The Multi-scale Multi-technique Multi-physics Framework Required to Model the Thermal Properties of Cement-Based Materials

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Abstract. The physical origins of the properties controlling the thermal response of nanoporous materials are fundamentally related to atomic-scale processes. Therefore, the techniques that enable assessing the nanoscale are required to properly understand the thermal properties of cement-based materials. In this paper, we review the techniques of classical molecular simulations that can be used to link the structure of materials to their thermal properties. We focus on the heat capacity, thermal expansion, and thermal conductivity. Results on various phases present in cement systems (tricalcium silicate, C-(A)-S-H, Friedel's salt, and ettringite) are presented. The fundamental property data provided on the thermal properties are valuable input for multiscale modeling and prediction of the thermal behavior of cement-based materials.

Keywords: Molecular simulations · Heat capacity · Thermal expansion · Quantum corrections

1 Introduction

Thermal deformations are a major cause of cracking in cement-based materials (e.g.[19,27]). Thermo-chemo analysis are critical for massive concrete structures [2,18,27]. The physical origins of the properties controlling the thermal response of micro- and mesoporous materials are fundamentally related to atomic-scale processes. Therefore, techniques well-suited to assess the atomistic scale are required to properly understand the thermal behavior of cement-based materials or, in a more ambitious perspective, bottom-up engineer materials with a target thermal performance.

Fundamental component data regarding the properties of the main phases present in cement systems are critical input in multiscale modeling [20]. However, such data is missing for some key phases (e.g., AF-phases). Also, the effects of water content in the thermal properties of hydrated phases (especially C-S-H and AF-phases, which exhibits variable water content) are not fully understood [9].

In this paper, we review the techniques of classical molecular simulations that can be used to link the structure of materials to their thermal properties. We focus on the following thermal properties: the heat capacity, thermal expansion, and thermal conductivity. We show that the molecular simulations of the heat capacity of materials with crystalline domains, as it is the case of crystalline phases (e.g., tricalcium silicate) or microporous hydrated phases (e.g., C-(A)-S-H, ettringite, AFm, alkali-silica crystalline products), requires the incorporation of quantum corrections. As a result, the thermal properties of tricalcium silicate, ettringite, Friedel's salt, and C-A-S-H computed from classical molecular dynamics are presented and confronted with experimental data available from the literature. The fundamental property data provided in this work for the thermal properties of these phases are valuable input for multiscale modeling and prediction of the thermal behavior of cement-based materials.

2   Thermal Properties from Molecular Simulations

Strategies based on finite difference and fluctuations approaches are presented. In the case of the finite difference, the property definition is used to define the simulation protocol.

2.1   Coefficient of Thermal Expansion

Finite Difference. The tensor of coefficients of thermal expansion is defined in the anisotropic framework as (.e.g. [8,36]):

$$\alpha_{ij} = \left[\frac{\partial \epsilon_{ij}}{\partial T}\right]_{\sigma_{ij}} \tag{1}$$

where σ_{ij} is the stress, T is the temperature, and the strain ϵ_{ij} is the second-order Lagrangian deformation tensor (also given in its general anisotropic form):

$$\epsilon_{ij} = \frac{1}{2}\left[\mathbf{h}_0^{-T}\mathbf{h}^T\mathbf{h}\mathbf{h}_0^{-1} - \mathbf{I}\right] \tag{2}$$

with $\mathbf{I}$ being the unit $3{\times}3$ matrix, $[.]^T$ being the transpose operator; the $\mathbf{h}$ matrix being the $3{\times}3$ matrix formed by arranging the lattice vectors as $\{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$, the reference state (at zero stress [36]) is denoted by the subscript 0.

In the finite difference approach, a number of simulations are run at the same stress σ_{ij} (of 1 atm) for various T in the vicinity of the target temperature. The derivative from Eq. 1 is finally evaluated assuming a linear behavior.

Fluctuation. In the fluctuation-dissipation approach, the thermal expansion tensor is obtained from the cross fluctuations of the strain ϵ_{ij} and the enthalpy H in an NσT simulation [8, 25, 36]:

$$\alpha_{ij} = \frac{\langle H\epsilon_{ij}\rangle_{N\sigma T} - \langle H\rangle_{N\sigma T}\langle \epsilon_{ij}\rangle_{N\sigma T}}{kT^2}. \tag{3}$$

where k is the Boltzmann constant, and $\langle . \rangle_{N\sigma T}$ is an NσT ensemble average.

2.2 Heat Capacity

Full Classical Estimates

Finite Difference. The heat capacity at constant volume C_v (respectively, the heat capacity at constant pressure C_p) is property quantifying how the internal energy E (respec., the enthalpy $H = E + PV$) varies with the temperature T:

$$C_V = \left[\frac{\partial E}{\partial T}\right]_V ; \ \ C_P = \left[\frac{\partial H}{\partial T}\right]_\sigma \tag{4}$$

A number of simulations are run at the same volume (for C_V) or stress (for C_P) for various T in the vicinity of the target temperature. The derivatives in the definitions are finally evaluated assuming a linear behavior.

Fluctuations. In a full classical approach, the heat capacity at constant volume C_V is computed from the fluctuations of the internal energy E [1]:

$$C_V = \frac{\langle E^2\rangle_{NVT} - \langle E\rangle^2_{NVT}}{kT^2} \tag{5}$$

The heat capacity at constant pressure C_P is computed from the fluctuations of the enthalpy H [1]:

$$C_P = \frac{\langle H^2\rangle_{N\sigma T} - \langle H\rangle^2_{N\sigma T}}{kT^2} \tag{6}$$

Semi-Classical Estimates. The high-frequency lattice dynamics require that some quantum corrections are introduced in the estimation of the heat capacity of phases with crystalline domains. In other words, whenever the lattice frequency f happens to be on the order of $\frac{kT}{h}$ quantum effects are not negligible (or in terms of angular frequency ω, whenever $\hbar\omega$ is on the order of kT), with h being the Planck constant (and $\hbar = h/(2\pi)$).

Studies on clinker phases show indeed that full-classical approaches lead to overestimations of the heat capacity [5, 10, 34].

A semi-classical approach [13], in which classical simulations are used to compute input in quantum-corrected expressions, can be used to get heat capacity

of crystal in agreement with the experimental evidence. In this semi-classical approach, the heat capacity at constant volume C_V is given by [32]:

$$C_V = \frac{dE_{vib}}{dT} = 3Nk \int_0^\infty \left(\frac{\hbar\omega \; n(\omega,T)}{kT} \right)^2 \exp\left[\frac{\hbar\omega}{kT} \right] g(\omega)d\omega \qquad (7)$$

where $n(\omega,T) = \frac{1}{\exp\left[\frac{\hbar\omega}{kT}\right]-1}$ is the Bose-Einstein distribution, and $g(\omega)$ is the density of the states [13] (see [21] for a detailed demonstration):

$$g(\omega) = \frac{1}{\pi} \int_{-\infty}^\infty \sum_j \frac{\langle m_j \mathbf{v}_j(t).\mathbf{v}_j(0)\rangle}{\langle m_j \mathbf{v}_j^2(0)\rangle} \exp\left[i\omega t\right] dt \qquad (8)$$

which is computed in the classical simulation using the mass-weighted velocity auto- correlation function $\langle m_j\mathbf{v}_j(t).\mathbf{v}_j(0)\rangle$, where m_j is the mass of particle j; $\mathbf{v}_j(t)$ is the velocity vector of particle j at time t, and "." is the scalar product. In the semi-classical approach, only the vibrational E_{vib} contribution for the internal energy is considered. The other contributions for the internal energy can be neglected: the translational and rotational contributions are negligible for temperatures below Debye temperature, and the lattice contribution is temperature-independent [13].

Hybrid Estimates. In hydrated minerals, it can be shown that the contribution of molecular water to the heat capacity is underestimated by semi-classical approaches [21]. An hybrid approach leads to experimentally sound estimates of the heat capacity of various hydrates minerals including clays [21], ettringite [17], C-A-S-H [29] and Friedel's salt [22]. In this hybrid approach, C_V of the hydrated mineral is computed using the semi-classical approach for the dry mineral $C_{v-min}^{semi-class}$ and the heat capacity of confined water C_{v-w}^{class} is computed using a full-classical approach [21]:

$$C_V = C_{v-w}^{class} + C_{v-min}^{semi-class} = C_{v-tot}^{class} - 3N_s k + C_{v-min}^{semi-class} \qquad (9)$$

Since the full classical approach applied to the dry mineral returns Dulong-Petit law (i.e., $C_{v-min}^{class} = 3N_s k$, where N_s is the number of atoms in the dry mineral), we can write the following expression used in the equation above: $C_{v-w}^{class} = C_{v-tot}^{class} - 3N_s k$.

Mayer's Relation. The specific heat capacity at constant volume and pressure can be readily obtained from each other, once the tensor of thermal expansion α_{ij} and the elastic stiffness tensor C_{ijkl} are known, using Mayer's relation (e.g.[40]):

$$c_P - c_V = \frac{T}{\rho} C_{ijkl}\alpha_{ij}\alpha_{kl}, \qquad (10)$$

where ρ is the density.

2.3   Thermal Conductivity

The full thermal conductivity tensor can be obtained from molecular simulations using equilibrium and non-equilibrium methods.

Non-Equilibrium Method. Non-equilibrium methods include direct thermostatting method [26], and reverse perturbation method [31].

Equilibrium Method. The main equilibrium method is the Green-Kubo formalism, detailed in the following. With Green-Kubo formalism, the thermal conductivity is the time integral of the ensemble average (denoted by $\langle . \rangle$ operator) of the auto-correlation of the heat flux J_i $(i = x, y, z)$ (e.g. [1]):

$$\lambda_{ij} = \frac{V}{kT^2} \int_0^\infty \langle J_i(0) \otimes J_j(t) \rangle dt \qquad (11)$$

where k is the Boltzmann constant, V is the volume, and $\otimes$ is the dyadic product. The heat flux vector is obtained from: $\mathbf{J}_p = \frac{1}{V} \left[\sum_p E_p \mathbf{v}_p - \sum_p \mathbf{S}_p \mathbf{v}_p \right]$ where E_p is the sum of the kinetics and potential energy, $\mathbf{v}$ is the velocity, and $\mathbf{S}_p$ is the stress tensor for atom p.

In some cases, the conductivity λ_{ij} computed from the standard Green-Kubo formalism might not converge. A solution to overcome this problem is to calculate the thermal conductivity tensor using the frequency-dependent response of the complex conductivity [39]:

$$\lambda_{ij}(\omega) = \frac{V}{kT^2} \int_0^\infty \langle J_i(0) \otimes J_j(t) \rangle \exp\left[i\omega t\right] dt \qquad (12)$$

The (static) thermal conductivity λ_{ij}^0 is obtained from fitting at the low frequency range the modulus $|\lambda_{ij}(\omega)|$ of the complex conductivity with the expression $|\lambda_{ij}(\omega)| = \lambda_{ij}^0 + A\omega^\xi$, where λ_{ij}^0, A and ξ are free parameters in the fitting procedure [34].

2.4   Molecular Models and Methods

Simulation are performed with LAMMPS [33]. Ewald summation with a desired relative error in forces of 10^{-5}, and tail corrections for the Lennard-Jones potential are adopted for long-range interactions. The adopted atomic structures and force fields are detailed in the following.

C$_3$S. The triclinic C$_3$S (T1) obtained by Golovastikov [15] is adopted. Interactions are described using the Consistent Valence Force Field (CVFF) [12]. More details and structural validation are given in ref. [5].

C-A-S-H. The bulk C-A-S-H structure proposed by [28] is adopted. Interactions are described using ClayFF [11]. More details and structural validation are given in Ref. [29].

Ettringite and Metaettringite. The ettringite structure resolved by Moore and Taylor [30] is adopted. AFFF [23,24] is used to describe interactions between atoms. Ettringite dehydrates at low RH ($< 1\%$), forming a more disordered phase called metaettringite. Metaettringite structures are obtained from the molecular simulations described in [24]. More details and structural validation are given in Refs. [23,24].

Friedel's Salt. The monoclinic structure resolved by [35] of the associated with ambient temperatures (noted LT hereon) is adopted. AFFF [23,24] is used to describe interactions between atoms in Friedel's salt. Parameters for chlorides are taken as in the original version of ClayFF [11]. The high-temperature (HT, at $313\,\mathrm{K}$) polymorph of Friedel's salt is obtained from simulations detailed in [22]. More details and structural validation are given in Ref. [22].

3   Results and Discussion

3.1   Thermal Expansion

The components of the tensor of coefficient of thermal expansion in the principal basis and the volumetric (i.e., $\alpha_v = Tr\ \alpha_{ij} = \alpha_{11} + \alpha_{22} + \alpha_{33}$) and linear (i.e., $\alpha_{lin} = \alpha_v/3$) coefficients of thermal expansion of phases studied here are gathered in Table 1. These results were obtained from molecular dynamics simulations using the fluctuation approach.

No experimental or simulation results are reported in the literature for the coefficient of thermal expansion of C-A-S-H and Friedel's salt. The results on C-A-S-H can be compared with the values reported for C-S-H obtained from molecular simulations of linear thermal expansion of $4.5 \pm 0.9 \times 10^{-5}$/K [34], and obtained from micromechanics inverse analysis 4.2×10^{-5}/K [14]. SImulations of the thermal expansion are provided only for monoclinic polymorphs of C_3S [10,34].

Experimental data on ettringite thermal expansion are reported by [16] following the crystallographic framework (in terms of lattice vector a, b, c): $\alpha_a = 4.2 \times 10^{-5}$K and $\alpha_c = 2.2 \times 10^{-5}$/K. In the hexagonal symmetry of the ettringite crystal, $\alpha_a = \alpha_b$ and a Cartesian frame $\alpha_{xx} = \alpha_{yy}$ is the vector a is aligned with x. Therefore, $\alpha_v = 10.6 \times 10^{-5}$/K. These values are fairly close to the one obtained from simulations when on take into account the standard deviations associated with the simulations of a few 10^{-5}/K. These results build confidence in using the simulation to get the properties of metaettringite, a phase for which almost no physical property has been experimentally assessed so far.

3.2   Specific Heat Capacity

Table 2 gathers the specific heat capacity obtained from molecular simulations. The semi-classical approach is adopted for C_3S (a non-hydrated phase). For the

Table 1. Coefficient of thermal expansion (in 10^{-5}/K) of phases relevant to cement systems obtained from molecular dynamics simulations using the fluctuation approach.

Phase	α_{11}	α_{22}	α_{33}	α_v	α_{lin}
C_3S	1.55	1.17	0.787	3.50	1.17
C-A-S-H	8.93	3.88	−0.52	12.33	4.11
Ettringite	7.61	5.03	2.83	15.45	5.15
Metaettringite	5.67-6.80	4.10–5.85	1.79-3.02	13.91–14.4	4.34–4.8
Friedel's salt LT	7.47	4.59	4.10	16.2	5.4
Friedel's salt HT	8.81	4.77	3.94	17.5	5.8

hydrated phases, a hybrid approach is adopted. Experimental or assessed data on c_p of hydrated phases are available in the literature: 1.006 to 0.849 kJ/(kg.K) for C-A-S-H [37]; 1.300 to 1.732 kJ/(kg.K) for ettringite [4,38] , and [4] 1.489 to 1.547 kJ/(kg.K) for metaettringite; 1.23 to 1.48 for Friedel's salt [3,7]. All these values compare well with the hybrid simulation results. In general, the heat capacity using full classical approaches leads to overestimations on the order of 50% (as is also the case for other hydrated phases such as clays [21]).

Table 2. Specific heat capacity (in kJ/(kg.K)) of phases relevant to cement systems obtained from molecular dynamics simulations using methods incorporating quantum corrections: semi-classical for C_3S, hybrid for the hydrated phases.

Phase	c_p	c_v
C_3S	0.687	0.673
C-A-S-H	1.048	1.023
Ettringite	1.845	1.746
Metaettringite	1.422–1.879	1.366–1.805
Friedel's salt LT	1.47	1.38
Friedel's salt HT	1.44	1.39

3.3   Thermal Conductivity

The components of the tensor of thermal conductivity in the principal basis and the volumetric (i.e., $\lambda_v/3 = Tr\lambda_{ij}/3$) thermal conductivity of C_3S and (meta)ettringite are displayed in Table 1. These results were obtained from molecular dynamics simulations using Green-Kubo formalism. The C_3S value can be compared with the estimates for cement particles' thermal conductivity of 1.55 W/(m.K) [6]. No experimental results exist in the literature for (meta)ettringite, therefore, the molecular simulation results can be helpful as the first available data for this phase. The thermal conductivity of other phases relevant to cement systems considered here (C-A-S-H and Friedel's salt) are yet to be provided.

Table 3. Components of the thermal conductivity tensor in the princiapl basis (in W/(m.K) and volumetric thermal conductivity of phases relevant to cement systems obtained from molecular dynamics simulations using the Green-Kubo formalism.

Phase	λ_{11}	λ_{22}	λ_{33}	λ_v
C_3S	4.33	0.52	0.28	1.71
Ettringite	4.87	2.33	1.13	2.78
Metaettringite	3.12-8.05	1.61–4.12	1.18-1.45	2.06–4.45

4   Conclusion

In this work, the techniques of classical molecular simulations enabling the estimation of thermal properties from the composition and atomic structure of crystalline and hydrated phases in cement systems were reviewed. As results, the thermal properties of tricalcium silicate (meta)ettringite, Friedel's salt (LT and HT), and C-A-S-H computed from classical molecular dynamics are presented and confronted with experimental data available from the literature. A good comparison with the available experimental data on thermal properties builds confidence in using molecular simulation to provide thermal properties data on the various phases in cement systems. Such data complete the information on component properties in cement systems, being valuable input for multiscale modeling and prediction of the thermal behavior of cement-based materials.

Perspectives include computing the thermal properties of other phases relevant to cement systems.

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