Heat transport in H$_2$O at ice-giant conditions from ab initio MD simulations

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(Dated: March 30, 2020)

The heat conductivity of different phases of water (liquid, solid, and super-ionic) occurring in the interior of ice giant planets are evaluated from equilibrium ab initio molecular dynamics, leveraging recent progresses in the theory and data analysis of heat transport in extended systems. As byproducts, we also obtain estimates for the diffusivity and the electrical conductivity, which are key parameters to model the internal structure and thermal history of water-rich planets and moons.

PACS numbers: 66.10.-x 61.20.Ja

Keywords: Transport properties, Molecular dynamics, Statistical analysis of time series, Cepstral analysis

Hydrogen and oxygen are two of the three most abundant elements in the universe, helium being the second. As a consequence, H$_2$O is thought to be a major constituent of celestial bodies formed far enough from their host star for it to condense [1]. Many moons of the outer solar system, such as Ganymede, Europa, and Enceladus, have rigid icy shells and interior water oceans, which are key for understanding the observed surface mass flux [2] and the generation of magnetic fields [3]. The ice giants, Uranus and Neptune, are thought to be composed primarily of H$_2$O [4]: throughout most of their interior, the large pressure and temperature (e.g. 240 GPa and 5000 K at half the radius of Uranus) favor a superionic (SI) phase, where oxygen ions are arranged in a crystalline lattice and protons diffuse freely like in a fluid [5, 6]. Partially-dissociated, liquid (PDL) water may instead be confined to the outermost third of the interior, where the superionic phase becomes unstable and the magnetic field is generated [7]. Outside the solar system, the observed characteristics of many exoplanets are also consistent with water-rich interiors [8].

The transport properties of different phases of H$_2$O occurring at high-pT conditions are key to any quantitative evolutionary model of water-rich celestial bodies. The reliability of such models stands in fact on the accuracy of heat and electrical conductivities, which determine the thermal and electromagnetic histories of the planets. In spite of the steady progress in diamond-anvil-cell and shock-wave technologies, the experimental investigation of transport properties of materials at planetary conditions is still challenging. In the specific case of H$_2$O, the electrical conductivity is only known with large uncertainties along the Hugoniot curve on a limited portion of the pT diagram, and nothing is known about the heat conductivity [6, 9–11].

Computer simulations may be our only handle on the properties of matter at physical conditions that cannot be achieved in the laboratory. In the case of water, they have allowed us to discover new phases [5] and to predict their properties at extreme pT conditions [6, 12] over an ever broader portion of its phase diagram [13]. The diverse local chemical environments that characterize the different relevant phases of water make classical force fields unfit for an accurate simulation of their properties, and call for a full quantum-mechanical, ab initio (AI), treatment of the chemical bond. Some transport properties of water at high pT conditions, such as ionic (H and O) diffusivities and the electrical conductivity have indeed been estimated using AI molecular dynamics (AIMD) simulations [14] and the Green-Kubo (GK) theory of linear response [15, 16]. However, it has long and widely been argued that quantum-mechanical simulation methods could not be combined with the GK theory, because the latter is based on a microscopic representation of the energy (current) density, which is evidently ill-defined at a quantum mechanical level [17]. The soundness of this objection, which would actually apply to a classical representation of the interatomic forces as well, was recently refuted for good by the introduction of a gauge invariance principle for transport coefficients [18–20]. In a nutshell, gauge invariance means that transport coefficients do not depend on the details of the microscopic representation of the conserved quantity being transported, as long as this representation sums to the correct value in the thermodynamic limit and its space correlations are short-ranged. This remarkable finding implies that any (good, in the above sense) local representation of the energy leads to the same heat conductivity, thus paving the way to a fully ab initio treatment of heat transport [18], which was recently generalized to multi-component systems [21].

In this work we leverage these recent theoretical advances to estimate the thermal conductivity and other transport coefficients of stoichiometric H$_2$O in the pT conditions to be found on ice giant planets, like Uranus and Neptune, from equilibrium AIMD simulations, exploring its solid, PDL, and SI phases.
Transport in macroscopic media is governed by the dynamics of hydrodynamic variables, i.e. by the long-wavelength components of the (current) densities of conserved extensive quantities [20, 22]. For short, we will dub such densities *conserved densities*, the corresponding currents *conserved currents*, while the macroscopic averages of the latter will be called *conserved fluxes*. The GK theory of linear response [15, 16] states that transport coefficients (i.e. conductivities) are integrals of the various flux time autocorrelation functions, which, according to the Wiener-Khintchine theorem [23, 24], are the zero-frequency values of the corresponding power spectra. An important concept in the theory of transport is that of *diffusive flux*: we say that a flux is diffusive if its power spectrum does not vanish [20, 21] at zero frequency. Gauge invariance states that two different representations (“gauges”) of a same conserved density that differ by the divergence of a bounded vector field are equivalent in that they give rise to macroscopic fluxes whose difference is non-diffusive, thus resulting in the same conductivity [18, 19].

When addressing heat transport, the relevant conserved quantities are the energy and the numbers of particles (or masses) of each atomic species. Since the total-mass flux itself (i.e. the total momentum) is a constant of motion, for a P-species system the number of independent conserved fluxes is equal to P (energy, plus P − 1 partial masses). Further constraints may reduce the number of relevant conserved fluxes. For instance, in solids, such as ordinary ice, atoms do not diffuse and there cannot be any macroscopic mass flow: energy flux is therefore the only relevant one. In molecular liquids, such as ordinary water, the partial mass fluxes of each atomic species are non-diffusive if the molecules do not dissociate. This is so because the integral of the difference between the individual total momenta of different atomic species is bound by the finite variation of the molecular bond lengths [18, 20]: also in this case, therefore, energy is the only relevant conserved quantity. On the contrary, the PDL and SI phases of water are truly multi-component systems, because the momentum of at least one atomic component is neither conserved nor is its integral bound by any molecular constraints.

Heat transport in multi-component systems has long been the subject of theoretical misconceptions and/or considered to be numerically intractable. For instance, the thermal conductivity is sometimes computed as the Green-Kubo integral of the energy flux, \( J_E \): \( \kappa \propto \int_0^\infty \langle J_E(t) J_E(0) \rangle dt \). This simplistic approach is manifestly wrong, as the resulting conductivity would depend on the arbitrary choice of the atomic formation energies. To see why this is so, let us consider the classical expression of the energy flux [20, 25]:

\[
\frac{1}{\Omega} \left[ \sum_{n=1}^N V_n \epsilon_n + \sum_{n,m} (R_n - R_m) F_{nm} \cdot V_n \right],
\]

where \( \Omega \) is the system’s volume, \( R_n \), \( V_n \), and \( \epsilon_n \) are the atomic positions, velocities, and energies, respectively, and \( F_{nm} = -\partial \epsilon_m / \partial R_n \) are inter-atomic forces. The heat conductivity cannot evidently depend on the arbitrary zero of the atomic energies. For instance, in *ab initio* calculations these energies differ in a pseudo-potential or in an all-electron scheme, whereas transport coefficients should not. A better choice would be to compute the heat conductivity from the Green-Kubo integral of the heat flux, defined as \( J_i = \mathbf{J}_E = \frac{1}{\Omega} \sum_{n=1}^P h_S N_S \mathbf{V}_S \), where \( h_S \) is the partial enthalpy of the S-th atomic species [26].

This approach has the advantage that \( \mathbf{J}_q \) is no longer sensitive to a rigid shift in the atomic energies; it is still an approximation, though, as it neglects the coupling between energy and mass flow (Soret effect) in the calculation of \( \kappa \). Even if, for several systems, it has been argued that the error in doing so is small [26], this argument cannot be taken for granted *a priori* for any generic system. Furthermore, the calculation of partial enthalpies is rather involved [27–29], and often the subject itself of crude approximations.

A rigorous methodology to deal with multi-component systems is provided by a combination of Onsager’s phenomenological approach [30] and the GK theory of linear response [15, 16]. In this approach the interactions among different conserved fluxes are explicitly accounted for as:

\[
J_i = \sum_j \Lambda_{ij} f_j,
\]

where \( J \) is a generic conserved flux, \( f \) a thermodynamic affinity, i.e. the average gradient of the intensive variable conjugate to a conserved quantity, and the suffixes enumerate in principle both different conserved quantities and the Cartesian components of their fluxes/affinities. In practice, in the following we will dispose of Cartesian components, and only enumerate different conserved fluxes/affinities, given that we will only be concerned with isotropic or cubic systems. Within the GK theory, the \( \Lambda \) coefficients are expressed as integrals of the time correlation functions of the relevant fluxes:

\[
\Lambda_{ij} = \frac{\Omega}{k_B} \int_0^\infty \langle \mathcal{J}_i(t) \mathcal{J}_j(0) \rangle dt,
\]

where \( \mathcal{J}_i(t) \) is the time series of the \( i \)-th flux. From now on, calligraphic fonts indicate samples of stochastic processes. The thermal conductivity is defined as the ratio between the energy flux and the temperature gradient, *when all the other conserved fluxes vanish*. In a two-component system this condition leads to the following expression for the heat conductivity:

\[
\kappa = \frac{1}{T^2} \left[ \Lambda_{EE} - \frac{|\Lambda_{EM}|^2}{\Lambda_{MM}} \right],
\]
where the $M$ suffix indicates the mass flux of one of the two components. The expression in square brackets is the inverse of the $EE$ matrix element of the inverse of the $2 \times 2$ matrix of the Onsager coefficients. In the general, multivariate, case, the heat conductivity is proportional to the Schur complement of the mass block in $\Lambda$. In Ref. 21 we have shown that this expression for the heat conductivity is invariant under the addition of an arbitrary linear combination of conserved fluxes (such as mass or adiabatic electronic charge) to the energy flux, and we named this further remarkable property of transport coefficients convective invariance.

Eq. (3) shows that this procedure is numerically ill-conditioned, because the estimator of the integral in Eq. (2) becomes a random walk as a function of the upper limit of integration, as soon as the integrand has exhausted all its weight, thus making the expression in Eq. (3) singular whenever the estimator of the denominator vanishes [31–34]. A solution to this problem is provided by multivariate cepstral analysis [21], briefly sketched below. According to the Wiener-Khintchine theorem [23, 24], the Onsager coefficients in Eq. (2) are proportional to the zero-frequency values of the flux cross power spectral density, $S_{ij}(\omega) = \int_{-\infty}^{\infty} \langle \tilde{J}_i(t)\tilde{J}_j(0) \rangle e^{i\omega t} dt$:

\[
\Lambda_{ij} = \frac{\Omega}{2k_B} S_{ij}(\omega = 0) \tag{4}
\]

\[
S_{ij}(\omega) = \lim_{\tau \to \infty} \langle \tilde{S}_{ij}^\tau(\omega) \rangle \tag{5}
\]

\[
S_{ij}^\tau(\omega) = \frac{1}{\tau} \tilde{J}_i^\tau(\omega)^* \cdot \tilde{J}_j^\tau(\omega) \tag{6}
\]

\[
\tilde{J}_j^\tau(\omega) = \int_0^\tau \tilde{J}_j(t)e^{i\omega t} dt. \tag{7}
\]

The continuity and smoothness of the power spectrum at low frequency can be leveraged to systematically reduce the noise affecting the estimator of its zero-frequency value, as explained below. According to the central-limit theorem, the flux processes, $\tilde{J}_i(t)$, are Gaussian because they are the space integrals of current densities, whose correlations are short-ranged. Stationarity implies that their Fourier transforms, Eq. (7), are normal deviates that for large $\tau$ are uncorrelated for $\omega \neq \omega'$. It follows that the sample spectrum of Eq. (6), aka the cross-periodogram, is a collection of complex Wishart random matrices [35] that are uncorrelated among themselves for different frequencies. Now, the Schur complement of a block of dimension $P-1$ in a Wishart matrix of order $P$ is proportional to a $\chi^2$ stochastic variable [21, 35]. We conclude that the Schur complement of the mass block, $\tilde{S}_E$, in the cross-periodogram given by Eq. (6), is the product of a smooth function of frequency, whose $\omega \to 0$ limit is the thermal conductivity we are after, times a set of independent, identically distributed, $\chi^2$ stochastic variables. By applying a low-pass filter to the logarithm of this quantity, one obtains a consistent estimator of the logarithm of the conductivity, as explained in Ref. 21, a procedure that is known as cepstral analysis in sound engineering and speech recognition applications [36].

\section*{RESULTS}

The heat and charge transport properties of different (solid, PDL, and SI) phases of water in the 1,000-3,000 K and 30-250 GPa pT range have been explored by Car-Parrinello (CP) \textit{ab initio} NVE molecular dynamics [37]. We believe that the CP Lagrangian formalism is particularly fit for transport simulations because the accurate conservation of the (extended) total energy allows one to generate long and stable trajectories without using thermostats. Figure 1 shows the phase diagram of water in such pT range. The SI-liquid (dashed) and ice-SI (dotted) phase boundaries are obtained from state-of-the-art shock-compression experiments [6]; Uranus’ isentrope (solid gray) from \textit{ab initio} simulations [38] is also reported. We have verified that a body-centered-cubic (BCC) to face-centered-cubic (FCC) transition in the oxygen lattice occurs for the SI phase at $P \approx 240$ GPa and $T \approx 3000$ K, in accordance with the results of Ref. 13. We then ran three simulations for the BCC-SI phase (blue circles) and one for the FCC-SI one (blue square). We also ran a simulation for solid ice X (green triangle) and a simulation for the PDL (orange triangle) at pT conditions where the fraction of dissociated molecules is $\sim10\%$ [39]. We have explicitly checked that the electron energy gap computed along the various MD trajectories is always way larger than $k_BT$, thus ruling out any direct electronic contributions to heat and charge transport. All the technical details of the simulations are reported in the Supplementary Information [40].

We start the discussion of our results by highlighting the importance of a multi-component analysis of the heat- and mass-flux time series resulting from our simulations. In Fig. 2 we display the power spectrum of the
energy flux of FCC-SI water at an average temperature \( T = 2920 \pm 90 \) K and pressure \( P = 257 \pm 2 \) GPa, evaluated according to two different prescriptions: blue lines refer to the plain spectrum of the energy flux computed within density-functional theory using the formulation of Ref. 18; orange lines indicate the “residual spectrum” computed by assuming that the mass flux vanishes, according to Eq. (3). The thick lines are the filtered spectra obtained via cepstral analysis. Inset: low-frequency zoom of with their estimated uncertainties.

Convective invariance can also be leveraged to reduce the statistical noise, and thus the uncertainty, on the estimated value of \( \kappa \), as explained in Ref. 21. The addition of one or more components to the set of conserved fluxes to be analysed decreases the total power of the reduced spectrum without affecting its value at zero frequency, thus making it smoother and the low-pass cepstral filter more efficacious. By adopting the adiabatic electron current as an additional flux, one obtains the refined result: \( \kappa = 12.8 \pm 1.0 \) W/(Km). Further details on the statistical analysis of our data can be found in the Supplementary Information[40].

Multi-component cepstral analysis, which has been performed using the thermocepstrum code [41], allows us to obtain accurate transport coefficients from relatively short AIMD trajectories, particularly for the strongly anharmonic exotic phases of water occurring at the high pT conditions of interest here. Figure 3 shows the values and the statistical uncertainties of the heat conductivity of different phases of water as a function of the length of the (reduced) energy-flux time series from which they are estimated. These data show that well-converged results with an uncertainty of \( \approx 15\% \) are obtained with trajectories as short as 10-20 ps. Not surprisingly, the more crystalline a phase is, the larger the uncertainty for a same trajectory length (ice X > super-ionic > liquid), due to the larger residual harmonicity of the structure.

Our results are summarized in Table I. In the pT-conditions examined here, the thermal conductivity of solid ice X is larger than that of the SI phase, which is itself larger than in PDL water. This is expected, again due to the decreasing level of harmonicity in going from a crystal lattice to a partially liquid and eventually fully liquid phase. We did not observe a significant dependence of \( \kappa \) upon the temperature for the SI phase in the explored range. The FCC-SI water has slightly larger heat conductivity than BCC-SI.

Pioneering AIMD simulations of charge transport in PDL water [14] revealed that, rather unexpectedly, a classical model of charge conduction where hydrogen and oxygen ions carry an integer charge whose magnitudes equal their formal oxidation numbers (\( q_H = +1 \) and \( q_O = -2 \)) yields the same conductivity that would be obtained from the exact quantum-mechanical expression of the electric current, based on Born’s effective charges. This surprising finding was explained in a recent paper of ours where it was shown to result from the combined effects of gauge invariance of transport coefficients and topological quantization of adiabatic charge transport [42]. Leveraging this result, we computed the electrical conductivity from the cepstral analysis of the classical
Table I. Results of the different NVE simulations. The temperatures and pressures are reported with their standard deviations. The uncertainty on the diffusivity is estimated via a 6 block analysis with \( \approx 10\text{-ps segments} \).

| phase | \( T \) [K] | \( P \) [GPa] | \( \rho \) [g/cm\(^3\)] | \( \kappa \) [W/(Km)] | \( \sigma \) [S/cm] | \( D \) [Å\(^2\)/ps] |
|-------|-------------|-------------|----------------|----------------|----------------|----------------|
| ice X | 1490 ± 50   | 182 ± 1     | 3.52           | 16.1 ± 1      | –              | –              |
| SI\(^\text{BCC}\) | 2470 ± 80   | 174 ± 2     | 3.39           | 9.4 ± 0.6     | 135 ± 7       | 4.88 ± 0.13 (H) |
| SI\(^\text{BCC}\) | 2950 ± 90   | 171 ± 2     | 3.35           | 10.7 ± 0.7    | 180 ± 5       | 7.41 ± 0.12 (H) |
| SI\(^\text{BCC}\) | 2910 ± 90   | 218 ± 2     | 3.61           | 9.9 ± 0.7     | 198 ± 9       | 7.38 ± 0.16 (H) |
| SI\(^\text{FCC}\) | 2920 ± 90   | 257 ± 2     | 3.82           | 12.8 ± 1.0    | 256 ± 8       | 7.17 ± 0.13 (H) |
| PDL   | 1970 ± 60   | 33 ± 1      | 2.04           | 4.1 ± 0.3     | 42 ± 3        | 3.10 ± 0.03 (H) |
|       |             |             |                | 0.92 ± 0.02 (O) |

\[
\mathcal{J}_Z = \frac{1}{\Omega} \left( q_H \sum_{n \in H} V_n + q_O \sum_{n \in O} V_n \right),
\]

where the \( V \)'s are ionic velocities. Interestingly enough, our simulations reveal a much stronger dependence of the electrical conductivity on pT-conditions than of the heat conductivity, in the range considered here. We remark a noticeable failure of the Nernst-Einstein equation, relating \( \sigma \) to the mere diffusivity \( D_H \), for SI water, a fact already remarked elsewhere for the same system [14] and other SI materials as well [43]: this is particularly evident by comparing the fourth and fifth lines of the Table I, which display a very similar value for the hydrogen diffusivity in BCC- and FCC-SI water, but a significant difference in \( \sigma \). Our results for the electrical conductivity are compatible with previous \textit{ab initio} simulations in PDL and SI water [14], and with the experimental data obtained from electrical impedance measurements along the liquid or pre-compressed Hugoniot [9–11], summarized in Fig. 4 of Ref. 6: \( \sigma \approx 150 \text{S/cm for the SI phase in the range 100-150 GPa and 2000-3000 K; and } \sigma \approx 30 \text{S/cm for the PDL phase at } \approx 30 \text{GPa and 2000 K.} \)

In this paper we have reported on the computation of the thermal and charge transport properties of water at the pressure and temperature conditions occurring in the interior of ice giant planets, made possible by recent advances in transport theory and data analysis. In the case of Uranus, our results have been instrumental in the development of a novel model of thermal evolution, featuring a frozen core and an anomalously low heat flow, resulting in the observed low luminosity of this planet. A detailed analysis of these findings is being reported elsewhere [44].

**DATA AVAILABILITY**

The data that support the plots and relevant results within this paper are available on the Materials Cloud Platform at [URL to be set once a DOI for the present paper is provided].

**ACKNOWLEDGMENTS**

This work was partially funded by the EU through the MAX Centre of Excellence for supercomputing applications (Projects No. 676598 and 824143), and by the US National Science Foundation under grant EAR-1853388. We are grateful to Riccardo Bertossa for technical help.

**AUTHOR CONTRIBUTIONS**

Every author contributed to all aspects of this work.

**COMPETING INTERESTS**

The authors declare no competing interests.

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AB INITIO SIMULATIONS

*Ab initio* molecular dynamics simulations were run using the plane-wave pseudo-potential method and the Car-Parrinello (CP) Lagrangian formalism [1], as implemented in the QUANTUM ESPRESSO suite of computer codes [2, 3]. We adopted norm-conserving pseudopotentials [4] from Ref. 5, which are accurate also at the present pT-conditions [6], and the PBE energy functional [7]. We employed a plane-wave energy cut-off of $E_{\text{cut}} = 110 \text{ Ry}$ for wave-functions and four times as much for the charge density. The fictitious electronic mass was set to 25 electronic masses and the integration time step to $\approx 0.0484 \text{ fs}$. These choices ensure adequate adiabatic decoupling of the electron fictitious dynamics from the ionic motion and conservation of the extended total energy in the relevant pT range considered here.

Flux time series were collected from $NVE$ simulations for at least 60 ps, after an initial $NPT$ equilibration of a few ps at the target pT conditions, followed by $\sim 4 \text{ ps}$ of further $NVE$ equilibration. $NPT$ simulations were run with a chain of three Nosé-Hoover thermostats [8] with a frequency of 60 THz, while pressure was controlled via Parrinello-Rahman barostat [9]. In order to minimize the effects of Pulay stresses, the kinetic energy functional was modified as: $G^2 \rightarrow G^2 + A \left[ 1 + \text{erf} \left( \frac{G^2 - E_0}{\sigma} \right) \right] \left[ \frac{1}{2} \frac{E_0}{\text{Ry}} \right]$, with $E_0 = 100 \text{ Ry}$, $A = 170 \text{ Ry}$, and $\sigma = 15 \text{ Ry}$.

FLUX TIME SERIES

The energy and charge fluxes, $J_E(t)$ and $J_Z(t)$, were sampled every 30 or 40 time steps of the original CP simulation ($\Delta t = 1.45 \text{ fs}$ or $1.94 \text{ fs}$), depending on the specific simulation. This sampling rate is high enough to make the flux power spectra vanish at the corresponding Nyqvist frequency, $f_{\text{Ny}} = 1/(2\Delta t)$, thus avoiding any aliasing effects. We verified that the energy band gap is far larger than $k_BT$ all along our simulations, thus excluding any possible non adiabatic effects in heat and charge transport at the pT conditions of interest here. The time series of the energy gap occurring in two different SI phases of water are reported in Fig. S1.

The energy flux was estimated using the expression derived in Ref. 11: the charge flux, $J_Z$, estimated from the classical expression derived from the formal oxidation numbers $q_H = +1$ and $q_O = -2$, according to the topological theory of adiabatic charge transport introduced in Ref. 12, and $ii)$ the standard quantum-mechanical one, $J'_Z$, that is the sum of the adiabatic electron-charge flux, $J_{el}$, and the classical current of the atomic cores ($Z_H = +1$ and $Z_O = +6$). The two expressions read:

$$J_Z = \frac{e}{\Omega} \left( q_H \sum_{n \in H} \mathcal{V}_n + q_O \sum_{n \in O} \mathcal{V}_n \right)$$  \hspace{1cm} (S1)

$$J'_Z = \frac{e}{\Omega} \left( Z_H \sum_{n \in H} \mathcal{V}_n + Z_O \sum_{n \in O} \mathcal{V}_n \right) + J_{el}.$$  \hspace{1cm} (S2)

The adiabatic electron charge current, $J_{el}$, can be computed as:

$$J_{el} = -\frac{2e}{\Omega} \Re \sum_v \langle \tilde{\phi}_c | \hat{J}_e | \phi_v \rangle,$$  \hspace{1cm} (S3)

where the sum runs over the occupied Kohn-Sham states, $\{ \phi_v \}$, and the orbitals

$$| \tilde{\phi}_c \rangle = \hat{P}_c \mathbf{r} | \phi_v \rangle,$$

$$| \hat{J}_e \phi_v \rangle = \hat{J}_e | \phi_v \rangle,$$  \hspace{1cm} (S4)
are the projections over the empty-state manifold of the action of the position operator over the \( v \)-th occupied orbital, and of its adiabatic time derivative [3]. The operators \( \hat{P}_v \) and \( \hat{P}_e = 1 - \hat{P}_v \) are projectors over the occupied- and empty-states manifolds, respectively. Equations (S4) are well defined in PBC and have been computed from standard density-functional perturbation theory [13].

**CEPSRAL ANALYSIS**

Transport coefficients were estimated by cepstral analysis of the flux time series, as explained in Refs. 14 and 15, using the *thermocepstrum* code [16]. This technique allows one to obtain accurate transport coefficients, as well as a quantitative estimate of their statistical accuracy, depending on two parameters: an effective Nyquist frequency, \( f^* \), used to limit the analysis to a properly defined low-frequency portion of the spectrum, and the number \( P^* \) of inverse Fourier (“cepstral”) coefficients of the logarithm of the spectrum in the low-frequency region thus defined. The estimated conductivities depend very little on \( f^* \), whereas an optimal value of \( P^* \) can be estimated in most cases by statistical model-selection techniques, as explained in Ref. 14. In our applications \( P^* \) is determined via the so-called *Akaike Information Criterion* [14, 17].

Figure S2 displays the sample power spectra of \( J_{el}, J_Z \) and \( J'_Z \), scaled in units such that the zero-frequency value is the electrical conductivity in S/cm. The faint lines are obtained by applying a moving average filter [18] with a window of 0.1 THz to the raw periodograms; the solid smooth lines are obtained by applying a cepstral filter [14] with the parameters reported in Table S1. The definitions \( J_Z \) and \( J'_Z \) lead to the same conductivity, even if their time series values differ, as is clear from the inset, in agreement with Ref. [12], where this finding was proved to be the consequence of gauge-invariance of transport coefficients and topological quantization of adiabatic charge transport in electronically gapped materials.

The application of the Arrhenius-like formula,

\[
\sigma^0 = \frac{e^2}{16\pi^2k_BT} \left[ q^2 N_H D_H + q^2 N_O D_O \left( 1 - \frac{3}{2} \gamma \right) \right],
\]

is based on the diffusivities \( D_X \) of the atoms and on the fraction \( \gamma \) of H atoms bound to oxygen atoms, gives, for PDL water, where \( \gamma \approx 10\% \), a conductivity \( \sigma^0 \approx 32 \text{ S/cm} \), in fair agreement with \( \sigma = 42 \pm 3 \text{ S/cm} \), obtained from the zero-frequency spectrum of \( J_Z \). Nonetheless, Eq. (S5) strongly underestimates the electrical conductivity of the SI phase (where \( D_O \) and \( \gamma \) vanish) since it neglects cross-correlations [19]: for instance, in SI phase with FCC oxygen structure at 2920 K and 257 GPa, \( \sigma^0 \approx 138 \text{ S/cm} \), while \( \sigma = 256 \pm 8 \text{ S/cm} \); in SI phase with BCC oxygen structure at 2470 K and 174 GPa, \( \sigma^0 \approx 83 \text{ S/cm} \), while \( \sigma = 135 \pm 7 \text{ S/cm} \).

As stated in the main text, a 3-variate analysis adopting the adiabatic electron current as an additional flux reduces the statistical uncertainty without affecting the estimate of the thermal conductivity, as shown in Fig. S3 (green). The 3-variate analysis produces a flatter spectrum featuring a reduced total, corresponding to a smaller number of cepstral coefficients, \( P^* \), thus ensuring a smaller statistical error.

A comprehensive summary of our results, along with the values of \( f^* \) and \( P^* \) used for cepstral analysis, is given in Table S2.
TABLE S1. Results of the different NVE simulations. \(N_{\text{H}_2\text{O}}\) is the number of H\(_2\)O stoichiometric units employed in the simulation. Temperature and pressures are reported together with their standard deviation. The last two simulations concern the defected structure, where one H\(_2\)O was removed.

| phase | \(N_{\text{H}_2\text{O}}\) | \(\rho\) [g/cm\(^3\)] | \(T\) [K] | \(p\) [GPa] | \(f^*\) [THz] | \(\kappa\) | \(\sigma\) [S/cm] | \(D\) \([\text{Å}^2/\text{ps}]\) |
|-------|----------------|-----------------|-------|--------|--------|--------|----------------|----------------|
| ice X | 128            | 3.52            | 1488 ± 45 | 182 ± 1 | 13.8   | 6      | 16.1 ± 1.1    | –              |
| SI\(_{\text{BCC}}\) | 128            | 3.39            | 2474 ± 78 | 174 ± 2 | 31.3   | 3      | 9.4 ± 0.6     | 135 ± 7        |
| SI\(_{\text{BCC}}\) | 128            | 3.35            | 2945 ± 88 | 171 ± 2 | 36.9   | 5      | 10.7 ± 0.7    | 180 ± 5        |
| SI\(_{\text{BCC}}\) | 128            | 3.61            | 2905 ± 86 | 218 ± 2 | 31.3   | 3      | 9.9 ± 0.7     | 198 ± 9        |
| SI\(_{\text{FCC}}\) | 108            | 3.82            | 2917 ± 93 | 257 ± 2 | 38.3   | 5      | 12.8 ± 1.0    | 256 ± 8        |
| PDL   | 128            | 2.04            | 1970 ± 60 | 33 ± 1  | 49.2   | 5      | 4.1 ± 0.3     | 42 ± 3         |
| d-ice X| 127            | 3.49            | 1523 ± 47 | 179 ± 1 | 18.1   | 8      | 17.0 ± 1.5    | < 0.1          |
| d-SI\(_{\text{BCC}}\) | 127            | 3.49            | 2302 ± 94 | 190 ± 2 | 38.3   | 6      | 11.6 ± 0.9    | 95 ± 3         |

in Tab. S1.

**DEFECTED STRUCTURE**

We also performed two further simulations—one in solid ice X and one in the SI phase with BCC oxygen structure—for defected structures where two H and one O atoms were removed, to preserve the stoichiometry of the ideal systems, resulting in a defect relative concentration of 1/128 ≈ 0.008. In the SI phase, vacancy hopping in the oxygen lattice is observed in the form of jumps of one or more than one O atoms within the same hopping event. From the mean square displacement of oxygen atoms with respect to their center of mass, we estimated the O self-diffusion coefficient as \(D_O \approx (8.5 \pm 0.6) \times 10^{-3} \text{Å}^2/\text{ps}\). The linear growth of the oxygen mean square displacement, together with the related statistical uncertainty from a 6-block analysis of 10ps segments, is reported in Fig. S4. On the contrary, in the defected ice X structure below the SI transition we observed no oxygen self-diffusion.

Even if such defect concentration is far larger than what it is expected to be at the pT-conditions of Uranus and Neptune from extrapolation of experimental data [20], it is still insufficient to strongly affect the thermal conductivity, when compared to the ideal-structure value. In fact, we obtained values for \(\kappa\) which are compatible with those of the ideal structures, namely \(\kappa \approx 17\) and \(\kappa \approx 12 \text{W}/(\text{Km})\) for the solid and the SI phases, respectively.

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