Intermolecular Forces Between Nanolayers of Crystalline Calcium-Silicate-Hydrates in Aqueous Medium

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Free Energy Perturbation Method

Free energy perturbation (FEP) is a well-established technique and is proven to be effective to calculate the free energy landscape along the path between the reference and the target system. In FEP, the free energy difference between two states can be calculated as

$$\Delta A = -\frac{1}{\beta} ln\langle exp(-\beta \Delta\lambda_i \Delta U)\rangle_i \tag{1}$$

where $\Delta\lambda_i = \lambda_{i+1} - \lambda_i$. We assign λ=0 for the reference state and λ=1 to target state. Any intermediate state takes a value between reference and target systems so that $0 < \lambda < 1$.

To capture the free energy difference landscape, we introduce M sub-stages and then calculate the free energy difference between two successive sub-stages. This approach is usually called

multi-stage free energy perturbation (MEFP). We note that in Eq. 1 the free energy difference can be in forward or backward direction. Due to the fact that in most systems (including the current one) the width of probability of potential energy difference in the forward direction $P_i(\Delta U_{i,i+1})$ and backward direction $P_{i+1}(\Delta U_{i+1,i})$ are different, the free energy calculation might be substantially different depending on the considered direction. To address this issue, we have applied the simple overlap sampling (SOS) technique. SOS is a simple yet effective approach to increase the accuracy of free energy calculations.[1] In this technique we can imagine the existence of an intermediate state between sub-stages λ_i and λ_{i+1}. The perturbation from each sub-stage to the intermediate state and therefore includes both forward and backward perturbation contribution (see Figure S1).

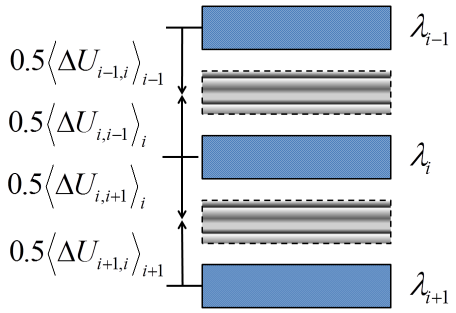

Figure S1 – Cartoon presentation of the perturbation states. Three successive sub-stages are denoted as λ_{i-1}, λ_i, λ_{i+1} illustrated with the blue pattern. The intermediate states are shown as grey stripe patterns. The energy perturbation from an actual sub-stage (blue patterns) to an imaginary state (grey stripe pattern) and vice versa is shown with the related notation used in this work.

Assuming a linear variation of the potential energy between two successive sub-stages (that is the energy between two states at the middle is the average of both states), free energy difference becomes,

$$\Delta A_{i,i+1} = -\frac{1}{\beta} ln \left[\frac{\langle \exp(-\beta \Delta U_{i,i+1}/2) \rangle_i}{\langle \exp(-\beta \Delta U_{i+1,i}/2) \rangle_{i+1}} \right] \tag{2}$$

where $\beta = \frac{1}{k_B T}$, and k_B is the Boltzmann constant and T is the system temperature. The forward and reverse perturbation from each state is presented in Figure S1. In this work, the temperature in all simulations is 300 °k. The charge of the atoms and their interaction are extracted from the

CSH-FF force-field. In the following, we elaborate on the face-to-face (FTF) and sliding FEP simulations along with the bootstrap resampling measurements.

Face-to-Face Interaction

In this study, we introduce 61 sub-stages between face to face (FTF) distances (ξ) from 0 to 12.25 Åto calculate the free energy difference landscape. Since we expect wider $P(\Delta U)$ at the shorter distances because of strong interlayer interaction, we choose a step size of 0.125 Åfor $0 \leq \xi \leq 2.5$ while for larger distances $2.5 < \xi < 12.25$ the step size is 0.25 Å. Since the FEP calculations are independent, we run parallel molecular dynamics (MD) simulations for each stage for 3 ns. During the MD runs we output the system configuration every 1 ps, keeping aside the first 0.5 ns to let the systems reach the equilibrium state. Then we perturb the second layer at each output configuration along the reaction coordinate, toward and opposite of the moving path. From here, we calculate the energy arising from forward and reverse perturbation used in Eq. 2. At each stage water molecules are removed from the interlayer spacing and placed outside. We consider infinitely long C-S-H layers by introducing periodic boundary condition in all directions. In order to test that the results for frozen case are reliable, we compare results of both cases in Figure S2. As it is evident from Figure S2, the equilibrium point (F = 0) shows a small shift toward zero, and the maximum force per area required to separate the layers is 5.8 GPa compared to 6.5GPa for frozen case. In total, the results do not show a considerable difference, while the computational cost and uncertainties of FEP results for simulation times in the scale of a few nanoseconds in the unfrozen case is much higher than the frozen case.

Sliding Interaction

To study the resistance against sliding of two C-S-H layers on top of each other, we perform FEP calculations along and perpendicular to the silicate chains. The choice of the directions are mainly because, force barriers are independent in these directions. Hence, we expect that the barriers along each arbitrary path can be defined as a function of the barriers experienced in these two directions.

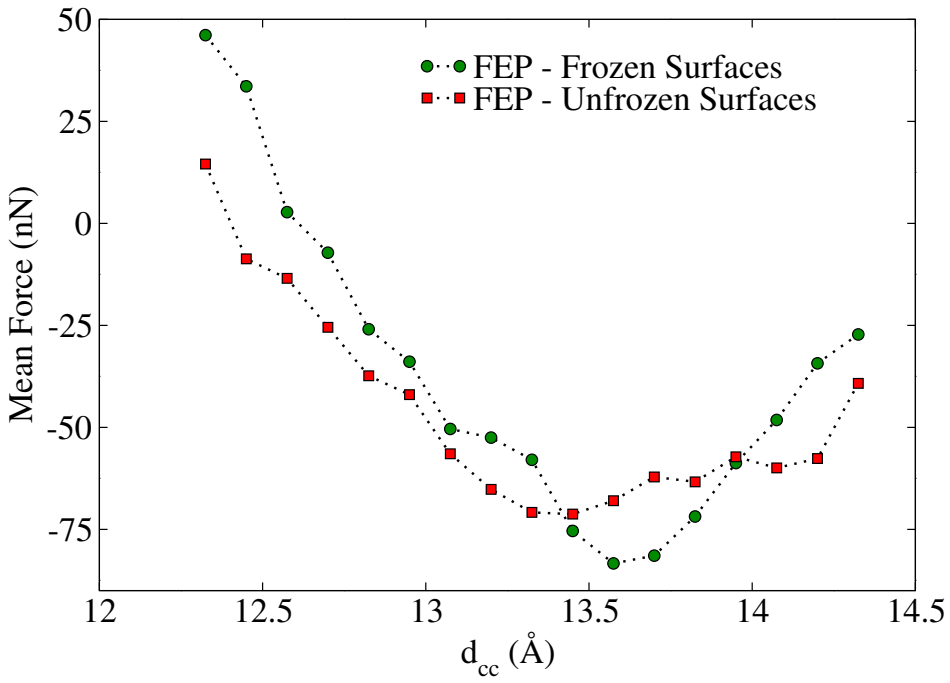

Figure S2 – A comparison between the FTF mean force for frozen and unfrozen cases below the distance of one layer of water.

Aside from interlayer calcium atoms, we let the bridging sites in layers move freely. To capture the force profile for the sliding case, we use the step size of 0.0625 Å. Given the periodicity length along x_1 and x_2,we perform 125 and 190 independent MD simulations respectively. The total simulation length is 1 ns and sampling is started after 200 ps where the systems reach the equilibrium state. We sample the MD trajectory every 0.5 ps corresponding to 1600 frames for each simulation.

Bootstrapping

To obtain the variability of the mean force calculated in this work, we use the bootstrap-resampling method. We notice that sampling of a random set of 100 frames would converge well to the results of FEP presented in this study. Consequently, we choose 1000 resamples of size 100 from the total population of the samples to estimate the shape of the mean distribution. We repeat this process for all MD simulations and then calculate the standard deviation for each simulation. Figure S3 to S5

show the standard deviation for ξ, x_1, and x_2 directions, respectively. Furthermore, the potential energy (U) during the sampling of the cases where the magnitude of the force is maximum is depicted in the inset. It is worth mentioning that for the FTF case, the standard deviation shows a jump at $d_{cc} \approx 14.7$ Åwhere we have doubled the size of the perturbation step. For all cases the standard deviation is within an acceptable range.

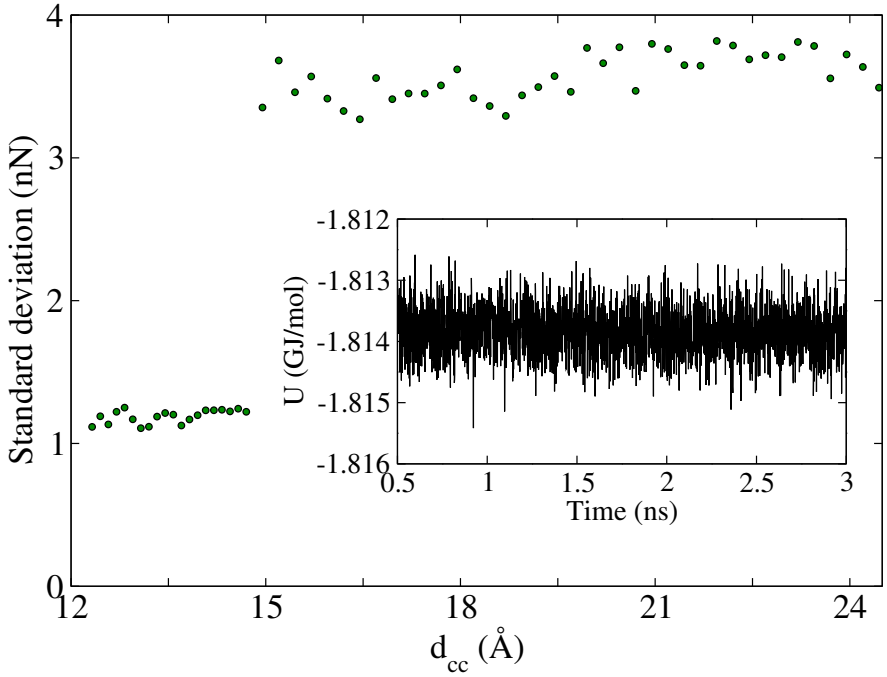

Figure S3 – Standard deviation of mean force calculation using FEP for FTF case. The inset shows the potential energy during the sampling at $d_{cc} = 13.5$Å.

Fitting the results

To fit the theoretical models to the FEP results, we used non-linear least square method with the cost function as follow:

$$E = \sum_{i=1}^{M} [FEP(x_i) - F_{th}(x_i)]^2 \tag{3}$$

then E is minimized using trust region algorithm. In trust region algorithm, we consider that we have an appropriate initial guess of the solution is available, then we seek an approximate point

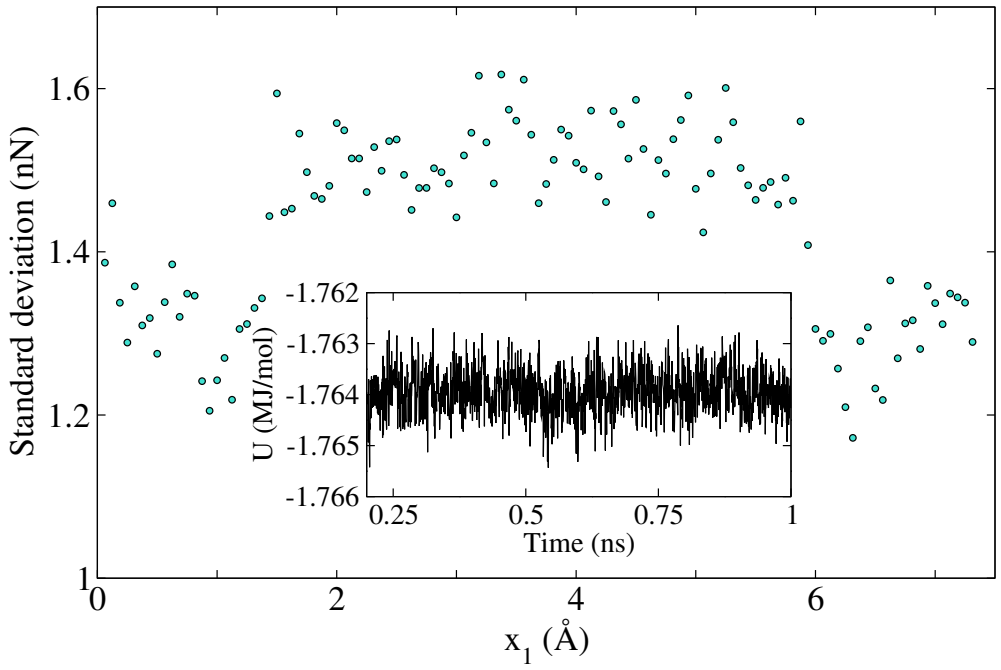

Figure S4 – Standard deviation of mean force calculation using FEP for sliding of unfrozen case along the x_1 direction. The inset shows the potential energy during the sampling at $x_1 = 6$Å.

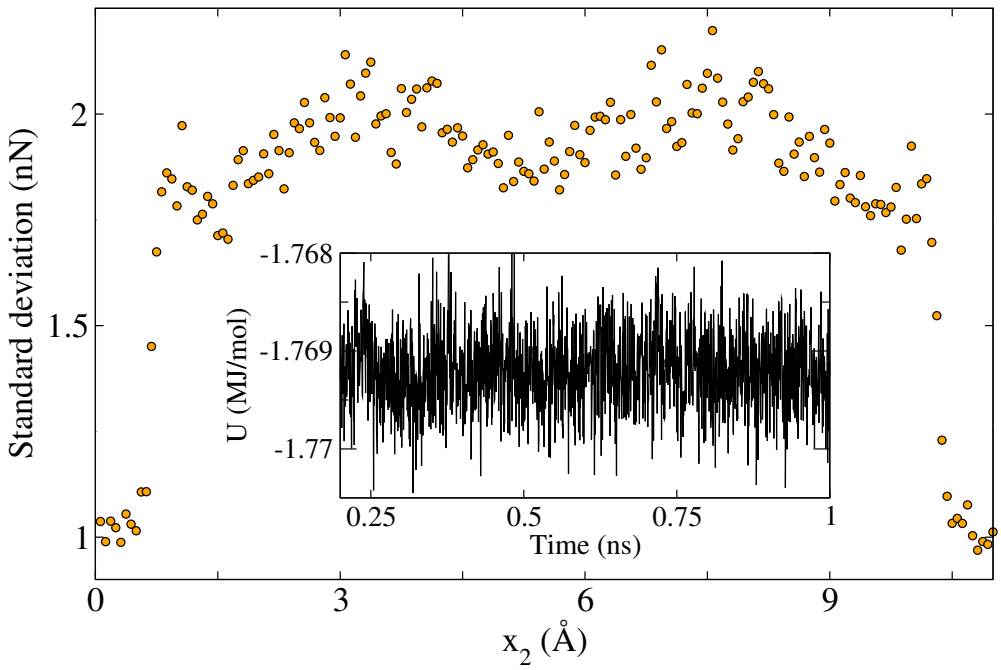

Figure S5 – Standard deviation of mean force calculation using FEP for sliding of unfrozen case along the x_2 direction. The inset shows the potential energy during the sampling at $x_2 = 10.5$Å.

closer to the solution in a limited (trusted) region around the current solution. The constants of the fitting for the FTF and sliding models are given in Table S1.

Table S1 – The theoretical model coefficients

Coef.	**value**	**Coef.**	**value**		**Coef.**	**value**	
	F^n		F_1^s	F_2^s		F_1^s	F_2^s
		b_0	0	0			
a_1	6046	b_1	-0.5557	0.0176	c_1	-25.78	-15.25
a_2	3.2	b_2	0.0676	-0.0174	c_2	1.567	-3.367
a_3	241	b_3	-0.06796	0.0175	c_3	-1.05	-2.448
a_4	2.3	b_4	-0.263	-0.0175	c_4	-3.043	-0.3317
a_5	-39	b_5	-0.2159	0.0176	c_5	1.995	-0.3054
a_6	1.6	b_6	0.1918	-0.0175	c_6	1.475	-0.3054
a_7	2.4	b_7	0.0544	0.0175	c_7	0.3582	-0.3085
		b_8	0.1246	-0.0175	c_8	0.7157	0.5505
		$\frac{2\pi}{l_p}$	0.8584	0.5712			

Material Properties

To calculate the elastic modulus, once the force is determined, we use the following equation:

$$E = \frac{d_{cc}}{S_{int}} \left(\frac{\partial \langle F^n \rangle}{\partial \xi} \right)_{d_0} \tag{4}$$

where d_0 is the distance in which the force is cancelled out (equilibrium point). S_{int} is the interaction area between the two layers. Similarly, we calculate the shear modulus using the sliding FEP results as,

$$G_i = \frac{d_{cc}}{S_{int}} \left(\frac{\partial \langle F_i^s \rangle}{\partial x_i} \right)_{x_0} \tag{5}$$

where i=1, and 2 represents the parallel and perpendicular direction to the silicate chains. x_0 is the position where the force is zero and lies at the beginning (ending) of each periodic length. We compute the surface energy of the FTF interaction as the ratio of the amount total potential of

mean force (PMF) required to separate two C-S-H layers and interaction area,

$$\gamma_s = \frac{PMF_{total}}{2 \times S_{int}} \tag{6}$$

where

$$PMF_{total} = -\int_{d_0}^{\infty} \langle F^n \rangle \, .d\xi \tag{7}$$

or alternatively

$$PMF_{total} = \sum_{i=n}^{N} \Delta A_{i,i+1} \tag{8}$$

where n is the number assigned to the closest sub-stage where the force is cancelled, and N is the number assigned to the largest distance sub-stage in the simulation.

References

(1) Chipot, C.; Pohorille, A. *Free energy calculations*; Springer-Verlag Berlin Heidelberg, 2007.