

Atomistic Simulations Of Silicate Species

Interaction With Portlandite Surfaces

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Supplementary Material

1 METADYNAMICS DETAILS

In addition to the collective variables, the parameters to be specified are the height (ω) and the width (σ_{CVX}) of the added Gaussian potentials with respect to the different collective variables CV as well as the frequency of addition τ_G for conventional as well as the temperature difference indicating the total fill height ΔT for well-tempered metadynamics¹. For the exploratory metadynamics these parameters were chosen as follows: and the following parameters were used for the metadynamics simulation:

$$\sigma_{CV1} = 0.2 \text{ \AA}, \sigma_{CV2} = 0.05 \text{ eV}, \omega = 0.02 \text{ eV and } \tau_G = 0.0525 \text{ ps.}$$

To calculate an energy profile, the choice of these parameters, especially for the conventional metadynamics, is much more critical. The well-tempered metadynamics,

developed by Barducci et al.¹ is also employed, has the advantage of less dependence on the initial parameters. Consequently the well-tempered simulation was carried out first and allowed a first estimate of the energy profile and its characteristics, such as the characteristic length scale Δs_{ch} and the characteristic well depth ΔF_{ch} . Almost the same parameters were chosen for all well-tempered metadynamics simulations: $T = 2700$ °K, $\sigma = 0.2$ Å and $\tau_G = 0.0525$ ps. Only one parameter changed: ω was 0.01 eV for the calculation of the complex formation and 0.005 eV for the adsorption calculations. The parameters of the non-tempered simulation were then chosen based on the results of the well-tempered metadynamics calculation, according to the guidelines by Laio et al.² to get an acceptable *a priori* error estimate. The full set of parameters used for the calculation can be found in Table 1. The final energy profile of the non-tempered metadynamics calculations has been averaged over several steps to reduce the error.

2 ERROR CALCULATIONS CA-SI COMPLEX

The main sources of error in this study are from metadynamics and the force field used. *A priori* the error of the conventional metadynamics simulation was estimated using the equation (1), where Δs_{max} is the size of the explored collective variable region, ΔF_e the maximal energy difference, T is the temperature D_α^{meta} is the diffusion coefficient of the collective variable α , t_{sim} is the total simulation time, σ is the width of the gaussian distribution and Δs_{ch} is the characteristic length scale². After the completion of both conventional and well-tempered calculations, the metadynamics error ϵ_{post}^{meta} on the energy profiles was estimated *a posteriori* as the standard deviation between the result for the non-tempered and the well-tempered calculation, averaged over the whole simulation domain, excluding the edges (~ 3 Å) to avoid an influence of the boundaries. The error estimates can be found in Table 1. The fact that the *a posteriori* error estimates are consistently lower than the *a priori* estimate indicates convergence and well-chosen collective variables for the

metadynamics calculations. Values of the different parameters used for the metadynamics simulation and the error calculations are listed in Table 1.

$$\bar{\epsilon}_{prior}^2 = \frac{\Delta s_{max}^2 \Delta F_e T (2\pi)^{\frac{2}{n}}}{D_{\alpha}^{meta} t_{sim}} \cdot \sum_{\vec{k}, k_{\alpha} \in (0,1,2,\dots), \vec{k}^2 \neq 0} \frac{1}{\vec{k}^2 \pi^2} e^{-\frac{\vec{k}^2 \pi^2 \sigma^2}{2 \Delta s_{ch}^2}} \quad (1)$$

In addition to the metadynamics error we have the force field error ϵ_{est}^{FF} , which is estimated by a method explained in the supplementary material of the previous paper of the authors³. In order to estimate the force field error, we need to know the energy of the part of the structure that is influenced by the collective variable. According to the Si-water and Ca-water radial distribution functions of separate molecular dynamics calculations (of a $CaSiO_2(OH)_2$ complex in a box with 2047 water molecules and of a Ca^{2+} and two OH^- ions in a water box with 2045 water molecules respectively), the hydration shell of the $CaSiO_2(OH)_2$ is comprised of about 71 water molecules and for the Ca^{2+} species of about 48 water molecules. Consequently, to estimate the total energy for the calculation of the complex formation we consider the energy of the whole simulation cell minus the energy of all but 119 of the water molecules in the cell. The number of water molecules considered and the estimated total energy can be found in Table 1. The estimated total error on the averaged free energy profile was the sum of the 95 % confidence interval ($\frac{1.96 \cdot \epsilon_{post}^{meta}}{\sqrt{2}}$) based on the a posteriori error estimate on the metadynamics calculations and the estimated force field error ϵ_{est}^{FF} (calculated according to the previously reported empirical relationship: $\epsilon_{est}^{FF} = 0.065 \cdot \Delta H + 0.00022 \cdot (\sum_j s_j^P |H_j^P| + \sum_i s_i^R |H_i^R|)$ where ΔH is the reaction enthalpy, s_i^R and s_j^P are the stoichiometric coefficients of the i^{th} reactant and j^{th} product respectively and H_i^R and H_j^P are the individual enthalpies of the i^{th} reactant and j^{th} product respectively³).

For the complex formation energy, the difference between the calculated and experimentally determined values was just outside the determined error estimate. One reason

could be that the empirical expression for the error estimate has not yet been thoroughly tested and the difficulty to judge the probability of a calculation falling outside of the estimated error interval. Additionally, there are several possible error sources that are not included in the error estimate such as the cutoff of the electrostatic interactions. To check if the cutoff distance affects the complex formation energy value, the well-tempered calculation was repeated with a larger cutoff (14.5 Å). The difference in errors between the two well-tempered calculations for the different cutoff was 0.08 eV and that for the two non-tempered calculations was 0.10 eV. These errors are similar to the method error estimated originally (0.07 eV) and smaller than the a priori error estimate (0.11 eV), indicating that the cutoff has little influence.

Table S1: Parameters used for the well tempered and non tempered metadynamics calculations of the Ca-Si complex and adsorption free energy profiles.

	Ca-Si Complex	Adsorption @ [0001]	
	$Ca - SiO_2(OH)_2$	$CaSiO_2(OH)_2$	$SiO_2(OH)_2^{2-}$
ΔT (°K)	-	-	-
D^{meta} ($10^{-9} \frac{m^2}{s}$)	1.2	0.015	0.015
Δs_{ch} [Å]	2	3	3
ΔF_{ch} [eV]	0.1	0.1	0.1
σ [Å]	0.2	0.3	0.3
ω [eV]	0.005	0.005	0.005
Δs_{max} [Å]	12	8	8
t_{sim} [ps]	1050	2240	2240
F_e [eV]	1	0.5	0.5
τ_G [ps]	0.0875	0.8400	0.8400
n_{H_2O} [-]	119	71	71

H_{tot}^{est} [eV]	-215.6	-195.6	-195.6
ϵ_{prior}^{meta} [eV]	0.11	0.10	0.05
ϵ_{post}^{meta} [eV]	0.07	0.10	0.04

3 REFERENCES:

- (1) Barducci, A.; Bussi, G.; Parrinello, M. Well-Tempered Metadynamics: A Smoothly Converging and Tunable Free-Energy Method. *Phys. Rev. Lett.* **2008**.
- (2) Laio, A.; Gervasio, F. Metadynamics: A Method to Simulate Rare Events and Reconstruct the Free Energy in Biophysics, Chemistry and Material Science. *Reports Prog. Phys.* **2008**.
- (3) Galmarini, S.; Bowen, P. Atomistic Simulation of the Adsorption of Calcium and Hydroxyl Ions onto Portlandite Surfaces - towards Crystal Growth Mechanisms. *Cem. Concr. Res.* **2015**, 1–29.