Solubility of water ice in metallic hydrogen: consequences for core erosion in gas giant planets

H. F. Wilson

Department of Earth and Planetary Science, University of California, Berkeley, CA 94720, USA.

and

B. Militzer

Departments of Earth and Planetary Science and of Astronomy, University of California, Berkeley, CA 94720, USA.

ABSTRACT

Using \textit{ab initio} simulations we investigate whether water ice is stable in the cores of giant planets, or whether it dissolves into the layer of metallic hydrogen above. By Gibbs free energy calculations we find that for pressures between 10 and 40 Mbar the ice-hydrogen interface is thermodynamically unstable at temperatures above approximately 3000 K, far below the temperature of the core-mantle boundaries in Jupiter and Saturn. This implies that the dissolution of core material into the fluid layers of giant planets of giant planets is thermodynamically favoured, and that further modelling of the extent of core erosion is warranted.

Subject headings: planets and satellites: Jupiter, planets and satellites: Saturn, molecular processes, convection

1. Introduction

According to core accretion models \cite{Mizuno1978}, giant gas planets such as Jupiter and Saturn formed via the accumulation of an proto-core of rock and ice which gained solid material until it reached sufficient size to begin accreting the gaseous component of the protosolar nebula. The existence of solid ice in the outer solar system promotes the rapid growth of the more massive protocores allowing the accretion of large quantities of gas necessary for Jupiter-sized planets. Giant planets thus have a dense core of rock and ice surrounded by a H-He envelope. It is not known, however, whether the initial dense core remains stable following the accretion of the H-He outer layer or whether the core erodes into the fluid hydrogen-rich layers above \cite{Stevenson1982, Guillot2004}.

The gravitational moments of Jupiter and Saturn, which have been measured by prior planetary missions and will be determined for Jupiter with unprecedented accuracy by the upcoming Juno mission, may be used in combination with interior models \cite{Militzer2008, Guillot2004, Hubbard2005, Saumon2004, Nettelmann2008} to estimate the mass of the present-day core, but it is unclear whether these masses correspond to the primordial core mass. It has been suggested \cite{Guillot2004, Saumon2004} that the present-day core mass of Jupiter may be too small to explain its formation by core accretion within the relatively short lifetime of the protosolar nebula \cite{Pollack1996}, although a more recent Jupiter model \cite{Militzer2008} predicted a larger core of 14–18 Earth masses which is consistent with core accretion. Furthermore, direct measurements of Jupiter’s atmosphere suggest a significant enhancement in the concentration of heavy ($Z > 3$) elements \cite{Niemann1996}, but it is unknown to what extent this should be attributed to a large flux of late-arriving planetesimals versus the up-
welling of core material. Determining the extent of core erosion is thus a major priority for understanding the interiors of giant planets and the process by which they were formed.

In this work we focus on water ice, presumed to be a major constituent of the core, and consider the question of whether it has significant solubility in fluid metallic hydrogen at conditions corresponding to the core-mantle boundaries of giant gas planets. Water ice is the most prevalent of the planetary ices (water, methane and ammonia) which may be assumed to make up the outermost layers of a differentiated rock-ice core (Hubbard 1981). At the conditions of temperature and pressure prevalent at giant planet cores, water ice is predicted (Cavazzoni et al. 1999; French et al. 2009) to be in either a fully atomic fluid phase in which oxygen and hydrogen migrate freely and independently, or in a superionic phase in which oxygen atoms vibrate around defined lattice sites while hydrogen atoms migrate freely. Assuming the existence of a core-mantle boundary at which water ice and the fluid H-He phase are in direct contact, the relevant question is the extent to which the system may lower its Gibbs free energy by the redistribution of the atoms of the ice phase into the fluid hydrogen. The extreme pressure and temperature conditions prevalent at giant planet core-mantle boundaries (8000–12000K and 8–18 Mbar for Saturn, 18000–21000K and 35–45 Mbar for Jupiter) are not yet obtainable in the laboratory, thus ab initio simulations provide the best available guide to determining the extent of core solubility.

2. Theory and Methodology

We used density functional molecular dynamics (DFT-MD) calculations and coupling constant integration (CCI) techniques to compute the Gibbs free energy of solvation, $\Delta G_{sol}$, of H$_2$O in fluid metallic hydrogen, i.e. the change in Gibbs free energy when an H$_2$O molecule is removed from the pure ice phase and dissolved in H. The free energy of solubility is computed from the free energies of three systems: pure ice, pure fluid H, and a mixed system in which the atoms of one water molecule are dissolved in $n$ atoms of hydrogen,

$$\Delta G_{sol} = G(OH_{n+2}) - [G(H_2O) + G(H_n)]$$  \hspace{1cm} (1)

where $G$(H$_2$O) is the energy per H$_2$O stoichiometric unit of the ice phase, and $G$(H$_n$) is obtained from an appropriately-scaled simulation of 128 H atoms. This quantity becomes more negative as solubility increases. A $\Delta G_{sol}$ of zero implies a saturation concentration of exactly one H$_2$O to $n$ H. In order to span the range of likely conditions for the core-mantle boundary of Jupiter and Saturn, we considered pressures of 10, 20 and 40 Mbar, at a range of temperatures from 2000 to 20000 K.

Computation of free energies from MD simulations is difficult since the entropy term is not directly accessible. Here we use a two-step CCI approach as previously applied by several authors (Alfe et al. 1999; Morales et al. 2009; Wilson and Militzer 2010) to compute free energies. The CCI method provides a general scheme for computing $\Delta F$ between systems governed by potential energy functions $U_1$ and $U_2$. We construct an artificial system $U_\lambda$ whose forces are derived from a linear combination of the potential energies of the two systems $U_\lambda = (1 - \lambda)U_1 + \lambda U_2$. The difference in Helmholtz free energy between the two systems is then

$$\Delta F = \int_0^1 \langle U_2 - U_1 \rangle_\lambda d\lambda,$$  \hspace{1cm} (2)

where the average is taken over the trajectories governed by the potential $U_\lambda$. We perform two CCIs for each $G$ calculation: first from the DFT-MD system to a system governed by a classical pair potential which we fit to the DFT dynamics of the system via a force-matching approach (Izvekov et al. 2004), and then from the classical system to a reference system whose free energy is known analytically.

2.1. Material phases

The material phases in question must be established prior to the Gibbs free energy calculations. At the pressure and temperature conditions of interest, hydrogen is a metallic fluid of H atoms in which molecular bonds are not stable. Water dissolved within hydrogen likewise is non-molecular, with a free O atom in an atomic H fluid. For water ice, the phase diagram at giant planet core pressures is divided into three regimes (Cavazzoni et al. 1999; Goldman...
et al. 2005; Mattsson and Desjarlais 2006; French et al. 2009): a low-temperature (< 2000 K) crystalline regime, an intermediate superionic regime in which oxygen atoms vibrate around fixed lattice sites while hydrogen atoms migrate freely, and a higher-temperature fully fluid regime in which both hydrogen and oxygen atoms are mobile. The transition between the crystalline and superionic regimes has not yet been studied in detail at high pressures but our simulations find that it occurs below 2000 K. The transition from superionic to fully fluid is found to occur in simulation at temperatures ranging from 8000 K for 10 Mbar and 13000 K for 50 Mbar [French et al. 2009]. Consequently our study includes the superionic and fully fluid ice phases.

Previous studies of superionic ice [Cavazzoni et al. 1999; French et al. 2009] have used an bcc arrangement of atoms for the oxygen sublattice. We found that such a lattice was stable at all points studied in the superionic regime except for 10 Mbar at 2000 and 3000 K. At these conditions we found that the oxygen sublattice was stable in the Pbca geometry which we recently reported to be the most stable zero-temperature structure for ice at 10 Mbar [Militzer and Wilson 2010]. At 10 Mbar and 5000 K, superionic ice with a bcc sublattice was stable but the Pbca was not. The bcc oxygen sublattice was found to be stable for 20 and 40 Mbar pressures at all temperatures studied in the superionic regime. Attempts to perform a superionic simulation in the Cmcn geometry reported by Militzer and Wilson [2010] to be the stable zero-temperature structure at these pressures resulted in an unstable system with a large anisotropic strain. We thus used a bcc oxygen sublattice for all superionic ice simulations, except the 2000 K and 3000 K simulations at 10 Mbar which used the oxygen sublattice from the Pbca phase, as indicated in Figure 1. While we cannot yet exclude the possibility of the existence of yet another superionic ice structure, we note that the differences between different ice phase energies are found to be on the order 0.1 eV per H$_2$O, and thus will not significantly affect our results about the stability of ice in giant planet cores.

2.2. Computation of Gibbs free energies

Our goal in this paper is to study the solubility of water ice in fluid hydrogen. Due to considerations arising from the entropy of mixing, the solubility of one material in another is never zero, however solubility at trace quantities is not sufficient for core erosion. In particular, we wish to know whether solubility is thermodynamically favored at concentrations significantly greater than the background concentration of oxygen in the fluid envelope of Jupiter or Saturn – this is equal to approximately one O atom to 1000 H atoms if we assume solar concentrations for the Jovian envelope and approximately one part in 300 if we assume a threefold enrichment for oxygen as observed for most other heavy elements [Mahaffy et al. 1998]. We begin by computing the Gibbs free energies of solubility for dissolving H$_2$O in pure H at one part in 125, and generalize later.

The coupling constant integration approach requires, as an integration end point, a reference system whose free energy may be computed analytically. It is important to ensure that the system does not undergo a phase change along the integration pathway since this may cause numerical difficulties in the integration. For the fluid systems, being pure hydrogen, hydrogen with oxygen, and ice at temperatures above the superionic-to-fluid transition, we used an ideal atomic gas as the reference system [Alfè et al. 1999; Morales et al. 2009; Wilson and Militzer 2010]. For superionic ice, we use as a reference system a combination of an ideal gas system for the hydrogen atoms with an Einstein crystal of oxygen atoms each oxygen tethered to its ideal lattice site with a harmonic potential of spring constant 30 eV/Å$^2$.

The DFT-MD simulations in this work used the Vienna Ab Initio Simulation Package (VASP) [Kresse and Furthmüller 1996] with pseudopotentials of the projector augmented wave type [Blöchl 1994] and the exchange-correlation functional of Perdew et al. [1996]. The pseudopotentials used had a core radius of 0.8 Å for hydrogen and 1.1 Å for oxygen. Wavefunctions were expanded in a basis set of plane waves with a 900 eV cutoff and the Brillouin Zone was sampled with $2 \times 2 \times 2$ $k$-points. The electronic temperature effects were taken into account via Fermi-Dirac smearing. A new set of force-matched potentials was fitted for each pressure-temperature conditions for each stoichiometry. All MD simulations used a 0.2 fs timestep. In the classical potential under superionic conditions, an additional harmonic potential
The first step of the free energy calculations was the determination of the appropriate supercell volumes for each system for each set of pressure and temperature conditions. This was accomplished via constant-pressure MD simulations (Hernández 2001) with a duration of 1.6 ps (0.6 ps for ice). DFT-MD trajectories were then computed in a fixed cell geometry in order to fit classical potentials. A run of 0.4 ps was found to be sufficient for fitting suitable potential. We then performed molecular dynamics runs 600 fs long (400 fs for ice) at five $\lambda$ values to integrate between the DFT and classical systems. Finally, we performed classical Metropolis Monte Carlo at 24 $\lambda$ values to integrate from the classical to the reference system.

3. Simulation results

Table I lists the total Gibbs free energies for each simulated system ($H_{128}$, $OH_{127}$ and ice) for each set of temperature and pressure conditions. Ice was confirmed to remain superionic except at the 20 Mbar/12000 K and 40 Mbar/20000 K conditions where it was fully fluid. The error bars on the computed $G$ values are dominated primarily by the uncertainty in the computed volume at the desired pressure, and secondarily by uncertainty in the $(U_{DFT} - U_{classical})\lambda$ term in the coupling constant integration. These free energies are combined using Equation [1] to give $\Delta G_{sol}$ representing the free energy change associated with removing an $H_2O$ from the ice phase and dissolving it in the hydrogen fluid at a concentration of molecule per 125 solute $H$ atoms. $\Delta G_{sol}$ increases strongly with temperature, but shows only a weak dependence on pressure within the 10–40 Mbar range under consideration. The $\Delta G$ values were found to be well converged with respect to wavefunction cutoff, k-point sampling to within the available error bars. The effect of the electronic entropy term on $\Delta G_{sol}$ was found to be less than 0.1 eV in all cases. From a linear interpolation through the adjacent data points we estimated the temperature at which $\Delta G_{sol}$ passes through zero as 2400 K ± 200 K at 40 Mbar, 2800 K ± 200 K at 20 Mbar, and 3400 K ± 600 K at 10 Mbar. As shown in Figure 1, this is clearly far lower than any reasonable estimate for the core-mantle boundaries for either Jupiter or Saturn. The onset of high solubility occurs within the portion of the phase diagram where ice is superionic, and does not coincide with either the superionic-to-fluid transition or the crystalline-to-superionic transition in ice.

The total $\Delta G$ of solubility may be broken down into three components: a $-U$ term from the potential energy, a $P\Delta V$ term from the volume difference, and a $-T\Delta S$ entropic term. Figure 2 shows this breakdown as a function of temperature for 20 Mbar. The breakdown for other pressures looks similar. The $-U$ term, representing the difference in chemical binding energy, provides approximately a 2 eV per molecule preference for ice formation at all temperatures where ice is superionic, but a much smaller preference for the 12000 K case where ice is fluid. The $PV$ term is indistinguishable from zero within the error bars, suggesting that this is not a pressure-driven transition, in contrast to recent results on the partitioning of noble gases between hydrogen and helium in giant planet interiors in which volume effects were found to be the dominant term (Wilson and Militzer 2010). The $-T\Delta S$ term dominates the temperature-dependent behavior, underlining that ice dissolution is indeed an entropy-driven process.

Given the Gibbs free energy of solubility for the insertion of one $H_2O$ into 125 H atoms we can determine an approximate Gibbs free energy of solubility at other concentrations, by neglecting the contribution of the oxygen-oxygen interaction and including only the entropic term arising from the mixing. Under these approximations, we obtain the expression

$$\frac{\Delta G_{sol}[m] - \Delta G_{sol}[n]}{k_B T} = (m + 2) \log \left( \frac{(m + 2)V_H + V_O}{(m + 2)V_H} \right) - (n + 2) \log \left( \frac{(n + 2)V_H + V_O}{(n + 2)V_H} \right) - \log \left( \frac{m + 2}{n + 2} \right),$$

where $V_H$ and $V_O$ are the effective volumes of each H and O atom in the fluid. This approxi-
formation becomes invalid as the oxygen-oxygen interaction term in the fluid oxygen phase becomes significant, however for our purposes it is sufficient to know that the saturation concentration is significantly higher than the background concentration. If a saturation concentration of oxygen in hydrogen does indeed exist then this may be expected to have a retarding effect on the erosion of the core.

We must also consider possibility that hydrogen and oxygen could dissolve separately from the H$_2$O mixture, leaving behind a condensed phase with stoichiometry other than H$_2$O. We tested two cases explicitly, computing the free energies of pure oxygen and one-to-one HO phases at the Jupiter-like 40 Mbar, 20,000 K set of conditions. Both O and HO were found to be in a fully fluid state at these temperature/pressure conditions. We found that HO had a free energy of solubility of -11.2 eV per oxygen, while pure oxygen had -22.8 eV per oxygen. Comparing to the -8.9 eV per oxygen solubility of H$_2$O, this suggests oxygen-rich condensed phases are less thermodynamically stable than the H$_2$O phase, and certainly far less favourable than dissolution of the dense phase into metallic hydrogen. We have also neglected the possibility of hydrogen-enriched dense phases such as H$_3$O. While it possible such phases may be somewhat energetically preferred to H$_2$O, it is extremely unlikely that the preference will be strong compared to the 8 – 12 eV per O unit preference for solubility.

In Figure 3 we plot the estimated $\Delta G_{\text{sol}}$ as a function of concentration for various computed temperatures at a pressure of 40 Mbar. A negative value of $\Delta G_{\text{sol}}$ means that it is thermodynamically favorable to dissolve further ice into the hydrogen phase at a given hydrogen-phase ice concentration, and the point at which $\Delta G_{\text{sol}}$ is zero is the saturation concentration. For 2000 K and 3000 K the saturation concentrations are estimated to be on the order of 1:500 and 1:20 respectively, while for higher temperatures the saturation concentration is much higher. Given that we neglect O–O interactions in the fluid hydrogen phase, it is difficult to precisely determine the saturation concentrations for higher temperatures. However, we may safely say that the saturation concentration for temperatures in excess of 3000 K is very much greater than the background oxygen concentration, and hence that solubility of ice into hydrogen at the core-mantle boundaries of Jupiter and Saturn is expected to be strongly thermodynamically favored.

4. Discussion

The consequences of core erosion for planetary evolution models have been previously considered by Stevenson (1982) and later Guillot et al. (2004). The effects of core erosion can potentially be detected either by orbital probes such as Juno or by atmospheric entry probes, since the redistribution of core material throughout the planet will manifest itself both by a smaller core (detectable from gravitational moments) and a higher concentration of heavy elements in the atmosphere than would be expected in a planet without core erosion. Once core material has dissolved into the metallic H layers, the rate at which core material can be redistributed throughout the planet is expected to be limited by double diffusive convection (Turner 1974; Huppert and Turner 1981). Since the higher density due to compositional gradients of the lower material interferes with the convection process, convection may be slowed significantly. Guillot et al. (2004) modelled the effect of core erosion under the assumptions of fully soluble 30 Mbar core in each planet. Under their assumptions up to 19 Earth masses could have been redistributed from Jupiter’s core but only 2 Earth masses from Saturn’s, the difference being Jupiter’s higher temperatures. While this prediction is subject to significant uncertainty in many aspects of the model, it does suggest that a redistribution of a significant fraction of the initial protocore is possible, at least in Jupiter. Further refinement of models for the upconvection of core material and its observable consequences may be fruitful. The effect of core erosion on the heat transport and mass distribution properties of Jupiter and Saturn should also be taken into account in future static models of these planets’ interiors.

These calculations can be expanded in several ways. We have neglected the presence of helium in the hydrogen-rich mantle, however due to the large magnitude of $\Delta G_{\text{sol}}$ and the chemical inertness of helium we do not expect the presence of helium in the mantle to significantly affect the solubility behavior. We have explicitly made the assumption that ice and hydrogen are in direct
contact, an assumption which might fail in one of two ways. If hydrogen and helium are immiscible at the base of the atmosphere then the core may make direct contact with a helium-rich layer. This, however, is unlikely in the context of the calculations of [Morales et al. (2009)] who predict hydrogen-helium immiscibility only far away from the cores of Jupiter and Saturn. The other possibility is that the ice layers of the core may be gravitationally differentiated, leaving ice beneath layers of the less dense planetary ices methane and ammonia. Since the bonding in these is similar to that in water ice one could assume that they show a similar solubility behavior, but this analysis is the subject of future work.

We have also considered only the structure of the present-day planet. As suggested by [Iaroslavitz and Podolak (2006)], a proper consideration of core solubility must also include solubility during the formation process, as dissolution of the icy parts of the core into the accreting hydrogen during the formation may result in the amount of ice on the core itself being small by the time the planet reaches its final size. A treatment of the formation processes for Jupiter and Saturn using ice solubilities derived from ab initio calculations may be valuable.

Our calculations strongly suggest that icy core components are highly soluble in the fluid mantle under the conditions prevalent at the core-mantle boundaries of Jupiter and Saturn. Since many recently-discovered exoplanets are more massive and hence internally hotter than Jupiter, it can be expected that any initial icy cores in these exoplanets will also dissolve. The presence of core erosion may allow models predicting a small present-day Jovian core to be made consistent with the large initial core required by core erosion, however models of the interior mass distribution of the planet will need to be revised to take the inhomogeneous composition of the lower layers implied by convection-limited core redistribution into account. Improved models which include core redistribution processes, combined with the data from the Juno probe, may assist in understanding the history and present structure of Jupiter and other planets in our own and in other solar systems.

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| P (Mbar) | T (K) | $G(\text{H}_{128})$ (eV) | $G(\text{H}_{127}\text{O})$ (eV) | $G(\text{Ice})$ (eV) | $\Delta G_{\text{sol}}$ (eV) |
|----------|-------|--------------------------|-----------------------------|------------------|-----------------|
| 10       | 2000  | 716.1(5)                 | 728.4(4)                    | 1800.2(22)*      | 0.97(62)        |
| 10       | 3000  | 672.2(3)                 | 683.9(4)                    | 1731.4(22)*      | 0.35(52)        |
| 10       | 5000  | 561.8(3)                 | 571.7(3)                    | 1311.5(11)       | -1.10(50)       |
| 20       | 2000  | 1308.3(1)                | 1332.8(2)                   | 2945.3(10)       | 0.61(24)        |
| 20       | 3000  | 1271.2(1)                | 1295.1(2)                   | 2895.8(9)        | 0.11(22)        |
| 20       | 5000  | 1173.0(3)                | 1195.3(2)                   | 2795.2(15)       | -1.91(37)       |
| 20       | 8000  | 989.7(7)                 | 1009.9(4)                   | 2536.5(15)       | -3.57(80)       |
| 20       | 12000 | 705.9(10)                | 722.5(6)                    | 2049.8(26)†      | -4.8(12)        |
| 40       | 2000  | 2161.5(1)                | 2205.5(1)                   | 5102.2(10)       | 0.18(14)        |
| 40       | 3000  | 2131.3(1)                | 2174.8(1)                   | 5062.6(10)       | -0.25(17)       |
| 40       | 5000  | 2046.0(3)                | 2087.9(2)                   | 4943.0(13)       | -1.69(30)       |
| 40       | 8000  | 1880.8(4)                | 1920.3(2)                   | 4701.3(13)       | -3.47(43)       |
| 40       | 20000 | 1011.6(17)               | 1041.1(14)                  | 3350.6(30)†      | -8.9(22)        |

Table 1: Gibbs free energies per simulation cell of fluid hydrogen, fluid hydrogen with oxygen, and ice at each temperature/pressure combination, along with the energy of solvation $\Delta G_{\text{sol}}$ per H$_2$O molecule. Ice systems marked with a star have H$_{128}$O$_{64}$ stoichiometry and an oxygen structure from the Pbca phase while other ice systems have H$_{108}$O$_{54}$ and a bcc oxygen sublattice. Ice systems marked with a dagger are fully fluid, while others are superionic.
Fig. 1.— (Color online) Computed location of the temperature at which saturation is reached at 1:125, as a function of pressure between 10 and 40 Mbar, with the shaded area corresponding to error bars, in relation to the approximate location of the superionic-to-fluid transition (French et al. 2009), and the approximate conditions corresponding to the core-mantle boundaries of Jupiter and Saturn. The points at which calculations have been undertaken are marked, with the shape and color of the symbols indicating phase of ice used in each calculation.
Fig. 2.— Breakdown of the computed $\Delta G_{sol}$ into contributions from the $\Delta U$, $P\Delta V$, and $-T\Delta S$ terms, as a function of temperature, at a pressure of 20 Mbar.
Fig. 3.— Estimated free energy of solubility $\Delta G_{\text{sol}}$ of ice in hydrogen as a function of oxygen concentration in the limit where oxygen atoms do not interact in the fluid phase, for various temperatures at a pressure of 40 Mbar. Shaded regions indicate error bars.