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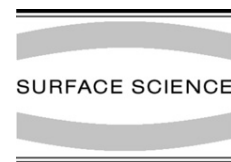


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Ice formation on kaolinite: Lattice match or amphotericism?

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Abstract

The long-standing belief that kaolinite is one of the most efficient natural ice nucleating agents because it provides a close lattice match to the basal plane of ice is called into question. Instead we show through an extensive series of first principles calculations that amphotericism is key to many of the interesting properties of kaolinite with regard to water adsorption and ice nucleation.

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Heterogeneous ice nucleation is a process of importance to a variety of scientific disciplines, such as atmospheric chemistry and biology [1]. Notably in environmental chemistry it is often the first step in cloud formation. Of the many varieties of microscopic dust particle in the upper atmosphere effective in encouraging the freezing of water, the clay mineral kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) plays a prominent role. Experimental studies indicate that kaolinite is an efficient ice nucleating agent and field studies of snow crystals find that kaolinite is often an abundant foreign material at the central nucleus of the crystals [2,3]. The standard explanation for why kaolinite is an effective nucleating agent is that the structure of its basal plane matches rather closely that of ice. Whilst water adsorption and ice nucleation on kaolinite has been widely examined [2–4], the simple questions of if and why water can wet kaolinite and if kaolinite can indeed support a stable epitaxial ice overlayer remain unanswered. Here we address these questions through a series of density-functional theory (DFT) calculations for the adsorption of water on the hydroxyl-

ated and siloxane (001) surfaces of kaolinite. We find that a flat 2D overlayer, with a stability that matches that of ice Ih, can indeed form on the hydroxylated (001) surface. By comparing the behavior of water on both (001) surfaces and through examination of the atomic and electronic structure of the stable overlayer that forms we conclude, however, that its stability is not a result of a favorable lattice match with the substrate but rather because the substrate is amphoteric with the ability to donate and accept H bonds.

The calculations reported here involve DFT within the plane-wave supercell approach as implemented in the CASTEP [5] code with ultra-soft pseudopotentials [6] and the PBE [7] exchange-correlation functional. The performance of the pseudopotentials has been carefully tested on a range of molecular and solid systems and a well-converged plane-wave cut-off of 700 eV used throughout. Monkhorst–Pack k -point meshes [8] with the equivalent of $4 \times 4 \times 1$ sampling within the surface Brillouin zone of a $p(1 \times 1)$ unit cell were used. All surface calculations were performed with a substrate model comprised of a single perfect layer of kaolinite (held in vacuum with periodic boundary conditions): on one side of the layer is a hydroxylated face and on the other a siloxane face. Although a perfect single layer of kaolinite carries a net dipole across the layer, calculations in cells without a net dipole revealed that the results for water

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adsorption were not affected by the dipole. Adsorption energies, E_{ads} , are defined here as

$$E_{\text{ads}} = (E_{n\text{H}_2\text{O}/\text{slab}} - E_{\text{slab}} - n \cdot E_{\text{H}_2\text{O}})/n,$$

where $E_{n\text{H}_2\text{O}/\text{slab}}$ and E_{slab} are the total energies of an n water adsorption system and the clean surface, respectively, and $E_{\text{H}_2\text{O}}$ is the total energy of an isolated water molecule in a 20 Å box. Within this definition a negative adsorption energy thus corresponds to an exothermic adsorption process. The reference bulk ice calculations have been computed with the same pseudopotentials and cut-off in a 12 molecule ice Ih model cell [9], in conjunction with a $4 \times 4 \times 4$ k -point mesh. The cohesive energy, E_{coh} , is defined here as

$$E_{\text{coh}} = (E_{\text{ice}} - 12 \cdot E_{\text{H}_2\text{O}})/12,$$

where E_{ice} is the total energy of the bulk ice Ih cell.

Kaolinite is a layered aluminosilicate. Each layer is neutral and held together through H bonds, which connect the siloxane (001) face of one layer to the hydroxylated (001) face of another. As a clay it is found in platy (several hundred nanometer to micrometer) crystals which predominantly expose (001) surfaces. The siloxane (001) face is said to interact with water weakly and the hydroxylated face strongly [4]. On the latter, each OH group is surrounded by a quasi-hexagonal arrangement of OH groups with bulk nearest neighbor O–O distances ranging from 2.77 to 3.45 Å [10]. With an equivalent O–O distance of 2.75 Å in ice Ih [11], there is an experimental mismatch that ranges from 0.02 Å (0.7%) to 0.70 Å (25%).¹ We note for future reference that upon cleavage of the (001) surface, our calculations predict that 1/3 of the OH groups are tilted and lie almost parallel to the surface (c.f. Fig. 1a and b). This orientational flexibility of the OH groups at the kaolinite surface is, as we will discuss, crucial to the ability of kaolinite to support a stable water overlayer.

Fig. 2 is a plot of E_{ads} versus coverage summarizing the results of an extensive series of DFT (PBE) calculations for water on the hydroxylated (001) surface. These calculations involved the examination of water monomers, 1D chains, clusters, and a range of 2D overlayers. We discuss here the results dealing with 2D overlayers on the hydroxylated surface, all with nominal coverage of 2/3 of a monolayer (ML), where 1 ML corresponds to one water molecule for every surface OH group. The overlayers tested include a conventional ice bilayer in which half of the water molecules are parallel to the surface and the other half are in the plane of the surface normal with one of their two OH groups pointing up into the vacuum (“H-up” bilayer model). The “H-down” analogue of this overlayer, in which the dangling OH groups are instead directed toward the substrate, was also considered. Different registries of these overlayers with the substrate were examined, as were proton

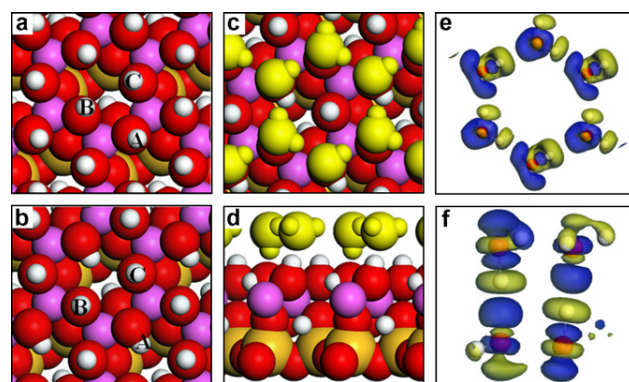


Fig. 1. (a, b) Hydroxylated (001) surface before cleavage (a, bulk truncated surface) and after cleavage (b, relaxed surface). The labels A, B and C illustrate that 1/3 of the surface OH groups tilt upon cleavage of the surface. (c, d) Top and side views of the H-down water overlayer. (e, f) Plots of electron density rearrangement: (e) the interaction within the overlayer is defined as $\Delta\rho = \rho_{\text{overlayer}/\text{slab}} + \rho_{\text{slab}} - \rho_{\text{H}_2\text{O_flat}/\text{slab}} - \rho_{\text{H}_2\text{O_down}/\text{slab}}$ and (f) the interaction between the overlayer and the substrate is defined as $\Delta\rho = \rho_{\text{overlayer}/\text{slab}} - \rho_{\text{slab}} - \rho_{\text{overlayer}}$, where $\rho_{\text{overlayer}/\text{slab}}$, ρ_{slab} , $\rho_{\text{H}_2\text{O_flat}/\text{slab}}$, $\rho_{\text{H}_2\text{O_down}/\text{slab}}$, and $\rho_{\text{overlayer}}$ are the electron densities of the water/kaolinite adsorption system, the clean kaolinite slab, the subset of flat-lying water molecules on the substrate, the subset of upright water molecules on the substrate, and the isolated gas phase overlayer, respectively. Blue (dark) regions indicate electron accumulation and yellow (bright) regions electron depletion at a value of 0.01 electrons/Å³. White, red, purple, and yellow spheres represent H, O, Al, and Si atoms, respectively. For clarity water molecules are colored yellow in (c) and (d), and in (e) six molecules of the overlayer only are shown, and in (f) only the substrate OH groups directly involved in H bonding with water are shown.

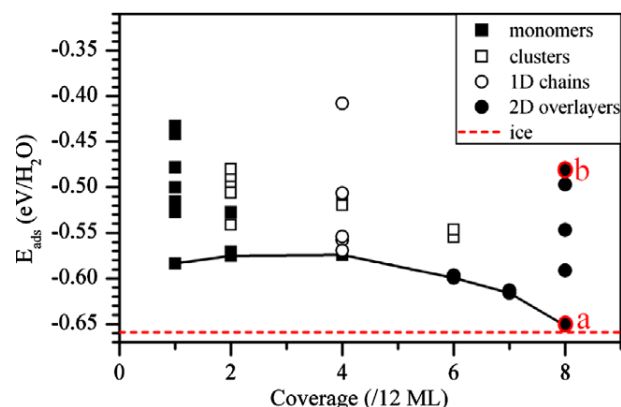


Fig. 2. E_{ads} of various water structures (monomers, clusters, 1D chains, and 2D overlayers) on the hydroxylated (001) surface of kaolinite as a function of coverage. The dashed line indicates the computed E_{coh} of ice Ih. The points labeled (a) and (b) at 2/3 ML indicate the H-down and H-up overlayer, respectively. The solid line is a guide to the eye connecting the lowest energy structures at each coverage considered.

ton ordered and partially proton disordered models² as well as mixed bilayer structures containing both H-up

¹ The corresponding DFT (PBE) distances computed here are 2.81–3.41 Å for the optimized surface of kaolinite and 2.71 Å for ice, yielding a rather similar theoretical mismatch of 3.7–25%.

² In ice terminology proton ordered bilayers have all the water molecules of each type (flat-lying and upright) in the same configuration. In proton disordered structures the water molecules have random configurations, whilst obeying the ice rules. See Ref. [11] for more details.

and H-down water molecules in a range of unit cells ($p(1 \times 1)$ to $p(3 \times 3)$) [12]. The most stable overlayer identified is shown in Fig. 1c and d. This is a H-down bilayer with each water molecule located approximately above a surface OH group. The structure shown is fully proton ordered. However, we did not observe an energetic difference between proton ordered and proton disordered structures so long as the upright water molecules remain in the H-down configuration. The E_{ads} of the periodic H-down overlayer is -0.65 eV/H₂O. This is noteworthy because it is essentially identical to the computed cohesive energy (E_{coh}) of ice Ih, -0.66 eV/H₂O. It has been argued that water has the ability to wet a substrate when E_{ads} matches or exceeds E_{coh} [13]. Thus, to within the accuracy of the current computational set-up, this overlayer has a stability matching that of ice and the potential to wet kaolinite. To test this finding, we have evaluated the relative energy of ice and the overlayer identified here with several other exchange-correlation functionals (PW91 [14], RPBE [15], PBE-WC [16]), but the conclusion that the overlayer is of comparable stability to ice is not altered (Table 1), since the largest difference between E_{ads} and E_{coh} is only 0.04 eV/H₂O. Likewise, the balance between E_{ads} and E_{coh} is not affected when corrections for zero point energies are taken into account: The zero point energy corrections to E_{ads} of the H-down overlayer and E_{coh} of bulk ice are both $+0.13$ eV/H₂O from our DFT (PBE) calculations. The high stability of the overlayer predicted here is also interesting because most previous calculations for adsorbed water overlayers, notably H-down bilayers on metals, are typically predicted to have adsorption energies at least 0.1 eV/H₂O less than is found here [17,18]. An interesting exception to this is the hydroxylated (0001) surface of α -quartz which, like kaolinite, supports a H-down overlayer equally stable to ice [19].

So why does a stable overlayer form on kaolinite? Examination of its structure reveals that optimal registry with the substrate is not necessarily the key issue. Indeed, on inspection, it is clear that the overlayer is considerably deformed from an ideal ice bilayer. First, it is a H-down overlayer that is favored rather than a conventional H-up bilayer. Second, the buckling between the O atoms, which in a conventional ice bilayer is 0.96 Å, 0.94 Å [11], is a mere 0.01 Å here. Thus, this is a flat layer rather than a bilayer, as can be seen from Fig. 1d. The idea that an ice-like overlayer is stable on kaolinite because of a small lattice mismatch with ice can further be tested by adsorbing bilayers on the siloxane (001) surface. Indeed the siloxane surface, with computed nearest neighbor O–O distances

ranging from 2.61 to 2.66 Å, offers a smaller lattice mismatch than the hydroxylated (001) surface. The most stable overlayer identified on the siloxane surface, however, with E_{ads} of -0.44 eV/H₂O is considerably less stable than the overlayer that forms on the hydroxylated surface. Thus it is apparent that favorable registry alone is not the origin of the stability of the overlayer on kaolinite. Instead we believe it is the amphoteric nature of the surface hydroxyl groups that is crucial. Specifically, the geometric flexibility of the surface hydroxyl groups allows them to act either as H bond acceptors or H bond donors depending on the orientation of the water molecules above them. As can be seen from Fig. 1c and d, beneath each flat-lying water molecule is a conveniently placed upwardly pointing OH from which it can accept a H bond. Likewise, beneath each upright down-pointing water is a flat-lying hydroxyl tilted so that it can readily accept a H bond from water. Through this flexibility of the substrate it is ensured that each water molecule is fully coordinated without any dangling H bonds.³ The H bonds in this system can be clearly seen in the electronic structures which lie behind our DFT simulations. Specifically in Fig. 1 electron density rearrangement plots revealing how the density changes upon creation of the water–water (Fig. 1e) and water–kaolinite (Fig. 1f) bonds are displayed. The density redistributions are characteristic of H bonding with depletion (accumulation) of electron density around the H(O) atoms involved in each bond. Further, from Fig. 1f, the different nature of the H bonds each type of water molecule makes with the substrate is clear with the flat-lying molecules acceptors of H bonds from the substrate and the upright molecules donors of H bonds to the substrate. Finally, by examining the lengths of the various H bonds in the adsorption system we obtain an indication of their relative strengths. The H bonds between the water molecules within the overlayer are in the range 1.95–2.14 Å, whereas the H bonds between the water molecules and the substrate are shorter at 1.73 Å and 1.83 Å for the upright and flat water molecules, respectively. Thus, in this adsorption system water appear to bond more effectively with kaolinite than they do with other water molecules.

In conclusion, a flat hexagonal water overlayer is predicted on the hydroxylated (001) surface of kaolinite. Every water molecule in this overlayer is fully coordinated with four H bonds and its stability matches that of ice, exceeding the predicted stability of similar overlayers on many other substrates. Its stability is not a consequence of a favorable lattice match with ice but rather because the substrate is amphoteric with the ability to accept and

Table 1

E_{ads} of the H-down overlayer on the hydroxylated surface and E_{coh} of ice Ih computed with several exchange-correlation functionals

	PBE	PW91	RPBE	PBE-WC
E_{ads}	-0.65	-0.67	-0.48	-0.73
E_{coh}	-0.66	-0.69	-0.49	-0.77

All values are in units of eV/H₂O.

³ The orientation of the hydroxyl groups is not dictated by our initial placement of the water overlayer. Putting instead flat-lying water molecules above initially flat-lying OH groups and/or down-pointing upright water molecules above initially upwardly pointing OH groups leads, upon optimization, to a structure equivalent to the one shown in Fig. 1.

donate H bonds. Overall this study reveals that the behavior of water on kaolinite is more complex and interesting than previously thought to be, highlighting the need for further theoretical and experimental work and the value of considering amphoterism more generally in studies of ice nucleation.

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