

## Molecular order and disorder of surfactants in clay nanocomposites

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### Supporting information

As supporting information we give the details of the clay models, force field and simulation methods.

### Clay model

We simulate three types of clay minerals: Wyoming montmorillonite, Cheto montmorillonite, and Vermiculite. Both montmorillonite clay minerals are dioctahedral, whereas Vermiculite is trioctahedral. The crystal structures of the three clay minerals also have a different layer charge, as well as a different distribution of substitutions in the tetrahedral ( $\text{Si}^{4+}$  by  $\text{Al}^{3+}$ ) and octahedral sheet. In the latter sheet,  $\text{Al}^{3+}$  is substituted by  $\text{Mg}^{2+}$  in case of the dioctahedral montmorillonites, whereas  $\text{Mg}^{2+}$  is substituted by  $\text{Al}^{3+}$  in case of Vermiculite. The unit-cell formula  $\text{M}_{0.625}[\text{Si}_{7.875}\text{Al}_{0.125}][\text{Al}_{3.5}\text{Mg}_{0.5}]\text{O}_{20}(\text{OH})_4$  corresponds to Wyoming montmorillonite, which has substitutions in both sheets, and a unit-cell layer charge of 0.625 e. Cheto montmorillonite has a unit-cell formula of  $\text{M}_{0.875}[\text{Si}_{8.00}][\text{Al}_{3.125}\text{Mg}_{0.875}]\text{O}_{20}(\text{OH})_4$ , only substitutions in the octahedral sheet, and a unit-cell layer charge of 0.875 e. Vermiculite has a unit-cell formula of  $\text{M}_{1.3125}[\text{Si}_{5.875}\text{Al}_{2.125}][\text{Al}_{0.8125}\text{Mg}_{5.1875}]\text{O}_{20}(\text{OH})_4$  and a unit-cell layer charge of 1.3125 e, with substitutions in the octahedral and tetrahedral sheets. In all structural formulas, 'M' represent monovalent alkylammonium molecules. We assumed an effective clay platelet thickness ( $z_{\text{clay}}$ ) of 9.5 Å. The total three-dimensional periodic simulation cell contains two clay layers and two interlayer spaces, and hence the z-dimension of the system ( $L_z$ ) corresponds to two times the basal spacing. The substitutions are carried out at randomly chosen coordinates obeying Lowensteins rule<sup>[1]</sup>. The set of atomic coordinates and partial charges describing the (unsubstituted) clay minerals are taken from Skipper et al.<sup>[2]</sup> and are given in Table 1.

**Table 1** The upper part of the table shows the coordinates and partial charges of atoms in the clay crystal structure of one unit-cell of montmorillonite<sup>[2]</sup>. For Vermiculite, this unit-cell is similar to the one of montmorillonite, with adaptations and additions given in the lower part of the table.

No.	Atom	x (Å)	y (Å)	z (Å)	q (e)	No.	Atom	x (Å)	y (Å)	z (Å)	q (e)
	Type						Type				
1	O	2.64	0.00	3.28	-0.8000	21	Al	7.04	6.09	0.00	3.0000
2	O	1.32	2.28	3.28	-0.8000	22	Al	7.04	3.05	0.00	3.0000
3	O	3.96	2.28	3.28	-0.8000	23	O	0.88	9.14	-3.28	-0.8000
4	O	0.00	0.00	1.06	-1.7175	24	O	2.20	6.86	-3.28	-0.8000
5	H	0.88	0.00	1.43	0.7175	25	O	-0.44	6.86	-3.28	-0.8000
6	Si	2.64	1.52	2.73	1.2000	26	O	3.52	9.14	-1.06	-1.7175
7	Si	0.00	3.05	2.73	1.2000	27	H	2.64	9.14	-1.43	0.7175
8	O	2.64	1.52	1.06	-1.0000	28	Si	0.88	7.62	-2.73	1.2000
9	O	0.00	3.05	1.06	-1.0000	29	Si	3.52	6.09	-2.73	1.2000
10	Al	4.40	1.52	0.00	3.0000	30	O	0.88	7.62	-1.06	-1.0000
11	Al	4.40	-1.52	0.00	3.0000	31	O	3.52	6.09	-1.06	-1.0000
12	O	0.00	4.57	3.28	-0.8000	32	O	3.52	4.57	-3.28	-0.8000
13	O	3.96	6.85	3.28	-0.8000	33	O	-0.44	2.29	-3.28	-0.8000
14	O	1.32	6.85	3.28	-0.8000	34	O	2.20	2.29	-3.28	-0.8000
15	O	2.64	4.57	1.06	-1.7175	35	O	0.88	4.57	-1.06	-1.7175
16	H	3.52	4.57	1.43	0.7175	36	H	0.00	4.57	-1.43	0.7175
17	Si	0.00	6.09	2.73	1.2000	37	Si	3.52	3.05	-2.73	1.2000
18	Si	2.64	7.62	2.73	1.2000	38	Si	0.88	1.52	-2.73	1.2000
19	O	0.00	6.09	1.06	-1.0000	39	O	3.52	3.05	-1.06	-1.0000
20	O	2.64	7.62	1.06	-1.0000	40	O	0.88	1.52	-1.06	-1.0000
4	O	0.00	0.00	1.06	-1.5200	21	Mg	7.06	6.09	0.00	2.0000
5	H	0.00	0.00	2.0176	0.5200	22	Mg	7.06	3.05	0.00	2.0000
10	Mg	4.40	1.52	0.00	2.0000	26	O	3.52	9.14	-1.06	-1.5200
11	Mg	4.40	-1.52	0.00	2.0000	27	H	3.52	9.14	-2.0176	0.5200
15	O	2.64	4.57	1.06	-1.5200	35	O	0.88	4.57	-1.06	-1.5200
16	H	2.64	4.57	2.0176	0.5200	36	H	0.88	4.57	-2.0176	0.5200
41	Mg	1.76	0.00	0.00	2.0000						
42	Mg	4.40	4.57	0.00	2.0000						

To describe the interactions of the alkylammonium molecules with each other and with the atoms of the clay platelets, we use an all-atom approach for the NH<sub>3</sub> head group and a united atom approach for the hydrophobic aliphatic tail. We call the aliphatic CH<sub>2</sub> and CH<sub>3</sub> groups united atoms, and denote these with C. We use the OPLS United Atom forcefield<sup>[3,4]</sup> with rigid bonds. The C-C, N-C, and, N-H bond-distances are 1.53, 1.51, and 1.01 Å, respectively. Bond-bending interactions<sup>[5]</sup> are computed by

$$u^{bend} = \frac{1}{2}k_{\theta}[\theta - \theta_{eq}]^2 \quad (1)$$

In this equation,  $u^{bend}$  is the bond-bending energy,  $k_{\theta}$  the force constant,  $\theta$  the bond-bending angle, and  $\theta_{eq}$  the equilibrium angle.  $k_{\theta}$  and  $\theta_{eq}$  depend on the atoms involved in the bond-bending (Table 2).

**Table 2 Parameters for the bond-bending potentials (Eq. 1) in the alkylammonium molecules<sup>[5]</sup>.**

	$k_{\theta}$ (kcal mol <sup>-1</sup> )	$\theta_{eq}$ (°)
C-C-C	126.0	112.4
N-C-C	160.0	111.2
H-N-C	70.0	109.5
H-N-H	70.0	109.5

The potential that describes torsion angles is

$$u^{tors} = \frac{1}{2}V_1[1 + \cos(\varphi)] + \frac{1}{2}V_2[1 - \cos(2\varphi)] + \frac{1}{2}V_3[1 + \cos(3\varphi)], \quad (2)$$

where  $V_1$  to  $V_3$  are specific parameters depending on the involved atoms (Table 3) and  $\varphi$  the dihedral angle.

**Table 3 Parameters for the torsion potentials (Eq. 2) in the alkylammonium molecules<sup>[3,6]</sup>.**

	$V_1$ (kcal mol <sup>-1</sup> )	$V_2$ (kcal mol <sup>-1</sup> )	$V_3$ (kcal mol <sup>-1</sup> )
C-C-C-C	1.411	-0.271	3.145
N-C-C-C	2.732	-0.229	0.485
H-N-C-C	0.000	0.000	0.347

Intermolecular atomic interactions, as well as intra-molecular atomic interactions between more than four (united) atoms, are described by a Lennard-Jones potential

$$u^{VDW} = \sum_{i=1}^N \sum_{j>i}^N 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (3)$$

where  $u^{VDW}$  is the Van der Waals energy,  $N$  the number of atoms,  $r_{ij}$  is the distance between atoms  $i$  and  $j$ . Using mixing rules<sup>[3]</sup>,  $\varepsilon_{ij}$  is defined as

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (4)$$

and  $\sigma_{ij}$  as

$$\sigma_{ij} = \sqrt{\sigma_i \sigma_j} \quad (5)$$

The parameters  $\varepsilon_i$  and  $\sigma_i$  depend on the type of atom and are given in Table 4.

**Table 4 Lennard-Jones parameters describing atomic interactions for alkylammonium molecules<sup>[3]</sup>.**

	$\sigma$ (Å)	$\varepsilon$ (kcal mol <sup>-1</sup> )	$q$ (e)
CH <sub>3</sub>	3.905	0.175	0.00
CH <sub>2</sub>	3.905	0.118	0.00
CH <sub>2</sub> (-N)	3.905	0.118	0.31
N	3.250	0.170	-0.30
H	0.000	0.000	0.33

Coulombic interactions are computed using

$$u^{Coul} = \sum_{i=1}^N \sum_{j>i}^N \left[ \frac{q_i q_j}{r_{ij}} \right] \quad (6)$$

where  $q_i$  and  $q_j$  denote the partial charges of atoms  $i$  and  $j$  (Table 4). We truncate and shift the Lennard-Jones potentials at 12.0 Å and apply periodic boundary conditions. The long-range Coulombic interactions are treated with the Ewald summation<sup>[7,8]</sup> with a precision of  $1.0 \cdot 10^{-6}$  for the molecular dynamics part of our simulations and a precision of  $1.0 \cdot 10^{-8}$  for the Monte Carlo volume changes. Using this precision and a cut-off of 12.0 Å we compute the necessary  $\alpha$  and the number of  $k$ -vectors<sup>[7]</sup>. The total potential energy ( $U$ ) is defined as the sum of the bond-bending, torsion, Van der Waals, and Coulombic energy:

$$U = u^{bend} + u^{tors} + u^{VDW} + u^{Coul} \quad (7)$$

### Simulation details

We use molecular dynamics as a method to generate new configurations that have the desired equilibrium distribution. To mimic the experimental setup we carry out molecular simulations in the  $NP_zT$  ensemble, which implies that the pressure normal to the clay layers is fixed and the basal spacing is allowed to fluctuate. In our communication we show a Monte Carlo formula for carrying out basal spacing changes, by scaling the clay platelets and alkylammonium molecules on the center of mass. In this formula, the relation between these  $z$ -dimensions is given by

$$L_z(n) = L_z(o) + [Ran() - 0.5] \cdot \Delta L_z^{\max}. \quad (8)$$

In this equation,  $Ran()$  is a uniformly distributed random number between 0 and 1 and  $\Delta L_z^{\max}$  is the maximum displacement. The latter is set in such a way that we obtain an acceptance of approximately 50% for the algorithm given in equation 14.

We start the simulations with randomly chosen molecular configurations at relatively large basal spacings of 24 Å or less. Depending on the type of clay mineral and carbon chain length, the total simulation time varies between 1.5 and 3.0 ns, and the total sampling time varies between 0.7 and 1.0 ns. Instead of defining a fixed simulation time, we simulate until the basal spacing converges to an equilibrium value. Especially the simulations with short carbon chain lengths equilibrate relatively rapidly, whereas longer carbon chain lengths require longer equilibration times.

### Configurational biased Monte Carlo

During the simulations we use a configurational bias Monte Carlo (CBMC) scheme to regrow the alkylammonium molecules. This technique is important to cross conformational barriers and thereby correctly sample the phase space. The procedure consists of a few steps. We randomly choose a molecule and generate 25 trial positions ( $k$ ) for a new position of the ammonium head group, including the first united atom bead. For each trial position we adjust the internal angles and orientation of the head group using an ordinary Metropolis algorithm. One of each 25 trial positions is selected with a certain probability

$$p_i(j) = \frac{\exp[-\beta u_i(j)]}{\sum_{l=1}^k \exp[-\beta u_i(l)]} = \frac{\exp[-\beta u_i(j)]}{w_i(n)}, \quad (9)$$

where  $u_i(j)$  is the potential energy of trial position  $j$ , and  $w_i(n)$  the Rosenbluth factor for united atom  $i$  of the new configuration.  $\beta$  is defined as  $1/k_B T$  with  $k_B$  the Boltzmann constant and  $T$  the temperature. The selected configuration is added to the system and is the starting point for growing the rest of the chain using equation 9, until the entire chain is regrown on a different position in the system. Once the whole chain is regrown we compute the total Rosenbluth factor of the new configuration  $W(n)$

$$W(n) = \prod w_i(n). \quad (10)$$

By regrowing the old chain at the same position and use  $k-1$  trial positions for each atom, we also compute the total Rosenbluth factor of the old configuration  $W(o)$

$$W(o) = \prod w_i(o). \quad (11)$$

If we would have moved the old chain to a new position in one step without CBMC, the acceptance rule would depend on the difference between the potential energies  $U(n)$  and  $U(o)$  of the new and old configurations, respectively, by

$$acc(o \rightarrow n) = \min(1, \exp[-\beta(U(n) - U(o))]). \quad (12)$$

The bias we introduce with CBMC is exactly removed by using the following acceptance rule<sup>[6]</sup>

$$acc(o \rightarrow n) = \min(1, W(n) / W(o)). \quad (13)$$

The procedure given above describes a full regrow of the alkylammonium molecules. In addition, we also carry out a partial regrow for which we only regrow the tail and do not move the ammonium head group and the first united atom. Since partial charges are only located on these atoms, we only have to recalculate the Van der Waals Energy for a partial regrow move. We regrow the alkylammonium molecules as much as necessary for achieving at least 1000 accepted new configurations in the simulation.

## References

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