First-Principles Equation of State Database For Warm Dense Matter Computations

Burkhard Militzer, F. Gonzalez, S. Zhang, K. Driver, F. Soubiran

UC Berkeley, UC Berkeley, LLE, LLNL, CEA
Outline

• Path integral Monte Carlo (PIMC) method
• Linear mixing approximation
• FPEOS database
• Comparison with different experiments
I. Path Integral Monte Carlo
Density functional molecular dynamics at lower T

Born-Oppenheimer approx. MD with classical nuclei:

\[ F = m \ a \]

Forces derived DFT with electrons in the instantaneous ground state.
Path integral Monte Carlo at high T > $10^4 \ldots 10^6$ K
Starting from Restricted PIMC Simulations of Hydrogen

PHYSICAL REVIEW LETTERS

VOLUME 73 17 OCTOBER 1994 NUMBER 16

Equation of State of the Hydrogen Plasma by Path Integral Monte Carlo Simulation
C. Pierleoni, 1,2, * D. M. Ceperley, 3 B. Bernu, 1 and W. R. Magro 3

VOLUME 76, NUMBER 8 PHYSICAL REVIEW LETTERS 19 FEBRUARY 1996

Molecular Dissociation in Hot, Dense Hydrogen
W. R. Magro, 1 D. M. Ceperley, 2 C. Pierleoni, 3 and B. Bernu 4
PIMC and DFT-MD Simulations of Hydrogen and Helium

Hydrogen

Helium

Temperature (K)

Pressure (GPa)

\( \Gamma < 1, \theta > 1 \) (classical regime)

\( \Gamma > 1, \theta < 1 \) (coupled and degenerate regime)


Restricted PIMC for fermions: How is the restriction applied?

Construct a **fermionic trial density matrix** in form of a Slater determinant of single-particle density matrices:

$$\rho_T(R,R',\beta) = \begin{vmatrix} \rho(r_1,r'_1,\beta) & \cdots & \rho(r_1,r'_N,\beta) \\ \vdots & \ddots & \vdots \\ \rho(r_N,r'_1,\beta) & \cdots & \rho(r_N,r'_N,\beta) \end{vmatrix}$$

Enforce the following nodal condition for all time slices along the paths:

$$\rho_T[R(t),R(0),t] > 0$$

This 3N-dimensional conditions eliminates all negative and some positive contribution to the path \( \rightarrow \) Solves the fermion sign problem approx.

Free-particle nodes:

$$\rho_0^{[1]}(r,r';\beta) = \sum_k e^{-\beta E_k} \Psi_k(r) \Psi_k^*(r')$$
Silicates: $\text{MgSiO}_3$
MgSiO$_3$: Principal Hugoniot Curve

Gonzalez, Soubiran, Peterson, Militzer, 
*Phys. Rev. B* 101 (2020) 024107
MgSiO$_3$ : Principal Hugoniot Curve

![Graph showing the principal Hugoniot curve for MgSiO$_3$. The graph includes multiple curves representing different physical processes such as melting curves, isentropes, and Hugoniot curves.]
MgSiO$_3$ : Principal Hugoniot Curve

CH plastics
Inertial confinement fusion experiments with plastic coated spheres of liquid H$_2$
PIMC and DFT-MD simulations performed for $\text{C}_2\text{H}$, CH, $\text{C}_2\text{H}_3$, CH$_3$ and CH$_4$.
CH Shock Hugoniot Curves: Comparison of Theory and Experiments
CH Shock Hugoniot Curves: Comparison of Theory and Experiments

CH Shock Hugoniot Curves: Comparison of Theory and Experiments

Pressure (TPa)

Shock compression ratio \( \rho/\rho_0 \)
CH Shock Hugoniot Curves: Comparison of Theory and Experiments
Linear Mixing
and
FPEOS database
Hugoniot Curves of **BN** and **B₄C**

Fully interacting EOS and Linear Mixing agree quite well.

Boron nitride
Zhang et al. PRB 2019

Boron carbide
Zhang et al. PRE 2020
Hugoniot Curves of **BN** and **B$_4$C**

Fully interacting EOS and Linear Mixing agree quite well.

**Boron nitride**
Zhang et al. PRB 2019

**Boron carbide**
Zhang et al. PRE 2020
Linear Mixing at Constant P and T
(Also called additive volume rule)

\[ V_{\text{mix}} = N_1 V_1 + N_2 V_2 , \]
\[ m_{\text{mix}} = N_1 m_1 + N_2 m_2 , \]
\[ E_{\text{mix}} = N_1 E_1 + N_2 E_2 , \]
\[ \rho_{\text{mix}} = \frac{m_{\text{mix}}}{V_{\text{mix}}} \]
Hugoniot Curves of $\text{MgO}$ and $\text{MgSiO}_3$
Results from fully interacting EOS and experiment.

Soubiran et al. JCP 2019

Gonzalez et al. PRB 2020

McCoy et al. PRB 2019

Millot et al. GRL 2020
Hugoniot Curves of MgO and MgSiO₃
Fully interacting EOS and Linear Mixing agree quite well.

Linear mixing works well for $T \gtrsim 2 \times 10^5 \text{K}$ and $\rho/\rho_0 \gtrsim 3.2$
Nonideal mixing effects in warm dense matter studied with first-principles computer simulations

Cite as: J. Chem. Phys. 153, 184101 (2020); doi: 10.1063/5.0023232
Submitted: 28 July 2020 • Accepted: 25 October 2020 • Published Online: 9 November 2020

Burkhard Militzer,¹,²,a) Felipe González-Cataldo,¹ Shuai Zhang,³ Heather D. Whitley,⁴ Damian C. Swift,⁴ and Marius Millot⁵
Nonlinear Mixing Effects in MgSiO$_3$

Fully interacting EOS and Linear Mixing agree quite well.

Linear mixing works well for $T \gtrsim 2 \times 10^5$K and $\rho/\rho_0 \gtrsim 3.2$
Hugoniot Curves of CO and CO$_2$

Experimental CO$_2$ Hugoniot agree with Linear Mixing result.

Crandall et al. PRL 2020
Hugoniot Curves of H$_2$O, H$_2$O$_2$, and Al$_2$O$_3$

Experimental H$_2$O Hugoniot agree with Linear Mixing result
### FPEOS: 11+10 Available Tables

<table>
<thead>
<tr>
<th>Material</th>
<th>Number of isochores</th>
<th>Minimum density [g cm(^{-3})]</th>
<th>Maximum density [g cm(^{-3})]</th>
<th>Minimum temperature [K]</th>
<th>Maximum temperature [K]</th>
<th>Number of EOS points</th>
<th>References</th>
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<tr>
<td>Hydrogen</td>
<td>33</td>
<td>0.001</td>
<td>798.913</td>
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<td>Helium</td>
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<td>0.387</td>
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<td>6736</td>
<td>5.174×10(^8)</td>
<td>284</td>
<td>[95, 96]</td>
</tr>
</tbody>
</table>
First-Principles Equation of State Database online http://militzer.berkeley.edu/FPEOS

First-Principles Equation of State (FPEOS) Database for Warm Dense Matter Computation

Authors: B. Militzer, F. Gonzalez-Cataldo, S. Zhang, K. P. Driver, F. Soubiran

With the goal in mind of making WDM computations more reliable and efficient, we make available our EOS tables for 11 elements and 10 compounds as well as the C++ computer codes for their interpolation. Python code is provided to generate graphs of shock Hugoniot curve, isentropes, isobars, and isothersms for compounds and user-defined mixtures. We put together this first-principles equation of state (FPEOS) database for matter at extreme conditions by combining results from path integral Monte Carlo and density functional molecular dynamics simulations of the elements H, He, B, C, N, O, Ne, Na, Mg, Al and Si as well as the compounds LiF, B4C, BN, CH4, CH2, C2H3, CH, C2H, MgO, and MgSiO3. For all these materials, we provide the pressure and internal energy over a wide density-temperature range from ~0.5 to 50 g/cc and from ~10^4 to 10^9 K. This database encompasses the results from approximately 5000 different first-principles simulations. It allows one to compute isobars, adiabats, and shock Hugoniot curves in the regime of L and K shell ionization. Invoking the linear mixing approximation, one can study the properties of user-defined mixtures at high density and temperature.


5000 first-principles calculations have been combined into our FPEOS database. So anyone can predict shock Hugoniot curves for a variety of compounds and mixtures. This will make warm dense matter calculations more reliable and efficient.
We propose to make EOS measurements along the Hugoniot with the Gbar platform of carbon-oxygen rich materials that resemble conditions in White Dwarf stars.

Graph made by D. Saumon

Glyoxal $\text{C}_2\text{O}_2\text{H}_2$  
comp:~/fpeos> fpeos binaryMixture EOS1=6 2.0 EOS2=18 2.0 rho0=1.27 E0=-227.8

Acetic acid $\text{C}_2\text{O}_2\text{H}_4$  
comp:~/fpeos> fpeos binaryMixture EOS1=6 2.0 EOS2=16 2.0 rho0=1.049 E0=-229.0