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Free energy of adsorption of water and calcium on the $\{10\,\bar{1}\,4\}$ calcite surface†

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Molecular dynamics simulations of the calcite–water interface have shown that the free energy of adsorption of water is relatively small compared to the previously calculated enthalpy of adsorption implying a large entropy change and that the free energy profile of a calcium adsorbing on the surface correlates with the solvent density; these calculations allow us to begin to address the rates of adsorption and desorption which are essential for studying growth and dissolution.

Atomistic simulations have been used successfully on many occasions to model the growth and dissolution of minerals by comparing the relative thermodynamic stability of different mechanisms,[1] surfaces[2] or impurities[3] for example. However, these calculations are limited by assuming that the rates of growth and dissolution are related to the energetics. Although very promising they do not contain kinetic information. Therefore, a new challenge for atomistic simulations is to calculate the rate of individual processes occurring at the mineral surface explicitly. To start to address these issues, we first investigated the case of a flat and stoichiometric mineral surface, namely the $\{10\,\bar{1}\,4\}$ calcite surface, in contact with an aqueous solution to calculate the residence time of water molecules on the surface and so gain further insight into the structure of the solvent at the interface. Then, we considered the case of a calcium ion approaching the surface from the bulk solution and calculated its free energy profile to determine the rate determining step in the adsorption process as well as its preferred sorption mechanism.

All molecular dynamics (MD) calculations were performed at 300 K in the NVT ensemble (constant number of particles, constant volume and temperature) using the computer code DL_POLY.[4] The potential parameters employed in this work have been described in previous papers.[2,5–7] In the simulation of the mineral surface in contact with bulk water, we calculated the free energy of a water molecule relative to its free energy in the bulk by integrating the average force in the direction perpendicular to the surface from the centre of the water slab to the surface over a 1 ns MD run. Fig. 1 shows the free energy profile of a water molecule approaching the surface as well as the water density relative to the bulk water density. The first thing to note from Fig. 1 is the "mirror symmetry" between the water density and free energy (only one face is shown). As has been seen before, both in theoretical[8,9] and experimental studies,[10] there is a distinct layering of the water at the interface. The density profile shows two peaks of similar height in the close vicinity of the surface at 2.2 and 3.2 Å followed by a large gap of very low water density and then a third peak at 5.0 Å. The amplitude of the oscillations then decreases and the density converges to that of bulk water. Fig. 1 suggests that there are two modes of adsorption on the surface: water molecules which are bonded through their oxygen atom to a surface calcium and those bonded *via* their hydrogen atom to a surface oxygen; we will call these mode I and II respectively. The free energy of adsorption is very similar for both modes, *i.e.* −2.8 and −2.4 kJ mol^{-1} for mode I and II respectively. It is not surprising, given the similar adsorption free energies, that the two modes of adsorption have an almost 1 : 1 ratio. Indeed, the average coordination per surface calcium for mode I is 1.01 and 0.86 for mode II. The free energy barrier to go from mode I to mode II is 5.6 kJ mol^{-1} and 5.3 kJ mol^{-1} to go back. Also a water molecule would have to overcome a free energy barrier of 6.2 kJ mol^{-1} to enter the second layer and 7.3 kJ mol^{-1} to escape from it.

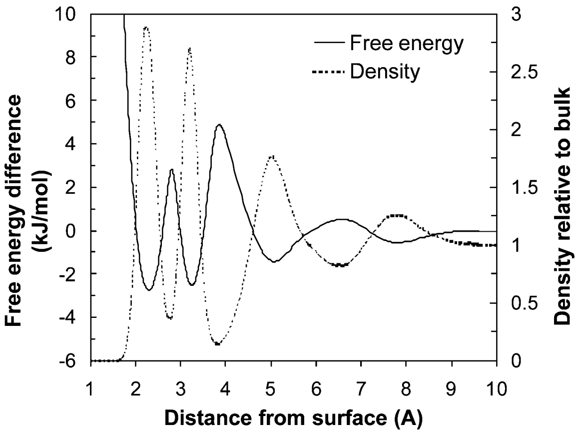

Fig. 1 Water density and free energy profile.

One interesting point to note here is that, although the adsorption energy calculated in precedent papers[2,7] is relatively high (about −45 kJ mol^{-1}), the free energy of adsorption is small (−2 to −3 kJ mol^{-1}). This implies that there is a large change in entropy, which almost cancels the enthalpy term, therefore the water molecules should show greater ordering near the surface. In order to try and demonstrate this, we calculated the orientation order parameter as function of distance to the surface as shown in Fig. 2. A value of −0.5 means that the water dipole is at right angles to the normal of the surface and a value of 1 indicates that it is perpendicular to the surface. Fig. 2 suggests that water molecules in the first layer tend to be lying flat on the surface whereas those in the second layer align their dipole with the normal to the surface and that there is no specific water orientation after about 4 Å. The two well-defined peaks show the high orientational order in the first few Å away from the surface. In order to evaluate to what extend the surface affects

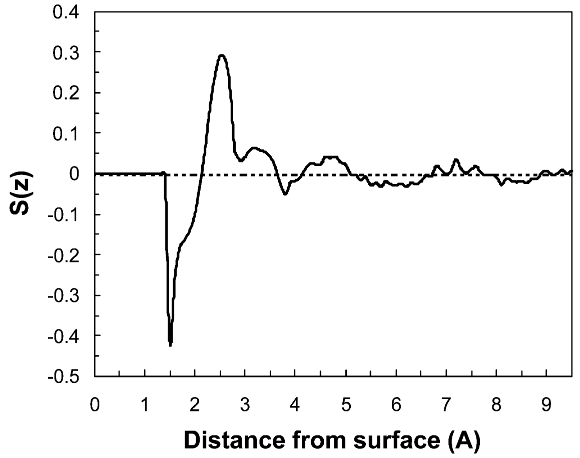

Fig. 2 Water orientation order parameter

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† Electronic supplementary information (ESI) available: free energy calculations. See http://www.rsc.org/suppdata/cc/b3/b311928a/

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the water diffusion, we calculated the water residence time in the different layers as shown in Table 1. The residence time of a water molecule in a layer increases as it approaches the surface. This shows that the water diffusion is further and further restrained as molecules get closer to the mineral surface. The information gained from the orientation order parameter and the water residence time suggests that the rotational and translational degrees of freedom are gradually reduced as water molecules approach the surface, which could justify the importance of the entropic term postulated earlier on.

In order to obtain the free energy profile of a calcium ion as a function of distance to the surface, we performed a series of 100 ps MD calculations where the metal ion is constrained at different heights above the surface. For each calculation, the force in the direction perpendicular to the surface is averaged to obtain one point of the calcium free energy profile in Fig. 3. Fig. 3 shows that the calcium free energy is correlated with the solvent density, with a trough in water density corresponding to a peak in the free energy. It also predicts that the rate determining step of adsorption is the formation of an inner sphere complex which is preferred over an outer sphere complex by about 5 kJ mol^{-1}. The outer sphere complex has an average coordination of 8.2 water molecules, which is the same as for a calcium ion in bulk water. When forming an inner sphere complex, it is coordinated on average to 6.4 water molecules and 1.0 surface oxygen and sits in a site which corresponds to a calcium lattice site if the crystal was extended. It is worth mentioning that when the calcium ion is pushed further in the lattice, there is a small energy well where the calcium ion is coordinated on average to 5.8 water molecules and 1.8 surface oxygens but positions itself outside a calcium lattice site. The free energy barrier to go from an inner sphere to an outer sphere complex is 18.5 kJ mol^{-1} which gives, according to transition state theory, a residence time for the inner sphere complex at the mineral surface of 385 ps assuming a transmission coefficient of one. To check the validity of this assumption, we calculated the transmission coefficient by first generating a pool of about 3000 configurations where the calcium ion is positioned at the transition state distance and then running each configuration for a short period of time, *i.e.* 1.4 ps. We extracted the transmission coefficient from the trajectories generated by taking the plateau value of the reactive flux correlation function,[11] which gave a transmission coefficient of 0.02. This shows that the transmission coefficient cannot be assumed to be one is such cases and thus the residence time for the inner sphere complex at the calcite surface increases to 19 ns.

Table 1 Water residence time as a function of distance from the surface

Water layer	Layer position/Å	Layert hickness/Å	Residence time/ps
1	2.2	1.3	300 ± 17
2	3.2	1.0	53 ± 5
3	5.0	2.7	16 ± 1
4	7.8	3.0	8.8 ± 0.5

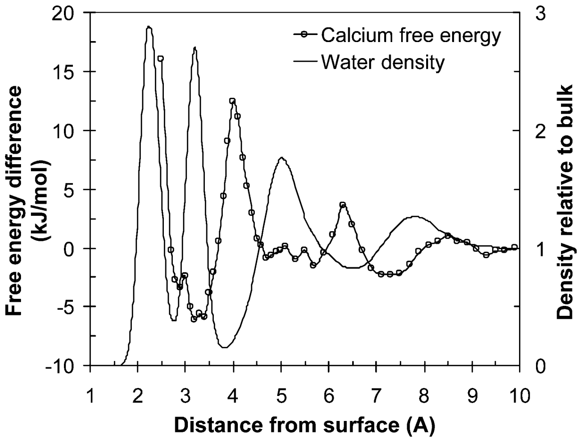

Fig. 3 Calcium free energy profile and water density.

In conclusion, this work highlights the importance of the entropic term in the calculation of the free energy of water adsorption on a mineral surface. Moreover, our calculations show that the mineral surface causes layering of the solvent in the vicinity of the surface, which in turn is responsible for the large oscillations in the free energy profile of a metal ion approaching the surface. In the future, we would like to investigate the effect of magnesium segregation at the surface on the structure of the calcite–water interface. Magnesium is known to form stronger bonds with water[12] and thus we can expect the water density profile and residence time to be modified, which could affect the calcium adsorption and thus the growth rate. Similarly, the free energy profile of a magnesium ion approaching the surface could show whether the adsorption process is related to the strength of the metal ion bond with water as it has been suggested.[13] In addition, the calculation of free energies of activation could be used in Kinetic Monte-Carlo simulations to model growth and dissolution over a long period of time.

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Notes and references

1 N. H. de Leeuw, S. C. Parker and J. H. Harding, *Phys. Rev. B*, 1999, **60**, 13792.
2 N. H. de Leeuw and S. C. Parker, *J. Phys. Chem. B*, 1998, **102**, 2914.
3 S. C. Parker, J. O. Titiloye and G. W. Watson, *Philos. Trans. R. Soc. London, Ser. A*, 1993, **344**, 37.
4 DL_POLY is a package of molecular simulation routines written by W. Smith and T. R. Forester, copyright The Council for the Central Laboratory of the Research Councils, Daresbury Laboratory at Daresbury, Nr. Warrington (1996).
5 A. Pavese, M. Catti, S. C. Parker and A. Wall, *Phys. Chem. Miner.*, 1996, **23**, 89.
6 N. H. de Leeuw and S. C. Parker, *Phys. Rev. B*, 1998, **58**, 13901.
7 S. Kerisit and S. C. Parker, *J. Phys. Chem. B*, 2003, **107**, 7676.
8 R. J. F. Leote de Carvalho and N. T. Skipper, *J. Chem. Phys.*, 2001, **114**, 3727.
9 M. I. McCarthy, G. K. Schenter, C. A. Scamehorn and J. B. Nicholas, *J. Phys. Chem.*, 1996, **100**, 16989.
10 L. Cheng, P. Fenter, K. L. Nagy, M. L. Schlegel and N. C. Sturchio, *Phys. Rev. Lett.*, 2001, **87**, 156103.
11 R. Rey and E. Guàrdia, *J. Phys. Chem.*, 1992, **96**, 4712.
12 J. Burgess, *Ions in Solution: Basic Principles of Chemical Interactions*, Ellis Horwood Ltd., Chichester, UK, 1988.
13 O. S. Pokrovsky and J. Schott, *Environ. Sci. Technol.*, 2002, **36**, 426.