoms will respond instantaneously to the deformation of the simulation box \[\text{[21, 25]}\]. Elastic parameters were calculated by the direct relations, where \( i \neq j \) are the \( x \), \( y \), and \( z \) coordinates:

\[
E_{ij} = \frac{\sigma_{ij}}{\varepsilon_{ii}} \quad G_{ij} = \frac{\sigma_{ij}}{\varepsilon_{ij}} \quad \nu_{ij} = -\frac{\varepsilon_{ii}}{\varepsilon_{jj}}
\]

(9)

2.3 Results

2.3.1 Static calculations

The stiffness constants, homogenized elastic constants and directional elastic moduli of M\(_1\) and M\(_3\) C\(_3\)S, computed by static MM method are reported in Table 1. Velez et al. measured elastic moduli of (147 \pm 5) GPa and (135 \pm 7) GPa by resonance frequency and nanoindentation respectively \[\text{[13]}\]. Boumiz et al. found the following values by acoustic measurements \[\text{[23]}\]:

\[
K = (105.2 \pm 0.5) \text{ GPa}
\]

\[
G = (44.8 \pm 0.6) \text{ GPa}
\]

\[
E = (117.6 \pm 0.8) \text{ GPa}
\]

\[
\nu = 0.314 \pm 0.017
\]

The values obtained with IFF agree relatively well with these experimental measurements. When compared to experimental results, the ClayFF tends to underestimate by a factor of approximately 2 the stiffness constants and thus the elastic constants. This very probably result from the non-bonded nature of atomic interactions in ClayFF, which neglect the covalent nature of O-Si bonds in silicates, thus decreasing the stiffness. The values obtained with this force field are close to previous calculations on the same M\(_3\) unit cell, obtained with the GULP code, via second derivative of the binding energy \[\text{[26]}\]. Employing the same code and computational method, the Young moduli, shear moduli, bulk moduli and Poisson’s ratio were determined on the M\(_3\) C\(_3\)S model proposed by de la Torre et al. \[\text{[27]}\], using a Buckingham force field \[\text{[17]}\] and ClayFF \[\text{[26]}\]. The homogenized elastic constants obtained by IFF are very close to those obtained by Manzano et al. with the Buckingham FF \[\text{[17]}\]. The homogenized elastic constants obtained for M\(_3\) C\(_3\)S with this FF are smaller than for M\(_1\) and closed to recent results from DFT calculations on T\(_1\) C\(_3\)S \[\text{[28]}\]. The lowest elastic modulus is obtained in the \( x \) and \( z \) direction for the M\(_1\) unit cell with the \( a \) parameter of the M\(_3\) unit cell.

The distributions of elastic moduli in space were created from the ELATE open-source Python module \[\text{[29]}\]. The resulting shapes are illustrated in Fig. 2. The M\(_3\) polymorph reveals a much more anisotropic elasticity than the M\(_1\) polymorph.

2.3.2 EMD calculations

EMD calculations where performed with the IFF at 0, 1, 2.5 and 5 5 GPa. The bulk moduli obtained by linear fitting of the hydrostatic pressure with respect to the volume variation are (101 \pm 2) GPa and (103 \pm 2) GPa for M\(_1\) and M\(_3\) C\(_3\)S polymorphs, respectively. A larger difference with static MM calculation is observed for M\(_1\). This could rely on the fact that the M\(_1\) model, which is not averaged, experienced a structural relaxation during the MD run.

As an important feature of the C\(_3\)S, the change in coordination between calcium cations Ca and oxygen in silicates (O\(_s\)) as a function of the hydrostatic pressure was analyzed by radial distribution function (RDF) (see Fig. 3). The increasing hydrostatic pressure seems to influence the C\(_3\)S structure at short range (\( \sim 4 \) Å). The second coordination shell is flattened and shifted to the left by the effect of the pressure. The same behavior is observed for both polymorphs.

\[
K = (105.2 \pm 0.5) \text{ GPa}
\]

\[
G = (44.8 \pm 0.6) \text{ GPa}
\]

\[
E = (117.6 \pm 0.8) \text{ GPa}
\]

\[
\nu = 0.314 \pm 0.017
\]

\[
K = \frac{V}{\varepsilon}
\]

(9)

where \( V \) is the volume of the crystal and \( \varepsilon \) is the strain.
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2.3.3 Stress-strain behaviour by NEMD and MM calculations

Next, the stress-strain curves of the NEMD simulations, and of the static MM calculation are plotted in Fig. 4. The general behavior of the M1 and M3 polymorphs seems similar. However, the compression strength seems to be larger for the M1 polymorph in the x direction, and for the M3 polymorph in the z direction. The structural correspondence of the (001) direction for the M1 unit cell with the (100) direction for the M3 unit cell explains this result. The elastic moduli and Poisson’s ratios obtained from these NEMD simulation are presented in Table 2. They are relatively close to values from previous stress controlled NEMD simulations [9].

The observed elastic behaviour seems to be stiffer for the MM than for MD due to the larger structural relaxation induced by the thermal motion and the dynamical strain increasing. Nonetheless, the elastic properties obtained are in relatively close to results from static MM calculations. While the static method provide a good representation of elastic properties, it does not allow to assess the yield stress properly, since no relaxation is permitted in the transversal directions. This restriction causes hardening for negative strains. The yield stress can be assessed by enthalpy minimization, but this such calculation is not trivial and the calculation can easily stuck in a local minima because the objective function is changing while the box dimensions change. On the other part, static calculations are very fast when compared with MD calculations. MM calculations in all directions on a M3 unit cell was performed in 4 minutes on 4 Intel Xeon Gold 5120 CPUs @2.20 GHz, while a MD calculation only in the x direction on a 2 x 4 x 3 M3 supercell was finalized in 3 hours and 28 minutes on 24 Intel Xeon Gold 5120 CPUs @2.20 GHz.
3 Thermal properties

During their lifetime, concrete undergoes temperature changes. The thermal expansion and contraction of concrete as temperature increases and decreases, is influenced by the aggregate type, the cement type, and the water cement ratio. As explained in the introduction of this chapter, the complete hydration of cement is never reached. Thus, although the aggregate type has the larger influence on the expansion and contraction of concrete, the thermal properties of hydrated and dry cement is of great interest. Thermal cracking of concrete generally occurs during the first days after casting. During the exothermic hydration of cement, the temperature rises, and drops faster on the surface than in the bulk. The surface tends to contract with the cooling and stress arises because the bulk remains hot, resulting in cracks. Naturally, this phenomenon occurs more likely in larger volumes. Considering a system of fixed volume being heated, the heat capacity is the partial derivative of its internal energy with respect to its temperature:

\[ C_V = \left( \frac{\partial E}{\partial T} \right)_V \]  

(10)

Because of a their lower compressibility when compared to gases, the internal energy of solids experience larger variation with volume. For this reason, their heat capacity is most of the time determined experimentally at constant pressure, as the partial derivative of enthalpy with respect to temperature:

\[ C_p = \left( \frac{\partial H}{\partial T} \right)_p \]  

(11)

Two methods are commonly used to compute the specific heat from a molecular dynamics simulation. In the canonical ensemble, one can derive the fluctuation relationship between specific heat and internal energy as follows:

\[ C_V = \left( \frac{\partial E}{\partial T} \right)_V = \left( \frac{\partial E}{\partial \beta} \right)_T \]  

(12)

with \( \beta = 1/k_B T \), where \( k_B \) is the Boltzmann constant. From thermodynamical laws, the specific heat capacities \( c_v \) and \( c_p \) at constant volume and pressure, respectively, are related by the equation:

\[ c_p - c_v = T \frac{\alpha^2}{\rho} \]  

(13)

where \( \rho \) is the density, \( \alpha = (1/V)(\partial V/\partial T)_p \) is the thermal expansion coefficient, and \( \beta = -(1/V)(\partial V/\partial P)_T \) is the compressibility, inverse of the bulk modulus \( K \).

3.1 Methods

By using fluctuation methods, the specific heat can be computed at any temperature with a single, long enough run. However, these methods rely strongly on the temperature relaxation parameter used to thermostat the system (and in the case of the NpT ensemble, on the pressure relaxation parameter) [30]. Moreover values obtained by fluctuation method depends on the time interval used for block averages [30], often leads to large uncertainties and to bad agreements with experimental results [31]. For this reason, non-fluctuation, or direct method, is preferred. It consists on running several simulations at finite temperature and calculating the time average energies for each one. The specific heat is calculated by definition, as the slope of the total energy with respect to the temperature, at the desired temperature. The chosen temperature increment must be large enough to compute accurately the variation.
Figure 5: Total phonon density of states (top), and partial density of states with VACF in insets (bottom) of $M_1$ and $M_3\text{C}_3\text{S}$ obtained with IFF and ClayFF.

| Temperature (K) | $\alpha$ (K$^{-1}$) | $\beta$ (Pa$^{-1}$) | $\rho$ (g cm$^{-3}$) | $c_p - c_v$ (J g$^{-1}$ K$^{-1}$) |
|----------------|----------------------|----------------------|-----------------------|----------------------------------|
| $M_1$          |                      |                      |                       |                                  |
| 200            | $4.6(18) \times 10^{-5}$ | $9.9(2) \times 10^{-12}$ | $3.147(5)$ | $0.013(14)$ |
| 300            | $4.4(15) \times 10^{-5}$ | $9.7(3) \times 10^{-12}$ | $3.160(4)$ | $0.019(13)$ |
| 400            | $5.0(23) \times 10^{-5}$ | $10.0(2) \times 10^{-12}$ | $3.147(6)$ | $0.032(30)$ |
| $M_3$          |                      |                      |                       |                                  |
| 200            | $3.6(14) \times 10^{-5}$ | $9.7(2) \times 10^{-12}$ | $3.139(5)$ | $0.009(8)$ |
| 300            | $4.0(16) \times 10^{-5}$ | $9.7(3) \times 10^{-12}$ | $3.151(4)$ | $0.016(13)$ |
| 400            | $4.8(15) \times 10^{-5}$ | $9.5(2) \times 10^{-12}$ | $3.128(6)$ | $0.031(21)$ |

Table 3: Thermal properties of $M_1$ and $M_3\text{C}_3\text{S}$. 
of energy between each simulation, but small enough, for the fitting to be representative.

The specific heat can also be computed from the velocity autocorrelation function (VACF) of atoms. Considering a solid made by quantum harmonic oscillator, the phonon density of states $g(\omega)$ is proportional to the Fourier transform of the velocity autocorrelation function of the atoms:

$$g(\omega) = \frac{1}{3NkT} \int_{-\infty}^{+\infty} \sum_{i=1}^{N} \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle e^{i\omega t} dt$$

(14)

where $k$ is the Boltzmann constant, $N$ is the number of atoms and $T$ is the temperature of the system. The occupational states of phonons follows a Bose-Einstein distribution $f_{BE}$ and at energy largely below the Debye temperature, the total energy of the system can be reduced to the vibrational energy $E_v$ [32, 33]:

$$E_v = \int_{0}^{+\infty} \hbar \omega \left( g(\omega)f_{BE}(\omega) + \frac{1}{2} \right) d\omega$$

(15)

The specific heat in $3Nk$ units is calculated from Eq. (10) as follows:

$$c_v = \frac{\int_{0}^{+\infty} \frac{u^2 e^u}{(1 - e^u)^2} g(\omega)d\omega}{\int_{0}^{+\infty} g(\omega)d\omega}$$

(16)

where $u = \hbar \omega/kT$.

Specific heat and expansion coefficient were computed on three replicas of $\text{C}_3\text{S}$ supercells. The simulations were performed in the NpT ensemble with the same MD parameters as previously. The systems were relaxed during 0.5 ns, and the data were collected for 1 ns. Within the direct method, the specific heat $c_p$ was computed by linear fitting of the enthalpy with respect to the temperature at five points around the temperature of interest (e.g., 280, 290, 300, 310 and 320 K to compute the specific heat at 300 K). The same method was employed to calculate the expansion coefficient, fitting the volume variation with respect to the temperature. To compute $c_v$ as function of the VACF with no external influence of thermostating or barostating, the relaxed system were equilibrated for 500 ps in the NVE ensemble, before running simulation of 100 ps, dumping the trajectory at each time step to be able to observe high vibrational frequencies. For the calculation using the ClayFF, a geometric mixing rule for LJ parameters was used in place of the original arithmetic mixing. Indeed, this mixing rule provides more accurate value of density obtained during NpT simulations. The VACF were computed on ten correlation windows of 10 ps on three replica for each polymorph.

3.2 Results

The phonon density of states (DOS) obtained from simulations in the NVE ensemble are presented in Fig. 5. The phonon DOS obtained for $M_1$ and $M_3$ are almost identical, so as the resulting specific heat. Thus the structural difference between both polymorph does not influence their thermal properties. However, the force field does affect the results. The main difference between the phonon DOS obtained with IFF and ClayFF relies principally in their description of bonds in silicate. In the case of IFF, where Si-O bonds are described by harmonic oscillators in addition to the short and long range description, the partial DOS (PDOS) of Os and Si atoms form a sharpened peak near 935 cm$^{-1}$, in agreement with infrared spectroscopy measurements [34], while the in-plane bending vibration of Os-Si-Os angle is measured as a band bellow 500 cm$^{-1}$ [34]. This bending contribution happens at larger frequencies in our results (near 550 cm$^{-1}$). Wave numbers $\omega$ bellow 500 cm$^{-1}$ are associated to stretching between calcium and oxygen atoms [32, 35], in agreement with the PDOS obtained with both IFF and ClayFF. For ClayFF, the purely non-bonded description of Si-Os bonds allows for more degrees of freedom of atoms. The PDOS obtained for Si and Os atoms are thus more sparse. Generally, for the IFF, a shift of the DOS is observed towards higher vibrational frequencies. No significant variation of the DOS was observed between 200, 300 and 400 K. The error on the calculation of the isobaric specific heat $c_p$ are mostly related to the $c_p - c_v$ quantity, calculated from simulations in the NpT ensemble. The values of $c_p - c_v$ were calculated at 200, 300 and 400 K and extrapolated linearly, because this quantity vary proportionally with temperature (see Eq. (13)). The expansion coefficient $\alpha$, the compressibility $\beta$, and the density $\rho$, computed from simulations in the NpT ensemble are presented in Table 3.

The specific heat $c_p$ obtained for $M_1$ and $M_3$ of $\text{C}_3\text{S}$ are plotted with respect to the temperature in Fig. 6.

Figure 6: Specific heat of $M_1$ and $M_3$ of $\text{C}_3\text{S}$ obtained by the direct and VACF method, plotted as function of the temperature. The transparent areas represent the error. Previously computed value from VACF calculation, as well as fitting of experimental measurements [37] and direct measurements [35] are plotted in addition to the results.

The values obtained at 300 K by the direct method are $0.86 \pm 0.10$ and $(0.87 \pm 0.04)$ J g$^{-1}$ K$^{-1}$ for $M_1$ and $M_3$, respectively, which is much larger than experimental measurements. As for the phonon DOS, no significant variation of $c_p$ was found between $M_1$ and $M_3$. The VACF method with ClayFF results in $c_p =$
(0.751 ± 0.013) J g\(^{-1}\) K\(^{-1}\), which is very close to experimental values of 0.756 J g\(^{-1}\) K\(^{-1}\)\(^3\) and 0.753 J g\(^{-1}\) K\(^{-1}\)\(^2\)\(^4\). The IFF provided a value slightly lower than experimental measurements: (0.723 ± 0.013) J g\(^{-1}\) K\(^{-1}\).

4 Cleavage Energies and Equilibrium Shapes

Surface energy is an important property of crystals since it can be an indicator of reactivity and give information on equilibrium shapes\(^5\). A practical way to compute the surface energy is to use three-dimensional periodicity. This method consists in creating a box composed by a slab in contact with a vacuum gap. The thickness must be sufficient so that the properties of the center of the slab converge to those of the bulk, and the vacuum region needs to be large enough, such that the surfaces do not interact through the boundaries. The cleavage energy is defined as the energy necessary to split a crystal along a specific plane. It is therefore the average of the energies of the two surfaces created. The cleavage energy is commonly computed as the difference between the slab and the bulk energy per layer. The authors performed surface energy calculations (PBC). Sun and Ceder documented some issues regarding the calculation of the bulk energy from Eq. (17)\(^9\),\(^43\). The systems with lower energies were selected to relax the surfaces to the configuration of lower energy\(^9\),\(^43\). The lowest energy plane is in the (100) direction, at 1.1 Å from the origin. The (100) direction of the M\(^1\) polymorph corresponds to the (001) direction of the M\(^3\) polymorph and vice-versa. For M\(^1\) polymorph, the lowest energy is in the (100) direction, at 1.1 Å from the origin. For M\(^3\) polymorph, the lowest energy is in the (100) direction, at 1.1 Å from the origin. The (100) direction of the M\(^3\) polymorph has many possible cleavage planes and the plane for which the lowest energy was computed has no equivalent in the M\(^3\) polymorph.

$$E_{\text{cleav}} = \frac{E_{\text{slab}} - E_{\text{bulk}}}{2A} \quad (17)$$

where \(E_{\text{slab}}\) and \(E_{\text{bulk}}\) are respectively the energies of slab and bulk systems, with the same number of atoms and stoichiometry, and \(A\) is the surface area of one side of the slab. Most of the time, the bulk energy computation by MD is performed running simulations in NpT ensemble on a supercell, with periodic boundary conditions (PBC). Sun and Ceder documented some issues regarding the calculation of the bulk energy from Eq. (17)\(^9\),\(^43\). Non-convergence arises from the difference between the converged bulk energy and the incremental increase of slab energy per layer. The authors performed surface energy computation calculating the bulk energy in different ways. The two methods which most improved the convergence were: 1) the calculation on basis transformed unit cells, eliminating inconsistencies in Brillouin zone integration and 2) the linear-fit relation introduced by Fiorentini and Methfessel\(^40\), giving an average of the bulk energy computed over several slabs of different thickness.

$$E_{\text{slab}}(N) = 2E_{\text{surf}} + NE_{\text{bulk}} \quad (18)$$

where \(N\) is the number of layers forming the slab in the perpendicular direction.

Another way mostly used in MD to compute the cleavage energy, preventing from any issue related to computation of the bulk energy, is to subtract the computed energies of unified and cleaved slabs, using the following equation:

$$E_{\text{cleav}} = \frac{E_{\text{cleaved}} - E_{\text{unified}}}{2A} \quad (19)$$

When the surfaces computed on both sides of the slab are symmetrically equivalent, the surface energy is equal to the cleavage energy. However, for most of the minerals, such an assumption cannot be effective for all the Miller indices, and, among various existing methods, Manzano et. al\(^8\) suggested to divide the slab in contact with a vacuum into two atomic groups and to computed the surface energy for each of them. Both groups have one side exposed to the vacuum region and the other in contact with the other group. The surface energy of each side of the slab can be computed as follow:

$$E_{\text{surf}} = \frac{E_{\text{slab}} - E_{\text{bulk}}}{A} \quad (20)$$

Obviously, if the subject of the study is a reconstructed, electrically neutral slab, the surface energies computed for both subslabs are considered equals and correspond to a cleavage energy. One should note that surface energies of asymmetrical, non-reconstructed surfaces can be computed by density functional theory or using a reactive force field. However, this is not in accordance with the classical electrostatic criteria stipulated by Tasker\(^41\),\(^42\) and could lead to unrealistic charge distribution. In addition to redistribution of the atomic charge on the two faces of the slab, other methods such as temperature gradients can be applied to assess more energetically favorable configurations, resulting in lower cleavage energies\(^9\),\(^43\).

4.1 Methods

The calculation of cleavage energies for multiple planes of the two monoclinic C\(_3\)S models under study involved creation of cleaved and unified systems. For non-symmetric planes, reorganization of superficial ions was performed to minimize superficial dipole moments. For each plane, five unified and cleaved systems were constructed with random distribution of surface species. A 10 nm vacuum was employed in cleaved systems. Series of steep temperature gradients were applied on ions within the uppermost and lowermost atomic layer of slabs in unified and cleaved systems. This method was previously employed and allows to relax the surfaces to the configuration of lower energy\(^9\),\(^43\). The systems with lower energies were selected to performed the calculation over 300 ps runs, after 200 ps equilibration runs. We refer the reader to ref.\(^35\) for more details on the method.

4.2 Results and discussion

The cleavage energy was computed classically from Eq. (19) and results are given in Table 4. The computed values are in the range of 1.14 to 1.55 J m\(^{-2}\) (1.32 J m\(^{-2}\) in average) for M\(^1\) C\(_3\)S, and 1.04 to 1.76 J m\(^{-2}\) (1.35 J m\(^{-2}\) in average) for M\(^3\) C\(_3\)S, in good agreement with previous atomistic simulation studies\(^8\),\(^44\). In general, the average values are very closed between the two models. The energies obtained for particular planes vary as a function of the structure of each polymorph, and is particularly influenced by coordination between calcium cations and oxygen atoms in silicates. The (100) direction of the M\(^1\) polymorph corresponds to the (001) direction of the M\(^3\) polymorph, and vice-versa. For M\(^1\) C\(_3\)S, the present calculation indicates that the lowest energy plane is in the (100) direction, at 2 Å from the origin. The (100) direction of the M\(^1\) polymorph has many possible cleavage planes and the plane for which the lowest energy was computed has no equivalent in the M\(^3\) polymorph.
Table 4: Cleavage energies of $M_1$ and $M_3\ C_3S$. Only the lowest energy plane is given in the (100) direction for $M_1$. Results for $M_3\ C_3S$ are from our previous study [38].

| $M_1\ C_3S$ | $M_3\ C_3S$ |
|--------------|--------------|
| Miller index | Cleavage energy (J m$^{-2}$) | Miller index | Cleavage energy (J m$^{-2}$) |
| (100)        | 1.04 ± 0.04  | (100)        | 1.39 ± 0.03  |
| (010)        | 1.41 ± 0.04  | (300)        | 1.14 ± 0.03  |
| (003)        | 1.20 ± 0.03  | (800)        | 1.17 ± 0.03  |
| (008)        | 1.20 ± 0.04  | (010)        | 1.55 ± 0.04  |
| (110)        | 1.45 ± 0.04  | (040)        | 1.31 ± 0.04  |
| (011)        | 1.51 ± 0.03  | (001)        | 1.38 ± 0.04  |
| (002)        | 1.17 ± 0.04  | (002)        | 1.45 ± 0.04  |
| (011)        | 1.17 ± 0.04  | (003)        | 1.31 ± 0.04  |
| (111)        | 1.43 ± 0.03  | (003)        | 1.33 ± 0.04  |

Figure 7: Equilibrium shapes of $M_1$ and $M_3\ C_3S$

The Wulff construction can give theoretical insights on the shape of a crystal at equilibrium. It is based on the assumption that a crystal growth in a such way that the Gibbs free energy of its surface is minimized. From the lowest energy obtained in each direction, the equilibrium shapes of $M_1$ and $M_3\ C_3S$ in Fig. 7 were created with the construction algorithm implemented in the pymatgen library [39, 45]. In the $M_1$ polymorph, the crystal grows only along three planes, while in the $M_3$, seven planes are available. Maki related that the equilibrium form of alite is usually made up of three special forms: one pedion and two rhombohedra [46].

The author proposed a morphology similar to the $M_1$ obtained by Wulff construction, though more flat and with only one rhombohedra form. Maki explains that the crystal form of alite changes during recrystallization from platelet to massive granules with well developed pyramidal faces (1011) and (1102) [47]. The ratio between the width and the length of the platelet is function of the environment during the growth. One should note that the obtained equilibrium shapes are not fully definitive, since they were determined on a relatively finite number of planes. More calculations would probably refine these shapes, and produce a more accurate prediction.

5 Conclusion

The mechanical and thermal properties of $M_1$ and $M_3\ C_3S$ were investigated, as well as cleavage energies and equilibrium shapes. The elastic constants were calculated by static and dynamical methods. The elastic constants found by Voigt-Reuss-Hill homogenization of the stiffness constants obtained in static calculation with IFF were found in good agreement with experimental measurements. However, the results obtained with ClayFF overestimated and underestimated experimental results, respectively. Isotropic distribution of elastic moduli in space was observed for the $M_1$ polymorph, whereas an
anisotropic distribution was found for M3. Bulk modulus was obtained by EMD, and elastic, shear modulus, as well as Poisson’s ratio were calculated by NEMD. The results are in good agreement with static calculations and experimental measurements.

Specific heat capacities were calculated by the direct method and from VACF. The direct method provides results greater than experimental measurements, and with much larger error than the VACF method. On the other hand, the VACF allowed to analyse the phonon density of states and provide results much more accurate. The results obtained with ClayFF are very close to previous experimental measurements, and results from IFF are slightly smaller. The DOS obtained from VACF are in good agreement with infrared spectroscopy measurements, and the differences between IFF and ClayFF arise mainly from the bond description of silicates.

Cleavage energy calculations were performed on both M1 and M3 C3S polymorphs, using a temperature gradient method to relax superficial ions to configurations of lower energy. The energies obtained for both polymorphs are in the same range. The resulting equilibrium crystal shapes, obtained by Wulff construction, are however different, but the planes of low index with lowest energies are the (100) and (001) for both polymorphs. The M1 construction possess three facets against seven for the M3 polymorph. The cleavage energies were calculated for a relatively limited number of planes, and further calculation could lead to even more accurate shapes.

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