Supplementary Information: Atomistic insight into the interaction of aspartic acid species with calcium carbonate: model development

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1 Force field

All the parameters for calcium carbonate and water were taken from Armstrong *et al.* [1] and Wu *et al.* [2] Atom labels, force field functional forms, intra-molecular parameters, and charges for aspartic acid species are reported in Schuitemaker *et al.* [3] (2023). Tables 1 and 2 contain the inter-molecular parameters involving aspartic acid species and changes with respect to Schuitemaker *et al.* [3] are highlighted in bold. This corresponds to FF2 in the paper. The parameters used for acetate were taken from Schuitemaker *et al.* [4] (2021), Table 1 reports those describing its interaction with calcium carbonate, with changes with respect to the original model highlighted in bold and labels as in original paper. The addition of a repulsive interaction between C4-O15 (carbon of carbonate and oxygen of acetate) prevents acetate from getting too close to carbonate as a consequence of the constraints in our metadynamics simulation; gas phase paring free energy profiles with and without this potential overlap, meaning that the addition of this potential will not affect surface binding results. A file containing the full potential model is shared in the Supplementary Information package.

Table 1 Buckingham and AB Lennard-Jones potentials for the interactions between aspartic acid species and calcium carbonate. The CO_3^{2-}-Asp potential is one of the options proposed in the paper, based on the assumption that the parameters developed for glycine,[4] derived from the interaction of methylammonium and acetate with calcite, can be used as such for aspartic acid. Labels are as in Schuitemaker *et al.* [3] (2023) for aspartate and Schuitemaker *et al.* [4] (2021) for acetate.

Buckingham	A [eV]	ρ [Å]	C [eV Å^6]	A-B Lennard-Jones	A [eV Å^6]	B [eV Å^{12}]
Ca^{2+}-Asp						
Ca - O71	2388.4841	**0.265011**	0.0	Ca - C72	12000.0	0.0
Ca - O75	2388.4841	**0.265011**	0.0	Ca - C74	12000.0	0.0
Ca - N73	22878.8	0.215023	0.			
CO_3^{2-}-Asp from glycine [4]						
O4 - H73	719.5374	0.25	0.0	O4 - H72	46.5625	0.0
O4 - H76	719.5374	0.25	0.0	O4 - H74	46.5625	0.0
O4 - C71	53.9625	0.57	0.0			
O4 - C75	53.9625	0.57	0.0			
Ca^{2+}-Acetate [4]						
Ca - O15	2388.4841	0.27151	0.0	Ca - C14	12000.0	0.0
CO_3^{2-}-Acetate [4]						
O4 - C15	67.475158	0.57	0.0	O4 - H14	34.0	0.0
C4 - O15	**67.475158**	**0.57**	0.0			

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Table 2 12-6 Lennard-Jones parameters for inter-molecular interactions involving aspartic acid species. The parameters for CO_3^{2-}-Asp are a second option proposed in the paper, revised from Schuitemaker *et al.* [3] where they had been derived from the inter-molecular aspartate-aspartate parameters in water. Labels are as in Schuitemaker *et al.* [3]

	ε [eV]	σ [Å]		ε [eV]	σ [Å]
Asp-Asp			**water-Asp**		
C71 - C71	0.00288	3.58118	O2 - C71	0.00440	3.36701
C71 - C72	0.00288	3.58118	O2 - C72	0.00440	3.36701
C71 - C74	0.00288	3.58118	O2 - C74	0.00440	3.36701
C71 - C75	0.00288	3.58118	O2 - C75	0.00440	3.36701
C71 - H72	0.00188	**3.15541**	O2 - H72	0.00288	2.74105
C71 - H74	0.00188	**3.15541**	O2 - H74	0.00288	2.74105
C71 - N73	0.00437	3.35146	O2 - N73	0.00332	3.47115
C71 - N76	0.00437	3.35146	O2 - N76	0.00332	3.47115
C71 - O71	0.00717	3.06654	O2 - O71a	0.00513	3.27240
C71 - O75	0.00717	3.06654	O2 - O75a	0.00513	3.27240
C72 - C72	0.00288	3.58118	O2 - O71b	0.00513	**3.27240**
C72 - C74	0.00288	3.58118	O2 - O75b	0.00513	**3.27240**
C72 - C75	0.00288	3.58118	H2 - H76	0.00123	2.45000
C72 - H72	0.00188	2.91541			
C72 - H74	0.00188	2.91541	**CO_3^{2-}-Asp**		
C72 - N73	0.00437	3.35146	C4 - H74	0.00188	2.91541
C72 - N76	0.00437	3.35146	C4 - N73	0.00437	3.35146
O71 - C72	0.00717	3.06654	C4 - N76	0.00437	3.35146
C72 - O75	0.00717	3.06654	O4 - C72	0.00717	3.06654
C74 - C74	0.00288	3.58118	O4 - H72	0.00468	2.49644
C74 - C75	0.00288	3.58118	O4 - C74	0.00717	3.06654
H72 - C74	0.00188	2.91541	O4 - H74	0.00468	2.49644
C74 - H74	0.00188	2.91541	O4 - N73	0.00152	3.98580
N73 - C74	0.00437	3.35146	O4 - N76	0.00152	3.98580
N76 - C74	0.00437	3.35146	C4 - C72	0.00288	3.58118
O71 - C74	0.00717	3.06654	C4 - C71	0.00288	3.58118
C74 - O75	0.00717	3.06654	O4 - O71	0.01788	2.62585
C75 - C75	0.00288	3.58118	O4 - O75	0.01788	2.62585
H72 - C75	0.00188	**3.15541**	C4 - C72	0.00288	3.58118
H74 - C75	0.00188	**3.15541**	C4 - H72	0.00188	2.91541
N73 - C75	0.00437	3.35146	C4 - C74	0.00288	3.58118
N76 - C75	0.00437	3.35146			
O71 - C75	0.00717	3.06654			
C75 - O75	0.00717	3.06654			
H72 - H72	0.00123	2.37341			
H72 - H74	0.00123	2.37341			
H72 - N73	0.00285	2.72839			
H72 - N76	0.00285	2.72839			
O71 - H72	0.00468	2.49644			
H72 - O75	0.00468	2.49644			
H74 - H74	0.00123	2.37341			
N73 - H74	0.00285	2.72839			
N76 - H74	0.00285	2.72839			
O71 - H74	0.00468	2.49644			
H74 - O75	0.00468	2.49644			
N73 - N73	0.00663	3.13647			
N76 - N76	0.00663	3.13647			
O71 - N73	0.00152	**4.05580**			
O71 - N76	0.00152	**4.05580**			
N73 - O75	0.00152	**4.05580**			
N76 - O75	0.00152	**4.05580**			
O71 - O71	0.01788	2.62585			
O71 - O75	0.01788	2.62585			
O75 - O75	0.01788	2.62585			

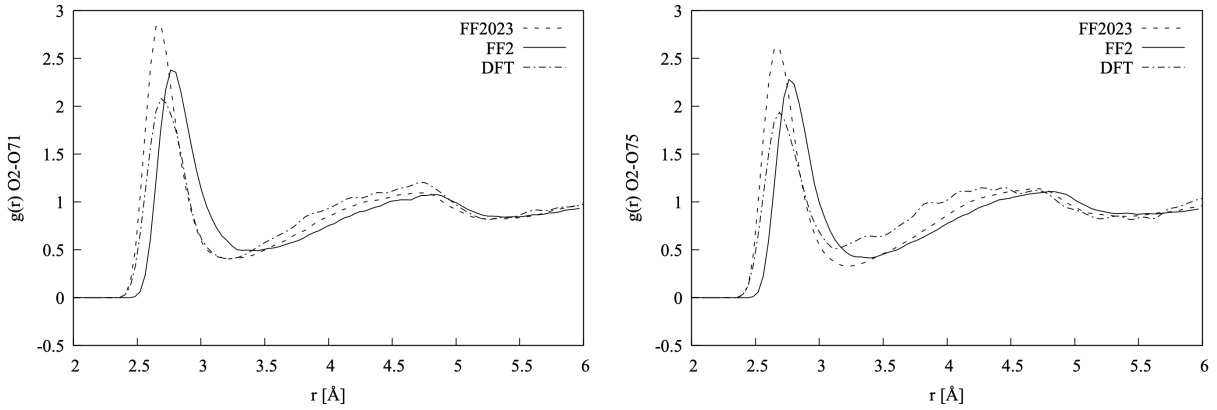

Fig. 1 Pairing distribution function between the oxygen of water (O2) and the oxygen of the carboxylate groups in L-Asp^{2-} (O71 and O75) with DFT, the force field from Schuitemaker *et al.* [3], and the force field in this work FF2

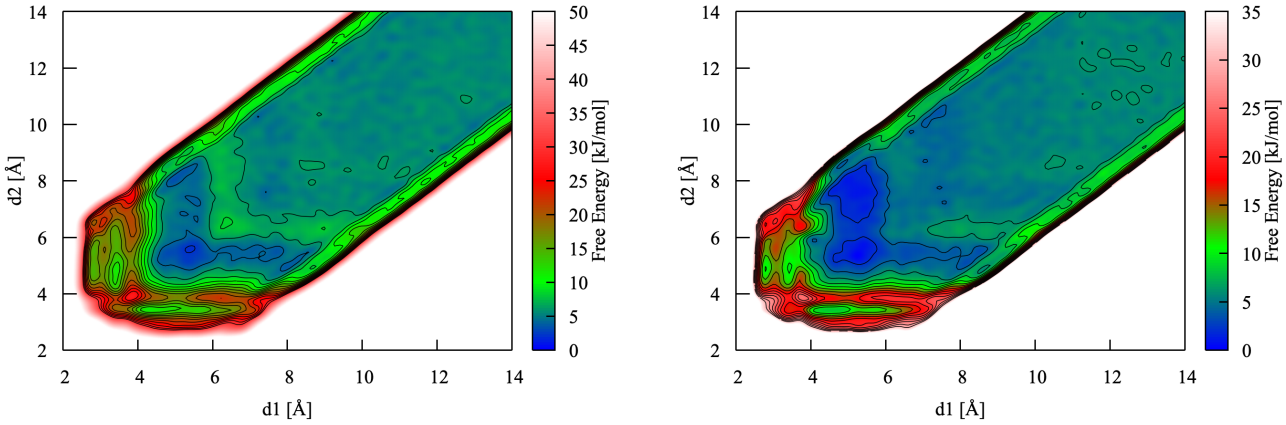

Fig. 2 Calcium aspartate pairing free energy projected along the distance between calcium and each carboxylate group (d1 and d2), obtained with FF2: Ca^{2+} L-AspZW^{-} (left) and Ca^{2+} L-Asp^{2-} (right).

2 Pairing distribution function

Figure 1 shows the pairing distribution function between the oxygen of water and the oxygen of the carboxylate groups in aspartate. Agreement/disagreement between the force field and DFT results is qualitative, given that DFT simulations have been run for only a few tens of ps.

3 Pairing free energy

The pairing free energy of calcium aspartate computed through metadynamics using the torsional angle and the distances between each of the carboxylate functional groups and calcium ($d1$ and $d2$) as collective variables. Figure 2 shows pairing free energy projected along $d1$ and $d2$, confirming a preference for solvent-shared interactions, while the formation of contact ion pairs is disfavoured. These projections are very similar to those obtained in Schuitemaker *et al.* [3], with contact ion pairing being slightly more disfavoured for Ca^{2+} L-Asp^{2-} with FF2. This is mostly due to calcium binding more strongly to water in Armstrong *et al.* [1]'s parametrization. More details and the 1-D profiles are in the main text.

References

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