Atom-in-jellium equations of state for cryogenic liquids

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Equations of state (EOS) calculated from a computationally efficient atom-in-jellium treatment of the electronic structure have recently been shown to be consistent with more rigorous path integral Monte Carlo (PIMC) and quantum molecular dynamics (QMD) simulations of metals in the warm dense matter regime. Here we apply the atom-in-jellium model to predict wide-ranging EOS for the cryogenic liquid elements nitrogen, oxygen, and fluorine. The principal Hugoniotst for these substances were surprisingly consistent with available shock data and Thomas-Fermi (TF) EOS for very high pressures, and exhibited systematic variations from TF associated with shell ionization effects, in good agreement with PIMC, though deviating from QMD and experiment in the molecular regime. The new EOS are accurate much higher in pressure than previous widely-used models for nitrogen and oxygen in particular, and should allow much more accurate predictions for oxides and nitrides in the liquid, vapor, and plasma regime, where these have previously been constructed as mixtures containing the older EOS.

INTRODUCTION

Many of the most common planet-forming substances contain oxygen, including silica and silicates, oxides such as alumina, MgO, and FeO, carbonates, water, and CO2. Some contain nitrogen, in particular ammonia. Equations of state (EOS) used to understand planetary impacts and giant planets and exoplanets are constructed in the warm, dense matter regime by mixing elemental EOS. EOS for constituents mixed in this way should be reasonably accurate at relevant atomic volumes and temperatures, which corresponds to high pressure compression of the corresponding cryogenic liquids. The third second-row diatomic cryogenic liquid, fluorine, is of practical interest as a component of LiF, which is widely used in high pressure experimental studies as an optical window or tamper. Fluorine is also a constituent of various polymers and chemical explosives, and is a component of ‘flibe,’ a possible coolant and in-situ breeder of tritium in thermonuclear reactors, where it would be subjected to heating and compression.

Shock wave data, usually used to calibrate high pressure EOS, are limited in range for the cryogenic liquids oxygen and nitrogen, and non-existent for fluorine. Widely-used semi-empirical EOS from the SESAME and LEOS libraries [1, 2] are thus limited in data for calibration or validation. The SESAME EOS for oxygen and nitrogen were constructed only for the molecular regime, using a model of molecular vibrations (MV) for the ion-thermal contribution with spherical symmetry and does not capture the relative orientation of neighboring atoms, smearing their charge into the uniform background jellium outside the Wigner-Seitz sphere [3]. However, atom-in-jellium calculations were subsequently found to be similarly accurate for the EOS of non-close-packed metals, and even for car-

ATOM-IN-JELLLEUM CALCULATIONS

The cryogenic liquids are an interesting test of electronic structure calculations of EOS. The atom-in-jellium model was originally expected to be suitable only for close-packed metals, as it represents the electron distribution with spherical symmetry and does not capture the relative orientation of neighboring atoms, smearing their charge into the uniform background jellium outside the Wigner-Seitz sphere [3]. However, atom-in-jellium calculations were subsequently found to be similarly accurate for the EOS of non-close-packed metals, and even for car-
bon and silicon [11], despite the importance of directional bonding in these elements near ambient conditions.

The diatomic cryogenic liquids are notable in that saturated interatomic bonds and van der Waals forces are essential to their behavior at low pressures and temperatures, processes which are not captured by the atom-in-jellium model. The atom-in-jellium EOS are thus not expected to be accurate at low pressures, and the interesting aspects of their performance are how close they match existing data at pressures where saturable bonding becomes less important, and their behavior at much higher pressures, not currently constrained by experimental data, in comparison to the theoretical treatments used in widely-used EOS, such as the Grüneisen or Thomas-Fermi (TF) models [14].

Simulations were performed using the same prescription as for the previous study [11]. For each elements, atom-in-jellium calculations were made over a range and density of states suitable for a general-purpose EOS: mass density $\rho$ from $10^{-4}$ to $10^3 \rho_0$ with 20 points per decade, and temperature $T$ from $10^{-3}$ to $10^5$ eV with 10 points per decade. The reference density $\rho_0$ was chosen to be that of the liquid cryogen; it should be noted that the choice of this density is purely a convenience in constructing a tabular EOS, where it is useful for the tabulation to include the starting state to reduce the sensitivity to interpolating functions. The EOS were not adjusted to reproduce any empirical data.

As was found in the previous study [11], the electronic wavefunctions were computed reliably down to 10 K or less for densities corresponding to condensed matter, and to 100 K or less for densities down to 0.1% of the ambient solid. At lower densities, calculations were completed successfully only for temperatures of several eV or more.

In contrast to the previous study, calculations of the ion oscillations gave imaginary Einstein frequencies for densities slightly above that of the cryogenic liquid. This behavior indicates the localization of electrons to an atom, and likely reflects the role of bonding orbitals and the resulting in no determination of an Einstein frequency, $\theta_0$, at the same mass density $\rho$, $\theta_0$, and $\rho_0$, so the EOS need not be valid near the unshocked state if these quantities can be obtained in a different way. This aspect is used in calculations of detonating high explosive, where the EOS of the reaction products can be used without any physical representation of the unshocked explosive [16]. For the present EOS, defined via the Helmholtz free energy $f$, the temperature $T$ was eliminated when solving the Rankine-Hugoniot equations.

To deduce a Hugoniot from atom-in-jellium EOS with unstable states around the initial cryogenic liquid ($\rho_0, T_0$), we first considered higher initial temperatures $T_0'$ at the same mass density, until a usable state was found, with specific internal energy from the atom-in-jellium calculation $E_0' = e_{\text{atom}}(\rho_0, T_0')$. A Hugoniot could then be calculated from this initial state. We then used a suitable previously-developed reference EOS to calcu-
late a difference in specific internal energy between the states:

$$\Delta e = e_{\text{ref}}(\rho_0, T'_0) - e_{\text{ref}}(\rho_0, T_0).$$  

We then recalculated the atom-in-jellium Hugoniot, defining the initial energy to be $e'_0 - \Delta e$. This approach essentially uses the specific heat capacity from the reference EOS to correct the atom-in-jellium state from a usable value at $t'_0$ to the desired $T_0$.

Experimental shock data were taken from the Marsh and van Thiel compendia [18, 19].

### Nitrogen

For nitrogen, the atom-in-jellium Hugoniot passed through the experimental measurements [20–25] around 50 GPa. At higher pressures, the Hugoniot was significantly stiffer than either the MV-based SESAME 5000 or the TF-based LEOS 70. The MV EOS omitted dissociation and ionization, and shows a Grüneisen-like behavior where the shock density approaches a limit asymptotically. The latter, TF, model exhibits a peak compression at a similar pressure to the atom-in-jellium EOS, except at a much higher density. The atom-in-jellium calculations exhibited a distinct feature around 5 g/cm$^3$ from ionization of the outer electrons. The maximum compression, although at a similar pressure to TF calculations, was at a significantly higher density. As for nitrogen, the atom-in-jellium result followed QMD/PIMC calculations of the Hugoniot [13], which in this case did not predict such a strong dissociation feature. In oxygen, the contribution of spin to the covalent bond is important [26]; the QMD calculations were spinless and thus underpredict the dissociation feature. Experimental data in the region of dissociation are relatively sparse, but measurements [22, 27] made consistently with those for nitrogen suggest a similar plateau. (Fig. 2)

### Oxygen

For oxygen, the atom-in-jellium Hugoniot passed slightly above the experimental data, and then closely tracked the Hugoniot for the MV-based SESAME 5010 to 1.5 TPa. At higher pressures, it exhibited a peak compression at 50 TPa, then approached the TF-based LEOS 80 for pressures above 1000 TPa. As with nitrogen, the atom-in-jellium calculations exhibited a distinct feature around 5 g/cm$^3$ from ionization of the outer electrons. The maximum compression, although at a similar pressure to TF calculations, was at a significantly higher density. As for nitrogen, the atom-in-jellium result followed QMD/PIMC calculations of the Hugoniot [13], which in this case did not predict such a strong dissociation feature. In oxygen, the contribution of spin to the covalent bond is important [26]; the QMD calculations were spinless and thus underpredict the dissociation feature. Experimental data in the region of dissociation are relatively sparse, but measurements [22, 27] made consistently with those for nitrogen suggest a similar plateau. (Fig. 2)

### Fluorine

For fluorine, the atom-in-jellium Hugoniot again exhibited a distinct feature around 7 g/cm$^3$ corresponding to ionization of the outer electrons, and a peak compression around 100 TPa. The peak compression was at a lower density than in the TFD-based SESAME 5040, and more localized in pressure. The atom-in-jellium EOS was constructed completely consistently with those for nitrogen and oxygen, with no empirical parameters, and so it is likely that the Hugoniot from SESAME 5040 is up to ~20% too dense. (Fig. 3)
the feature originates from ionization of the electrons in the excitation of electron shells became significant and the atom-in-jellium Hugoniot calculation for oxygen.

The relatively different behavior of TF-based EOS from atom-in-jellium calculations: higher for nitrogen but lower for oxygen, and with much greater difference than the empirical/TF models. From the atom-in-jellium EOS should be more reliable than the empirical/TF models.

The atom-in-jellium calculations were not able to reproduce the feature in the Hugoniot of nitrogen and oxygen associated with dissociation. Fluorine is likely to exhibit a similar feature, though likely much smaller than that of oxygen, as the trend should correlate with the energy of the covalent bond: 9.79, 5.15, and 1.63 eV for N$_2$, O$_2$, and F$_2$ respectively, at STP. Recent spinless QMD results reproduced the dissociation feature fairly well in nitrogen but appeared to underpredict it in oxygen.

Consistently with recent results from PIMC and QMD simulations where available, the atom-in-jellium EOS indicate that widely-used EOS for nitrogen, oxygen, and fluorine have significant inaccuracies in the dense plasma regime, densities of several grams per cubic centimeter and temperatures above a few electron-volts.

**CONCLUSIONS**

We have constructed wide-ranging EOS for nitrogen, oxygen, and fluorine using the atom-in-jellium model, including ion-thermal and cold curve energies as well as the electron-thermal energy for which atom-in-jellium calculations have been used most widely. Although the ion-thermal calculations were not valid around the cryogenic liquid states for these elements, which are stabilized by interatomic bonding and van der Waals forces not captured by the atom-in-jellium model, it was possible to calculate shock Hugoniots from these initial states by correcting preheated calculations to obtain a reasonable starting energy.

Apart from a regime affected by dissociation in N$_2$, the atom-in-jellium Hugoniots matched predictions based on QMD and PIMC where they were available.

As was found with solid elements, despite disagreements at low pressures, shock Hugoniots derived from the atom-in-jellium EOS were close to or matched shock data at pressures approaching around 100 GPa. At higher pressures, where no shock data currently exist, there were substantial differences between the Hugoniots from atom-in-jellium EOS and those from other EOS using a Thomas-Fermi treatment of the electrons or neglecting dissociation and ionization. As the atom-in-jellium EOS were calculated self-consistently, without any empirical adjustment to match data for any of these elements, this deviation is likely to reflect inaccuracies in the pre-

**DISCUSSION**

It is instructive to compare the systematic behavior of the atom-in-jellium EOS with previous, semi-empirical EOS for the Hugoniots of these cryogenic liquids. Where experimental Hugoniot data are available, the atom-in-jellium EOS is inaccurate at low pressures, as expected given its inability to capture the details of interatomic forces, but becomes close to or coincident with shock data at pressures of several tens to $O(100)$ GPa. As the shock pressure increases, the atom-in-jellium EOS was found to track surprisingly close to the molecular EOS in the SESAME library, deviating when effects from the excitation of electron shells become significant and the molecular EOS would then be inaccurate. As has been found for other elements, the atom-in-jellium Hugoniot exhibited a relatively sharp peak in compression compared with the broader peak characteristic of a TF treatment of the electrons. For the elements considered here, this feature originates from ionization of the electrons in the K-shell. Interestingly, the peak compression in the TF-based EOS models varied non-systematically from the atom-in-jellium calculations: higher for nitrogen but lower for oxygen, and with much greater difference than was found previously for more common standard elements. Indeed, unlike the standard elements, the TF calculation of post-peak compression only matched the atom-in-jellium calculation for oxygen.

In reality, because TF theory is inadequate around ambient conditions, TF-based EOS are typically a combination of an empirical Grüneisen fit to shock data where it exists, coupled to TF theory at higher temperatures. The relatively different behavior of TF-based EOS from atom-in-jellium for these cryogenic liquids reflects the scarcity of shock data. This observation highlights the value of the atom-in-jellium calculations: although inad-
vious EOS. These inaccuracies are likely to mean that EOS for planetary materials such as oxides and silicates, constructed in the warm dense matter regime by mixing previous elemental EOS such as these, may well be inaccurate for applications such as the internal structure of giant planets and collisions.

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