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This copy of the ESI replaces the previous version published on 29th December 2023 to correct typographical errors in Table 4

Supplementary Information
New model of aspartic acid species in aqueous calcium carbonate growth environments: challenges and perspectives

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1 Force field

Atoms are labelled as in Figure 1 with water oxygen and hydrogen atoms labelled as H2 and O2, respectively. Parameters for water and calcium carbonate are reported in Raiteri *et al.*[1] and in Wu *et al.*[2]. Charges, intra- and inter-molecular parameters for aspartic acid species are reported in Tables 1, 2, 3, and 4.

The energy of intra-molecular bonds (E_{bond}), angles (E_{angles}), dihedral angles ($E_{dihedrals}$), and improper angles ($E_{improper}$) for aspartic acid species is defined as follows:

$$E_{bond} = K(r - r_0)^2 \tag{1}$$
$$E_{angle} = K(\theta - \theta_0)^2 \tag{2}$$
$$E_{dihedral} = K[1 + cos(n\phi - d)] \tag{3}$$
$$E_{improper} = K_2 d^2 + K_4 d^4 \tag{4}$$

Van der Waals interactions between calcium and aspartic acid species are modelled trough either a Lennard-Jones potential in its *AB* form, E_{LJ-AB}, or a Buckingham potential, E_B:

$$E_{LJ-AB} = \frac{A}{r^{12}} - \frac{B}{r^6} \tag{5}$$

$$E_B = A \cdot e^{-\frac{r}{\rho}} - \frac{C}{r^6} \tag{6}$$

All other van der Waals interactions are described with a Lennard-Jones potential, E_{LJ}:

$$E_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{7}$$

All Coulomb and van der Waals interactions have a cutoff radius at 9.0 Å; all van der Waals interactions except from those between aspartic acid species and water have a tapering function from 6.0 Å. 1-4 intra-molecular interactions are considered for 12-6 Lennard-Jones (weighting 0.5) and Coulomb (weighting 1.0) terms.

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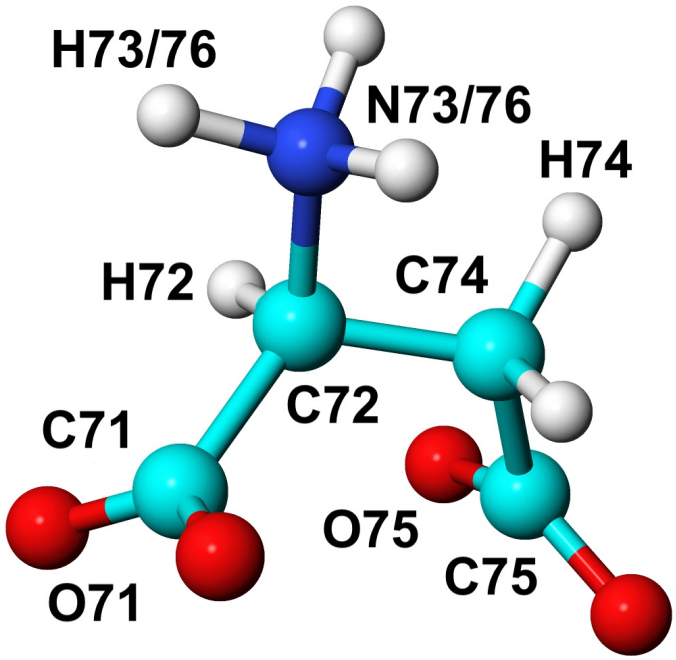

Fig. 1 Ball and stick representation of L-Asp ZW^-. O atoms are coloured in red, C atoms in cyan, H atoms in white and N is coloured in blue. Labels correspond to the atom types as defined in the force field. Labels 73 and 76 refer to the amino group in Asp ZW^- and in Asp^{2-}, respectively.

Table 1 Force field charges. Labels as in Figure 1

Atom Type	Partial charges, $\|e\|$
C71	0.499000
O71	-0.702000
C72	0.198000
H72	0.024000
N73	-0.449000
H73	0.326000
N76	-0.923000
H76	0.226000
C74	-0.241000
H74	0.070000
C75	0.715000
O75	-0.730000

Table 2 Intra-molecular interactions for aspartic acid species. Parameters as in equations 1 to 4. Labels as in Figure 1

bond	K [eV Å^{-2}]	r [Å]	improper	K_2 [eV Å^{-2}]	K_4 [eV Å^{-4}]
C72-H72	15.618400	1.0963000	C71 - C72 - O71 - O71	8.35870000	360
C74-H74	15.618400	1.0963000	C75 - C74 - O75 - O75	8.35870000	360
C71-O71	24.765100	1.2516000			
C75-O75	24.765100	1.2516000			
C72-N73	13.162300	1.4658000			
N73-H73	20.528750	1.0250000			
C72-N76	13.162300	1.4658000			
N76-H76	20.528750	1.0250000			
C71-C72	11.482000	1.5100000			
C74-C75	11.482000	1.5650000			
C72-C74	7.899100	1.5300000			

angle	K [eV $\circ^{-2}$]	r [°]	dihedral	K [eV]	n	d [°]	weighting
C71 - C72 - N73	1.5441000	114.70000	N73 - C72 - C74 - C75	0.00005403	6	180	0.0
C71 - C72 - N76	1.5441000	114.70000	N76 - C72 - C74 - C75	0.00005403	6	180	0.0
C71 - C72 - H72	1.9992000	109.26000	H74 - C74 - C72 - C71	0.00703640	3	360	0.0
C71 - C72 - C74	1.5441000	114.33000	C75 - C74 - C72 - C71	0.00703640	3	360	0.0
O71 - C71 - C72	2.8160500	115.04000	H74 - C74 - C72 - H72	0.00703640	3	360	0.0
O71 - C71 - O71	5.0780000	129.92000	C75 - C74 - C72 - H72	0.00703640	3	360	0.0
C72 - C74 - H74	2.0952500	110.33000	H74 - C74 - C72 - N73	0.00005403	6	180	0.0
C72 - N73 - H73	3.1083500	106.11000	H74 - C74 - C72 - N76	0.00005403	6	180	0.0
C72 - N76 - H76	3.1083500	106.11000	O71 - C71 - C72 - N73	0.00005403	6	180	0.0
C72 - C74 - C75	1.5441000	114.33000	O71 - C71 - C72 - N76	0.00005403	6	180	0.0
H72 - C72 - N73	1.5303500	111.73000	H72 - C72 - C71 - O71	0.00005403	6	180	0.0
H72 - C72 - N76	1.5303500	111.73000	C74 - C72 - C71 - O71	0.00005403	6	180	0.0
H72 - C72 - C74	1.9992000	109.26000	C72 - C74 - C75 - O75	0.00005403	6	180	0.0
N73 - C72 - C74	1.5441000	114.70000	O75 - C75 - C74 - H74	0.00005403	6	180	0.0
H73 - N73 - H73	1.6219500	105.67000	C71 - C72 - N73 - H73	0.00703640	3	360	0.0
N76 - C72 - C74	1.5441000	114.70000	C71 - C72 - N76 - H76	0.00703640	3	360	0.0
H76 - N76 - H76	1.6219500	105.67000	H73 - N73 - C72 - H72	0.00703640	3	360	0.0
C74 - C75 - O75	2.8160500	115.04000	H76 - N76 - C72 - H72	0.00703640	3	360	0.0
H74 - C74 - C75	1.9992000	107.26000	H73 - N73 - C72 - C74	0.00703640	3	360	0.0
H74 - C74 - H74	1.5441000	106.05000	H76 - N76 - C72 - C74	0.00703640	3	360	0.0
O75 - C75 - O75	5.0780000	129.92000					

Table 3 Force field parameters for the interactions between aspartic acid species and calcium (Equations 5 and 6). Labels as in Figure 1

Buckingham	A [eV]	ρ [Å]	C [eV Å^6]	A-B Lennard-Jones	A [eV Å^6]	B [eV Å^{12}]
Ca - O71	2388.4841	0.271511	0.	Ca - C72	12000.0	0.0
Ca - O75	2388.4841	0.271511	0.	Ca - C74	12000.0	0.0
Ca - N73	22878.8	0.215023	0.			

Table 4 Force field parameters for the 12-6 Lennard-Jones interactions, as in Equation 7. Labels as in Figure 1; for water-Asp interactions only, O71a and O75a refer to Asp ZW^-, and O71b and O75b refer to Asp^{2-}.

	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	2.91541	O2 - H72	0.00288	2.74105
C71 - H74	0.00188	2.91541	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	3.37115
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	3.17240
C72 - C74	0.00288	3.58118	O2 - O75b	0.00513	3.17240
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	2.91541	C4 - C75	0.00288	3.58118
H74 - C75	0.00188	2.91541	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	3.98580			
O71 - N76	0.00152	3.98580			
N73 - O75	0.00152	3.98580			
N76 - O75	0.00152	3.98580			
O71 - O71	0.01788	2.62585			
O71 - O75	0.01788	2.62585			
O75 - O75	0.01788	2.62585			

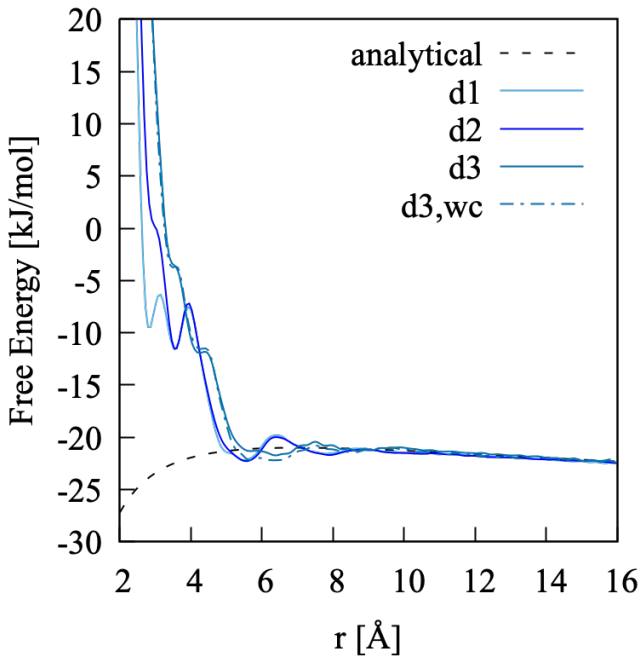

Fig. 2 Pairing free energy of Ca-Asp ZW^- along distances (Ca-O71), d2 (Ca-O75), d3 (Ca-COM, where COM is the centre of mass of Asp ZW^-) and d3,wc (d3 with water coordination of calcium as a collective variable).

References

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