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Estimating the quantum effects from molecular vibrations of water under high pressures and temperatures

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Abstract

We present a simple model which estimates the influence of quantum effects from molecular vibrations on the equation of state of water under high pressures and temperatures. This model is combined with an *ab initio* equation of state of water generated by quantum molecular dynamics (QMD) simulations employing density functional theory for the electrons and a classical algorithm for the ions. We calculate the specific heat capacity as well as the principal Hugoniot curve, especially the Hugoniot temperature, in accordance with experiments.

1. Introduction

The equation of state (EOS) of water under high pressures and temperatures is of general interest and has applications in astrophysics and shock physics. For temperatures lower than 1000 °C and pressures up to 1 GPa the EOS table by Wagner and Pruß [1] founded on experimental data is available while the SESAME 7150 EOS table [2] is widely used for higher pressures and temperatures. Analytical expressions for the EOS data which are based on experimental results exist for a wide range of temperatures and densities [3–5]. Recently, *ab initio* EOS data were calculated via quantum molecular dynamics (QMD) simulations [6, 7] which employ density functional theory (DFT) for the electrons and classical molecular dynamics for the ions. *Ab initio* approaches do not rely on empirical potentials for the interaction like chemical models [8] nor do they use an experimental data base. The only approximation in the DFT is the exchange–correlation functional; in [6] the generalized gradient approximation of Perdew, Burke and Ernzerhof [9] was employed and the Vienna *ab initio* simulation package (VASP) [10–13] served as a numerical implementation of the procedure. EOS data were generated for temperatures between 1000 and 24 000 K and densities up to 15 g cm⁻³, a region which is still largely out of reach of present experimental techniques but nevertheless relevant for modelling of the interiors of giant planets [6, 14–16]. Good agreement was found between the QMD EOS and diamond anvil cell experiments at 300 K up to 1.26 Mbar [17] while the SESAME 7150 EOS overestimates

the density in that region considerably. A more detailed introduction to the theoretical background of QMD simulations can be found elsewhere (see Gillan *et al* [18]).

However, the QMD simulation method lacks contributions from the quantum effects of the ionic motion which influence the caloric EOS $u(T, \rho)$. Such effects, although in principle also accessible through extended but even more numerically expensive *ab initio* methods [19], can be estimated by using the harmonic oscillator approximation for the three linear independent vibrations of the water molecule. We show that experimental values of the heat capacity and the principal Hugoniot temperature [20, 21] are reproduced by this approach.

2. Heat capacity of molecular water

Considering a classical ideal gas model for water molecules, the specific heat capacity per mole is $c_v^{\text{id}} = 6R$, where R is the universal gas constant. It is composed of 1.5 R from the translational, 1.5 R from the rotational (rigid rotator) and 3 R from the three vibrational (harmonic oscillator) degrees of freedom. With the aim of estimating the quantum effects of the internal degrees of freedom at temperatures of 1000 K and above, only the vibrational degrees of freedom need to be considered since the characteristic temperatures of vibration, $T_i = \hbar\omega_i/k_B$, are of the same order of magnitude, in numbers $T_1 = 5262$ K, $T_2 = 5404$ K and $T_3 = 2295$ K [22]. The treatment of the quantum mechanical harmonic oscillator

(QMHO) is found in textbooks of statistical physics (see e.g. [23]), which leads to the expression

$$c_v^{\text{QMHO}}(T) = R \sum_{i=1}^3 \frac{T_i^2 \exp(T_i/T)}{T^2 [\exp(T_i/T) - 1]^2}. \quad (1)$$

The respective heat capacity of the three oscillators is always smaller than the classical value of $3R$ at finite temperatures.

First we compare the heat capacity of the QMD EOS [6] with the table of Wagner and Pruß [1] by calculating the internal energy through a series of five QMD simulations at 0.912 g cm^{-3} at temperatures of 800, 900, 1000, 1100 and 1200 K using the same simulation parameters as in [6] which produce well-converged results. We obtain the molar heat capacity as $c_v^{\text{QMD}}(1000 \text{ K}, 0.912 \text{ g cm}^{-3}) = 8.4(\pm 0.8)R$ by linear regression. The respective value of [1] is $c_v^{\text{WP}}(1000 \text{ K}, 0.912 \text{ g cm}^{-3}) = 5.8R$, well below the QMD value. Subtracting the classical $3R$ and adding the result of equation (1) to the QMD value, we find the quantum-corrected value as $c_v^{\text{QMD+QMHO}}(1000 \text{ K}, 0.912 \text{ g cm}^{-3}) = 6.4(\pm 0.8)R$ which is in agreement with Wagner and Pruß. Thus, we apply the QMHO model for the molecular vibrations also to higher temperatures and densities.

At this point we have to note that the pressure of the QMD EOS [6] at 0.912 g cm^{-3} and 1000 K exceeds the pressure of Wagner and Pruß [1] and SESAME 7150 [2] by 20%. This is probably due to the lack of attractive van der Waals forces in the exchange–correlation functional [9]. For this reason, we recommend using the 1000 K QMD pressure isotherm from [6] only above 1.25 g cm^{-3} . However, this limitation does not apply to the isotherms at higher temperatures from [6] because the experimental EOS data of Brodholt and Wood [24] at 1450 and 1600 °C are reproduced by the QMD EOS.

3. Dissociation of the water molecules and quantum corrections to the caloric EOS

The QMHO model can only be applied to intact water molecules. Increasing temperature and density force the molecules to dissociate. Hence we have to introduce a chemical picture that yields the fractions of water molecules $\alpha(T, \rho) = N_{\text{H}_2\text{O}}(T, \rho)/N_{\text{O},\text{total}}$ out of the QMD simulations which are performed in the physical picture consisting of hydrogen and oxygen ions and electrons [6]. Different ways to obtain the fraction of water molecules, or also other ion species like OH^- and H_3O^+ , have been reported in the literature. For instance, Schwegler *et al* [25] have matched each hydrogen ion to its nearest oxygen ion at each time step. The number of hydrogen ions associated with each oxygen ion is counted and a distribution of molecules and ions is obtained. This definition is free from parameters but also counts hydrogen ions in scattering states which pass an oxygen ion in a short time as bound. It is therefore likely to overestimate the occurrence of bound hydrogen ions. To avoid this, Goldman *et al* [7, 26] and Mattsson and Desjarlais [27] have defined a critical radius r_{cut} around each oxygen ion in which a hydrogen ion must stay for a particular time t_{cut} to be counted as bound to that particular oxygen ion. This allows us to sort out transient hydrogen ions

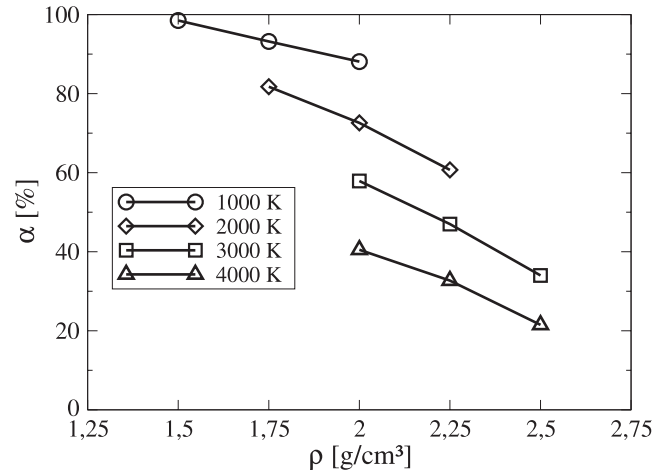


Figure 1. Fraction of water molecules dependent on temperature and density in the regime relevant for the principal Hugoniot curve. The degree of dissociation increases with density and with temperature.

but includes the bond length r_{cut} and the bond time t_{cut} as parameters which must be chosen intuitively. However, both methods can yield similar fractions of water molecules or water ions [7, 25–27] since the results are sensitive to the choice of parameters [27]. In this work, we combine both methods and obtain the fraction of water molecules as follows: at every time step, we match each hydrogen ion to its nearest oxygen ion and obtain a distribution of oxygen ions with one, two, three etc hydrogen ions associated with it in the same way as Schwegler *et al* [25] did. But we count such an ion aggregation as a water molecule only if an oxygen ion retains the same two hydrogen ions as its nearest neighbours for a certain time interval Δt . Thus, we have only the time interval Δt as a free parameter. In the limit $\Delta t = 0$ our approach corresponds exactly to the model of Schwegler *et al* [25] and yields the same results. For our purpose of examining quantum mechanical effects in the molecular vibrations, we find that $\Delta t = 21 \text{ fs}$ is a suitable choice because this is the full period of the slowest vibration ($t = 2\pi\hbar/k_B T_3$) of a water molecule. We display our results of the density and temperature dependent fraction of water molecules $\alpha(T, \rho) = N_{\text{H}_2\text{O}}(T, \rho)/N_{\text{O},\text{total}}$ in figure 1; they are in good agreement with the values found by Goldman *et al* [7].

Using the same method to detect also OH^- and H_3O^+ ions, although their effective charges cannot be determined via this procedure, we observed only 4% or less of H_3O^+ and 12% or less of OH^- ions in the entire density–temperature plane considered in the QMD simulations of [6]. Most of the protons are either bound in water molecules or free. Therefore, we will neglect OH^- and H_3O^+ ions in our thermodynamic considerations. Similar observations were made by Goldman *et al* [7] and Wu *et al* [28]. This finding is also in agreement with the Raman scattering experiments of Holmes *et al* [29] along the principal Hugoniot curve where H_3O^+ could not be detected. Goldman *et al* [7] report higher concentrations of OH^- ions and lower concentrations of H_3O^+ in their simulations which is probably due to the slightly different way of counting the species (see above).

Table 1. Thermal $p(T, \varrho)$ and caloric $u(T, \varrho)$ EOS of fluid water.

T (K)	ϱ (g cm ⁻³)	p (kbar)	u (kJ g ⁻¹)
1000	0.912	12.0	-72.72
1000	1.0	18.6	-72.73
1000	1.246	43.5	-72.68
1000	1.5	88.1	-72.29
1000	1.75	158	-71.71
1000	1.9	207	-71.18
1000	1.994	246	-70.86
2000	1.0	36.8	-69.75
2000	1.5	120	-68.98
2000	1.76	196	-68.20
2000	2.0	304	-67.21
2000	2.25	448	-65.80
3000	2.0	357	-63.36
3000	2.25	503	-61.84
3000	2.5	694	-60.14
4000	0.9972	59.5	-62.8
4000	1.5	165	-61.3
4000	1.994	385	-59.1
4000	2.25	550	-57.5
4000	2.5	776	-55.7

After having identified the fraction of molecules, we can apply the equation

$$u^{\text{QMD+QMHO}}(T, \varrho) = u^{\text{QMD}}(T, \varrho) + \alpha(T, \varrho) \frac{R}{M_{\text{H}_2\text{O}}} \left[\sum_{i=1}^3 T_i \left(\frac{1}{2} + \frac{1}{\exp(T_i/T) - 1} \right) - 3T \right] \quad (2)$$

to the caloric EOS data ($[u] = \text{kJ g}^{-1}$) of the QMD simulations performed in [6] in the fluid phase above 1000 K. It adds the contributions of the QMHO and subtracts the classical vibrational energies, both scaled with the fraction of water molecules $\alpha(T, \varrho)$. The molar mass of water is $M_{\text{H}_2\text{O}} = 18.0 \text{ g mol}^{-1}$. We present the caloric EOS data $u^{\text{QMD+QMHO}}(T, \varrho)$ for temperatures between 1000 and 4000 K in table 1. The data are compatible with the those given in [6].

4. Results for the principal Hugoniot curve

The principal Hugoniot curve is calculated via

$$2(u - u_0) = (p + p_0)(v_0 - v) \quad (3)$$

which connects the thermodynamic states occurring in planar shockwave experiments starting from defined initial conditions (subscript 0) [30]. The expression is evaluated for different isotherms of the theoretical EOS tables (SESAME 7150 [2], QMD from [6], and the EOS from this work). The thermodynamic quantities are the pressures $p = p(T, \varrho)$ and $p_0 = 1 \text{ bar}$, the specific volumes $v = \varrho^{-1}$ and $v_0 = \varrho_0^{-1} = (0.998 \text{ g cm}^{-3})^{-1}$, and the specific internal energies $u = u(T, \varrho)$ and u_0 .

Special attention has to be paid to water at ambient conditions: although liquid water is molecular, the molecules are embedded in a network of hydrogen bonds [31] which perturbs the vibrations and rotations of the molecules. For instance, the specific heat capacity of water under ambient

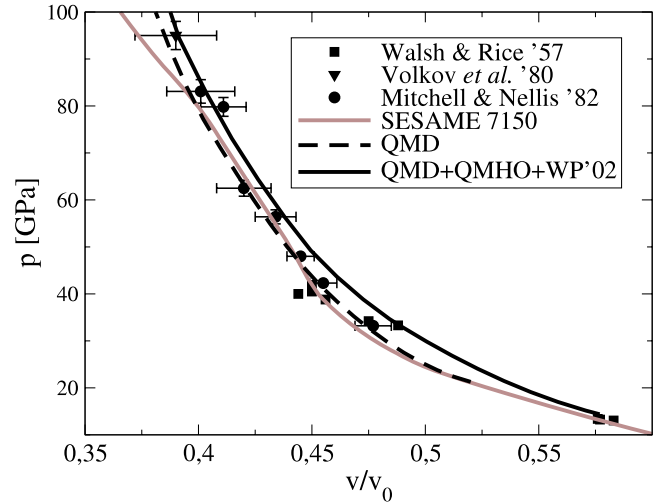


Figure 2. Comparison of the theoretical principal Hugoniot curves obtained by the SESAME 7150 EOS [2] (grey), by QMD simulations [6] (dashed black), and with the QMHO correction from this work (solid black). The experiments of Walsh and Rice [32], Volkov *et al* [33] and Mitchell and Nellis [34] are reproduced by all theoretical EOS, whereas the least compressible Hugoniot curve is derived from the present model.

conditions is $\approx 9R$ [1] which is not matched by the QMHO model employed in this work. Therefore, we use the table of Wagner and Pr u  [1] and equalize the internal energy with the QMD+QMHO value at the mutual data point (1000 K and 0.912 g cm^{-3}) to calculate the energy of the initial condition u_0 for the principal Hugoniot curve.

The three theoretical EOS (SESAME 7150 [2], QMD from [6], and QMD + QMHO from this work) agree well with the experiments [32–34] in the pressure versus compression plane (see figure 2). The effect of the QMHO correction on the QMD EOS is small in that representation; the density is shifted slightly to lower values.

However, the influence on the Hugoniot temperature is significant. We compare the calculated Hugoniot curves in the pressure versus temperature plane in figure 3. The SESAME 7150 EOS and the pure QMD EOS predict Hugoniot temperatures which are too low. The inclusion of the QMHO vibrations for the water molecules into the QMD EOS as well as the use of the Wagner and Pr u  [1] ground state energy yields temperatures within the experimental error bars. As a special case, we also apply formula (2) to the EOS data of [6] with $\alpha(T, \varrho) = 1$, assuming that all water molecules remain undissociated for the whole density and temperature range. The respective curve (dotted line in figure 3, not shown in figure 2 because no visible differences appear in that representation) is very close to that obtained by taking the dissociation into account properly. This illustrates the weak dependence of the vibrational quantum effects on the degree of dissociation, which is important since the procedure of determining the concentration of molecules in QMD simulations is not parameter free, as discussed above. At temperatures higher than 5000 K the quantum effects do not need to be considered any further; their contribution to the caloric EOS becomes insignificant.

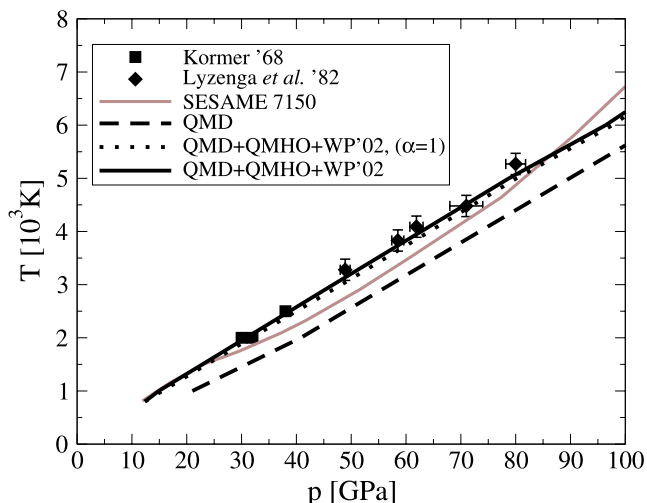


Figure 3. Temperature along the principal Hugoniot curve. The experimental data from Lyzenga *et al.* [21] are represented by the diamonds with error bars and the data of Kormer [20] by the squares. The SESAME 7150 EOS [2] (grey) as well as the pure QMD EOS [6] (dashed black) predict Hugoniot temperatures which are too low. With the QMHO correction of this work applied to the QMD EOS (solid black) a good agreement with the experiment is achieved. The dotted line is a calculation where the dissociation of the water molecules is neglected ($\alpha = 1$ in formula (2)).

Lastly, the majority of the water molecules do not dissociate until the temperature reaches values of about 3000 K (see figure 1). Results within the error bars for the Hugoniot temperature are already obtained without considering the dissociation of water molecules when applying formula (2), see figure 3. We thus conclude that the major contributions to the vibrational quantum effects are contained in the harmonic oscillator approximation for the vibrations of H_2O molecules.

5. Conclusions

We have estimated the influence of quantum effects from molecular vibrations of water molecules under high pressures and temperatures. It is shown that an *ab initio* EOS model in combination with the harmonic oscillator approximation yields the specific heat capacity as well as the Hugoniot temperature in good agreement with experimental data. A table containing the quantum-corrected *ab initio* EOS is given.

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Note added in proof. After the acceptance of this work, we were informed about a related approach to include quantum nuclear vibrational effects into *ab initio* EOS data and its application to water and methane [35]. It employs the *ab initio* power spectrum instead of experimental vibrational frequencies and yields similar results for the water Hugoniot temperature.

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