Magnesium oxide at extreme temperatures and pressures studied with first-principles simulations

Permalink
https://escholarship.org/uc/item/0rh739x2

Journal
The Journal of Chemical Physics, 151(21)

ISSN
0021-9606 1089-7690

Authors
Soubiran, François
Gonzalez-Cataldo, Felipe
Driver, Kevin P
et al.

Publication Date
2019-12-07

DOI
10.1063/1.5126624

Peer reviewed
Magnesium Oxide at Extreme Temperatures and Pressures
Studied with First-Principles Simulations

François Soubiran,1,2,∗ Felipe González-Cataldo,1 Kevin P. Driver,1,3 Shuai Zhang,1,4 and Burkhard Militzer1,5,†

1Department of Earth and Planetary Science, University of California, Berkeley, CA 94720, USA
2École Normale Supérieure de Lyon, Université Lyon 1, Laboratoire de Géologie de Lyon, CNRS UMR 5276, 69364 Lyon Cedex 07, France
3Lawrence Livermore National Laboratory, Livermore, California 94550, USA
4Laboratory for Laser Energetics, University of Rochester, Rochester, NY 14623, USA
5Department of Astronomy, University of California, Berkeley, CA 94720, USA

(Dated: January 7, 2020)

We combine two first-principles computer simulation techniques, path integral Monte-Carlo and density functional theory molecular dynamics, to determine the equation of state of magnesium oxide in the regime of warm dense matter, with densities ranging from 0.35 to 71 g cm−3 and temperatures from 10,000 K to 5 × 108 K. These conditions are relevant for the interiors of giant planets and stars as well as for shock wave compression measurements and inertial confinement fusion experiments. We study the electronic structure of MgO and the ionization mechanisms as a function of density and temperature. We show that the L-shell orbitals of magnesium and oxygen hybridize at high density. This results into a gradual ionization of the L-shell with increasing density and temperature. In this regard, MgO behaves differently from pure oxygen, which is reflected in the shape of the MgO principal shock Hugoniot curve. The curve of oxygen shows two compression maxima, while that of MgO shows only one. We predict a maximum compression ratio of 4.66 to occur for a temperature of 6.73 × 107 K. Finally we study how multiple shocks and ramp waves can be used to cover a large range of densities and temperatures.

I. INTRODUCTION

The discovery of numerous exoplanets [1] has renewed the interest in materials at extreme conditions since their behavior determines a planet’s internal structure and evolution. Laboratory experiments and computer simulations have both contributed significantly to the characterization of matter at extreme conditions. Developing accurate equations of state (EOS) for candidate materials is necessary not only to infer planetary formation scenarios, but also to understand how materials respond to extreme conditions including those present in high-velocity impacts, shock compression, and inertial confinement fusion (ICF) experiments [2]. These applications require an EOS that is able to describe different degrees of ionization, as the temperatures can increase by several orders of magnitude during these dynamic compression events. Inconsistencies in the EOS can lead to incorrect interpretations of the experiments or to contradicting planet formation scenarios that arise, for example, from different relations between isentropes and melting curves [3].

Magnesium oxide (MgO) is one of the most abundant minerals in the Earth’s interior and is considered to be a primary building block of planetary formation [4, 5]. It is commonly used as a representative mantle material in exoplanet modeling [4, 6–8]. Shock compression experiments on SiO2 [9, 10] and MgO [5, 11, 12], combined with first principle calculations, demonstrated that these mantle minerals become electrically conducting in the fluid phase. Super-Earth planets can thus generate magnetic fields within their mantles [13]. At ambient conditions, MgO has the rock-salt (B1) structure which is known from experiments to be stable up to at least 227 GPa [14]. Around 500 GPa, it is predicted to transform into the CsCl (B2) structure [15–17], which is believed to be the only stable phase up to at least 40 Mbar, a pressure at which MgO remains solid at least up to 20 000 K [18]. Together with silica (SiO2), MgO is one of the endmembers on the last-stage dissociation of MgSiO3 [16, 19–21].

Recent experiments using plate impacts have measured the shock Hugoniot of a single-crystal MgO preheated to 1850 K, reaching temperatures up to 9100 K and providing a complete EOS for pressures below 250 GPa [22]. The principal Hugoniot of MgO has been explored in the solid and in the liquid phases using plate impacts up to 1200 GPa [23]. More extreme conditions have been achieved with laser-driven shocks [24], providing measurements of the reflectivity, specific heat, and Grüneisen parameter up to 2300 GPa and 64 000 K. According to these experiments, the commonly used tabulated EOSs, such as SESAME and LEOS, have underpredicted the temperature for a given pressure in liquid MgO. Although the melting curve of MgO has been explored with first-principles simulations up to 4000 GPa [25], the properties of the liquid have not been studied for temperatures higher than a few thousand K [26, 27], where significant ionization can take place and an accurate description is required in order to interpret the latest high-temperature experiments on MgO. Recently, the properties of the MgSiO3 plasma have been reported in the warm-dense matter regime [28], where it was shown that the K-shell...
ionization of the oxygen atoms is the cause of a compression maximum along the principal Hugoniot of MgSiO$_3$. This provides an insight into the properties of silicates in the warm-dense matter regime, but a full picture is far from complete. Therefore, a consistent EOS that spans a wide range of temperatures and pressures is needed in order to provide a quantitative picture that accounts for the changes in MgO properties with pressure and temperature.

Path integral Monte Carlo (PIMC) methods have gained considerable interest as a state-of-the-art, stochastic first-principles technique for computing the properties of interacting quantum systems at finite temperature. This formalism results in a highly parallelizable implementation and an accurate description of the properties of materials at high temperature where the electrons are excited to a significant degree [29–33]. The application of the PIMC method to first and second-row elements has been possible due to the development of free-particle [34, 35] and Hartree-Fock nodes [36]. The latter approach enables one to efficiently incorporate localized electronic states into the nodal structure, which extends the applicability of the path integral formalism to heavier elements and lower temperatures [37, 38]. Furthermore, PIMC treats all electrons explicitly, avoiding the use of any pseudopotentials. The PIMC simulation time scales as $1/T$, proportional to the length of the paths, which is efficient at high-temperature conditions, where most electrons including the K shell are excited. The accuracy of PIMC at intermediate temperatures has been shown [39, 40] to be in good agreement with predictions from density functional theory molecular dynamics (DFT-MD) simulations.

Kohn-Sham DFT [41, 42] is a first-principles simulation method that determines the ground state of quantum systems with high efficiency and reasonable accuracy, which has made it a workhorse of computational materials science. It has thus gained considerable use for many years. The introduction of the Mermin scheme [43] enabled the inclusion of excited electronic states, which extended the applicability range of the DFT method to higher temperatures. The combination of this method with molecular dynamics has been widely applied to compute the EOS of condensed matter, warm dense matter (WDM), and dense plasmas [44–47]. It is often the most suitable computation method to derive the EOS under a wide range of conditions because it accounts for both electronic shell and bonding effects. The main source of uncertainty in DFT is the use of an approximate exchange-correlation (XC) functional. The error in the XC functional is generally a negligible fraction of the internal energy, which is the most relevant quantity for the EOS and the derivation of the shock Hugoniot curve [48]. However, the range of validity of this assumption in the WDM regime remains to be verified for different classes of materials through the comparison with laboratory experiments and other simulation methods like PIMC.

In this work, we combine the PIMC and DFT-MD methods to study the properties of MgO in the regime of WDM. The combination of both methods allows us to test the validity of the approximations in the methods. We study the regimes of thermal and pressure ionization of the electronic shells and provide an equation of state that spans a wide range of temperatures and pressure. We describe the electronic properties of liquid MgO and show how the band gap between s and p states closes upon compression, and provide a structural characterization of the liquid. Finally, we compare our PIMC/DFT-MD shock Hugoniot curves with widely used models and experiments.

II. SIMULATIONS METHODS

We perform first-principles computer simulations of magnesium oxide for a range of extreme density and temperature conditions that we illustrate in Fig. 1. At high temperature, we employ path integral Monte Carlo (PIMC) simulations and at lower temperatures we use standard Kohn-Sham density functional theory molecular dynamics (DFT-MD) calculations.

A. PIMC

PIMC is a state-of-the-art first-principles technique for simulating interacting quantum systems at finite temperature. The fundamental techniques for the simulations of bosonic systems were developed in Ref. [49] and later reviewed in Ref. [34]. Subsequently the algorithm was ex-
tended to simulate fermionic systems by introducing the restricted paths approach [35, 50, 51]. The first results of this simulation method were reported in the seminal work on liquid $^3$He [51] and dense hydrogen [52]. In subsequent articles, this method was applied to study hydrogen [53–58], helium [29, 39, 59], hydrogen-helium mixtures [60] and one-component plasmas [61–63]. In recent years, the PIMC method was extended to simulate plasmas of various first-row elements [30, 40, 47, 64–66] and with the development of Hartree-Fock nodes, the simulations of second-row elements became possible [32, 36–38].

This PIMC method is based on the thermal density matrix of a quantum system, \( \hat{\rho} = e^{-\beta \hat{H}} \), that is expressed as a product of higher-temperature matrices by means of the identity \( e^{-\beta \hat{H}} = (e^{-\tau \hat{H}})^M \), where \( M \) is an integer and \( \tau \equiv \beta / M \) represents the step time of a path integral in imaginary time. The path integral emerges when the operator \( \hat{\rho} \) is evaluated in real space,

\[
\langle R | \hat{\rho} | R' \rangle = \frac{1}{N!} \sum_{P} (-1)^{P} \int_{R \to P R'} dR_{t} e^{-S[R_{t}]} .
\]  

Here, we have already summed over all permutations, \( P \), of all \( N \) identical fermions in order project out all antisymmetric states. For sufficiently small time steps, \( \tau \), all many-body correlation effects vanish and the action, \( S[R_{t}] \), can be computed by solving a series of two-particle problems [49, 67, 68]. The advantage of this approach is that all many-body quantum correlations are recovered through the integration over all paths. The integration also enables one to compute quantum mechanical expectation values of thermodynamic observables, such as the kinetic and potential energies, pressure, pair correlation functions and the momentum distribution [34, 69]. Most practical implementations of the path integral techniques rely on Monte Carlo sampling techniques because the integral has \( D \times N \times M \) dimensions (\( D \) is the dimension in space) and, in addition, one needs to sum over all permutations. The method becomes increasingly efficient at high temperature because the length of the paths scales like \( 1 / T \). In the limit of low temperature, where few electronic excitations are present, the PIMC method becomes computationally demanding and the MC sampling can become inefficient. Still, the PIMC method avoids any exchange-correlation approximation and the calculation of single-particle eigenstates, which are embedded in all DFT calculations.

The only uncontrolled approximation within fermionic PIMC calculations is the use of the fixed-node approximation, which restricts the paths in order to avoid the well-known fermion sign problem [35, 50, 51]. Addressing this problem in PIMC is crucial, as it causes large fluctuations in computed averages due to the cancellation of positive and negative permutations in Eq. (1). We solve the sign problem approximately by restricting the paths to stay within nodes of a trial density matrix that we obtain from a Slater determinant of single-particle density matrices,

\[
\rho_{T}(R, R'; \beta) = \left| \left| \rho^{[1]}(r_{i}, r_{j}'; \beta) \right| \right|_{ij} ,
\]

that combined free and bound electronic states [36, 38],

\[
\rho^{[1]}(r, r'; \beta) = \sum_{k} e^{-\beta E_{k}} \Psi_{k}(r) \Psi_{k}^{*}(r')
\]

\[
+ \sum_{l=1}^{N} \sum_{s=0}^{n} e^{-\beta E_{s}} \Psi_{s}(r - R_{l}) \Psi_{s}^{*}(r' - R_{l}) .
\]

The first sum includes all plane waves, \( \Psi_{k} \) while the second represents \( n \) bound states \( \Psi_{s} \) with energy \( E_{s} \) that are localized around all atoms \( l \). Predictions from various slightly differing forms of this approach have been compared in Ref. [37]

All PIMC simulations used periodic boundary conditions and treated 80 electrons, 4 Mg and 4 O nuclei explicitly. We enforced the nodal constraint in small steps of imaginary time of \( \tau = 1 / 8192 \) Ha$^{-1}$, while the pair density matrices [70] were evaluated in steps of $1 / 1024$ Ha$^{-1}$. This results in using between 2560 and 5 time slices for the temperature range that is studied with PIMC simulations here. These choices converged the internal energy per atom to better than 1%. We have shown the associated error is small for relevant systems at sufficiently high temperatures [71].

### B. DFT-MD

Kohn-Sham (KS) DFT-MD [41, 42] is a well-established method to compute the properties of matter in the warm dense matter regime. We thus used the DFT-MD code VASP [72] to perform simulations up to 2 millions Kelvin to complement the PIMC calculations. We restricted our DFT-MD calculations to a range of 2- to 12-fold the ambient density of MgO. We placed from 4 to 32 MgO formula units in a cubic box with periodic boundary conditions. It has been shown in previous work that such a small cell is not detrimental to the accuracy of the EOS data under such high temperatures [38, 66, 73]. To keep the temperature constant, we used a Nosé thermostat [74, 75]. The timestep was adapted to the density and the temperature and ranged from 8.33 as to 0.25 fs for a total duration of several hundred time steps to ensure a relevant estimation of the thermodynamic quantities.

Regarding the DFT calculations, we used the Mermin scheme [43] and employed projector augmented wave [76] pseudopotentials. We were however limited to the existing pseudopotentials of VASP and opted for hard ones with a $ls^{2}$ frozen core for both magnesium and oxygen. The PAW sphere radius was 1.75 bohr for Mg and 1.1 bohr for O. We used the generalized gradient approximation Perdew–Burke–Ernzerhof (PBE) [77] functional for the lowest densities as it has shown to give good results for MgO [13]. At high density the pseudopotentials in PBE were unable to give proper results and we switched
to the local density approximation (LDA). We have a very good agreement between both functionals at 4-fold compression (see paragraph III A). For very high temperatures, the Mermin approach requires computation of the excited states even for low occupation numbers. That is why we computed up to 6000 bands even for the reduced cell size of 8 atoms when we reached temperatures above $10^6$ K. This high number of bands ensured that we computed all the bands up to an energy level associated to an occupation of $10^{-5}$. The systematic error due to this band cut-off is below 0.1%. The energy cut-off for the plane wave basis set had also to be increased at high temperatures up to 7000 eV. We sampled the Brillouin zone with the $\Gamma$ point only which was found to be sufficient for the convergence of the thermodynamic quantities under the conditions of interest.

For the calculation of the density of state (DOS), we used the KS eigenenergy on snapshots sampled every 500 time steps to compute an instantaneous DOS. To obtain a smooth curve, we replaced each eigenvalue by a gaussian centered on the eigenenergy and with an RMS width of 0.5 eV. Each instantaneous DOS was aligned on its Fermi energy so that we could average them. The average DOS was the re-shifted by the average value of the Fermi energy. We also computed the projected DOS (pDOS). Each eigenstate was locally projected on spherical harmonics centered on each nucleus. We could then average the contributions to the DOS by species and by harmonics level.

### III. RESULTS AND DISCUSSION

#### A. Equation of state

![Graph of reduced equation of state](image)

**FIG. 2.** Reduced equation of state of MgO from 2 to 12-fold compression from ambient density as a function of temperature as predicted by DFT (diamonds) and PIMC (circles). The top panel is the relative difference between the total pressure $P$ and the pressure $P_0$ of an ideal gas of nuclei and a Fermi gas of electrons. The bottom panel is the difference between the total internal energy $E$ and the energy $E_0$ of an ideal gas of nuclei and a Fermi gas of electrons. Different isochores have been shifted apart for clarity.

The internal energies that were derived in the VASP DFT-MD simulations with LDA and PBE functionals were shifted respectively by $-273.6020398$ and $-274.9006146$ Ha per MgO formula unit in order to make them compatible with the all-electron energies that we obtained with the PIMC simulations.

In Fig. 2 we plotted the relative excess pressure and energy with respect to an ideal gas of nuclei and Fermi gas of electrons. Regarding the DFT part solely, there is good agreement between LDA and PBE calculations at 4-fold compression ensuring a smooth transition from one data set to another. As temperature increases, DFT becomes too computationally expensive around the same conditions that PIMC first becomes viable. For MgO we managed to obtained good agreement between PIMC and DFT at 1,347,305 K. Near this temperature, the relative difference in the pressure is less than 3.5%, and the difference in the energy ranges from 2.5 to 5.3 Ha/nucleus. These are maximum differences between

![Graph of temperature-pressure conditions](image)

**FIG. 3.** Temperature-pressure conditions for the PIMC and DFT-MD calculations along isochores corresponding to the densities of 0.1-fold (upper left curve) to 20-fold (right curve) the ambient density. The shock Hugoniot curves with and without radiation effects were included as well as a number of isentropes.
PIMC and DFT-MD, as they are reported for the 12-fold compression case, where we are most severely affected by pseudo-potential overlap and frozen core effects. Globally, the agreement is very satisfactory.

With our PIMC simulations, we were able to reach densities as low as 0.1 times the ambient density but not with DFT because of numerical limitations (both in computer time and in memory needs). For high densities, DFT was limited by the pseudo-potentials available, preventing any simulations beyond 12-fold compression. However, as can be seen in Fig. 3 our data set still covers an extremely wide range of pressures and temperatures. Our entire EOS table is provided as supplementary material. This allows to benchmark other faster but more approximate EOS methods for a wide range of conditions.

To extrapolate the present EOS towards other conditions it is possible to use other approximations such as the fully ionized plasma [78] for high densities or a chemical model at low density. Such an approach has been recently performed on H-He mixtures [79]. It is also possible to improve the EOS by a careful characterization of the free energy using thermodynamic integration. This work has been performed on H-He at temperatures relevant for the interior of giant planets [80].

B. Electronic and Ionic Structures

From PIMC simulations, a measure of the degree of ionization can be obtained from the integrated nucleus-electron pair correlation function, \( N(r) \), given by

\[
N(r) = \left\langle \frac{1}{N_I} \sum_{e,I} \Theta(r - ||\vec{r}_e - \vec{r}_I||) \right\rangle, \tag{5}
\]

where \( N(r) \) represents the average number of electrons within a sphere of radius \( r \) around a given nucleus of atom of type \( I \). The summation includes all electron-nucleus pairs and \( \Theta \) represents the Heaviside function. Fig. 4 shows the integrated nucleus-electron pair correlation function for temperatures from \( 1 \times 10^6 \) K to \( 65 \times 10^6 \) K and densities from 0.357 g cm\(^{-3}\) (0.1-fold) to 71.40 g cm\(^{-3}\) (20-fold compression). For comparison, the \( N(r) \) functions of an isolated nucleus with a doubly occupied 1s orbital were included. Unless the 1s state is ionized, its contribution will dominate the \( N(r) \) function at small radii of \( r < 0.2 \) Bohr radii. For larger radii, contributions from other electronic shells and neighboring nuclei will enter. Still, this is the most direct approach available to compare the degree of 1s ionization of the three nuclei.

At 0.1-fold compression, the comparison with the corresponding curves for the isolated nuclei shows that the ionization of the 1s states of the Mg nuclei occurs over the temperature interval from 2.0 to \( 8.1 \times 10^6 \) K. Conversely, the ionization of 1s state of the oxygen nuclei occurs from 1.3 to \( 4.0 \times 10^6 \) K, which reflects the difference in binding energy that scales with the square of the nuclear charge, \( Z \). Consistent with this interpretation, one finds no evidence of an ionization of the 2s states of Mg nuclei at \( 1.0 \times 10^6 \) K while those of the oxygen nuclei are partially ionized, as the comparison with calculations of isolated nuclei in Fig. 4 shows.

When the density is increased from 0.1- to 1.0-fold compression (second row of panels in Fig. 4), the degree of 1s ionization is reduced. For the Mg and O nuclei, the \( N(r) \) functions at small \( r \) are closer to doubly occupied 1s state than they were before. This trend continues as we increase the density to 4.0 and 20-fold compression. The degree of 1s ionization is consistently reduced with increasing density when the results are compared for the same temperature. Most noticeable are the deviations for a temperature of \( 8.1 \times 10^6 \) K. At 0.1-fold compression the 1s states of both nuclei are essentially fully ionized while they still appear to be partially occupied for this temperature at 20-fold compression.

In Fig. 4, we also show the electron-electron pair correlation functions, \( g(r) \), that we derived from our all-electron PIMC simulations. Without any Coulomb interactions, this function would equal 1 for all \( r \) for electron pairs with opposite spin. This is also true for pairs with the same spin for large distances, but for small \( r \), this function must drop to zero because of Pauli exclusion. The trend for very small \( r \) can be seen in right column of Fig. 4 where we plot the \( g(r) \) functions for the fully interacting MgO system. For all other \( r \) values, these functions are substantially modified by the Coulomb interaction effects, as expected. At low density and low temperature, one finds strong positive correlations that reflect the fact that electrons with both types of spins occupy bound states at the same nuclei. With increasing temperature, the electrons become ionized and the positive correlation disappears. At small \( r \) Pauli exclusion dominates which introduces difference into the pair correlation functions between electrons with parallel and opposite spin. For large \( r \), these function are always very similar.

For lower temperature conditions that we studied with DFT-MD simulations, one can derive information about the electronic properties by analyzing the Kohn-Sham eigenstates. In Fig. 5 we plotted the density of states (DOS) for \( 10^5 \) K at three different densities. The full DOS shows that the system becomes increasingly pressure ionized with increasing density. Peaks in the DOS, that are narrow at low density, broaden and merge with the continuum of free states. In the KS-DFT framework, we can also approximately decompose the DOS into contributions from different nuclei and orbital character. We included the results from various such projections in Fig. 5. At 2-fold compression, the first two peaks correspond to the L shell of magnesium while the M-shell states have already merged with the continuum. The second set of two peaks between \(-20\) and \( 20 \) eV correspond to the s and p orbitals of oxygen L-shell. We retrieve a very similar feature in our simulations for pure oxygen [73] that showed oxygen orbitals that could be
As the density is increased, we can still identify two L-shell peaks of magnesium: a first one (L\(_d\)) with s character and a second (L\(_\Pi,III\)) with p character. However, already at 6-fold and much more at 10-fold compression, both types of orbitals hybridize and form very broad peaks without a clear gap. For oxygen, the s-type peak has already disappeared at 6-fold which is very different from predictions for pure oxygen [82]. However, it reminds one of the electronic properties of the carbon in dense plastics [66]. This phenomena is likely caused by the hybridization of the p orbital of magnesium with the s and p orbitals of oxygen. This produces a very large broadening of the oxygen L-band which gradually merges with the continuum with increasing density. The observed hybridization of magnesium and oxygen orbitals has thus consequences for the ionization state of MgO at extreme conditions. These effects will be difficult to reproduce with average atom models that describe mixtures of dense atoms as a collection of noninteracting species.

With the nuclear configurations extracted from the MD trajectories, we can determine the local structure of the plasma as a function of the density and temperature. In Fig. 6, we illustrate changes in this structures with a series of pair correlation functions. With increasing density and decreasing temperature, the liquid becomes more structured and the peaks in the correlation functions increase. Under no conditions we found a signature of a stable molecular bond between Mg and O species. How-
ever, the Mg and O nuclei exhibit positive correlations that are slightly stronger than that between the other pairs. This was seen in Ref. [83] and is due to an imbalance in their respective charge states. In comparison to our recent work [33] on boron nitride (BN) which shows a structure-less feature in $g(r)$ at $5 \times 10^4$–$10^5$ K, our results on MgO show that correlation remains up to $5 \times 10^5$ K. This is consistent with the electronic structure analysis above and indicates that an average-atom approach would be less trustworthy for MgO at below $5 \times 10^5$ K, higher than that for BN ($10^5$ K) because of the deeper K shells of Mg and O than B and N.

C. Single and Multi Shock Hugoniot Curves

Dynamic shock compression experiments allow one to directly measure the equation of state and other physical properties of hot, dense fluids. Such experiments are often used to determine the principal Hugoniot curve, which is the locus of final states that can be obtained from different shock velocities. Density functional theory has been validated by experiments as an accurate tool for predicting the shock compression of a variety of different materials [44–46].

During a shock wave experiment, a material whose initial state is characterized by an internal energy, pressure, and volume, $(E_0, P_0, V_0)$, will change to a final state denoted by $(E, P, V)$ while conserving mass, momentum, and energy. This leads to the Rankine-Hugoniot relation [84],

$$\left(E - E_0\right) + \frac{1}{2}(P + P_0)(V - V_0) = 0.$$  \hspace{1cm} (6)

Here, we solve this equation for our computed first-principles EOS data set, only in the liquid phase. We obtain a continuous Hugoniot curve by interpolating the EOS data with splines as a function of $\rho$ and $T$. The Hugoniot curve for the liquid state only depends on the liquid EOS and the initial point, but not on the path followed in the solid phases. In order to obtain the principal Hugoniot curve, we used initial conditions based on the energy and pressure of ambient, solid MgO in the B1 phase computed with static DFT calculations at the experimental density of 3.570 g cm$^{-3}$ ($V_0 = 18.7478216$ Å$^3$/MgO). Depending on which DFT functional we use, we obtained two slightly different initial energies, $E_{0}^{\text{LDA}} = -274.6138119$ and $E_{0}^{\text{PBE}} = -275.3370951$ Ha/MgO. The difference between these two values is small compared the $\sim 50,000$ Ha/MgO that the internal energy changes along the shock Hugoniot curve in the temperature interval that we study here. However, one would want to make reasonable choice to minimize the error that arises from choosing a particular DFT functional. Thus, when we evaluate the $(E - E_0)$ term in Eq. 6, we use values derived with the same functional. When we use PIMC values for $E$, we combine
FIG. 6. Nuclear pair correlation functions 2-fold (left), 4-fold (middle) and 10-fold compression (right column) at different temperatures given in the legend. The different rows show these functions for Mg-Mg, Mg-O, and O-O pairs of nuclei.

them with $E_0^\text{PBE}$ because this has work well in Ref. [37]. The resulting shock Hugoniot curve has been added to Figs. 1, 3, 7, 8, and 9.

The principal Hugoniot curve in Fig. 7 and 8 exhibits a wide pressure interval where the compression ratio exceeds 4.0, the asymptotic value for a non-relativistic ideal gas. Such high compression values are the result of excitations of internal degrees of freedom [29], which increase the internal energy term in Eq. (6). Consequently, the second term in this equation becomes more negative, which reduces the volume $V$ and thus increases the compression ratio. Indeed, at a pressure of 18666 GPa and a temperature of 525 000 K, the shock compression ratio starts to exceed 4, which are conditions where the $L$ shell electrons are already ionized. The bulk of the high compression region is dominated by the ionization of the K shell (1s) electrons of the Mg and O nuclei. However, instead of two separate compression peaks, we see a broad region of increased compression indicating that the two peaks have merged due to interaction effects [39].}

No experimental data are available in the K- and L-shell ionization regimes yet. In the TPa regime, we obtain an excellent agreement between our predictions and the experimental data by Root et al. [23] and McCoy et al. [24] (see Fig. 8), which underline the robustness of our DFT-MD calculations.

The highest compression ratio of 4.66 is reached for $6.73 \times 10^7$ K and 421 000 GPa, which coincides in pressure with the upper compression maximum of the shock Hugoniot curve of pure silicon, which has also been attributed to K shell ionization [36]. Based on this comparison and the K shell ionization analysis of MgO in Fig. 4 we conclude that the upper part of the high compression region in Fig. 7 is dominated by the ionization of the K shell electrons of the Mg nuclei while the lower end around $10^5$ GPa and $2 \times 10^6$ K, marks the beginning of the K shell ionization of the oxygen ions as Fig. 4 confirms. However, in shock compressed pure oxygen, the K shell ionization peak occurs for lower P and T. We attribute this difference to interaction effects in hot, dense MgO.
that can shift the compression peaks along the Hugoniot curve to higher temperatures and pressures and reduce the peak compression [39].

It is interesting to note that we do not see a separate compression maximum for the L shell ionization while such maxima were seen in simulations of pure nitrogen and oxygen [38, 64]. In Figs. 7 and 8, we instead see a slight lowering in temperature, or pressure respectively, from approximately 3.2 to 4.2-fold compression, which we attribute to the L-shell ionization of the Mg and O nuclei because the same shape was seen in simulations of dense CH plastic and associated with the ionization of the L-shell of the carbon nuclei (see Fig. 3 of Ref. [66]). We conclude that L shells of the Mg and O nuclei are ionized gradually, as it occurs in dense carbon and boron materials [33, 40, 47]. This interpretation is consistent with the electronic structure observed in Fig. 5 where the oxygen and magnesium electronic states are strongly hybridized at high compression.

The Hugoniot curves in Figs. 7 and 8 show a small shoulder at 4.3-fold compression. We determined this to be a robust feature even though we switch between DFT-MD and PIMC data sets in this regime. Our EOS table (see supplementary material in section ??) is sufficiently dense so that different interpolation schemes for the pressure and internal energy yield consistent results. For example, even with linear interpolation we have obtained very similar Hugoniot curves.

Very approximately, we added relativistic and radiation effects to the Hugoniot curves in Fig. 7. Under the assumption of complete ionization, the relativistic corrections were derived for an ideal gas of electrons. This increases the shock compression ratio for \( P > 7 \times 10^6 \) GPa and \( T > 10^8 \) K.

Considering an ideal black body scenario, we derived the photon contribution to the EOS using \( P_{\text{radiation}} = \frac{4\pi \sigma}{3c}T^4 \) and \( E_{\text{radiation}} = 3P_{\text{radiation}}V \), where \( \sigma \) is the Stefan-Boltzman constant and \( c \) is the speed of light in vacuum. We find that radiation effects are important only for temperatures above \( 2 \times 10^7 \) K, which is above the temperature necessary to completely ionize the 1s orbitals of Mg and O species.

In Fig. 9, we show a number of double-shock Hugoniot curves. Various points along the principal Hugoniot curve were chosen as initial conditions for a second shock that compresses the material again reaching densities that are much higher than can probed with single shocks. If one starts from the high compression point on the principal Hugoniot curve, one can reach densities of \( 65 \text{ g cm}^{-3} \). However, the compression ratio is typically not as high because the strength of the interaction effects increases and this lowers the compression ratio. For the secondary shock Hugoniot curves that we show in Fig. 9, the maximum compression ratio varied between 4.51 and 3.97 while the maximum compression ratio of the principal Hugoniot curve was 4.66.

Fig. 9 also compares our secondary Hugoniot curves with our isentropes and isotherms. For weak second shocks, the secondary Hugoniot curves and isentropes almost coincide, which implies that the second shock produces very little irreversible heat. As the strength of the second shock increases, more and more irreversible heat is generated.

In Fig. 10, we compare an isentrope with various multi-shock Hugoniot curves in order to determine how closely one can trace an isentrope by breaking up a sin-
FIG. 9. Single and double shock Hugoniot curves are compared with a family of isentropes. For weak second shocks, minimal shock heating is introduced and the secondary Hugoniot curves behave like isentropes. For stronger second shocks, the heating is substantial and the resulting Hugoniot curve is similar to the shock curve for a precompressed sample.

ingle shock into multiple smaller shocks. All curves start from 20 000 K, twice the ambient density, and 1386 GPa. The isentrope [85] was derived from our EOS table using $\frac{dT}{dP}|_S = -\frac{T}{\rho V} \frac{dP}{dE}|_V$. For weak shocks, the Hugoniot curve does not deviate much from an isentrope. For strong shocks, a substantial amount of shock heating occurs. The resulting single-shock Hugoniot curves are thus much hotter than an isentrope when both are compared for the same pressure. The discrepancy depends significantly on pressure, which reflects the fact that the final shock density cannot exceed 4.7-fold the initial density (Fig. 7). To reach a large final shock pressure, a substantial pressure contribution must come from the thermal pressure, which requires high temperatures.

One can, however, get arbitrarily close to isentropic compression by breaking up a single shock experiments into multiple weaker shocks. The purpose of Fig. 10 is to assess quantitatively how well this method works for shocks in MgO and to determine how much shock heating still occurs if the shock is broken up into $N = 2$–10 steps. In our multi-shock calculations, we successively solve Eq. 6 to connect the intermediate shock states. In order to obtain the lowest possible shock temperature for a given number of shocks, we keep the final shock pressure fixed while we carefully adjust the temperatures of the intermediate shocks until we determined the global minimum of the final shock temperature with sufficient accuracy.

As expected, all the resulting multi-shock Hugoniot curves converge to an isentrope for weak shocks. For strong shocks such as $P_{\text{final}}/P_{\text{initial}} \approx 31$, we find the temperature of single-shock temperature is 8.36 times higher than the corresponding temperature on the isentrope. If this shock is broken up into two, well-chosen smaller shocks, the final shock temperature be reduced to 4.00 times the value on the isentrope. If three, four, five, or even ten shocks are employed the final shock temperature can, respectively, be reduced to 2.64, 2.02, 1.72, or 1.29 times the isentropic value. This are substantial reductions compared to the single-shock temperatures.

IV. CONCLUSION

By combining results from PIMC and DFT-MD simulations, we provided a consistent EOS table for MgO in the regime of warm, dense matter (see supplemental material), which includes conditions where the K- and L-shell electrons of both nuclei are ionized. The ionization of the L-shell only introduces a small increase in compression along the shock Hugoniot curve. The K shell ionization of both nuclei, however, introduces a broad temperature interval where shock compression exceeds values of 4.5. The maximum compression ratio of 4.66 is reached for conditions of 6.378 000 K and $\rho = 2\rho_0$ were chosen as initial conditions. The circles represent the DFT-MD simulation points that we used in this analysis.
the ionization processes. It will make it challenging for other theoretical methods to approximate the properties of MgO by combining EOS tables of Mg and O without fully taking into account their interaction effects. But it also demonstrates that elements with a relatively close atomic number may be strongly influenced by one another. This could have some significance for ICF experiments and for stellar interior opacities where the radiative properties and thus the ionization stage is of essence.

**SUPPLEMENTARY MATERIAL**

We provide our equation of state as a table in text format. The columns contain the following quantities.

| No. | Description |
|-----|-------------|
| 1   | Simulation method: PIMC, DFT-MD with GGA (PBE) or LDA functional. |
| 2   | Volume per MgO formula unit in Angstrom³. |
| 3   | Mass density in g cm⁻³. |
| 4   | Temperature in Kelvin. |
| 5   | Pressure in GPa. |
| 6   | Internal energy in Hartree per MgO formula unit. |
| 7   | 1-σ uncertainty of pressure. |
| 8   | 1-σ uncertainty of energy. |

10: 1-σ uncertainty of energy.

**ACKNOWLEDGMENTS**

This work was in part supported by the National Science Foundation-Department of Energy (DOE) partnership for plasma science and engineering (grant DE-SC0016248), by the DOE-National Nuclear Security Administration (grant DE-NA0003842), and the University of California Laboratory Fees Research Program (grant LFR-17-449059). F.S. was in part supported by the European Union through a Mari Sklodowska-Curie action (grant 750901). F.G.-C. acknowledges support from the CONICYT Postdoctoral fellowship (grant 74160058). Computational support was provided by the Blue Waters sustained-petascale computing project (NSF ACI 1640776) and the National Energy Research Scientific Computing Center.

[1] The Extrasolar Planets Encyclopedia http://exoplanet.eu/
[2] B.A. Hammel, S.W. Haan, D.S. Clark, M.J. Edwards, S.H. Langer, M.M. Marinak, M.V. Patel, J.D. Salmonson, and H.A. Scott. High-mode rayleigh-taylor growth in nif ignition capsules. *High Energy Density Physics*, 6(2):171 – 178, 2010. ICHED 2009 - 2nd International Conference on High Energy Density Physics.
[3] D. E. Fratanduono, M. Millot, R. G. Kraus, D. K. Spaulding, G. W. Collins, P. M. Celliers, and J. H. Eggert. Thermodynamic properties of MgSiO₃ at super-Earth mantle conditions. *Phys. Rev. B*, 97(21):214105, jun 2018.
[4] Diana Valencia, Masahiro Ikoma, Tristan Guillot, and Nadine Nettelmann. Composition and fate of short-period super-Earths. *Astronomy & Astrophysics*, 516(section 4):A20, jun 2010.
[5] R. M. Bolis, G. Morard, T. Vinci, A. Ravasio, E. Bambrik, M. Guarguagliani, M. Koenig, R. Musella, F. Remus, J. Bouhet, N. Ozaki, K. Miyanishi, T. Sekine, Y. Sakawa, T. Sano, R. Kodama, F. Guyot, and A. Benuzzi-Mounaix. Decaying shock studies of phase transitions in MgO-SiO₂ systems: Implications for the super-Earths’ interiors. *Geophysical Research Letters*, 43(18):9475–9483, 2016.
[6] Sara Seager, M. Kuchner, C. A. Hier-Majumder, and Burkhard Militzer. Mass-Radius Relationships for Solid Exoplanets. *The Astrophysical Journal*, 669(2):1279–1297, nov 2007.
[7] Diana Valencia, Richard J. O’Connell, and Dimitar D. Sasselov. The role of high-pressure experiments on determining super-Earth properties. *Astrophysics and Space Science*, 322(1-4):135–139, 2009.
[8] F W Wagner, N Tosi, F. Sohl, H Rauer, and T Spohn. Rocky super-Earth interiors. *Astronomy & Astrophysics*, 541:A103, may 2012.
[9] D. G. Hicks, T. R. Boebly, J. H. Eggert, J. E. Miller, P. M. Celliers, and G. W. Collins. Dissociation of Liquid Silica at High Pressures and Temperatures. *Phys. Rev. Lett.*, 97(2):025502, 2006.
[10] M Millot, N a Dubrovinskaia, A Černok, S Blaha, L Dubrovinsky, DG Braun, PM Celliers, GW Collins, JH Eggert, and R Jeanloz. Shock compression of stishovite and melting of silica at planetary interior conditions. *Science*, 347(6220):418–420, 2015.
[11] R Stewart McWilliams, Dylan K Spaulding, Jon H Eggert, Peter M Celliers, Damien G Hicks, Raymond F Smith, Gilbert W Collins, and Raymond Jeanloz. Phase transitions and metatization of magnesium oxide at high pressure and temperature. *Science*, 338(6112):1330–1333, 2012.
[12] K Miyanishi, Y Tange, N Ozaki, T Kimura, T Sano, Y Sakawa, T Tsuchiya, and R Kodama. Laser-shock compression of magnesium oxide in the warm-dense-matter regime. *Phys. Rev. E*, 92(2):023103, 2015.
[13] François Soubiran and Burkhard Militzer. Electrical conductivity and magnetic dynamos in magma oceans of Super-Earths. *Nature Communications*, 9(1):3883, dec 2018.
[14] Thomas S Duffy, Russell J Hemley, and Ho-kwang Mao. Equation of state and shear strength at megabar pressures: Magnesium oxide to 227 gpa. *Physical Review Letters*, 74(8):1371, 1995.
[15] Anatoly B. Belonoshko and Leonid S. Dubrovinsky. Molecular dynamics of NaCl (B1 and B2) and MgO (B1) melting; two-phase simulation. *American Mineralogist*, 81(3-4):303–316, apr 1996.
[16] Brian Boates and Stanimir a. Bonev. Demixing Instability in Dense Molten MgSiO$_3$ and the Phase Diagram of MgO. Physical Review Letters, 110(13):135504, mar 2013.

[17] J. Bouchet, F. Bottin, V. Recoules, F. Remus, G. Morard, R. M. Bolis, and A. Benuzzi-Mounaix. Ab initio calculations of the B1-B2 phase transition in MgO. Physical Review B, 99(9):094113, mar 2019.

[18] Hugh F. Wilson and Burkhard Militzer. Rocky Core Solubility in Jupiter and Giant Exoplanets. Physical Review Letters, 108(11):111101, mar 2012.

[19] Taku Tsuchiya, Jun Tsuchiya, Koichiro Umemoto, and Renata M. Wentzcovitch. Phase transition in MgSiO$_3$ perovskite in the earth’s lower mantle. Earth and Planetary Science Letters, 224(3-4):241–248, aug 2004.

[20] Koichiro Umemoto and Renata M. Wentzcovitch. Two-stage dissociation in MgSiO$_3$ post-perovskite. Earth and Planetary Science Letters, 311(3-4):225–229, nov 2011.

[21] Koichiro Umemoto, Renata M. Wentzcovitch, Shunqing Wu, Min Ji, Cai-zhuang Wang, and Kai-ming Ho. Phase transitions in MgSiO$_3$ post-perovskite in super-Earth mantles. Earth and Planetary Science Letters, 478:40, 2017.

[22] O. V. Fat’yanov, P. D. Asimow, and T. J. Ahrens. Thermodynamically complete equation of state of mgo from true radiative shock temperature measurements on samples preheated to 1850 k. Phys. Rev. B, 97:024106, Jan 2018.

[23] Seth Root, Luke Shulenburger, Raymond W. Lemke, Daniel H. Dolan, Thomas R. Mattsson, and Michael P. Desjarlais. Shock Response and Phase Transitions of MgO at Planetary Impact Conditions. Physical Review Letters, 115:198501, 2015.

[24] C. A. McCoy, M. C. Marshall, D. N. Polsin, D. E. Fratanduono, P. M. Celliers, D. D. Meyerhofer, and T. R. Boehly. Hugoniot, sound velocity, and shock temperature of mgo to 2300 gpa. Phys. Rev. B, 100:014106, Jul 2019.

[25] Takashi Taniuchi and Taku Tsuchiya. The melting points of MgO up to 4 TPa predicted based on the ab initio thermodynamic integration molecular dynamics. Journal of Physics: Condensed Matter, 56(1-2):201–209, feb 2018.

[26] Dario Alfè. Melting Curve of MgO from First-Principles Simulations. Physical Review Letters, 94(23):235701, jun 2005.

[27] Nico de Koker and Lars Stixrude. Self-consistent thermodynamic description of silicate liquids, with application to shock melting of MgO periclase and MgSiO$_3$ perovskite. Geophysical Journal International, 178(1):162–179, jul 2009.

[28] Felipe González-Cataldo, François Soubiran, Henry Peterson, and Burkhard Militzer. Path Integral Monte Carlo and Density Functional Molecular Dynamics Simulations of Warm, Dense MgSiO$_3$. Phys. Rev. B., submitted.

[29] B. Militzer. First principles calculations of shock compressed fluid helium. Phys. Rev. Lett., 97:175501, Oct 2006.

[30] L. X. Benedict, K. P. Driver, S. Hannel, B. Militzer, T. Qi, A. A. Correa, A. Saul, and E. Schwegler. A multiphase equation of state for carbon addressing high pressures and temperatures. Phys. Rev. B, 89:224109, 2014.

[31] K. P. Driver and B. Militzer. First-principles simulations and shock Hugoniot calculations of warm dense neon. Phys. Rev. B, 91(4):045103, jan 2015.

[32] S. X. Hu, B. Militzer, L. A. Collins, K. P. Driver, and J. D. Kress. First-principles prediction of the softening of the silicon shock hugoniot curve. Phys. Rev. B, 94:094109, Sep 2016.

[33] Shuai Zhang, Amy Lazicki, Burkhard Militzer, Lin H. Yang, Kyle Caspersen, Jim A. Gaffney, Markus W. Däne, John E. Pask, Walter R. Johnson, Abhiraj Sharma, Panhian Suryanarayana, Duane D. Johnson, Andrey V. Smirnov, Philip A. Sterne, David Erskine, Richard A. London, Federica Coppari, Damian Swift, Joseph Nilsen, Art J. Nelson, and Heather D. Whitley. Equation of state of boron nitride combining computation, modeling, and experiment. Phys. Rev. B, 99:165103, Apr 2019.

[34] D. M. Ceperley. Path integrals in the theory of condensed helium. Rev. Mod. Phys., 67:279–355, Apr 1995.

[35] David Ceperley. Monte carlo and molecular dynamics of condensed matter systems. volume 49, page 443. Editrice Compositori, Bologna, Italy, 1996.

[36] Burkhard Militzer and Kevin P. Driver. Development of Path Integral Monte Carlo Simulations with Localized Nodal Surfaces for Second-Row Elements. Phys. Rev. Lett., 115(17):176403, oct 2015.

[37] Shuai Zhang, Kevin P. Driver, François Soubiran, and Burkhard Militzer. Equation of state and shock compression of warm dense sodium—A first-principles study. J. Chem. Phys., 140(7):074505, feb 2017.

[38] Kevin P. Driver, François Soubiran, and Burkhard Militzer. Path integral Monte Carlo simulations of warm dense aluminum. Phys. Rev. E, 97(6):063207, jun 2018.

[39] B. Militzer. Path integral Monte Carlo and density functional molecular dynamics simulations of hot, dense helium. Phys. Rev. B, 79:155105, Apr 2009.

[40] Shuai Zhang, Burkhard Militzer, Lorin X. Benedict, François Soubiran, Philip A. Sterne, and Kevin P. Driver. Path integral Monte Carlo simulations of dense carbon-hydrogen plasmas. J. Chem. Phys., 148(10):102318, mar 2018.

[41] P. Hohenberg and W. Kohn. Inhomogeneous electron gas. Phys. Rev., 136:B864–B871, Nov 1964.

[42] W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. Phys. Rev., 140:A1133–A1138, Nov 1965.

[43] N. David Mermin. Thermal properties of the inhomogeneous electron gas. Phys. Rev., 137:A1441–A1443, Mar 1965.

[44] Seth Root, Rudolph J. Magyar, John H. Carpenter, David L. Hanson, and Thomas R. Mattsson. Shock compression of a fifth period element: Liquid xenon to 840 gpa. Phys. Rev. Lett., 105:085501, Aug 2010.

[45] Xiaoli Wang, Fubo Tian, Liancheng Wang, Tian Cui, Bingbing Liu, and Guangtian Zou. Structural stability of polymeric nitrogen: A first-principles investigation. J. Chem. Phys., 132(2):024502, 2010.

[46] Thomas R. Mattsson, Seth Root, Ann E. Mattsson, Luke Shulenburger, Rudolph J. Magyar, and Dawn G. Flicker. Valicado. Compositori, Bologna, Italy, 1996.

[47] Thomas R. Mattsson, Seth Root, Ann E. Mattsson, Luke Shulenburger, Rudolph J. Magyar, and Dawn G. Flicker. Validating density-functional theory simulations at high energy-density conditions with liquid krypton shock experiments to 850 gpa on sandia’s z machine. Phys. Rev. B, 90:184105, Nov 2014.

[48] Shuai Zhang, Burkhard Militzer, Michelle C. Gregor, Kyle Caspersen, Lin H. Yang, Jim Gaffney, Tadashi Ogitsu, Damian Swift, Amy Lazicki, D. Erskine, Richard A. London, P. M. Celliers, Joseph Nilsen, Philip A. Sterne,
and Heather D. Whitley. Theoretical and experimental investigation of the equation of state of boron plasmas. *Phys. Rev. E*, 98(2):023205, aug 2018.

[48] Valentin V. Karasiev, Lázaro Calderín, and S. B. Trickey. Importance of finite-temperature exchange correlation for warm dense matter calculations. *Phys. Rev. E*, 93:063207, Jun 2016.

[49] E. L. Pollock and D. M. Ceperley. Simulation of quantum many-body systems by path-integral methods. *Phys. Rev. B*, 30:2555–2568, Sep 1984.

[50] D. M. Ceperley. Fermion nodes. *Journal of Statistical Physics*, 63(5-6):1237–1267, jun 1991.

[51] D. M. Ceperley. Path-integral calculations of normal liquid 3He. *Phys. Rev. Lett.*, 69:331–334, Jul 1992.

[52] C. Pierleoni, D. M. Ceperley, B. Bernu, and W. R. Magro. Equation of state of the hydrogen plasma by path integral monte carlo simulation. *Phys. Rev. Lett.*, 73:2145–2149, Oct 1994.

[53] W. R. Magro, D. M. Ceperley, C. Pierleoni, and B. Bernu. Molecular dissociation in hot, dense hydrogen. *Phys. Rev. Lett.*, 76:1240–1243, Feb 1996.

[54] Burkhard Militzer, William Magro, and David Ceperley. Characterization of the state of hydrogen at high temperature and density. *Contributions to Plasma Physics*, 30(1-2):151–154, 1999.

[55] Burkhard Militzer. *Path Integral Monte Carlo Simulations of Hot Dense Hydrogen*. PhD thesis, University of Illinois at Urbana-Champaign, 2000.

[56] Burkhard Militzer and D. M. Ceperley. Path Integral Monte Carlo Calculation of the Deuteron Hugoniot. *Phys. Rev. Lett.*, 85(9):1890–1893, aug 2000.

[57] B. Militzer and D. M. Ceperley. Path integral monte carlo simulation of the low-density hydrogen plasma. *Phys. Rev. E*, 63:966404, May 2001.

[58] B. Militzer, D. M. Ceperley, J. D. Kress, J. D. Johnson, L. A. Collins, and S. Mazevet. Calculation of a deuteron double shock hugoniot from ab initio simulations. *Phys. Rev. Lett.*, 87:275502, Dec 2001.

[59] Burkhard Militzer. Correlations in hot dense helium. *Journal of Physics A: Mathematical and Theoretical*, 42(21):214001, may 2009.

[60] Burkhard Militzer. Hydrogen–helium mixtures at high pressure. *Journal of Low Temperature Physics*, 139(5):739–752, Jun 2005.

[61] M. D. Jones and D. M. Ceperley. Crystallization of the one-component plasma at finite temperature. *Phys. Rev. Lett.*, 76:4572–4575, Jun 1996.

[62] E. L. Pollock and B. Militzer. Dense plasma effects on nuclear reaction rates. *Phys. Rev. Lett.*, 92:021101, Jan 2004.

[63] B. Militzer and E. L. Pollock. Equilibrium contact probabilities in dense plasmas. *Phys. Rev. B*, 71:134303, Apr 2005.

[64] K. P. Driver and B. Militzer. First-principles equation of state calculations of warm dense nitrogen. *Phys. Rev. B*, 93:064101, Feb 2016.

[65] Kevin P. Driver and Burkhard Militzer. First-principles simulations of warm dense lithium fluoride. *Phys. Rev. E*, 95(4):043205, 2017.

[66] Shuai Zhang, Kevin P. Driver, François Soubiran, and Burkhard Militzer. First-principles equation of state and shock compression predictions of warm dense hydrocarbons. *Phys. Rev. E*, 96(1):013204, jul 2017.

[67] Vincent Natoli and David M Ceperley. An optimized method for treating long-range potentials. *Journal of Computational Physics*, 117(1):171–178, 1995.

[68] B. Militzer. Computation of the high temperature coulomb density matrix in periodic boundary conditions. *Comp. Phys. Comm.*, 204:88, 2016.

[69] B. Militzer, E.L. Pollock, and D.M. Ceperley. Path integral Monte Carlo calculation of the momentum distribution of the homogeneous electron gas at finite temperature. *High Energy Density Physics*, 30(October 2018):13–20, jan 2019.

[70] B Militzer. Computation of the high temperature Coulomb density matrix in periodic boundary conditions. *Computer Physics Communications*, 204:88–96, jul 2016.

[71] Kevin P. Driver and Burkhard Militzer. All-Electron Path Integral Monte Carlo Simulations of Warm Dense Matter: Application to Water and Carbon Plasmas. *Phys. Rev. Lett.*, 108(11):115502, mar 2012.

[72] G Kresse and D. Joubert. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B*, 59(3):1758–1775, jan 1999.

[73] Kevin P. Driver, François Soubiran, Shuai Zhang, and Burkhard Militzer. First-principles equation of state and electronic properties of warm dense oxygen. *J. Chem. Phys.*, 143:164507, 2015.

[74] Shuichi Nosé. A unified formulation of the constant temperature molecular dynamics methods. *J. Chem. Phys.*, 81:511–519, 1984.

[75] Shuichi Nosé. Constant Temperature Molecular Dynamics Methods. *Prog. Theor. Phys. Suppl.*, 103:1, 1991.

[76] P E Blöchl. Projector augmented-wave method. *Phys. Rev. B*, 50(24):17953–17979, 1994.

[77] John P. Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.*, 77(18):3865–3868, oct 1996.

[78] G. Chabrier and A. Y. Potekhin. Equation of state of fully ionized electron-ion plasmas. *Phys. Rev. E*, 58:4941, 1998.

[79] G. Chabrier, S. Mazevet, and F. Soubiran. *Astrophys. J.*, 872:51, 2019.

[80] B Militzer and W B Hubbard. Ab Initio Equation of State for Hydrogen-Helium Mixtures With Recalibration of the Giant-Planet Mass-Radius Relation. *Astrophys. J.*, 774:148, 2013.

[81] General Atomic and Molecular Electronic Structure System (GAMESS). Visit http://www.msg.ameslab.gov/gamess/ for more information.

[82] Kevin P. Driver, François Soubiran, Shuai Zhang, and Burkhard Militzer. Comparison of path integral Monte Carlo simulations of helium, carbon, nitrogen, oxygen, water, neon, and silicon plasmas. *High Energy Density Physics*, 23:81–89, 2017.

[83] Daniel Cebulla and Ronald Redmer. \{<|i|><|j|>\}Ab initio\{<|i|><|j|>\} simulations of MgO under extreme conditions. *Phys. Rev. B*, 89(13):134107, 2014.

[84] Y. B. Zeldovich and Y. P. Raizer. *Elements of Gasdynamics and the Classical Theory of Shock Waves*. Academic Press, New York, 1968.

[85] B. Militzer and W. H. Hubbard. *Astrophys. and Space Sci.*, 322:129, 2009.