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Article

Structural and Thermodynamic Properties of Magnesium-rich Liquids at Ultrahigh Pressure

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Abstract: We explore the structural properties of Mg, MgO and $MgSiO_3$ liquids from *ab initio* computer simulations at conditions are relevant for the interiors of giant planets, stars, shock compression measurements and inertial confinement fusion experiments. Using path integral Monte Carlo and density functional theory molecular dynamics, we derive the equation of state of magnesium-rich liquids in the regime of condensed and warm dense matter, with densities ranging from 0.32 to 86.11 g cm^{-3} and temperatures from 20 000 K to 5×10^8 K. We study the electronic structure of magnesium as a function of density and temperature and the correlations of the atomic motion. We find an unexpected local maximum in the pair correlation functions that emerges at high densities, which decreases the coordination number of elemental magnesium and reveals a higher packing. We do not observe this phenomenon in other magnesium liquids that maintain a rather constant coordination number.

Keywords: density functional theory, silicates, coordination number

1. Introduction

Magnesium-rich liquids are significant minerals in planetary science because they represent the main constituent of magma oceans [1] that formed when iron and silicates phase separated during the formation of Earth and super-Earth planets [2–4]. Sizable magma oceans have been predicted to persist over long periods of time [5]. Understanding how the properties magnesium-rich liquids change with pressure and temperature will thus enable us to better constrain the models of formation and evolution of rocky planets [6]. Magnesium-rich liquids also provide valuable information for inertial confinement fusion (ICF) experiments, where materials are exposed to extreme conditions [7–9] that transform liquids into warm dense matter and dense plasmas that are difficult to understand. State-of-the-art laboratories, including the National Ignition Facility (NIF) at Lawrence Livermore National Laboratory, the Omega laser at the University of Rochester, the Z machine at Sandia National Laboratory, and the SLAC laboratory, regularly investigate these conditions to explore matter in the high-energy density regime, exploring matter in the high-energy density regime by probing materials at ultrahigh pressure and temperature conditions never explored before, but that are present at the interior of white dwarf stars [10], rocky exoplanets [11,12], and giant planets like Jupiter [13,14]. While these experiments have accessed the warm dense matter regime and were able to achieve fusion conditions recently [15], theoretical methods have difficulties accessing this regime due to the strong level of ionization, which makes interpretation of experimental measurements a hard task.

The properties of magnesium-rich liquids are very interesting. Their Grüneisen parameter increases upon compression [16] and the heat capacity can increase beyond the ideal gas limit upon ionization [17]. MgO, SiO_2 and $MgSiO_3$ are all insulators in the solid phase but they all become modest electronical conductors in liquid form at high enough

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temperature and pressure, which implies that super-Earth planets can generate magnetic fields in their mantle [5,18]. The structure of liquid magnesiosilicates varies substantially with compression [19–21]. Some melts, such as $MgSiO_3$, are good solvents for water. The solubility was found to increase with pressure, which has important consequences for the Earth's mantle [22]. At high temperatures, it is also important to identify the thermal and pressure ionization regimes [23], as they modify the properties of the liquid as it becomes partially ionized. Recent *ab initio* calculations predicted mixed coordination numbers for silica between the 6-fold coordinated pyrite-type phase and the 9-fold coordinated Fe_2P-type phase at high pressure, as well as the formation of superoxides such as SiO_3 and SiO_6, which may exist in the mantle of super-Earth planets [24].

In this study, we perform *ab initio* simulations of the liquids Mg, MgO, and $MgSiO_3$ using a combination of density functional theory molecular dynamics (DFT-MD) and path integral Monte Carlo (PIMC), providing a detailed characterization of the structure of the liquids.

2. Simulation methods

Rigorous discussions of the PIMC [25–27] and DFT-MD [28–30] methods have been provided in previous works, and the details of our simulations have been presented in some of our previous publications [17,31–33]. Following earlier publications on hydrogen and helium, PIMC and DFT-MD simulations have been combined to study the properties of materials with core electrons in the regime of warm dense matter such as lithium fluoride [34], boron [35], aluminum [31], oxygen [36], silicon [37,38], hydrocarbons [38,39], and superionic water [40,41]. However, the structure of magnesium liquids has not been explored in detail in this regime of extreme conditions. We combine PIMC [42] and and DFT-MD simulations as implemented in the Vienna Ab initio Simulation Package (VASP) [43] to generate a consistent Equation of State (EOS) for Mg, MgO, and $MgSiO_3$ that spans across a wide range of ultrahigh temperatures and pressures.

For DFT-MD simulations, we employ Kohn-Sham DFT simulation techniques as implemented in the Vienna Ab initio Simulation Package (VASP) [43] using the projector augmented-wave (PAW) method [44,45], and molecular dynamics is performed in the NVT ensemble, regulated with a Nosé thermostat. The time step was adapted to the density and the temperature, ranging from 0.16 to 0.44 fs for simulation times from 1000 to 16 000 time steps, to ensure a reliable estimation of the thermodynamic quantities. The pseudopotentials used in our DFT-MD calculations freeze the electrons of the 1s orbital (He-core), which leaves 10, 12, and 6 valence electrons for Mg, Si, and O atoms, respectively. Exchange-correlation effects are described using the Perdew, Burke, and Ernzerhof [46] (PBE) generalized gradient approximation (GGA). However, for elemental Mg, the provided Mg PBE pseudopotential did not give proper results for high densities, so we switched to the local density approximation (LDA). We proceed in a similar way with MgO, the highest densities were also simulated using the LDA functional. As shown in Ref. [47], the choice of the pseudopotential in ab initio simulations of Mg has very little effects on the computed thermodynamic properties. We obtain a very good agreement between both functionals for a number of densities. Electronic wave functions are expanded in a plane-wave basis with a energy cut-off as high as 7000 eV in order to converge total energy. Size convergence tests with up to a 65-atom simulation cell at temperatures of 10 000 K and above indicate that pressures are converged to better than 0.6%, while internal energies are converged to better than 0.1%. We find, at temperatures above 500 000 K, that 15-atom supercells are sufficient to obtain converged results for both energy and pressure, since the kinetic energy far outweighs the interaction energy at such high temperatures [31,48]. The number of bands in each calculation was selected such that orbitals with occupation as low as 10^{-4} were included, which requires up to 14 000 bands in an 15-atom cell at 2×10^6 K and two-fold compression. All simulations are performed at the Γ point of the Brillouin zone, which is sufficient for high temperature fluids, converging total energy to better than 0.01% compared to a grid of k-points.

3. Results

In this section, provide a detailed characterization of the magnesium-rich liquids that we have obtained from our *ab initio* simulations of Mg [33], MgO [32], and $MgSiO_3$ [17], spanning the condensed matter, warm dense matter and plasma regimes. Computations were performed for a series of densities and temperatures ranging from 0.321–86.11 $g\,cm^{-3}$ and 10^4–10^8 K. The full range of our EOS data points is shown in temperature-density and pressure-density space in Fig. 1, along with the shock Hugoniot curve of each material.

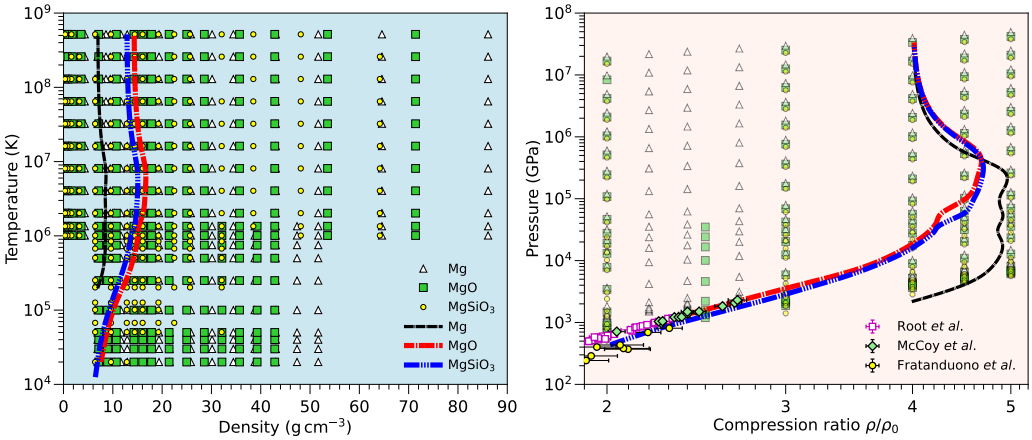

Figure 1. Temperature-density conditions of our PIMC and DFT-MD simulations. The thick dashed lines correspond to the shock Hugoniot curves that we derived for Mg, MgO, and $MgSiO_3$, with initial densities $\rho_0 = 1.736\ g\,cm^{-3}$, $3.570\ g\,cm^{-3}$, $3.208\ g\,cm^{-3}$, respectively. The full EOS for each material is available in Refs [17,23,32,49]. Shock Experiments on MgO from McCoy *et al.* [50], and Root *et al.* [51], and shock experiments on $MgSiO_3$ from Fratanduono *et al.* [52], are included for comparison.

The ideal mixing approximation has been shown to perform well for temperatures above 10^5 K. [53], and the magnitude of nonideal mixing effects was found to be small in this regime, leading to shock Hugoniot curves of MgO and $MgSiO_3$ that are reproduced with sufficient accuracy by combining the EOSs of the elemental substances with the additive volume rule. This concept was extended to other mixtures [49] and good agreement the shock Hugoniot curves of H_2O and CO_2 was found between laboratory measurements and theoretical predictions based on the linear mixing approximation. However, this approximation breaks down at lower temperatures, where chemical bonds play an increasingly important role. These bonds change the structure of the liquid, modifying the atomic coordination. Here we will study how the structure of the liquid changes with density and temperature. We will demonstrate that coordination of magnesium ions is sensitive to presence of silicon and oxygen.

3.1. Radial Distribution Function

The atomic trajectories obtained from DFT-MD simulations can be used to study the local structure of the liquids. Using the radial distribution function, defined by

$$g_{\alpha\beta}(r) \equiv \frac{V}{4\pi r^2 N_\alpha N_\beta} \left\langle \sum_{i=1}^{N_\alpha} \sum_{j\neq i}^{N_\beta} \delta\left(r - \|\vec{r}_{ij}\|\right) \right\rangle = \frac{V}{4\pi N_\beta r^2} \frac{dN_\beta(r)}{dr}, \tag{1}$$

we can obtain a measure of the structure of the liquid, which depends on temperature and density. Here, N_α and N_β are the total number of nuclei of type α and β, respectively that are contained in the volume V, while $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ is the separation between nuclei i and j. $N_\beta(r)$ is the total number of nuclei of species β within a sphere of radius r around a nuclei of type α [54,55]. This function, $g_{\alpha\beta}(r)$, can be interpreted as the probability of finding a particle of type α at a distance r from a particle of type β.

In Fig. 2, we compare radial distribution functions of liquid magnesium over a wide range of temperatures and densities. For every density, we observe that the average distance to the nearest neighbor, given by the location of the first maximum of the $g(r)$, slightly decreases with increasing temperature. At 6.89 g cm^{-3}, this distance shifts from 1.9 Å at 20 000 K to 1.8 Å at 100 000 K. This 5% decrease is caused by stronger collisions and higher kinetic energy. As expected, the distance to the nearest neighbors depends strongly on density. At the highest density explored (51.67 g cm^{-3}), this distance decreased to 0.96 Å. This value does not depend much on temperature.

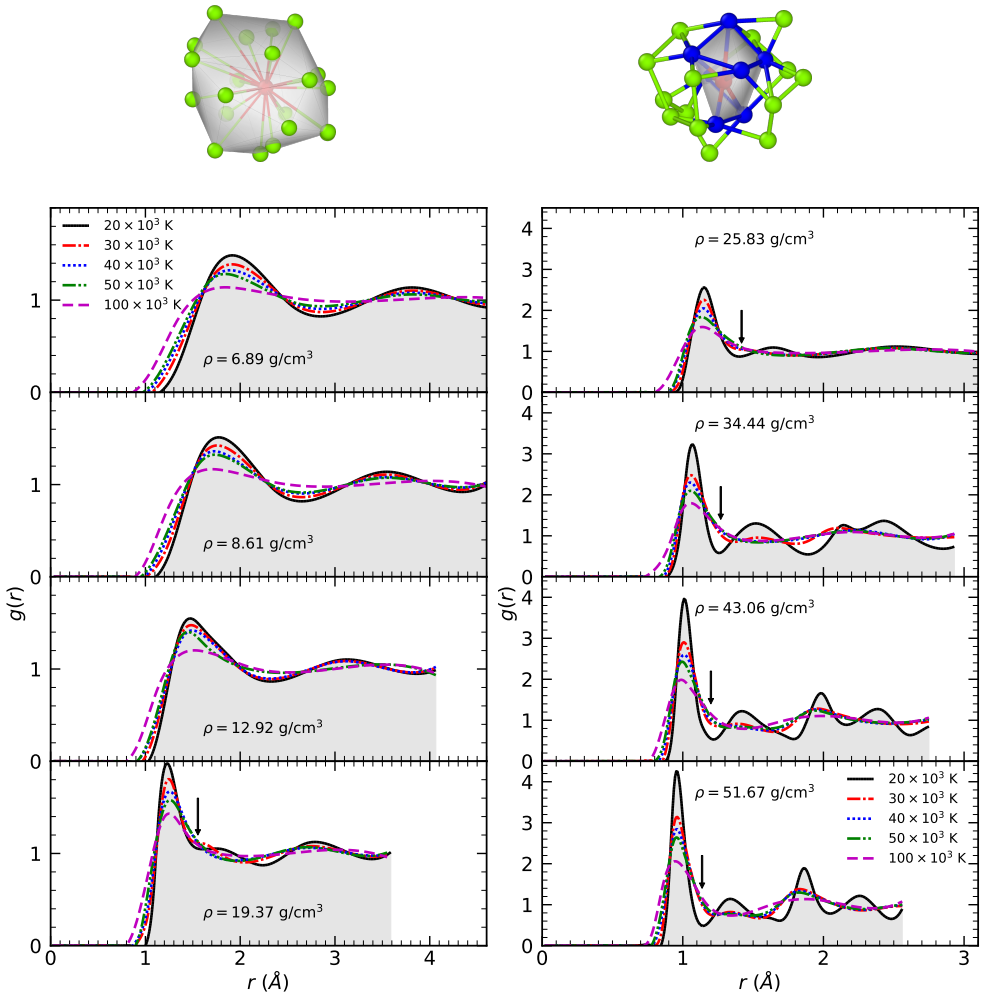

Figure 2. Radial distribution function of liquid elemental magnesium at 8 different densities as a function of temperature. The diagrams on the top correspond to the typical environment of a magnesium atom: surrounded by an average of 18 nearest neighbors within 2.39 Å at 12.92 g cm^{-3} and 20 000 K (left), and surrounded by a closer shell of only 6 to 7 neighboring atoms at 25.83 g cm^{-3} and 20 000 K. For the three highest densities in our simulations ($\rho \geqslant 34.44$ g cm^{-3}), the system freezes into an simple cubic structure at 20 000 K, which corresponds to the stable phase of Mg observed experimentally at pressures exceeding 1 TPa, the highest pressures ever reported in experiments of Mg to date [56] . The arrows indicate the location of an emerging intermediate local minimum.

We can also observe in Fig. 2 that the shape of the all $g(r)$ curves at a low densities is fairly similar. All curves have two well-defined maxima and two minima. However, for densities of 19.37 g cm^{-3}and higher, the liquid becomes significantly more structured. The curve develops an additional intermediate local maxima that result in a new local minimum at $\sim$ 1.55 Å. As density increases, this intermediate maximum becomes more pronounced. In our simulations at 20 000 K, the system freezes into the simple cubic phase

for densities of 34.44 g cm^{-3} and higher, which corresponds to pressures higher than 24381 GPa. This simple cubic phase has been observed experimentally at pressures of 1 TPa [56]. With crystal structure search methods, a series of other high-pressure structures including body-centered cubic, face-centered cubic, and simple hexagonal and simple cubic phases have been predicted for magnesium [57]. When this crystallization happens in our MD simulations, the subtle features of the liquid $g(r)$ functions become amplified. But for temperatures of 30 000 K and above, we found that the system remained in a liquid state for all densities. Still the local minimum at $r_{\mathrm{min}} \sim 1.55$ Å persisted. We will discuss these changes in terms of the atomic coordination number in the next section.

3.2. Coordination Number

A further measure of the structure of the liquid is the coordination number, given by

$$C_{\alpha\beta} = \frac{4\pi N_\beta}{V} \int_0^{r_{\mathrm{min}}} r^2 \, g_{\alpha\beta}(r) \, dr \tag{2}$$

where $C_{\alpha\beta}$ is defined to be the number of atoms of type β that are within a spherical region of radius r_{min}, centered at an atom of species α [54]. Here, we adopted the usual convention that r_{min} is the location of the first minimum of the radial distribution functions $g_{\alpha\beta}(r)$. The integrated nucleus-nucleus pair correlation function, given by $N_\beta(r)$ in Eq. (1), can be employed to define a coordination number in Eq. (2) when evaluated at the location of the first minimum, that is, $N_\beta(r_{\mathrm{min}}) = C_{\alpha\beta}$.

In Fig. 3, we show the radial distribution functions of liquid elemental magnesium at 30 000 K and the corresponding integrated nucleus-nucleus pair correlation functions, $N(r)$. The shaded areas in the top panel highlights the interval $[0, r_{\mathrm{min}}]$ over which the integration in Eq. (2) is performed. As density increases, the position of the first local maximum shifts to smaller distances and the peak becomes narrower, which indicates that the distance to first neighbors is decreasing. r_{min}, also decreases with increasing density, reducing the total area below the curve and, hence, the coordination number.

As the atoms get closer, the liquid develops a new structure, which is reflected in the intermediate local maximum that starts developing in the $g(r)$ for densities higher than 25.83 g cm^{-3} at 30 000 K, as we can see in Fig. 3, which corresponds to a pressure of 13147 GPa. The typical environment of a magnesium atom, after this intermediate local maximum develops, is shown at the top of Fig. 2, where a new shell of nearest neighbors forms. The slope $(dE/d\rho)_T$ is positive, therefore pressure ionization is likely to take place [23]. As described in the previous section, a transition occurs in the liquid for higher densities, where a new intermediate maximum appears, which abruptly decreases the value of r_{min} and, hence, the coordination number.

In Fig. 4, we show the resulting Mg-Mg coordination number in liquid magnesium for a wide range of temperatures and densities. As we can observe in the figure, the coordination number first increases from 14 to 18 at $T = 20\,000$ K and then abruptly drops to 7, consistent with the diagram shown in Fig. 2. Something similar occurs at $T = 30\,000$ K, where the coordination number drops from 18 to 8. This is an indication that the system prefers a coordination similar to the simple cubic structure, where the coordination number is 6. For higher temperatures, this intermediate maximum never develops for this range of densities, but it is likely to appear for $\rho > 60$ g cm^{-3}. For $T > 30\,000$ K, the coordination number remains between 13 and 18 at all densities.

3.3. Electronic Density of states

We also identified changes in the electronic structure of Mg at conditions where structure of the liquid changes and the new intermediate $g(r)$ maximum appears. At ultrahigh pressure, solid magnesium has been predicted to assume an electride structure [56–58]. In Fig. 5, we show the electronic density of occupied states (DOS) together with the electronic localization function (ELF) for liquid Mg at 30 000 K. In the DOS, we observe with increasing density a clear broadening of the 2s and 2p energy bands and a shift of

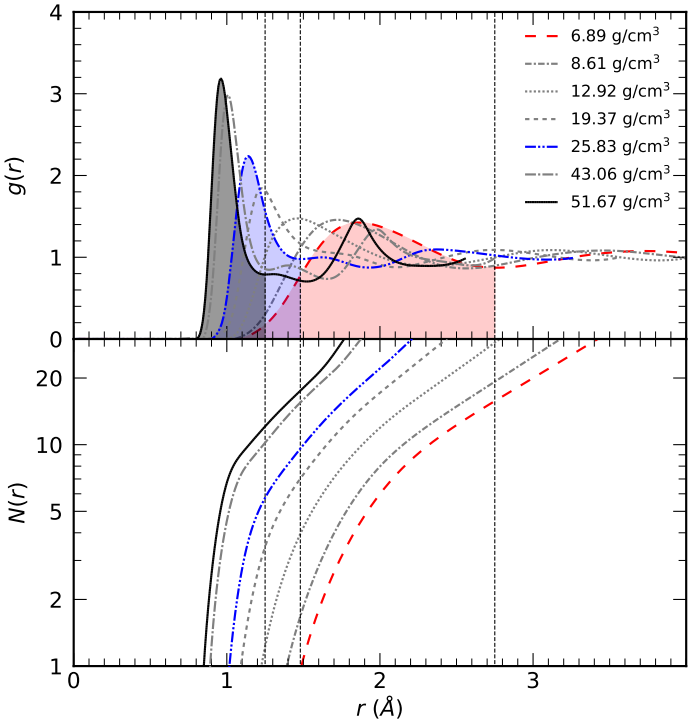

Figure 3. Radial distribution functions, $g(r)$, of liquid Mg at $T = 30\,000$ K (top panel) and the corresponding integrated nucleus-nucleus pair correlation functions, $N(r)$ (bottom panel). For densities higher than 25.83 g cm^{-3}, the $g(r)$ function develops an intermediate maximum, which decreases the area below the curves and, consequently, the coordination number. The vertical bars indicate the location of the first minimum for the highlighted $g(r)$ functions, corresponding to 6.89, 25.83, and 51.67 g cm^{-3}.

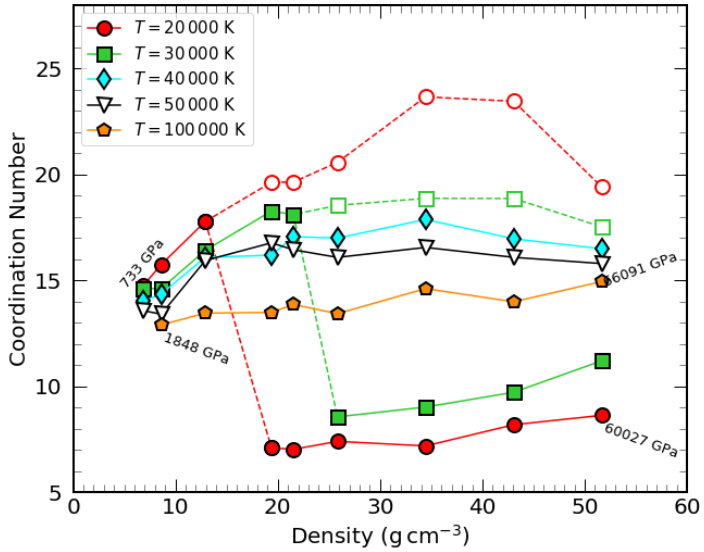

Figure 4. Coordination number C_{Mg-Mg} of liquid magnesium as a function of density for five different temperatures. For densities higher than 25.83 g cm^{-3}, the $g(r)$ function develops an intermediate maximum, which increases the coordination number. The labels next to the symbols in the right panel indicate the pressure of selected simulations, and the open symbols indicate the coordination number obtained if we ignore the intermediate minimum and perform the integration in Eq. (2) up to the next local minimum.

the eigenvalues towards lower energies. This broadening does not affect the electrons in the conduction band (3s) in a significant way. However, at 21.53 g cm^{-3}, the broadening of the other bands is significant and almost closes the gap between the 2s and 2p bands. According to Ref. [33], these conditions fall in the regime of pressure ionization where the effects of thermal ionization are expected to be small. The ELF depicts location of electronic charge in the between void between the nuclei, which is the typical electride behavior that results from the repulsion of core electrons. For the simple cubic phase of Mg, this has recently been reported by a experimental-theoretical study [56]. With *ab initio* methods, this has been predicted to occur in many solid structures at high pressure [59]. In Fig. 5, we show that also the Mg liquid exhibits electride behavior, which shares similarities to earlier predictions for liquid iron [60].

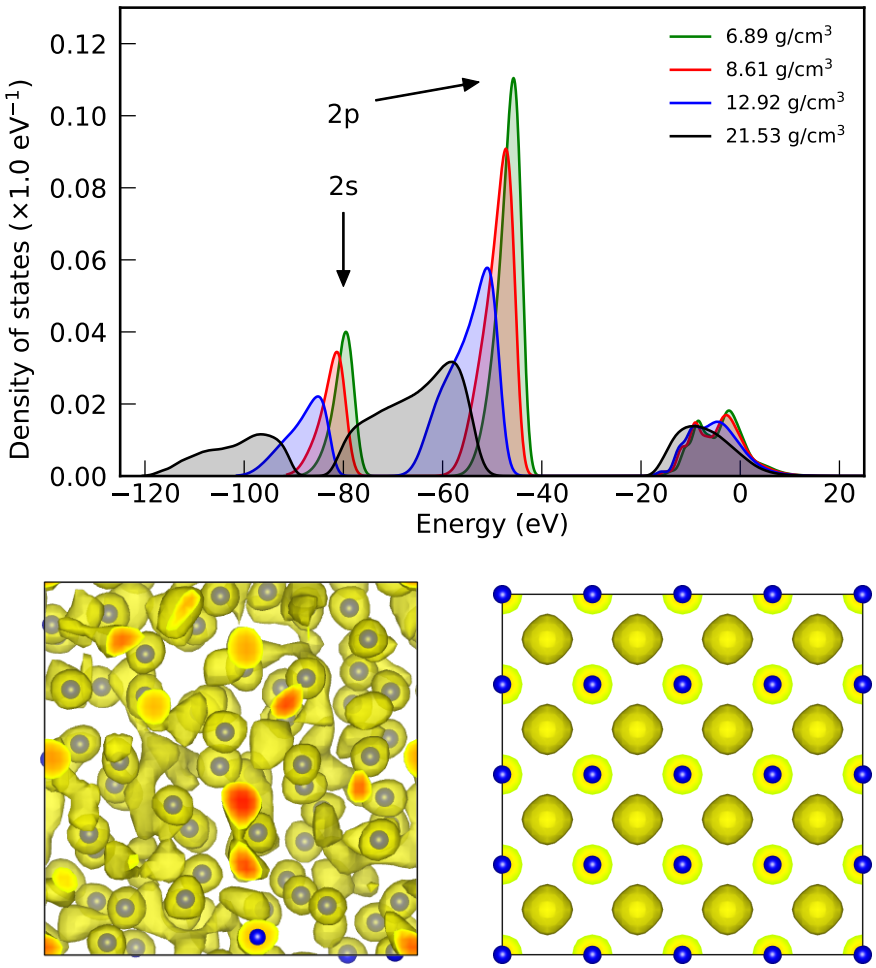

Figure 5. Top: Electronic density of occupied states of Mg based on our DFT-MD simulations at different densities for a temperature of 30 000 K. The energies of all MD configurations were shifted so that the Fermi energies are aligned at $E = 0$ eV. Bottom: ELF function of liquid (left) and solid Mg in the simple cubic phase (right) at 25.83 g cm^{-3}. In the solid phase (right), the electronic charge (yellow pockets) is localized in the voids between the nuclei, which depicts the typical electride behavior that has been predicted with *ab initio* method to occur in many solid structures including K [58,61,62] and Mg [56]. Here we also find the Mg liquid to exhibit electride behavior (left), which has been predicted to occur in liquid Fe [60].

3.4. MgO and $MgSiO_3$

We do not observe an intermediate maximum or similar structural change in our simulations of MgO. In Fig. 6, we plot the radial distribution functions (left panel) of MgO which show that the peaks becomes more pronounced with increasing density, but there

is no significant change in the topology of these functions as we observed in elemental Mg, indicating that the structure of the liquid varies smoothly with both temperature and density. At densities of 24.99 g cm^{-3} and higher, the Mg-Mg and O-O coordination increases, as shown by the separation of the radial distribution function in two distinctive peaks that separates the first nearest neighbors from the second nearest neighbors.

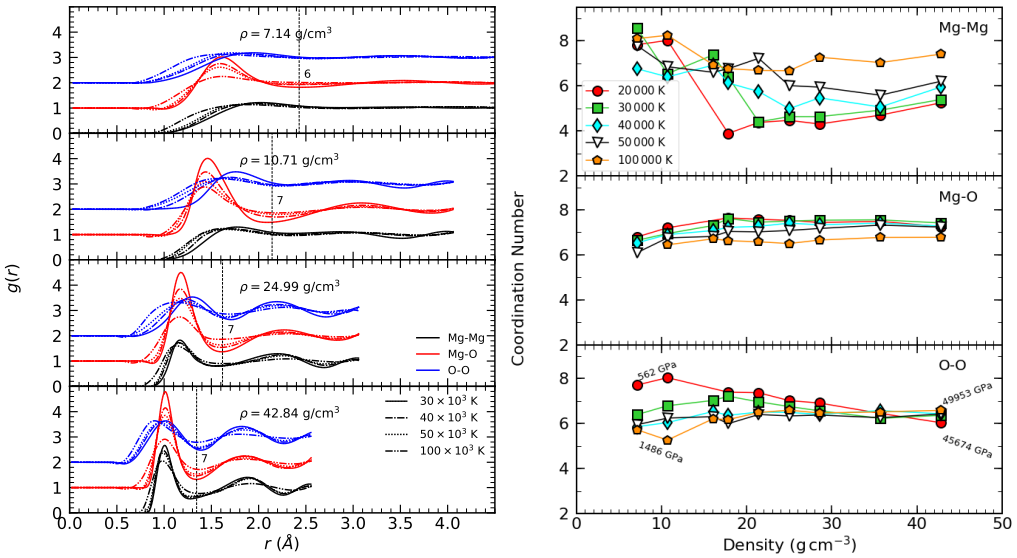

Figure 6. Coordination number of liquid MgO (right panel) as a function of density for five different temperatures. The radial distribution functions of MgO (left panel) show the location of the first local minimum (vertical bars for Mg-O), used to calculate the coordination number using Eq. (2). The small number near the vertical bars indicate the Mg-O coordination number at that local minimum. The Mg-O and O-O $g(r)$ functions have been shifted upwards for clarity. The four text labels in the lowest right panel indicate the pressure in the simulations at the lower and highest temperatures for two density values.

The Mg-Mg coordination number is much higher in liquid, elemental Mg (∼14) than in liquid MgO. In the presence of oxygen, the Mg-Mg coordination number decreases from 8 to 4-6 with increasing density, as we observe in the right panel of Fig. 6. However, this lower coordination is comparable to that of elemental Mg (∼7-10) if the density of that system is high and the temperature is low, as we showed in Fig. 4. The Mg-O coordination number was found to be around 7 for all temperatures and densities, consistent with previous studies of MgO at high temperatures and densities [19]. Similarly, the O-O coordination number remained approximately 6. This is smaller that the value found for the molecular fluid GeO_2 liquid, where the average O-O coordination number was found to be around 9 and a Ge-O coordination number of 2 at 1500 K and low temperatures [63,64]. This is not the case of MgO, which behaves as an atomic fluid. This is comparable to silica, which is predicted to a have a mixed coordination between the 6-fold coordinated pyrite-type phase and the 9-fold coordinated Fe_2P-type phase at high pressure [24]. Therefore, coordination numbers with oxygen between 6 and 9 are expected at these conditions.

In the case of $MgSiO_3$, the Mg-O coordination number is also between 6 and 8, as we can see in Fig. 7, but slightly larger than 8 at some densities. The Mg-Mg $g(r)$ functions in the left panel show that magnesium atoms are not correlated, with no clear signature of a local minimum at most of the conditions that allows to identify a layer of first nearest neighbors. When the identification is possible, the Mg-Mg coordination number in $MgSiO_3$ lies between 2 and 4. While the Mg-O coordination number seems to decrease with density, the Si-O coordination number increases with increasing density, regardless of the temperature, from 6 to 8. The O-O coordination number is larger in the $MgSiO_3$ liquid than in the MgO liquid, reaching values between 7 to 9 in the latter case, while MgO

shows an average of 6 for most conditions. Regarding the distance to nearest neighbors, or bond length, we find that the Mg-O bond length is larger in $MgSiO_3$ than in MgO. For a comparable denisity of $\sim$25 g cm^{-3}, this distance is 1.3 Å in $MgSiO_3$, while for MgO, this distance is about 1.2 Å. At all conditions, the Si-O bond length is smaller than the Mg-O, and both are larger than the O-O bond length. As in the case of MgO, there no signature of an abrupt structure transition, as we observed in pure Mg.

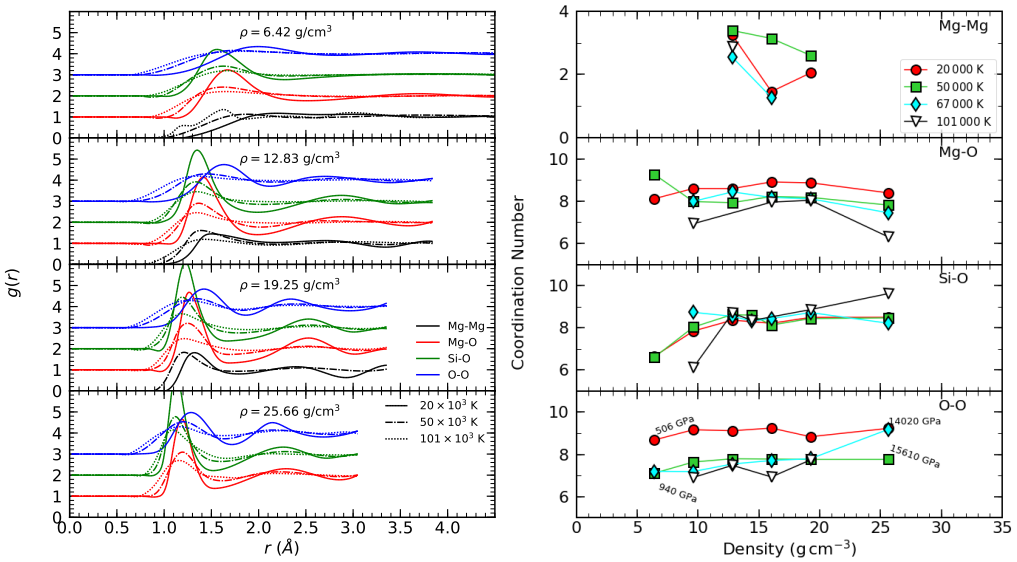

Figure 7. Coordination number of liquid $MgSiO_3$ (right panel) as a function of density for four different temperatures. The radial distribution functions of $MgSiO_3$ (left panel) show the location of the first local minimum, used to calculate the coordination number using Eq. (2). The Mg-O, Si-O, and O-O $g(r)$ functions have been shifted upwards for clarity. The text labels on top of the symbols of the right panel indicate the pressure of the sample at the corresponding density and temperature.

4. Conclusions

We have studied the structural properties of magnesium liquids in a broad range of temperatures and densities using *ab initio* simulations. We found evidence of a structural transition in liquid Mg around 20 g cm^{-3}, where the emergence of a new intermediate maximum in the radial distribution function leads to an abrupt decrease in the coordination number with increasing density for low temperatures. The structural change in liquid elemental magnesium is an indication of a transition to electride-type behavior, consistent with recent experimental finding of electride phases of Mg at ultrahigh pressure [56]. This transition does not occur in the other magnesium liquids, MgO and $MgSiO_3$, where compression introduces only gradual changes in the coordination. Under no conditions we found a signature of a stable molecular bond between Mg and O species. However, the Mg and O nuclei exhibit positive correlations that are stronger than those between the other pairs. The presence of silicon increases the O-O coordination number, which is larger in $MgSiO_3$ than in MgO. The Mg-O bond length is smaller in MgO when compared to $MgSiO_3$ at similar conditions, and it is always larger that the Si-O bond length within the same $MgSiO_3$ liquid. We did not observe the formation of any molecule, making Mg, MgO, and $MgSiO_3$ atomic fluids at the conditions studied.

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Data Availability Statement: The equation of state of Mg, MgO, and $MgSiO_3$ can be found in the supplementary material of Refs. [17,32,33], respectively.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

DFT-MD	Density Functional Theory Molecular Dynamics
PIMC	Path Integral Monte Carlo
VASP	Vienna Ab initio Simulation Package

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