Electronic supplementary materials

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A molecular dynamics simulation study on the tensile and compressive behavior of hydrated kaolinite

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Coulombic interactions, van der Waals interactions, bond stretching, and angle bending are included in this force field. Coulomb potential describes the electrostatic interaction, expressed in Eq. (S1):

$$E_{\text{coul}} = \frac{e^2}{4\pi\epsilon_0}\sum_{i\neq j}\frac{q_i q_j}{r_{ij}} \tag{S1}$$

where q_i and q_j denote the charges of atom i and j; e is the charge of an electron; and ϵ_0 is the constant 8.85419×10^{-12} F/m, which represents the dielectric permittivity of vacuum.

The van der Waals energy is calculated using the Lennard-Jones (12-6) function; see Eq. (S2). $D_{o,ij}$ and $R_{o,ij}$ can be calculated with the arithmetic and geometric mean rule (Eqs. (S3) and (S4)), respectively.

$$E_{\mathrm{VDW}} = \sum_{i \neq j} D_{o,ij} \left[\left(\frac{R_{o,ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{o,ij}}{r_{ij}} \right)^{6} \right] \quad \text{(S2)}$$

$$R_{o,ij} = \frac{1}{2} \left(R_{o,i} + R_{o,j} \right) \quad \text{(S3)}$$

$$D_{o,ij} = \sqrt{D_{o,i} D_{o,j}} \quad \text{(S4)}$$

Bond stretching energy and angle bending energy can be expressed as Eqs. (S5) and (S6):

$$E_{\text{bond stretch}} = k_1 \left(r_{ij} - r_0 \right)^2 \quad \text{(S5)}$$

$$E_{\text{angle bend}} = k_2 \left(\theta_{ijk} - \theta_0 \right)^2 \quad \text{(S6)}$$

where k_1 and k_2 are the force constants, r_{ij} is the actual bond distance between atoms i and j, θ_{ijk} is the bond angle, and r_0 and θ_0 are the equilibrium bond distance and bond angle, respectively.

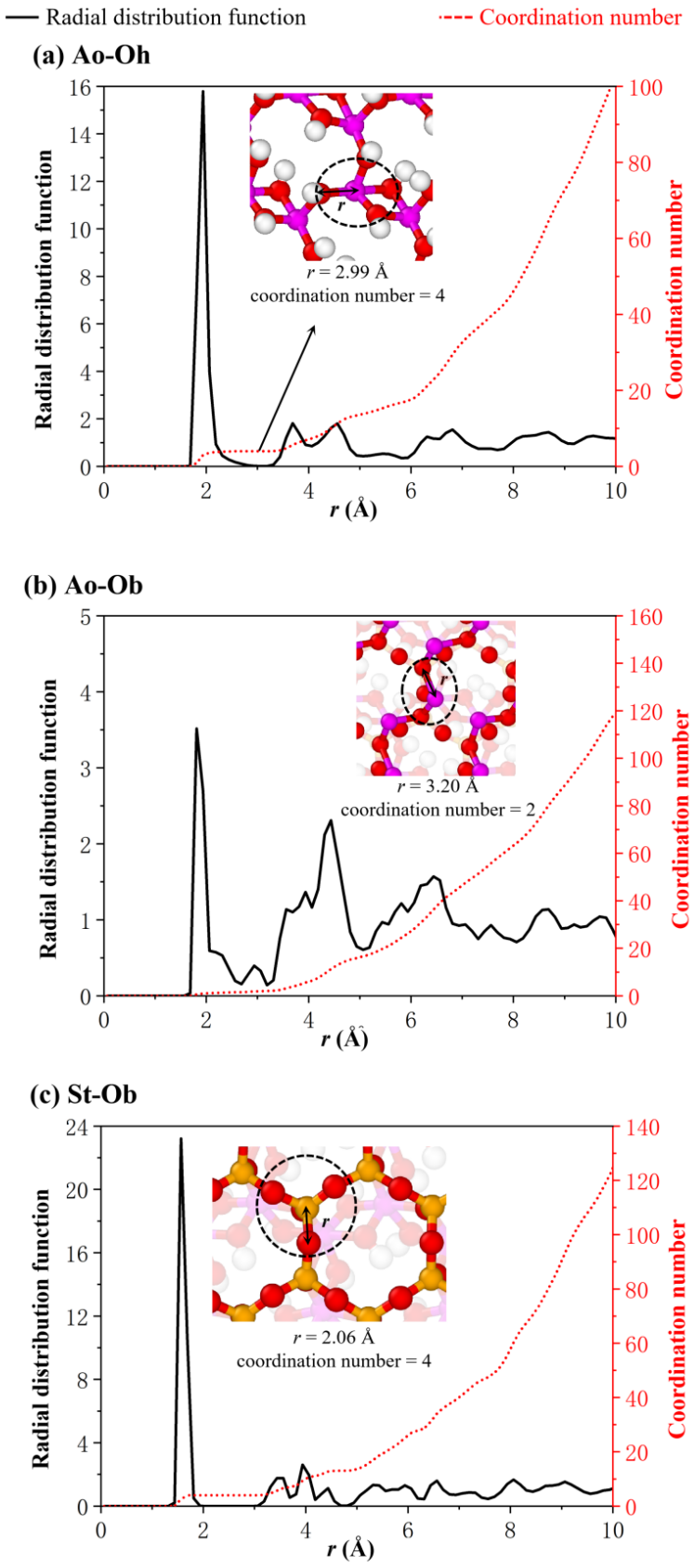

Fig. S1 Radial distribution function (RDF) of Ao-Oh, Ao-Ob, and St-Ob

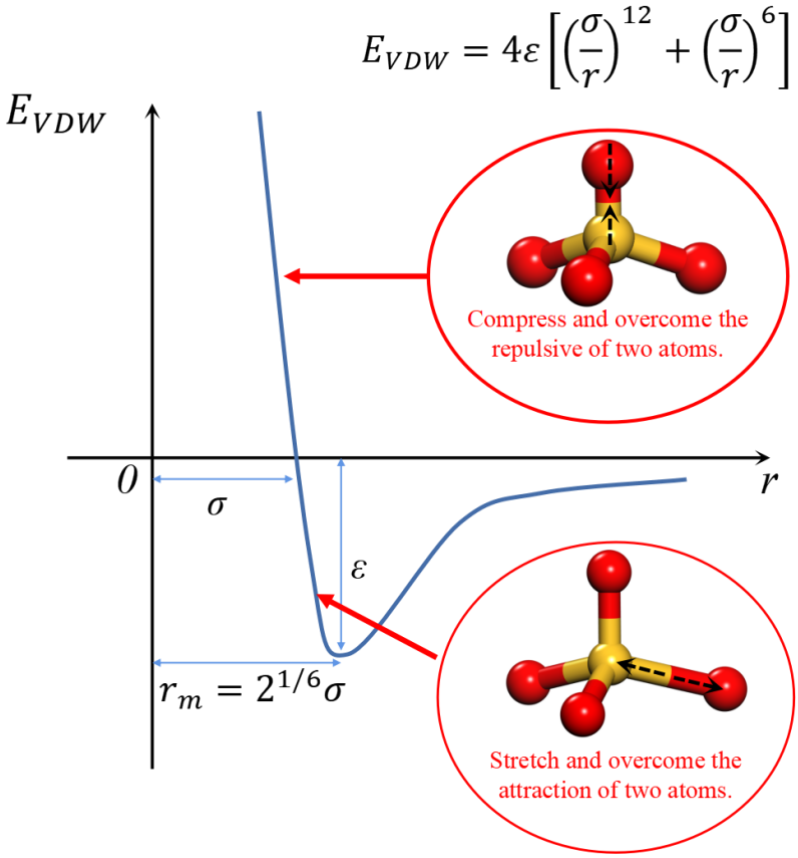

Fig. S2 Curve of van der Waals potential energy

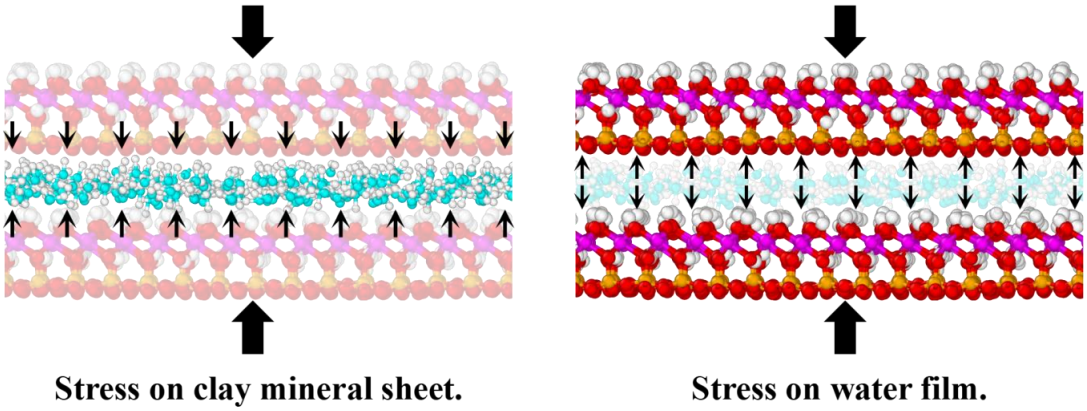

Fig. S3 Compressive stress on clay mineral sheet and water film when hydrated kaolinite is compressed along the *z*-direction

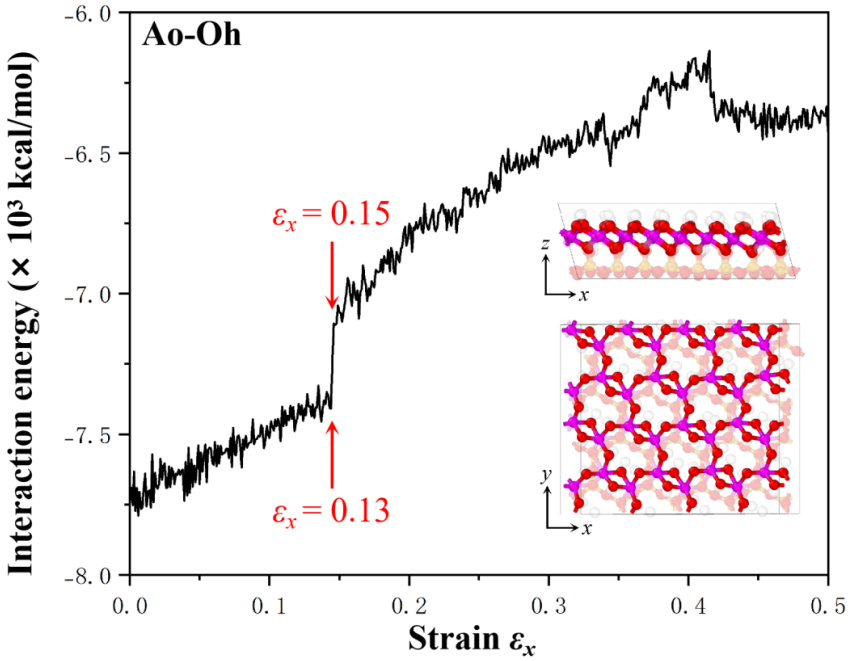

Fig. S4 Interaction energy of atomic pairs Ao-Oh when 4*a*×2*b*×1*c* kaolinite supercell was stretched along the x-direction

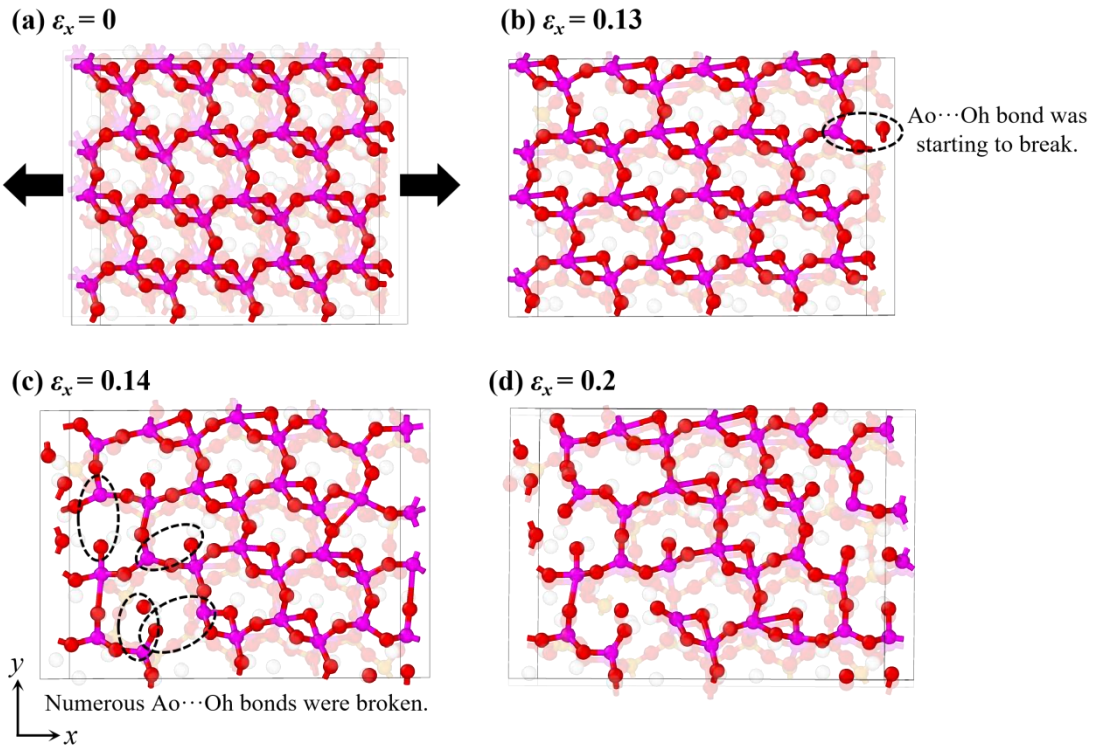

Fig. S5 Snapshots of when 4*a*×2*b*×1*c* kaolinite supercell was stretched along the *x*-direction

As shown in Figure S1, the length of Ao-Oh bond has been proven as 2.99 Å. Based on this, we connected virtual bonds to Ao and Oh at a distance of 2.99 Å in a simple model of 4a × 2b × 1c supercell. The bond-breaking phenomenon of kaolinite can be observed.

As shown in Figure S4, when conducting the same tensile simulation, a sudden change phenomenon at εx = 0.13 was also observed in the interaction energy curve. As shown in Figure S5, it can be observed that when ε_x = 0.13, Ao ··Oh covalent bond breakage did indeed begin to occur. As kaolinite was further stretched (Figure S4c), numerous Ao ··Oh covalent bonds were broken. In summary, it can be considered that the method of explaining bond breaking phenomenon through the interaction energy curve is feasible.

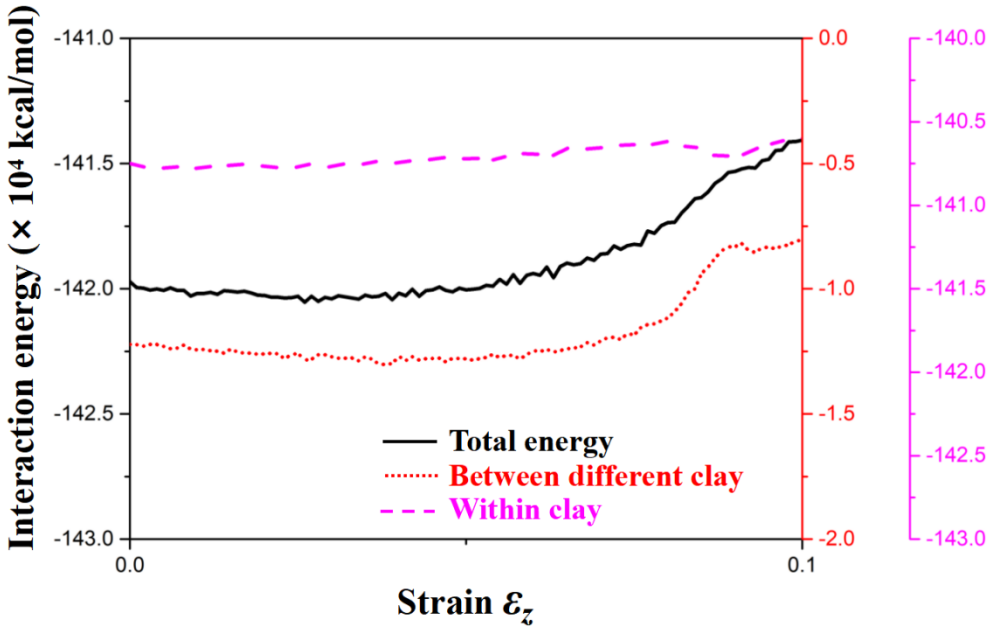

Fig. S6 Total interaction energy of clay-clay, the interaction energy between different clay mineral sheets, and that within clay mineral sheet

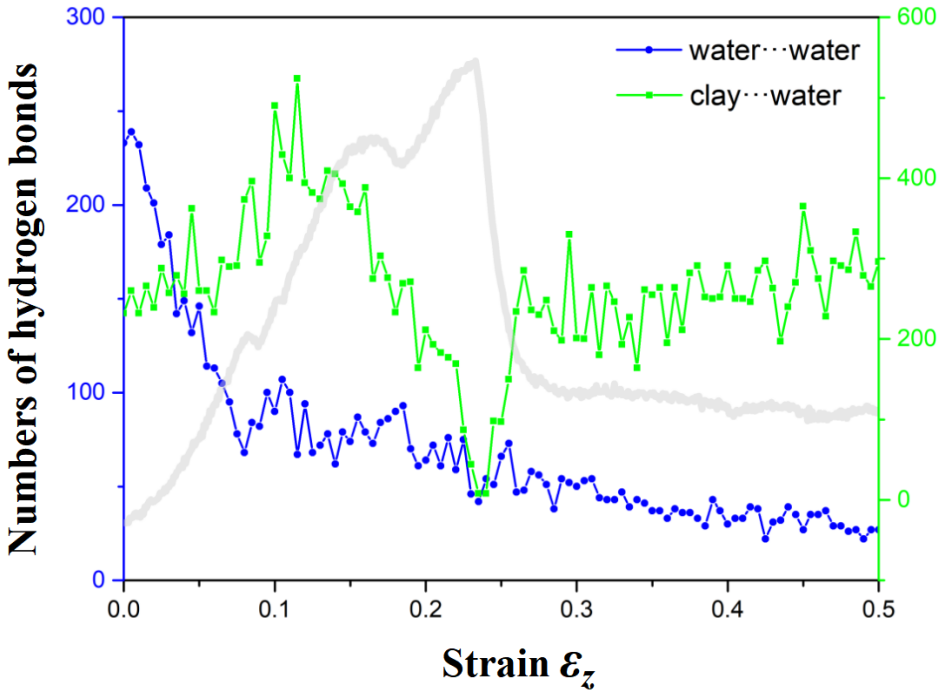

Fig. S7 Numbers of hydrogen bonds of water ···water and clay ···water when kaolinite with one layer of water film is compressed along the *z*-direction. The criterion for judging hydrogen bond is that the cut-off distance of O-H is 2.4 Å, and the cut-off angle of H-O-H is 30 °

Table S1 The failure strain and strength of five systems when stretching along the *x*-direction and compressing along *z*-direction.

Layers of Water Film	Tensile Failure Strain	Tensile Failure Strength (GPa)	Compressive Failure Strain	Compressive Failure Strength (GPa)
No water	0.13	10.28	0.21	−19.39
One		9.44	0.23	−16.34
Two		7.45	0.24	−15.02
Three		8.75	0.25	−15.63
Four		8.31	0.28	−14.34