Final Report

1. Cover Page

DOE Award Number: DE-SC0010517
Sponsoring Program Office: Office of Science
Recipient: The Regents of the University of California
Project Title: Path Integral Monte Carlo Simulations of Warm Dense Matter and Plasmas

Principal Investigator:
Burkhard Militzer, Associate Professor
407 McCone Hall, University of California, Berkeley, CA 94720-4767
militzer@berkeley.edu, (510) 643-7414

Submission Date: April 24, 2013
Grant Period: 08/15/13 to 8/14/2017 including a one-year no cost extension
Final Report: January 13, 2018

Abstract

New path integral Monte Carlo simulation (PIMC) techniques will be developed and applied to derive the equation of state (EOS) for the regime of warm dense matter and dense plasmas where existing first-principles methods cannot be applied. While standard density functional theory has been used to accurately predict the structure of many solids and liquids up to temperatures on the order of 10,000 K, this method is not applicable at much higher temperature where electronic excitations become important because the number of partially occupied electronic orbitals reaches intractably large numbers and, more importantly, the use of zero-temperature exchange-correlation functionals introduces an uncontrolled approximation.
Here we focus on PIMC methods that become more and more efficient with increasing temperatures and still include all electronic correlation effects. In this approach, electronic excitations increase the efficiency rather than reduce it. While it has commonly been assumed such methods can only be applied to elements without core electrons like hydrogen and helium, we recently showed how to extend PIMC to heavier elements by performing the first PIMC simulations of carbon and water plasmas [Driver, Militzer, *Phys. Rev. Lett.* 108 (2012) 115502]. Here we propose to continue this important development to extend the reach of PIMC simulations to yet heavier elements and also lower temperatures. The goal is to provide a robust first-principles simulation method that can accurately and efficiently study materials with excited electrons at solid-state densities in order to access parts of the phase diagram such the regime of warm dense matter and plasmas where so far only more approximate, semi-analytical methods could be applied.

1. What are the major goals of the project?

Given that a rigorous and consistent theoretical description of high energy density materials has been identified as a central goal in national energy and defense science programs, such as inertial confinement fusion (ICF), we have been developing new path integral Monte Carlo (PIMC) techniques to study plasmas composed of heavier elements such as iron and other third-row elements. Our primary goal is to derive equations of state (EOS) and transport properties in the regime of WDM and dense plasmas where existing first-principles methods cannot be applied. While standard density functional theory (DFT) has been used to accurately predict the structure of many solids and liquids up to temperatures on the order of 100,000 K, this method is not applicable at much higher temperature because the number of partially occupied electronic orbitals reaches intractably large numbers or the use of finite-temperature free energy functionals in orbital-free DFT introduces an uncontrolled approximation. On the other hand, DFT-based orbital-free and average-atom methods are extremely efficient at high temperatures, but tend to oversimplify the quantum mechanical effects that may be crucial for success in inertial confinement fusion and defense science studies. Development of PIMC offers the chance to produce the optimal tool for such high temperature regimes.

In our work, we focus on PIMC methods that become more and more efficient with increasing temperatures and still include all electronic correlation effects. In this approach, electronic excitations increase the efficiency rather than reduce it. While it had commonly been assumed this method could only be applied to elements without core electrons, we showed that PIMC with free-particle nodes works well for all first-row elements (*Physical Review Letters* **108** (2012) 115502). Most recently, we extended the applicability range of all-electron PIMC to second-row elements by adopting localized nodal surfaces (*Physical Review Letters* **115** (2015) 176403). To simulate third-row elements efficiently under WDM conditions, our goal is to develop a new method to remove core electrons by introducing *pseudo-nodes*. We explain our approach step by step and present preliminary results.

Application-wise, our aim was to achieve the ability to perform PIMC simulations of heavier elements because of their fundamental importance for WDM and astrophysics. In our latest efforts, we succeeded in simulating key first- and second-row materials such as hydrocarbons, LiF, Na, Mg, MgO, and Al.

Our collaborators at LLNL, Lorin Benedict, Heather Whitley and Phil Sterne, used our PIMC EOS data both as comparisons to existing semi-empirical, EOS-generating schemes, and as input for continuum radiation hydrodynamics simulations. This has allowed us to relate our PIMC results to macroscopic continuum studies of materials response. An emphasis will be placed on benchmarking such methods for plasmas of heavy elements at the very high temperatures (~100 eV) and low densities that are generated when Hohlraum radiation heats the ablator material in indirect drive laser experiments. Results from changes to the EOS will be of immeasurable importance to the designers at the National Ignition Facility (NIF) and at other facilities.

Starting with our EOS of our ablator materials, doped CH and Be, our collaborator at LLE, Suxing Hu, will perform real-time simulations of laser fusion experiments at the Omega laser and at the NIF to determine how sensitive the compression path depends on the ablator EOS. Since Suxing also has experience in performing orbital-free DFT calculations, we have ongoing

efforts to compare predictions from this method with PIMC results. In joint publications, we aim to analyze the accuracy of different free-energy functionals in order to understand why existing orbital-free DFT calculations do not predict compression peaks along the shock Hugoniot curve that we see with PIMC. The peaks are caused by the ionization of various electron shells, which may be crucial for fine-tuning ICF experiments, akin to known M-band preheating effects in gold.

Our PIMC EOS calculations will benchmark and possibly replace semi-analytical EOS tables like QEOS or SESAME, which will impact the hydrocode simulation community and will affect the design of NIF targets. Our PIMC results will also help to improve the accuracy of orbital-free DFT and average-atom simulations. We currently have one post doc being trained in the relevant simulation techniques. We typically train one undergraduate, summer students every year during paid, eight-week long internship position. This gives young students valuable exposure to research experiences on key DOE research problems and high-performance computing platforms, and begins to groom the future of our community. The students' effort usually leads to a presentation at a research conference and a publication.

2. What was accomplished under these goals?

The team of the PI performed a large set of calculations for **hydrocarbons** (C_nH_m) in order to compare with the experimental results that teams of Tilo Döppner and Annie Kritcher (both LLNL) obtained from spherically converging shock wave experiments on the gigabar platform at NIF. For the first time, we have PIMC simulations that accurately predict 1s compression peak along the shock Hugoniot curve of CH. We learned how strong the imprint of many-body effects are under conditions where the 1s electrons are ionized. We further construct coherent equations of state (1184 data sets in total) for a series of hydrocarbon materials with various C:H ratios (2:1, 1:1, 2:3, 1:2, and 1:4) over the range of 0.07-22.4 g/cm^3 and 6.7x10^3-1.29x10^8 K. We found that the Hugoniot curves of carbon and CH compounds have only one compression peak (from 1s electrons) while O, N, and Ne have two peaks (from 1s and 2nd shell electrons). This is because their electronic structures are different. Analysis of the electronic density of states reveals the L-shell eigenstates are merging in carbon, while they remain distinct for higher-Z elements. A shoulder develops along the Hugoniot curve of CH at compression ratio between 3.3-4.3, which may be traced back to the start of the ionization of the 1s electron shell of carbon. We predicted the Hugoniot curve of polystyrene to be ~5% softer at maximum compression than that predicted by orbital-free DFT and other Thomas-Fermi-based approaches.

Our results provide benchmark-quality EOSs that surpasses that of semi-empirical and Thomas-Fermi-based methods in the warm dense matter regime. By comparing our first-principles EOS to the LEOS 5112 model for CH, we validate the specific heat assumptions in this model but suggest that the Grueneisen parameter is too large at low temperature. By investigating the atomic structure and chemical bonding, we show a drastic decrease in the lifetime of chemical bonds in the pressure interval of 0.4-4 megabar. We find the assumption of linear mixing to be valid for describing the EOS and the shock Hugoniot curve of the dense, partially ionized hydrocarbons under consideration. We therefore use the linear mixing approximation and make predictions of the shock compression of the practically important glow-discharge polymers and investigate the effects of oxygen content and C:H ratio on their Hugoniot curve.

Finally we performed PIMC and DFT-MD calculations to explore warm dense matter states of **aluminum**. Our equation of state (EOS) simulations cover a wide density-temperature range of 0.1-32.4 g/cm^3 and 10^4-10^8 K. Since PIMC and DFT-MD accurately treat effects of atomic shell structure, we find compression maxima along the principal Hugoniot curve attributed to K-shell and L-shell ionization, with a peak compression of rho/rho$_0$=4.90 at T=628.0 eV and P=3.6 Gbar. Subsequent multi-shock analysis reveals how closely one may track an isentrope in off-Hugoniot experiments. The results provide a benchmark for widely used EOS tables, such as SESAME, QEOS, and models based on Thomas-Fermi and Average Atom techniques. Finally, we compute pair-correlation functions, heat capacity, and the electronic density of states to reveal an evolving plasma structure and ionization process driven by thermal and pressure ionization.

More recently, we collaborate with Heather Whitley and experimental colleagues at LLNL to apply similar approach to investigate the EOS and shock compression of other low-Z element and compounds (**B, B_4C, and BN**), which are important ablator materials in dynamic compression experiments. We examine the sensitivity of the fusion yield to the EOS of these candidate ablator materials in radiation-hydrodynamic simulations of a direct-drive implosion. These results are useful for systematic improvement of existing EOS models and helpful in guiding the design of future gigabar experiments.

Pursuing our exploration of the second-row elements and because we are interested in mixtures, we studied **MgO** with our now-standard method of combining PIMC and DFT calculations. We performed the DFT simulations from 7.1 to 42.6 g/cm^3 and from 10^4 to 1.3x10^6 K. For these calculations, we had to switch from GGA to LDA because the pseudo-potentials available for GGA were not suited for high density calculations. The PIMC calculations were performed on a wider range of parameters, namely 0.36 to 53.5 g/cm^3 and 1.3x10^6 K up to 5.2x10^8 K, since they do not have the same technical limitations as DFT-MD. We thus were able to produce a consistent EOS table for MgO and we are still in the process of analyzing and interpreting our results. In parallel, we also studied the properties of pure magnesium. We used a similar grid of points and a similar strategy regarding the combination of GGA and LDA calculations as well as PIMC for higher temperatures. The aim is to characterize the properties of the MgO mixture with respect to the pure species Mg and O and to quantify the magnitude of the non-ideal effects. While the EOS table is now complete, we still have to finalize the analysis of the non-ideal effects.

Postdoc Felipe Gonzalez and our undergraduate summer intern, Henry Peterson, performed simulations of hot, dense **NaCl** as well as **argon** in order to complete our studies of the second row of elements. We performed PIMC and DFT-MD simulations. Upon inspection, this project turned out to be much more challenging than expected. We did not succeed in getting good agreement between our PIMC and DFT-MD results. This was caused by limitations in the DFT pseudopotentials that are available for VASP DFT-MD code. For chlorine and argon only pseudopotentials with frozen neon cores have been constructed, which prevented us from performing DFT-MD at sufficiently high temperature.

Henry and Felipe then moved on to performing calculations of warm dense states for both **$MgSiO_3$** and **Mg_2SiO_4** by combining PIMC at high temperatures and DFT-MD at lower temperatures; thus, a coherent equation of state was obtained for the density-temperature range of 6.41-32.1 g/cm^3 and 10^4-10^8 K. Pressures and internal energies computed with DFT-MD and PIMC agree for intermediate temperatures, showing the methods are consistent.

Ongoing analysis of these simulations will be used to characterize the electronic structure of the evolving plasma, as well as providing the Hugoniots for both materials.

4. How have the results been disseminated to communities of interest?

Publications (since last annual report):

S. Zhang, B. Militzer, L. X. Benedict, F. Soubiran, K. P. Driver, P. A. Sterne, "Path integral Monte Carlo simulations of dense carbon-hydrogen plasmas", J. Chem. Phys. 148 (2018) 102318

S. Zhang, K. P. Driver, F. Soubiran, B. Militzer "First-principles Equation of State and Shock Compression Predictions of Warm Dense Hydrocarbons", Phys. Rev. E 96 (2017) 013204.

K. P. Driver, B. Militzer, "First-principles simulations of warm dense lithium fluoride", Phys. Rev. E 95 (2017) 043205.

Kevin Driver, François Soubiran, Shuai Zhang, Burkhard Militzer, “Comparison of Path Integral Monte Carlo Simulations of Helium, Carbon, Nitrogen, Oxygen, Water, Neon, and Silicon Plasmas”, High Energ. Dens. Phys. 23, 81-89 (2017).

François Soubiran, Burkhard Militzer, Kevin Driver, Shuai Zhang, “Properties of hydrogen, helium, and silicon dioxide mixtures in giant planet interiors”, Phys. Plasmas 24, 041401 (2017).

Shuai Zhang, Kevin Driver, François Soubiran, Burkhard Militzer, “Equation of state and shock compression of warm dense sodium—A first-principles study”, J. Chem. Phys. 146, 074505 (2017).

Shuai Zhang, Kevin Driver, François Soubiran, Burkhard Militzer, “Path Integral Monte Carlo Simulations of Warm Dense Sodium”, High Energ. Dens. Phys. 21, 16-19 (2016).

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 (2016) 094109.

K. P. Driver, F. Soubiran, and B. Militzer, “Path Integral Monte Carlo Simulations of Warm Dense Aluminum”, resubmitted to Phys. Rev. E (2018).

Talks:

B. Militzer, "Path Integral Monte Carlo Simulations of Warm Dense Matter", 20th Biennial Conference of the APS Topical Group on Shock Compression of Condensed Matter (SCCM 2017), invited presentation, St. Louis, MO, 2017.

B. Militzer, “Path Integral Monte Carlo Simulations of Warm Dense Matter”, ICTP Workshop on Understanding Quantum Phenomena with Path Integrals: From Chemical Systems to Quantum Fluids and Solids, invited presentation, Trieste, Italy, 2017.

B. Militzer, “Path Integral Monte Carlo Simulations of Partially Ionized Plasmas”, Workshop on Current Challenges in the Physics of White Dwarfs, invited presentation, Santa Fe, NW, 2017.

F. Soubiran, "Path Integral Monte Carlo and Density Functional Theory Molecular Dynamics Simulations of Warm Dense Plastic, Oxygen, and Sodium", invited presentation, International Workshop on Warm Dense Matter Vancouver, B.C., Canada, 2017.

B. Militzer, “Path Integral Monte Carlo Simulations of Dense Plasmas”, 20th anniversary workshop for the NSF-DOE partnership in basic plasma science and engineering, Washington, DC, 2017.

S. Zhang, "First-principles study of equation of state and shock compression of warm dense sodium and other low-Z materials", APS March Meeting, New Orleans, LA, 2017.

Posters:

K. Driver, “First-Principles Equation of State and Shock Hugoniot Calculations of Lithium Fluoride and Sodium”, AGU Fall Meeting, San Francisco, CA, USA, 2016.

S. Zhang, “First-principles equation of state and shock compression of warm dense hydrocarbons and sodium”, LLNL Postdoc Poster Symposium, Livermore, CA, USA, 2017.

F. Soubiran, “Electronic transport properties of silicates at conditions of super-Earth interiors", International Workshop on Warm Dense Matter Vancouver, B.C., Canada, 2017.

S. Zhang, “First-principles equation of state and shock compression of warm dense hydrocarbons and sodium”, Telluride School on Stochastic Approaches to Electronic Structure Calculations, Telluride, CO, USA, 2017.

5. What do you plan to do during the next reporting period to accomplish the goals?

We plan on finalizing our CH calculations since the first experimental results have been obtained at the Gbar platform at NIF.

We will continue our PIMC method development to extend the method to heavier elements and to make the sampling in the low temperature regime more efficient, where is it most difficult for PIMC.

We will continue our current efforts to characterize various important silicates at extreme conditions.

We are also in contact with Heather Withley LLNL to start a joint project to perform simulations of various boron-rich compounds since they will be used in the next generation of NIF ablators.

1. What is the impact on the development of the principal discipline(s) of the project?

Our results have been accepted as benchmarks for other theoretical methods developed in the community. While our PIMC simulations methods are very demanding computationally, they contain the most physics and rely on minimal approximations only. Charley Starrett (LANL) and his team regularly compares with our findings.

From our recent paper with Suxing Hu, we learned that the energy and the heat capacity, that one obtains with OF-MD simulations, are inaccurate because this method cannot accurately capture the shell effects of the atom.

We showed that the Hugoniot curve of CH compounds can be obtained with fairly good accuracy by invoking the linear mixing approximation and relying solely on the EOS tables of C and of H while neglecting all interaction effects. This simplifies the characterization of ternary mixtures tremendously.

2. What is the impact on other disciplines?

We expect our comparison between PIMC and OF-MD results will eventually lead to more accurate OF-MD methods, or at least to a closer scrutiny of the predictions with current methods.

Our theoretical prediction of the shock Hugoniot curve of CH do not agree for the high pressures with the experimental findings by Annie Kritcher. This is a point of concern and further investigations are needed. However, our theoretical findings have already led to a closer scrutiny of the data analysis procedure in a regime where the shock wave converged to reach the most extreme pressure and disentangling density from opacity effects is most challenging.

3. What is the impact on the development of human resources?

Three postdocs, one PhD student and one undergraduate student were trained in simulations of matter at extreme conditions. They learned about the challenges and the importance of this field. They acquired knowledge about on-going experimental activities at national laboratories. This grant help shape their careers various ways. For example, former postdoc Kevin Driver has been hired into staff scientist position at Lawrence Livermore National Laboratory (LLNL). Former PhD student, Shuai Zhang, has been hired into a postdoc position at LLNL. He now pursues a career in warm dense matter simulations and collaborates with multiple experimental groups at LLNL and elsewhere.