

AFFF: an empirical force field for AF-phases in cement systems

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1. Introduction

AFFF is a reparametrization of ClayFF [1] and Cannon et al. [2] sulfate force fields. Water and hydroxide are modeled using the SPC/E (extended simple-point charge) water model [3]. The idea of revisiting ClayFF is to better reproduce structural features and to improve the estimates of physical properties of AF-phases.

AFFF has been used to molecular model:

- Elastic properties of ettringite, monosulfoaluminate and tricalcium aluminate [4].
- Sorption-induced deformations and hysteresis under sorption in ettringite [5].
- Thermal conductivity, heat capacity, thermal expansion of ettringite and metaettringite [6].
- Friedel's salt thermoelastic properties.

2. Force field details

The potential energy of the system is modeled by a sum of the contributions from the short-range interactions (van der Waals forces and steric repulsion), the electrostatic (Coulombic) interactions, and the 2- and 3-body interactions (bonds and angles, respectively):

$$U^{Tot} = U^{VdW} + U^{Coul} + U^{Bond} + U^{Angle} \quad (1)$$

The nonbond interactions are described by the Lennard-Jones (12-6) potential :

$$U^{VdW} = 4 \sum_{i \neq j, i,j \text{ nonbonded}} \epsilon_{ij}^{LJ} \left[\left(\frac{\sigma_{ij}^{LJ}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}^{LJ}}{r_{ij}} \right)^6 \right] \quad (2)$$

where r_{ij} is the distance between the particles i and j ; ϵ_{LJ} and σ_{LJ} are empirical parameters. The parameters for the Lennard-Jones potential are defined only for the same atom type. The Lorentz-Berthelot mixing rule is used to compute the Lennard-Jones contribution for dissimilar nonbond atoms pairs.

The Coulomb potential describes the electrostatic contribution:

$$U^{Coul} = \frac{e^2}{4\pi\epsilon_0} \sum_{i \neq j, i,j \text{ nonbonded}} \frac{q_i q_j}{r_{ij}} \quad (3)$$

where q_i is the partial charge of a particle i , e is the elementary charge, and $\epsilon_0 = 8.85419 \times 10^{-12}$ F/m is the dielectric permittivity of vacuum.

Table 1 shows the nonbond parameters and partial charges defined for AFFF.

Hydroxide is also modeled based on SPC/E water but with an oxygen O_H partial charge of $q = -0.8988e$. It must be noted that using the partial charges employed by Kalinichev and Kirkpatrick [7], ettringite will exhibit a net charge of $-1.86 e$ per $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot nH_2O$. Ettringite columns bear a positive structural charge of $1.25e/nm$ that is balanced by the sulfate ions present in the channels [8]. The partial charges in AFFF ensure ettringite electroneutrality. Accordingly, in tricalcium aluminate modeling, the electroneutrality was ensured by adjusting O_H partial charges.

The van der Waals interactions involving Al and Ca are modeled using ClayFF parameters. Kalinichev and Kirkpatrick [7] used the partial charges of octahedral Al ($q = 1.5750e$) and hydroxide Ca ($q = 1.0500e$) proposed in ClayFF to model ettringite. In AFFF, the partial charges of Al ($q = 1.05e$) and Ca ($q = 1.6e$) species are obtained based on the quantum mechanical calculations reported by Liu et al. [9]. Note that this partial charge of Ca is closer to the value of the octahedral calcium reported in ClayFF of $1.36e$.

ClayFF in its original version does not provide sulfate interactions. The nonbonded parameters for sulfates in AFFF are a reparametrization of the results reported by Cannon et al. [2]. The original parameters of the Cannon et al. force field, which are developed for aqueous sulfate solutions, do not provide S- O_S distances consistent with sulfate in ettringite structure. The LJ diameter of S-S pairs interactions is $\sigma_{LJ} = 3.55 \text{ \AA}$ with Cannon et al. force field; simulations of ettringite using this σ_{LJ} yields average S- O_S bonds lengths of exceeding 2 \AA . The experimental S- O_S bond lengths in ettringite range from 1.31 to 1.56 \AA [10]. The σ_{LJ} for S pairs proposed in AFFF yields S- O_S distances that are in agreement with the experimental values observed in ettringite [4].

With AFFF, bond interactions are defined hydroxides, water molecules, and sulfates (since this version [5]). The bond

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Table 1: AFFF: Nonbond parameters and partial charges. * Reparametrization proposed in AFFF.

Species and Symbol	partial charge [e]	ϵ_{LJ} [kJ/mol]	σ_{LJ} [Å]
water hydrogen, H_w	0.4238	-	-
water oxygen, O_w	-0.8476	0.650	3.166
hydroxyl hydrogen, H_H	0.4238	-	-
hydroxyl oxygen, O_H (AFm)	-0.96547*	0.650	3.100*
hydroxyl oxygen, O_H (AFt)	-0.8988*	0.650	3.166
oxygen, O (C_3A)	-1.15*	0.650	3.100*
sulfate oxygen, O_S	-1.0	0.839	3.15
sulfur, S	2.0	1.046	0.1*
aluminium, Al	1.05*	5.56×10^{-6}	4.27
calcium, Ca (AFt, C_3A)	1.6*	2.10×10^{-5}	5.56
calcium, Ca (AFm)	1.6*	2.10×10^{-5}	5.10*
chloride, Cl	-1.0	0.4184	3.981

Table 2: AFFF: Bond parameters.

	k_b [kJ/mol]	r_0 [Å]
O_w-H_w	2318.476	1.0
O_H-H_H	2318.476	1.0
O_S-S	418.96	1.47
	k_a [kJ.mol $^{-1}$.rad $^{-2}$]	θ_0 [°]
$H_w-O_w-H_w$	191.50	109.47
O_S-S-O_S	3347.2	109.47

(2-body) and angle (3-body) interactions are described by harmonic potentials:

$$U^{Bond}(r_{ij}) = k_b (r_{ij} - r_0)^2 \quad (4)$$

$$U^{Angle}(\theta_{ij}) = k_a (\theta_{ij} - \theta_0)^2 \quad (5)$$

where k_b and k_a are the rigidity of the bond and angle, respectively; r_0 and θ_0 are the equilibrium distance and angle, respectively.

Table 2 shows the bonded parameters used in AFFF based on SPC/E water model [3]. The imposed equilibrium bond length of $r_0=1$ Å for OH groups in ettringite columns and water molecules can be compared to the experimental values reported by Hartman and Berliner [11] on deuterated (D) ettringite: DH bond length varies from 0.913 to 0.986 Å for hydroxyls, and from 0.926 to 1.103 Å for DH in water molecules. The same authors report water molecule angles ranging from 97.6 to 116.5°. The equilibrium bond length r_0 of OH groups (O_H-H_H) in the kuzelite structure reported by Allmann [12] is in average 0.844 Å [13]; this value is adopted for the bond parameters of layer hydroxide in AFFF.

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