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Assessment of mechanical, thermal properties and crystal shapes of monoclinic tricalcium silicate from atomistic simulations

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Abstract

The two most common polymorphs in industrial alite, M1 and M3, were characterized at the molecular scale. Different methods were employed and discussed to assess mechanical properties and specific heat of both polymorphs. The calculated homogenized elastic moduli and specific heat were found in good agreement with experimental measurements. A comparative analysis of spacial Young's modulus reveal isotropic and anisotropic spacial distribution for M₁ and M₃ respectively. A more isotropic compressive strength is also reported for M₁ when compared to M₃ polymorph. Cleavage energies computation allowed to proposed equilibrium shapes for both polymorph, with significant differences. While the lowest cleavage energies were found along (100) and (001) for both polymorphs, the constructed M₁ crystal possesses 3 independent facets, against seven for the M₃ polymorph.

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

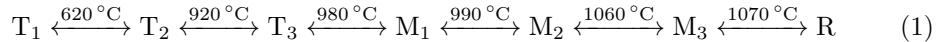
1. Introduction

The research in cementitious materials is experiencing new challenges mainly due to the need to preserve the environment and save energy. To reduce CO₂ emissions and energy cost of production, alternative binders are under study [1]. However, ordinary Portland cement (OPC) should continue to be employed for a long time and understanding of its principal constituents is primordial for its improvement. Another way to reduce the environmental impact of Portland cement is to enhance its reactivity which will involve less content of cement in concrete for the same strength. Since alite is the principal phase of Portland clinker that most contributes to strength development of Portland cement and particularly at early ages, a deep understanding of its properties is crucial to

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11 improve its quality and reactivity. Alite is a tricalcium silicate (C_3S) with minor oxides
 12 usually called impurities. It presents a large grade of polymorphism depending on dif-
 13 ferent factors, among them: the nature and the amount of impurities, the temperature
 14 of preheating or burning [2]. Seven structures were reported in industrial alite: three
 15 triclinic (T_1 , T_2 and T_3), three monoclinic (M_1 , M_2 and M_3), and a rhombohedral form
 16 R. These polymorphs appear via successive and reversible phase transitions [3]:



17 It is well known that impurities in alite stabilize high temperature polymorphs at low
 18 temperatures [3, 4]. The two main C_3S polymorphs present in industrial clinker are M_1
 19 and M_3 . According to Maki and Goto [5], MgO in clinker promotes the stable growth of
 20 alite in favor of the occurrence of M_3 . In contrary, decreased MgO/SO₃ ratio lead to M_1
 21 stabilization [2, 5]. It was also reported that preheating of the raw meal may result in
 22 the disappearance of the M_3 polymorph [2]. This modifications in the structure of C_3S
 23 can have a significant impact on strength as reported in few experimental results in the
 24 literature [2, 6]. The transformation of M_3 to M_1 polymorph may result in a 10% increase
 25 in the compressive strength [2]. The origin of this observed variation in strength could be
 26 explained by a greater amount of non-bonding electrons in oxygens of M_1 C_3S , leading
 27 to a higher reactivity when compared to the M_3 polymorph. The impact of structure at the
 28 atomic level via molecular modelling and simulation should be helpful to improve our
 29 understanding of Portland cement.
 30

31 Over recent years, the properties of cementitious materials were addressed using atom-
 32 istic models, with particular attention on the main hydration product of OPC: calcium
 33 silicate hydrates (C-S-H) [7, 8]. In comparison, only few studies at the atomic scale fo-
 34 cused on OPC clinker phases [9]. Computation of thermal and mechanical properties at
 35 the molecular scale can provides important information on the behaviour of OPC clinker
 36 and hydrated product. From the computation of surface energies, crystal shapes can be
 37 theoretically constructed for different polymorphs and help to understand morphological
 38 changes [10]. The knowledge of preferential cleavage planes and crystal shapes of C_3S
 39 polymorphs is fundamental to understand their growth during the clinkering process [11].
 40 It could also explain C_3S dissolution mechanisms [12] or cleavage modes during clinker
 41 grinding [13, 14]. Determination of such properties by experimental methods are most
 42 of the time limited, especially in the case of surface energies [15]. In all cases, a proper
 43 synthesis procedure of pure C_3S is necessary, and the determination of the amount of
 44 each polymorph in a sample is neither trivial nor accurate [16].

45 In this work, the mechanical, thermal and surface properties of M_1 and M_3 C_3S (the
 46 main forms of alite encountered in industrial OPC [17]) were characterized by molecular
 47 dynamics (MD) simulations. The present article is divided into four sections: crystal
 48 structures and force fields, mechanical properties, thermal properties, and cleavage ener-
 49 gies and equilibrium shapes. The last three sections include a description of the method
 50 employed and a presentation and discussion of results. To finish, a general conclusion
 51 resumes the different findings.

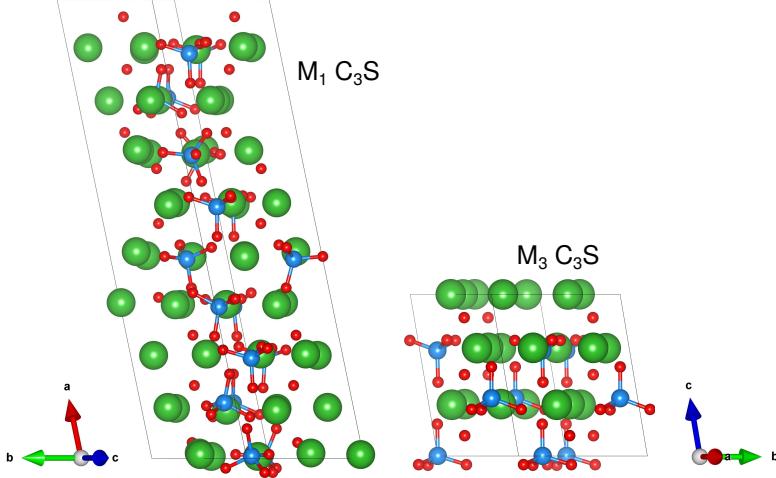


Figure 1: Unit cells of $M_1 C_3 S$ (cell parameters: $a = 27.874 \text{ \AA}$, $b = 7.059 \text{ \AA}$, $c = 12.257 \text{ \AA}$, $\beta = 116.03^\circ$) [17] and $M_3 C_3 S$ (cell parameters: $a = 12.235 \text{ \AA}$, $b = 7.073 \text{ \AA}$, $c = 9.298 \text{ \AA}$, $\beta = 116.31^\circ$) [18]. Color code: calcium cations in green, oxygen anions and silicate oxygen in red and silicon atoms in blue

2. Crystal structures and force fields

The atomistic systems investigated were built from the pure M_1 [17] and M_3 [18] crystal structures depicted in Fig. 1. While the latter has already been used [13, 19, 20], this is the first time that a $M_1 C_3 S$ model has been employed in a MD investigation, despite of its predominance in alite of Portland clinker with high SO_3 content [5]. Regarding atomic structural organization along the (010) direction, and b parameters, the two cells are very close. 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 (040) plane of the 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 equal. 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 .

Understanding the mechanical properties of $C_3 S$ is important for various reasons; among them: 1) 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 [21, 22], and mainly at early ages; 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 concerning 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 [23]. The elastic properties are typically determined by nanoindentation experiments and at the macroscale by resonance frequency measurements [24, 25]. Nanoindentation experiments are most of the time performed on hydrated mortar or cement paste [22, 26–

77 28], and more rarely on pure and doped clinker phases [24]. Unhydrated clinker phases
 78 are known to exhibit stiffnesses by 3–5 times larger and hardnesses by one order of
 79 magnitude larger than hydrated phases [22, 24, 29].

80 Two force fields (FF) introduced in the *cemff* database [9] were employed to describe
 81 atomic interactions in C₃S: INTERFACE FF (IFF) [13, 30] and ClayFF [31]. The PCFF
 82 implementation of IFF, used inhere, includes quadratic bonded terms for covalent bonds
 83 in silicates, an electrostatic term and a 9-6 Lennard-Jones (LJ) potential for short-range
 84 interactions:

$$E_{IFF} = \sum_{ij} \sum_{n=2}^4 K_{r,ij} (r_{ij} - r_{0,ij})^n + \sum_{ijk} \sum_{n=2}^4 K_{\theta,ij} (\theta_{ij} - \theta_{0,ij})^n \\ + \frac{1}{4\pi\varepsilon_0\varepsilon_r} \sum_{ij} \frac{q_i q_j}{r_{ij}} + \sum_{ij} \varepsilon_{0,ij} \left[2 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^9 - 3 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2)$$

85 ClayFF is a general force field initially developed to describe interfaces between clays
 86 and water [31], and in particular adsorption of ions for, inter alia, environmental appli-
 87 cation. It uses a flexible single point charge (SPC) water model and its potential energy
 88 includes a 12-6 Lennard-Jones potential:

$$E_{ClayFF} = K_{r,ij} (r_{ij} - r_{0,ij})^2 + K_{\theta,ij} (\theta_{ij} - \theta_{0,ij})^2 \\ + \frac{1}{4\pi\varepsilon_0\varepsilon_r} \sum_{ij} \frac{q_i q_j}{r_{ij}} + \sum_{ij} \varepsilon_{0,ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (3)$$

89 For dehydrated species, its interaction potential is the sum of a 12-6 LJ potential and
 90 electrostatic interactions. ClayFF does not account explicitly for covalent bonding in sil-
 91 icates, and larger charges are used for silicon atoms (2.1e) when compared to IFF (1.0e).
 92 The ionic nature of these bonds is thus overestimated in ClayFF, and impacts substan-
 93 tially computed surface tension [13]. We also expect an influence of this assumption on
 94 the elastic behaviour [30]. Results in better agreement with experimental measurements
 95 are expected with IFF, for which parameters were optimized especially for C₃S [13]. Ev-
 96 ery simulation in the present paper were performed with the LAMMPS simulation code
 97 [32]. A 12 Å cutoff, and an Ewald summation with precision of 10⁻⁵ were adopted for
 98 short-range and long-range interaction, respectively.

99 3. Mechanical properties

100 3.1. Methods

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

1. Static optimization methods are typically applied at 0 K, or where anharmonical vibrations can be neglected, although lattice vibration frequency can be included through quasi-harmonic approximation techniques [33]. In this case, a small strain $\Delta\varepsilon_j$ is applied positively and negatively in each direction j : 105
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$$\begin{aligned} C_{ij}^+ &= -\frac{\sigma_i(\Delta\varepsilon_j) - \sigma_i(0)}{\Delta\varepsilon_j} \\ C_{ij}^- &= \frac{\sigma_i(-\Delta\varepsilon_j) - \sigma_i(0)}{\Delta\varepsilon_j} \end{aligned} \quad (4)$$

The stiffness constants can be obtained by averaging C_{ij}^+ and C_{ij}^- and the symmetric constants: 109
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$$C_{ij} = \frac{C_{ij}^+ + C_{ij}^- + C_{ji}^+ + C_{ji}^-}{4} \quad (5)$$

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 multiple steps followed by an energy minimization after each step. The stiffness constants are therefore obtained by linear regression on the desired strain range. 111
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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: 117
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$$\sigma_{ij} = \frac{\sum_k^N m_k v_{ki} v_{kj}}{V} + \frac{\sum_k^N r_{ki} f_{kj}}{V} \quad (6)$$

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. 119
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2. Time integration methods use equilibrium MD (EMD) or non-equilibrium (NEMD) simulations to compute the deformation of the simulation box while controlling the stress or vice versa. In EMD, the equilibrium is reached before each production run, which provides time-averaged values of the computed properties. 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 fixed 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 simulation box is thus allowed to relax in the other directions. 122
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The elastic properties of M_1 and $M_3 C_3 S$ were first computed from the static MM calculation method on unit cells. The enthalpy of the cell was minimized at 0 GPa, allowing free movement of atoms and cell parameters. Then a deformation was applied in the desired direction and 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 133
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139 Eq. (5). The unit cells experienced maximal deformations of ± 0.2 , with increments of
 140 1×10^{-4} , but the values C_{ij}^{\pm} were obtained by linear fitting on values from zero to ± 0.02
 141 deformation. Homogeneous values of bulk and shear moduli for large crystals randomly
 142 dispersed were obtained by calculating Reuss and Voigt bounds. The Voigt-Reuss-Hill
 143 (or VRH) estimation for monoclinic crystals is obtained as the arithmetic average of
 144 Voigt and Reuss bounds on bulk and shear modulus [34–36].

145 In order to determine elastic properties at finite temperature supercells of 1296
 146 atoms ($1 \times 4 \times 2$ and $2 \times 4 \times 3$, with dimensions $27.87 \text{ \AA} \times 28.24 \text{ \AA} \times 24.52 \text{ \AA}$ and $24.47 \text{ \AA} \times 28.29 \text{ \AA} \times 27.89 \text{ \AA}$, for M_1 and $M_3 C_3 S$ respectively) were created from the unit cells
 147 presented in Fig. 1. For each polymorph, three replicas were created by using different
 148 seeds for the initial velocities of atoms. Equilibration runs were performed during 500 ps
 149 at 300 K in the NpT ensemble at hydrostatic pressure σ varying between 0 and 15 GPa,
 150 followed by a production run of 1 ns. Nose-Hoover thermostat and barostat [37, 38]
 151 were employed with the Verlet algorithm [39] to integrate Newton’s equations of motion.
 152 Long-range interaction were computed with an Ewald summation with precision of 10^{-5}
 153 and a cutoff of 10 \AA was applied for van der Waals interactions.

154 The bulk modulus K was calculated from EMD simulations in the NpT ensemble
 155 with incremental equilibrium pressure. In NEMD simulations, the supercells underwent
 156 1 ns runs of compression and tension at a strain rate of $1 \times 10^8 \text{ s}^{-1}$ up to 20 %, while
 157 maintaining the pressure to 0 GPa in the other directions. The stress components were
 158 computed from Eq. (6). No noticeable influence was reported for rates of one order
 159 of magnitude above and bellow $1 \times 10^8 \text{ s}^{-1}$. This is predictable because the resulting
 160 dislocation velocity is $\sim 0.28 \text{ m s}^{-1}$ for the largest dimension. This dislocation velocity
 161 is large when compared to macroscale tests, but is negligible compared to the velocity
 162 of acoustic waves in $C_3 S$. Based on the values of bulk modulus K , Poisson’s ratio
 163 ν and density ρ from previous acoustic measurements, compressive and shear waves are
 164 calculated as 7200 and 3700 m s^{-1} respectively [40]. This ensures that atoms will respond
 165 instantaneously to the deformation of the simulation box [41, 42]. Elastic parameters
 166 were calculated by the direct relations, where $i \neq j$ are the x , y and z coordinates:

$$\begin{aligned} E_{ii} &= \frac{\sigma_{ii}}{\varepsilon_{ii}} \\ G_{ij} &= \frac{\sigma_{ij}}{\varepsilon_{ij}} \\ \nu_{ij} &= -\frac{\varepsilon_{ii}}{\varepsilon_{jj}} \end{aligned} \quad (7)$$

168 3.2. Results and discussion

169 The stiffness constants, homogenized stiffness constants and elastic moduli of M_1 and
 170 $M_3 C_3 S$, computed by static MM method, as well as experimental results from literature,
 171 are reported in Table 1. ClayFF tends to underestimate by a factor of approximately 2
 172 the stiffness constants and thus the elastic moduli. This very probably results from the
 173 non-bonded nature of atomic interactions in ClayFF, where the covalent nature of O-Si
 174 bonds in silicates is underestimated, thus decreasing their stiffness. Previous calculations
 175 on the same M_3 unit cell, via second derivative of the binding energy with the GULP
 176 code, lead to very similar results [43]. The homogenized elastic moduli computed with
 177 IFF agree relatively with experiments. The values obtained for $M_3 C_3 S$ are smaller than

	M ₁		M ₃		Exp.
	IFF	ClayFF	IFF	ClayFF	Boumiz et al. ^a [40] Velez et al. [24]
C_{11}	185.2(2)	89.3(2)	219.6(3)	118.6(2)	
C_{12}	62.11(9)	29.6(4)	77.54(9)	34.81(7)	
C_{13}	61.73(8)	27.83(7)	52.79(7)	35.98(5)	
C_{15}	17.35(3)	-0.12(7)	4.0(1)	17.69(4)	
C_{22}	216.1(3)	112.6(5)	216.0(3)	85.9(3)	
C_{23}	70.77(9)	33.31(8)	52.72(8)	27.95(8)	
C_{25}	-8.38(2)	-4.7(3)	-21.7(9)	1.39(4)	
C_{33}	212.7(3)	100.2(3)	189.6(2)	95.4(1)	
C_{35}	-9.2(3)	-7.93(3)	-34.04(2)	6.65(3)	
C_{44}	66.54(3)	34.93(4)	37.0(7)	33.01(5)	
C_{46}	-4.954(7)	-3.958(8)	-6.39(8)	3.28(5)	
C_{55}	66.44(3)	31.35(4)	43.4(6)	38.22(4)	
C_{66}	65.17(3)	32.21(4)	67.65(7)	32.16(6)	
K	111.1	53.2	104.7	53.9	105.2(5)
G	66.7	33.5	54.3	33.5	44.8(6)
E	166.8	83.0	139.0	83.2	117.6(8)
ν	0.250	0.240	0.279	0.243	0.314(17)
E_{11}	151.5	77.2	176.9	91.2	
E_{22}	180.6	96.2	174.6	71.7	
E_{33}	177.3	84.4	147.2	80.4	
E_{44}	66.2	34.4	36.3	32.7	
E_{55}	63.1	30.6	34.9	35.3	
E_{66}	64.8	31.7	66.5	31.8	

Table 1: Stiffness constants and elastic moduli of M₃C₃S obtained by static MM, in GPa. ^a Acoustic measurements. ^bResonance frequency. ^c Nanoindentation.

for M_1 and close to recent results from DFT calculations on the $T_1 C_3S$ [44]. Very similar results were obtained by Manzano et al. [29], employing the Buckingham FF and a $M_3 C_3S$ model proposed by de la Torre et al. [45]. The lowest elastic modulus is obtained in the x and z direction for the M_1 and M_3 polymorph respectively. This result is predictable because of the correspondence of the c parameter of the M_1 unit cell with the a parameter of the M_3 unit cell. Spacial distributions of Young's modulus were plotted with the ELATE open-source Python package [46] and reveal a much more anisotropic elasticity for M_3 than for $M_1 C_3S$ (see Fig. 2).

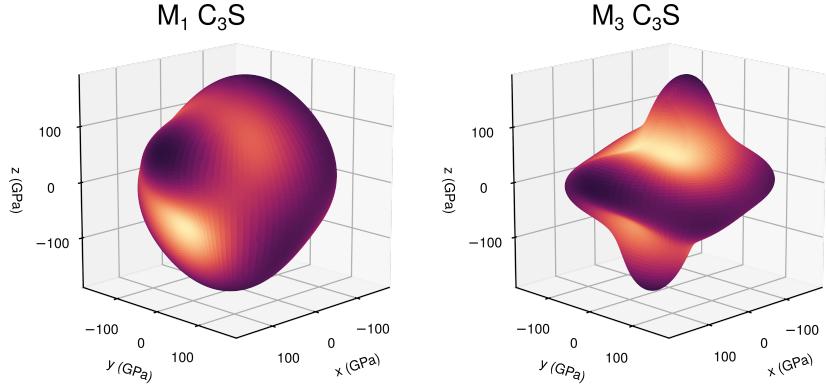


Figure 2: Spacial distribution of Young's modulus for the $M_1 C_3S$, and $M_3 C_3S$ computed with IFF using the static MM method.

EMD calculations were performed with the IFF at 0, 1, 2.5 and 5 GPa. The bulk moduli obtained by linear fitting of the hydrostatic pressure with respect to the volume variation are (101 ± 2) GPa and (103 ± 2) GPa for M_1 and $M_3 C_3S$ 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_3S , the change in coordination between calcium cations Ca and oxygen in silicates (Os) 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_3S structure at short range ($\sim 4 \text{ \AA}$). 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.

The stress-strain curves for NEMD and static MM simulations are plotted in Fig. 4. The general behavior of the M_1 and M_3 polymorphs seems similar. However, the compressive strength seems to be larger for the M_1 polymorph in the x direction, and for the M_3 polymorph in the z direction. The structural correspondence of the (001) direction for the M_1 unit cell with the (100) direction for the M_3 unit cell explains this result. As already noticed for the elastic behaviour (see Fig. 2), a more isotropic yield behaviour is observed for M_1 when compared to M_3 . The difference in compressive strength along the x and z directions is greater for $M_3 C_3S$ (~ 15 and 30 GPa) than for $M_1 C_3S$ (~ 21 and 16 GPa). The elastic moduli obtained from these NEMD simulation are presented in Table 2. They are in good agreement with values from previous stress controlled NEMD

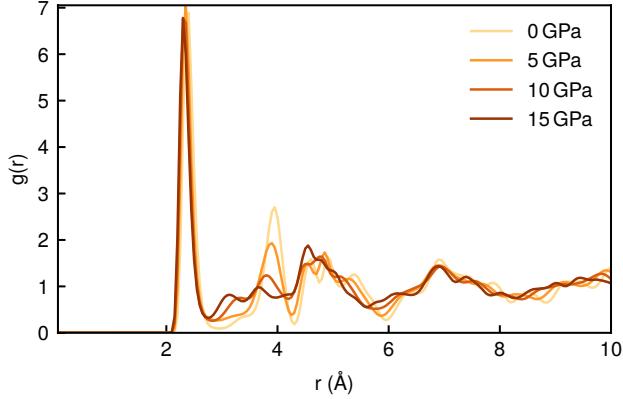


Figure 3: Radial distribution function of Ca-Os pairs as a function of the hydrostatic pressure for $M_3 C_3 S$, with IFF. The RDF obtained for the M_1 polymorph is very similar.

simulations on $M_3 C_3 S$ [13] and $T_1 C_3 S$ [47].

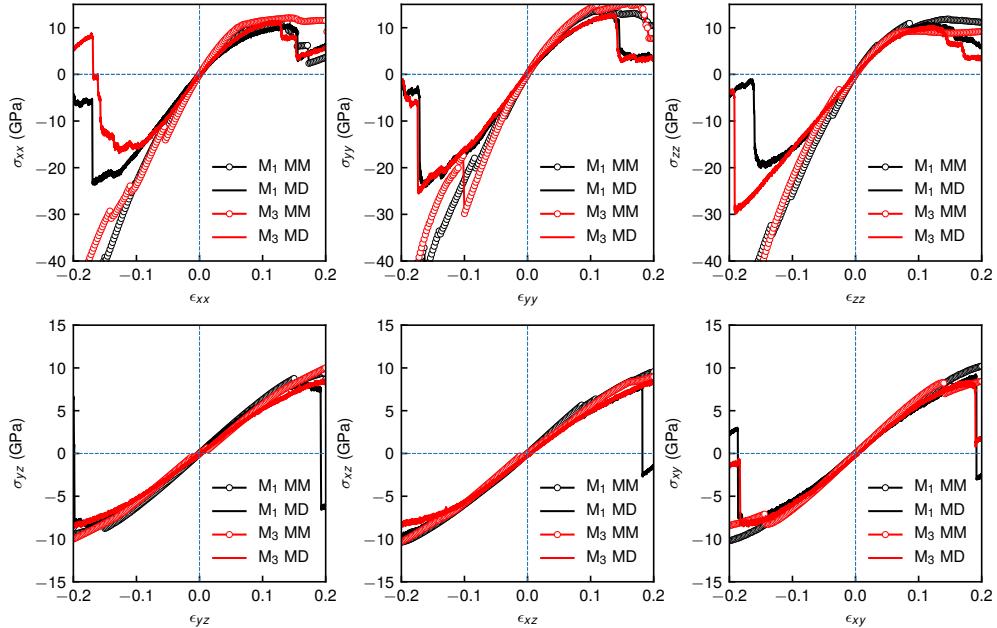


Figure 4: Stress-strain curves obtained by NEMD and MM calculations with IFF.

MM simulations results in a stiffer elastic behaviour than for MD simulations, due to the larger structural relaxation induced by the thermal motion. Nonetheless, the values obtained by these two methods are in good agreement. The static calculation method provides a good representation of elastic properties and is very fast, but does not allow to assess the yield stress properly, in particular in compression, since no relaxation is

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	M ₁	M ₃	M ₃ ^a [13]
$E_{11} = E_{xx}$	141.8(2)	168.5(2)	152(6)
$E_{22} = E_{yy}$	164.4(2)	166.0(2)	176(3)
$E_{33} = E_{zz}$	155.8(2)	154.9(1)	103(11)
$E_{44} = G_{yz}$	62.6(5)	57.16(6)	
$E_{55} = G_{xz}$	59.22(7)	57.42(6)	
$E_{66} = G_{xy}$	59.77(5)	64.35(6)	
$\nu_{12} = \nu_{xy}$	0.220(1)	0.297(1)	0.303(42)
$\nu_{13} = \nu_{xz}$	0.236(2)	0.227(2)	0.273(43)
$\nu_{21} = \nu_{yx}$	0.241(2)	0.290(1)	0.225(21)
$\nu_{23} = \nu_{yz}$	0.239(2)	0.215(1)	0.197(27)
$\nu_{31} = \nu_{zx}$	0.245(2)	0.200(1)	0.372(41)
$\nu_{32} = \nu_{zy}$	0.230(1)	0.200(1)	0.299(58)

Table 2: Elastic moduli obtained from NEMD simulations with IFF. ^aResults from previous stress controlled NEMD.

permitted in the transversal directions. This restriction causes hardening for negative strains. The yield stress could be assessed by enthalpy minimization, but such calculation is not trivial and the calculation can easily stuck in a local minima because the objective function is changing while the simulation box dimensions change.

4. Thermal properties

During its 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. 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. The assessment of vibrational spectra and specific heat of cement phase is a first step toward a microstructural modelling and further understanding of heat propagation in the cement paste.

4.1. Methods

In the canonical ensemble, one can derive the fluctuation relationship between specific heat and internal energy E :

$$C_V = \frac{1}{kT^2} \langle (\Delta E)^2 \rangle \quad (8)$$

where k is the Boltzmann constant. 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) [48]. Moreover values obtained by fluctuation method depends on the time interval used for block averages [48], often leads to large uncertainties and to bad agreements with experimental results [49]. 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 internal energy with respect to the temperature, at the desired temperature. The chosen temperature increment must be large enough to compute accurately the variation of energy between each simulation, but small enough, for the fitting to be representative.

The specific heat capacity 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:

$$g(\omega) = \frac{1}{3NkT} \int_{-\infty}^{+\infty} \sum_{i=1}^N \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle e^{i\omega t} dt \quad (9)$$

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 internal energy of the system can be reduced to the vibrational energy E_v [50, 51]:

$$E_v = \int_0^{+\infty} \hbar\omega \left(g(\omega) f_{BE}(\omega) + \frac{1}{2} \right) d\omega \quad (10)$$

The specific heat c_v in $3Nk$ units is calculated as the partial derivative of internal energy with respect to temperature:

$$c_v = \frac{\int_0^{+\infty} \frac{u^2 e^u}{(1 - e^u)^2} g(\omega) d\omega}{\int_0^{+\infty} g(\omega) d\omega} \quad (11)$$

where $u = \hbar\omega/kT$. One has to note that the phonon spectrum computed this way is semi-classical and is different from the quantum phonon spectrum [52]. Although the Eq. (9) includes quantum effects, the density of states is obtained by classical MD. We consider that this method is applicable at standard temperature and that anharmonic interactions are negligible.

Most of the time, experimental measurement of specific heat capacities is performed at constant pressure. From thermodynamics, the specific heat capacities at constant volume and pressure c_v and c_p , are related by the equation:

$$c_p - c_v = T \frac{\alpha^2}{\rho\beta} \quad (12)$$

where ρ 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 .

Specific heat and thermal expansion coefficient were computed on three replicas of C₃S 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 avoid the external influence of thermostating or barostating, the relaxed systems 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.

4.2. Results and discussion

	Temperature (K)	α (K^{-1})	β (Pa^{-1})	ρ ($g cm^{-3}$)	$c_p - c_v$ ($J g^{-1} K$)
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 $M_3 C_3S$.

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 sharp peak near 935 cm^{-1} , in agreement with infrared spectroscopy measurements [53], while the in-plane bending vibration of Os-Si-Os angle is measured as a band below 500 cm^{-1} [53]. This bending contribution happens at larger frequencies in our results (near 550 cm^{-1}). Wave numbers ω below 500 cm^{-1} are associated to stretching between calcium and oxygen atoms [50, 54], 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

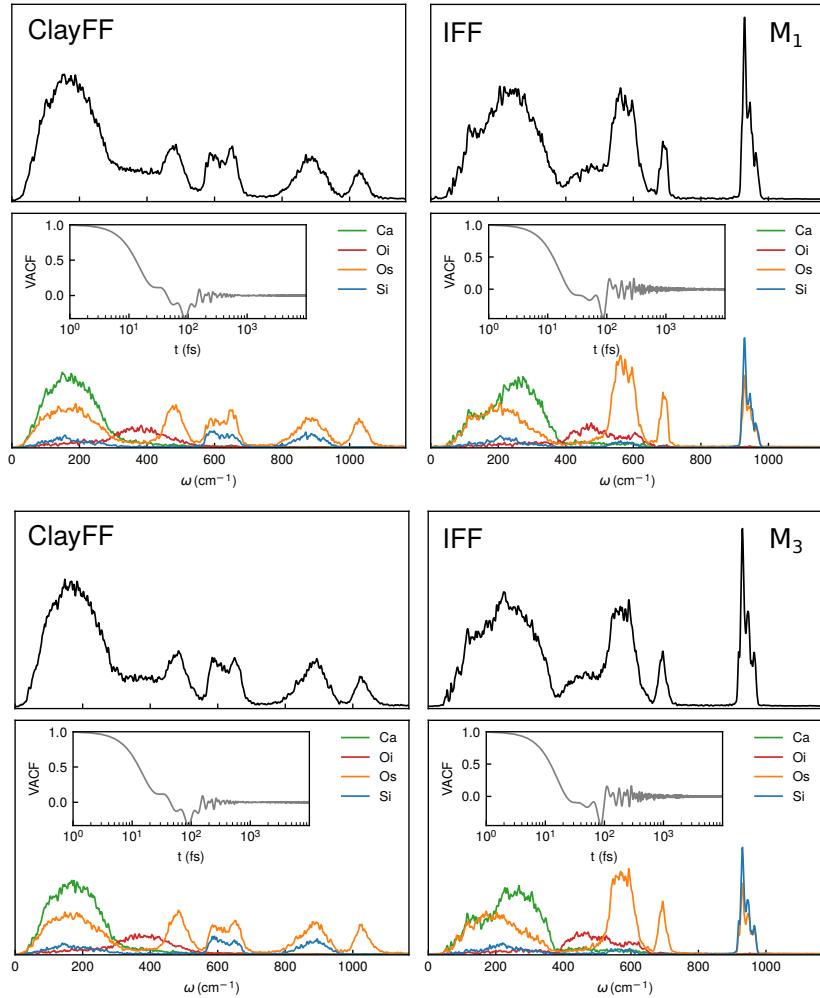


Figure 5: Total phonon density of states (top), and partial density of states with VACF in insets (bottom) of M_1 and M_3 C_3S obtained with IFF and ClayFF.

301 200, 300 and 400 K and extrapolated linearly, because this quantity vary proportionally
 302 with temperature (see Eq. (12)). The thermal expansion coefficient α , the compressibility β ,
 303 and the density ρ , computed from simulations in the NpT ensemble are presented
 304 in Table 3.

305 The specific heat c_p obtained for M_1 and $M_3 C_3S$ are plotted with respect to
 306 the temperature in Fig. 6. The values obtained at 300 K by the direct method are
 307 0.86 ± 0.10 and $(0.87 \pm 0.04) J g^{-1} K^{-1}$ for M_1 and $M_3 C_3S$ respectively, which is much
 308 larger than experimental measurements. As for the phonon DOS, no significant variation
 309 of c_p was found between M_1 and M_3 . The VACF method with ClayFF re-
 310 sults in $c_p = (0.751 \pm 0.013) J g^{-1} K^{-1}$, which is very close to experimental values of
 311 $0.756 J g^{-1} K^{-1}$ [55] and $0.753 J g^{-1} K^{-1}$ [56]. The IFF provided a value slightly lower
 312 than experimental measurements: $(0.723 \pm 0.013) J g^{-1} K^{-1}$.

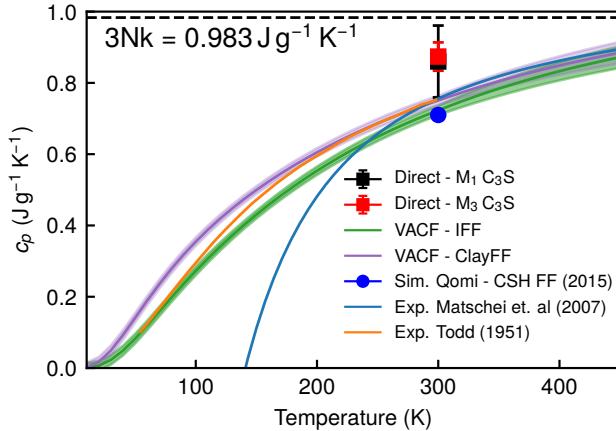


Figure 6: Specific heat of M_1 and $M_3 C_3S$ obtained by the direct and VACF method, plotted as function of the temperature. The transparent areas represent the error. Previously computed value from VACF calculation, as well as fitting of experimental measurements [55] and direct measurements [56] are plotted in addition to the results.

313 5. Cleavage energies and equilibrium shapes

314 In the current section, the cleavage energies of M_1 and $M_3 C_3S$ were calculated from
 315 energy difference of cleaved and unified slabs. From these energies, the crystal shapes of
 316 both polymorphs were constructed using the Wulff construction method [57].

317 5.1. Methods

318 The calculation of cleavage energies for multiple planes of the two monoclinic C_3S
 319 models under study involved creation of cleaved and unified systems. For non-symmetric
 320 planes, reorganization of surface ions was performed to minimize superficial dipole mo-
 321 ments. For each plane, five unified and cleaved systems were constructed with random
 322 distribution of surface species. A 10 nm vacuum was employed in cleaved systems. Series
 323 of steep temperature gradients were applied on ions within the uppermost and lowermost

M ₁ C ₃ S	
Miller index	Cleavage energy (J m ⁻²)
(100)	1.04 ± 0.04
(010)	1.41 ± 0.04
(040)	1.76 ± 0.03
(003)	1.20 ± 0.03
(008)	1.20 ± 0.04
(110)	1.45 ± 0.04
(101)	1.51 ± 0.03
(011)	1.17 ± 0.04
(111)	1.43 ± 0.03

M ₃ C ₃ S	
Miller index	Cleavage energy (J m ⁻²)
(100)	1.39 ± 0.03
(300)	1.14 ± 0.03
(800)	1.17 ± 0.03
(010)	1.55 ± 0.04
(040)	1.31 ± 0.04
(001)	1.38 ± 0.04
(002)	1.45 ± 0.04
(003)	1.31 ± 0.04
(00̄3)	1.33 ± 0.04
(008)	1.22 ± 0.04
(00̄8)	1.22 ± 0.04

Table 4: Cleavage energies of M₁ and M₃ C₃S. Only the lowest energy plane is given in the (100) direction for M₁. Results for M₃ C₃S are from our previous study [58].

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 [13, 59]. The systems with lower energies were selected to performed the calculation over 300 ps runs, after 200 ps equilibration runs. For more details on the method, we refer the reader to ref. [58]

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5.2. Results and discussion

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The cleavage energy was computed classically from Eq. (13) and results are given in Table 4.

$$E_{cleav} = \frac{E_{cleaved} - E_{unified}}{2A} \quad (13)$$

The computed values are in the range of 1.14 to 1.55 J m⁻² (1.32 J m⁻² in average) for M₃ C₃S, and 1.04 to 1.76 J m⁻² (1.35 J m⁻² in average) for M₁ C₃S, in good agreement with previous atomistic simulation studies [19, 60]. In general, the average values are very close between the two models. The energies obtained for particular planes vary as a function of the structure of each polymorph, and are particularly influenced by

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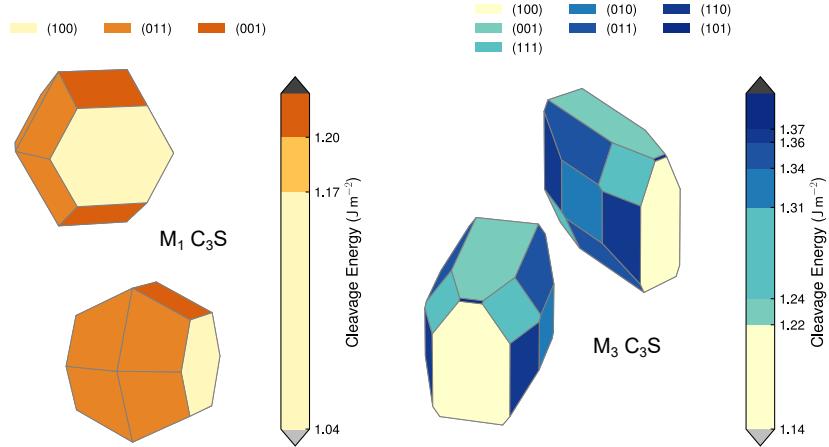


Figure 7: Equilibrium shapes of M_1 and M_3 C_3S

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 $M_1 C_3S$, 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.

The Wulff construction can give theoretical insights on the shape of a crystal at equilibrium [57]. It is based on the assumption that a crystal grows in such a way that the Gibbs free energy of its surface is minimized [61]. This results in a proportional relationship between the surface energy of a facet and its distance from the crystal center. 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 [15, 62]. 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 [63]. 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 (10 $\bar{1}$ 1) and (1102) [64]. 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.

6. Conclusion

This research aimed to provide knowledge at the atomic scale on the influence of alite polymorphism on its mechanical and thermal properties as well as on its equilibrium shape. The two main polymorphs of C_3S in industrial OPC, M_1 and M_3 , were inves-

tigated. This knowledge may contribute to the understanding of the influence of alite polymorphism on the variation in strength of Portland cement. This work also provide input data that are necessary in microscale modelling of Portland cement hydration and the development of its mechanical and thermal behavior [65, 66]. Cleavage energy values may improve our understanding of alite reactivity and dissolution kinetic, and crystal shapes could help for identification of polymorphs by SEM. In addition, this study explored and discussed different calculation methods and compared the performance of two force fields widely used to described cementitious systems.

The elastic constants were calculated by static and dynamical methods. The moduli 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. An isotropic distribution of elastic moduli in space was observed for the M₁ polymorph, whereas an anisotropic distribution was found for M₃. The assessment of stress-strain curves for both polymorphs also indicates a more anisotropic behaviour for M₃ C₃S regarding the yield compressive stress. 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 in 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. These calculations allowed the construction of equilibrium shapes which are significantly different. The M₁ crystal possess three facets against seven for the M₃ polymorph. The energies obtained for both polymorphs are in the same range. Despite different morphologies, low index crystal planes with the lowest energies are the (100) and (001) for both polymorphs. 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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