Phase behaviours of superionic water at planetary conditions

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Most water in the Universe may be superionic, and its thermodynamic and transport properties are crucial for planetary science but difficult to probe experimentally or theoretically. We use machine learning and free-energy methods to overcome the limitations of quantum mechanical simulations and characterize hydrogen diffusion, superionic transitions and phase behaviours of water at extreme conditions. We predict that close-packed superionic phases, which have a fraction of mixed stacking for finite systems, are stable over a wide temperature and pressure range, whereas a body-centred cubic superionic phase is only thermodynamically stable in a small window but is kinetically favoured. Our phase boundaries, which are consistent with existing—albeit scarce—experimental observations, help resolve the fractions of insulating ice, different superionic phases and liquid water inside ice giants.

Water is the dominant constituent of Uranus’s and Neptune’s mantles, and superionic water is believed to be stable at depths greater than about one-third of the radius of these ice giants. Water superioncity is marked by exceptionally high hydrogen diffusivity and ionic conductivity, as hydrogen atoms become liquid-like while oxygen atoms remain solid-like on a crystalline lattice. Although superionic water was postulated over three decades ago, its optical properties (it is partially opaque) and oxygen lattices were only accurately measured recently, and many properties of this hot ‘black ice’ are still uncharted.

Amongst the many mysteries regarding superionic water, the location of various coexistence lines over a large range of pressure (P) and temperature (T), including the melting line, the insulating ice to superionic transition line and the phase boundaries between competing superionic phases, are essential for understanding the formation, evolution, interior structure and magnetic fields of planets. However, these lines and even the possible types of oxygen lattice for superionic water have long been debated. Initial computational studies proposed a face-centred cubic (fcc) oxygen lattice, whereas early first-principles electronic structure molecular dynamics (FPMD) considered a body-centred cubic (bcc) superionic phase as a high-temperature analogue of ice X. Later FPMD studies again proposed an fcc oxygen lattice and suggested a close-packed and (at pressures higher than 1 TPa) a P21/c (ref. 18) oxygen lattice. In superionic water experiments, sample preparation is extremely challenging, hydrogen positions cannot be determined and temperature measurements in dynamical compression experiments are not straightforward. Notably, recent dynamical compression experiments combined with X-ray diffraction (XRD) found a superionic phase with an fcc oxygen lattice, ice XVIII, above 2,000 K (ref. 19). Static compression experiments combined with synchrotron XRD suggest a triple point between liquid, ice VII’ and ice VII” (a bcc superionic phase) at 14.6 GPa and 850 K (ref. 19).

Theoretical modelling of high-pressure water is also difficult. No reliable empirical force fields are available for this system. FPMD simulations are computationally expensive, and are thus confined to short trajectories and small system sizes, which may introduce artefacts leading to contradictory results on the phase boundaries between superionic and diffusivity between various studies based on the same assumption on the underlying electronic structure. Furthermore, most FPMD simulations treat nuclei as classical point masses and ignore their wave-like nature, despite light elements such as hydrogen exhibiting strong nuclear quantum effects (NQEs). Molecular dynamics combined with the Feynman path integral (PIMD) can be used to treat the NQEs, but PIMD multiplies the computational cost by another factor of about 20 (ref. 20). However, machine learning potentials (MLPs) can help overcome these limits by first learning an accurate data-driven model of atomic interactions from first-principles calculations, and then driving large-scale simulations at an affordable computational cost. MLPs have thus helped reproduce the low-pressure phase diagram of water and elucidate the nucleation behaviour of gallium, the liquid–liquid transition of high-pressure hydrogen and the structural transition mechanisms in disordered silicon.

In this study, we construct an MLP for high-pressure water using an artificial neural network architecture based on Perdew–Burke–Ernzerhof (PBE) density functional theory. Combining the MLP with advanced free-energy methods, we predict the properties of superionic and liquid water at the PBE level of theory, using large system sizes and long timescales and considering NQEs. We elucidate the mechanisms for ice–superionic transitions and hydrogen transport, map the high-pressure water phase diagram and probe the kinetics of phase transition.

Hydrogen diffusivity in superionic phases

The hydrogen diffusion coefficient $D_H$ is the key feature of superionic water, and can be used to derive the ionic conductivity, which is crucial for modelling the magnetic field geometry of Uranus and Neptune. We considered the aforementioned bcc and fcc lattices of oxygen, and a hexagonal close-packed (hcp) lattice that has a low-temperature ice analogue with the Pbcm space group. The insulating structures became superionic when the temperature...
The dashed lines in Fig. 1 indicate the associated transition temperatures $T_\lambda$ defined by $D_\lambda = 10^{-4} \text{ cm}^2 \text{s}^{-1}$. The bcc phase has a higher $T_\lambda$ compared with the fcc and hcp phases. At $T > T_\lambda$, $D_\lambda$ in all three superionic phases shows no distinct difference, which is in agreement with ref. 9 and in contrast with ref. 8. The distributions of hydrogen positions are shown in the contour plots of Fig. 1: at low temperature hydrogen atoms are confined to their equilibrium sites, whereas in the superionic phases only a fraction are.

We focused on the hydrogen diffusion in the fcc lattice at 300 GPa, as the results at other pressures and for bcc and hcp lattices are similar (Supplementary Section 6D). When the lattice remains stable, Fig. 2a shows that $D_\lambda$ changes rapidly but smoothly across the ice–superionic transition region, and increases gradually as a function of $T$ when the system is fully superionic. To rationalize such behaviour, we used an interstitial formation model\textsuperscript{17} to describe the free energy of the system:

\[ f(x, T) = (e_0 - T_\lambda) x - \frac{\lambda}{2} x^2 + k_B T \left[ x \ln x + (1 - x) \ln (1 - x) \right], \]

where $x$ is the fraction of the conducting hydrogen, $s_0$ is the entropy gain for creating a conducting atom in the unit cell from a confined atom, as the former has a higher accessible volume, $e_0$ and $\lambda$ are the energy scales for interstitial formation and interaction, respectively, and $k_B$ is the Boltzmann constant. Upon equilibration, equation (1) reaches a minimum and the equilibrium fraction $x(T) = \text{arg min}_x f(x, T)$. We used a Speedy–Angell power law\textsuperscript{28}

\[ D = D_0 \left[ \left( \frac{T}{T_0} \right) - 1 \right]^{\nu}, \]

where $D_0$ and $\nu$ are constants and $T_0$ being a singular temperature, to model the diffusivity of conducting hydrogen atoms in the lattice, and assume that the confined hydrogen atoms have negligible diffusivity, so that overall $D_\lambda(T) = x(T)D$. We fitted $x(T)D$ to the computed $D_\lambda$ for bcc, fcc and hcp phases at various conditions (one example is shown as the black curve in Fig. 2a, all fits are in the Supplementary Fig. 13), and the fits are excellent over the entire range of thousands of kelvin considered. Figure 2b shows $x(T)$ from the fits for the fcc lattice at different pressures, which exhibits rapid increase at $T \approx 2,000 \text{ K}$ corresponding to the ice–superionic water transitions. At $T > T_\lambda$, $x(T)$ increases slowly and reaches about 0.8 at 3,000 K, consistent with the observation in Fig. 1 that a fraction of hydrogen atoms are close to the equilibrium sites even in fully superionic phases.

The interstitial model (equation (1)) sheds light on the driving force of the superionic transition: $s_0$ competes with the energetic cost $e_0$ of interstitial formation and wins at high temperature. The interaction between interstitial $\lambda$ affects the nature of the transition: $x(T)$ will exhibit a smooth crossover, which is the case observed here, when $\lambda \leq 4 e_0/(2 + s_0)$, and a first-order phase transition in $T$ otherwise. The smooth crossover in this case explains the facile ice–superionic water transitions and the lack of hysteresis. A similar framework can be used to understand how to tune the conductivity of ambient-pressure superionic materials used for solid-state fuel cells and solid-electrolyte applications\textsuperscript{14,16}.

**Chemical potentials of superionic and liquid water**

The thermodynamic stability of different phases is governed by their chemical potentials $\mu$. However, computing $\mu$ for the superionic phases is difficult, because these phases are half solid/half liquid, and because the thermodynamic integration method cannot
be applied across first-order boundaries that might exist between a number of phases (ice VII, VII', VII'', X) all sharing the bcc oxygen lattice\textsuperscript{13,16}. To circumvent these difficulties, we instead computed their chemical potentials relative to the liquid, $\mu_{\text{MLP}}^{\text{bcc}} - \mu_{\text{MLP}}^{\text{fcc}}$ in umbrella sampling\textsuperscript{31} simulations on superionic–liquid coexistence systems (illustrated in Fig. 3) at different pressures between 15 and 200 GPa and temperatures close to melting points using the MLP. In these coexistence systems, oxygen atoms in the liquid phase diffuse around (and the ones in the superionic phase stay on) the bcc, fcc or hcp lattices. Meanwhile, hydrogen atoms travel in and out between the two phases, as illustrated by a few trajectories in Fig. 3.

The difference in $\mu$ between two superionic phases can simply be obtained from the coexistence simulations, for example $\mu_{\text{bcc}} - \mu_{\text{fcc}} = (\mu_{\text{bcc}} - \mu_{\text{PBE}}) - (\mu_{\text{fcc}} - \mu_{\text{PBE}})$. We used thermodynamic integration along isotherms and isobars to calculate the chemical potential differences at other conditions where the two phases remain metastable. We then promoted the MLP results to the PBE level by adding $\mu - \mu_{\text{MLP}}$ computed from free-energy perturbation, which removes the small residual errors in the MLP partly due to its lack of long-range electrostatics\textsuperscript{19,32}. Finally, we performed PIMD simulations using the MLP, and obtain $\mu_{\text{PBE}}$ values at the PBE level that include NQEs.

The melting curves ($T_m$) of bcc and fcc lattices, indicated using the purple and the blue lines in Fig. 4a,b, respectively, are similar to each other at $P \geq 40$ GPa, and noticeably different from previous single-phase melting and solidification FPMD calculations\textsuperscript{8}. At $P < 100$ GPa (Fig. 4b), our $T_m$ lie roughly between the experiments based on a laser-heated diamond anvil cell with XRD at $P \leq 45$ GPa (ref. 13) and the direct observation of motion in the laser-speckle pattern at $P \leq 90$ GPa (refs. 33,43). Our results are presented up to 220 GPa, and agree with a single point at about 190 GPa and 4,800 K in the precompressed shockwave experiment\textsuperscript{4}.

Figure 4a shows $\mu_{\text{bcc}} - \mu_{\text{fcc}}$, and the hatched area indicates the statistical uncertainty bounds of the coexistence line $T(\mu_{\text{bcc}} = \mu_{\text{fcc}})$. The bcc lattice is stable at low temperature as well as low pressure ($P \ll 75$ GPa), and this stability region includes both the insulating ice and the superionic bcc phase, which are separated by $T_s$ (the solid green line in Fig. 4a). The superionic bcc phase has a narrow stability region, and becomes less stable at higher pressure. Previous calculations of the boundary between competing superionic phases were conflicting and scattered: thermodynamic integration calculations using FPMD at 3,000 K (ref. 8) (the brown line), constant-pressure single-phase FPMD at 2,200 K and 3,000 K (ref. 10) (the pink line with the bounds of the transition pressure between bcc and close-packed phases) and analytic models combined with FPMD\textsuperscript{9} (the grey curve). Our boundary has small statistical uncertainty owing to the large-scale simulations. Notably, our boundary is fully compatible with the pressure–temperature conditions where bcc (red circles) and fcc (orange circles) phases were observed in the XRD measurements\textsuperscript{8}.

Fig. 3 | Hydrogen atoms diffuse easily between the superionic and the liquid phases. The liquid–fcc superionic interface of a water system with 20,736 atoms at 100 GPa and 3,250 K (on the melting curve) is shown. The oxygen atoms are red and the hydrogen atoms are white. The yellow, green and blue lines show the trajectories of three hydrogen atoms during a 75 ps molecular dynamics simulation run using the MLP.
Figure 4c shows that the hcp phase becomes more favourable at higher pressure, and is slightly more stable than fcc above ~400 GPa. Overall, the magnitude of $\mu_{\text{hcp}} - \mu_{\text{fcc}}$ is very small across 100 GPa ≤ P ≤ 800 GPa and 2,000 K ≤ T ≤ 5,500 K, of less than 10 meV per H$_2$O formula unit, compared with the thermal energy of 0.3 eV per degree of freedom at a few thousand kelvin. This hints that fcc and hcp phases can coexist at these conditions, which has been observed in FPMD simulations at P > 280 GPa in ref. 15. To further confirm this, we simulated superionic water growing from liquid water supercooled at 3,000 K, 100 GPa (one example shown in Fig. 4d). The starting configuration has a pure hcp oxygen lattice with close-packed planes parallel to the interface, and the oxygen lattice gradually grows into a state of mixed stacking. This indicates that, for a system of finite size, the equilibrium oxygen lattice in the fcc region of stability (shown in Fig. 4a) may have a finite fraction of mixed stacking. Such stacking can be revealed by XRD measurements, and we provide the simulated diffraction patterns (Supplementary Fig. 21) as a guide.

**Superionic-liquid interfacial free energies**

The phase synthesized in experiments may not be the stable phase suggested by the phase diagram (Fig. 4a,c), but instead a metastable phase with a lower activation barrier to nucleation 16. The interfacial free energy $\gamma$ dominates the nucleation rate by entering as an exponential of a cubic power 16 and is a key quantity in the modelling of kinetics of phase transition during dynamical compression experiments 17,28. We computed fcc/bcc–liquid interfacial free energies $\gamma$ for the (100), (111) and (110) interfaces at T = 3,250 K and P = 100 GPa (on $T_m^b$) using the capillary fluctuation method (see Supplementary Section 6f and ref. 79). For bcc, $(\gamma_{100}, \gamma_{111}, \gamma_{110}) = (16.7 \pm 0.3, 17.0 \pm 0.2, 2,168 \pm 0.2) \text{meV Å}^{-2}$, and for fcc, $(24.5 \pm 0.4, 24.1 \pm 0.4, 24.2 \pm 0.4) \text{meV Å}^{-2}$. We assume that hcp is likely to have similar $\gamma$ values as fcc owing to their shared close packing.

Both bcc and fcc phases have small anisotropy in term of $\gamma$, suggesting that the equilibrium shapes of superionic nuclei in liquid water are near spherical. The bcc superionic phase has much lower $\gamma$ compared with the fcc phase at the given condition, suggesting that a bcc lattice is easier to nucleate and thus kinetically favoured. Crucially, dynamic compression experiments 24, pulsed laser heating in the diamond anvil cell 24,25 and FPMD simulations have short timescales, so in these settings the bcc superionic phase may form even at conditions where it is not as stable as the fcc phase. This kinetic effect sheds light on the discrepancy between recent experimental measurements 24,21.

Our phase boundaries of water at planetary conditions can be used to determine the fractions of insulating ice, superionic water and liquid water in the interior of ice giants. Compared with previous theoretical results shown in Fig. 4, which are sparse and contradictory, we were able to quantitatively map the phases of superionic water across a large part of the phase diagram (10 GPa ≤ P ≤ 800 GPa, 500 K ≤ T ≤ 5,500 K) and provide a mechanistic understanding of the ice-superionic water transition. Our results suggest that, for
finite systems, a close-packed superionic phase with mixed stacking is stable over a wide temperature and pressure range (Fig. 4), whereas the superionic bcc phase is stable in a small region at $P \leq 75 \text{ GPa}$ and $T \leq 2,500 \text{ K}$ but may be kinetically favoured due to its lower interfacial free energy with the liquid. Planets have billions of years to evolve and to reach equilibrium, but dynamic compression experiments and FPMD simulations are bound to have short timescales—the kinetic factors probed in our study therefore help bridge the gap. The planetary interior models illustrated in Fig. 4a combined with our phase diagram imply a transition from liquid water to superionic water deep inside the ice giants. This transition zone will see a liquid–superionic water interface, with hydrogen atoms diffusing across the interface between the two phases, as we see in Fig. 5, carrying electrical charges and heat across such interfaces in the icy planets.

Our quantitative understanding of superionic water sheds light into the interior structure, evolution and dynamo process of planets such as Uranus and Neptune, and also of the increasing number of icy exoplanets. We suggest that static and dynamic compression experiments are performed to discover the close-packed phase with mixed stacking, and to investigate the preferential nucleation of bcc phases. Furthermore, our framework can be used to discover and characterize superionic electrolyte materials, as well as new superionic phases of other components such as ammonia, salts and related mixtures that are relevant for planetary science.

Online content
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Data availability
The data supporting the findings of this study are available within the paper, and a detailed description of the calculations is included in the Supplementary Information. All original data generated for the study and the machine learning potential for high-pressure water constructed in this study are in the Supplementary Information and available via GitHub at https://github.com/BingqingCheng/superionic-water.

Code availability
All necessary input files for simulations and a Python notebook for data analysis are in the Supplementary Information.

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Author contributions
B.C., M.B. and S.H. conceived the study. B.C. performed the simulations related to the MLP. M.B., C.J.P. and S.H. performed the FP calculations. B.C. M.B. and S.H. analysed the data. All authors wrote the paper.

Competing interests
The authors declare no competing interests.

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