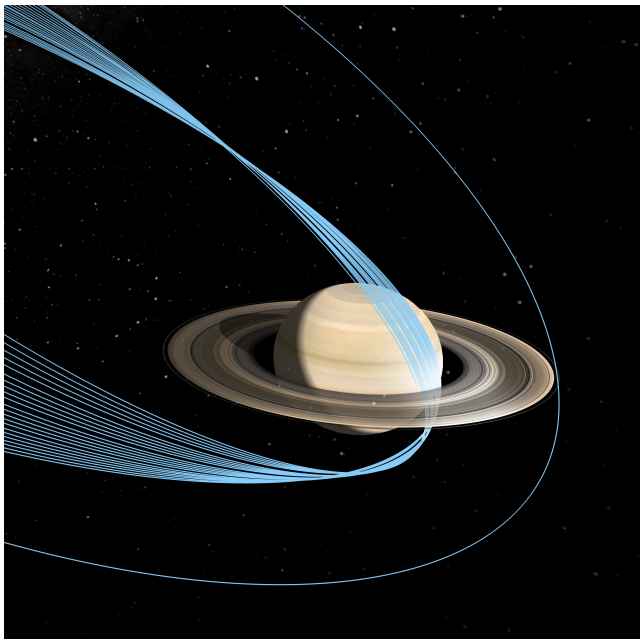
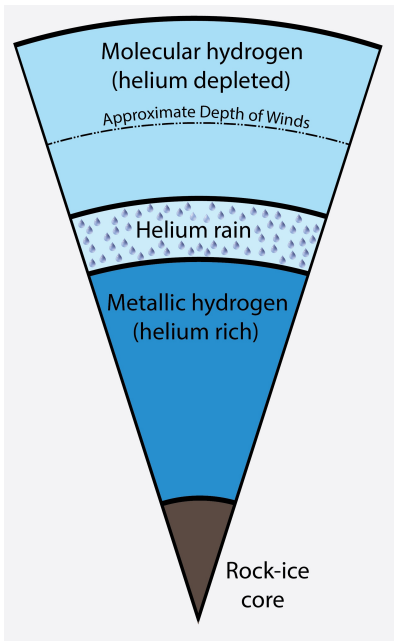
First-Principles Equation of State Database for Warm Dense Matter Computation

Burkhard Militzer, UC Berkeley **F. Gonzalez,** UC Berkeley **S. Zhang,** LLE **H. Peterson,** UC Berkeley **K. Driver,** LLNL **F. Soubiran,** CEA **T. Kovacevic,** UC Berkeley **R. Domingos,** UC Berkeley **H. Whitley,** LLNL **M. Millot,** LLNL **D. Swift,** LLNL **S. Stewart,** UC Davis **R. Jeanloz,** UC Berkeley **R. Falcone,** UC Berkeley

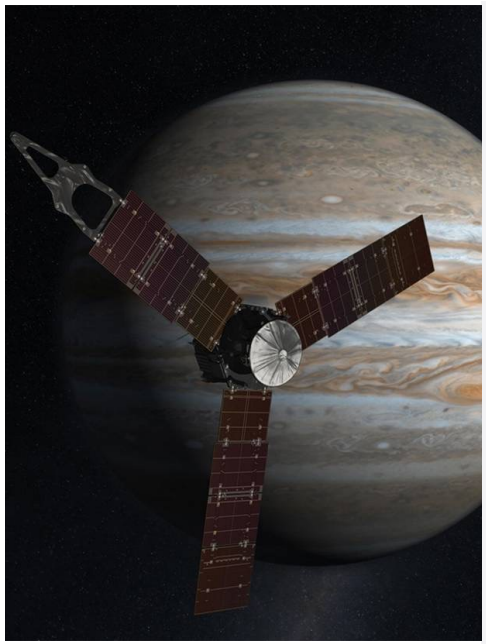
Models for the Interiors of Jupiter and Saturn to Match Gravity Measurements of *Juno* and *Cassini* Spacecrafts



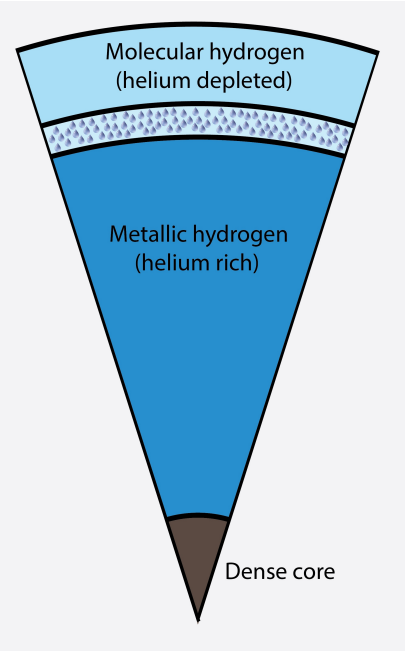
Cassini's Gran Finale orbits inside rings



Saturn's interior

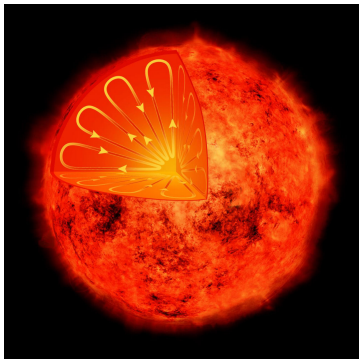


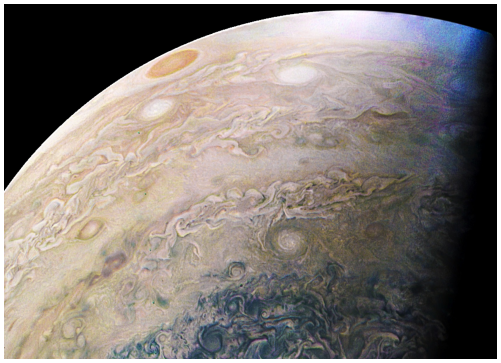
Juno spacecraft



Jupiter's interior

Center for Matter under Extreme Conditions (CMEC)



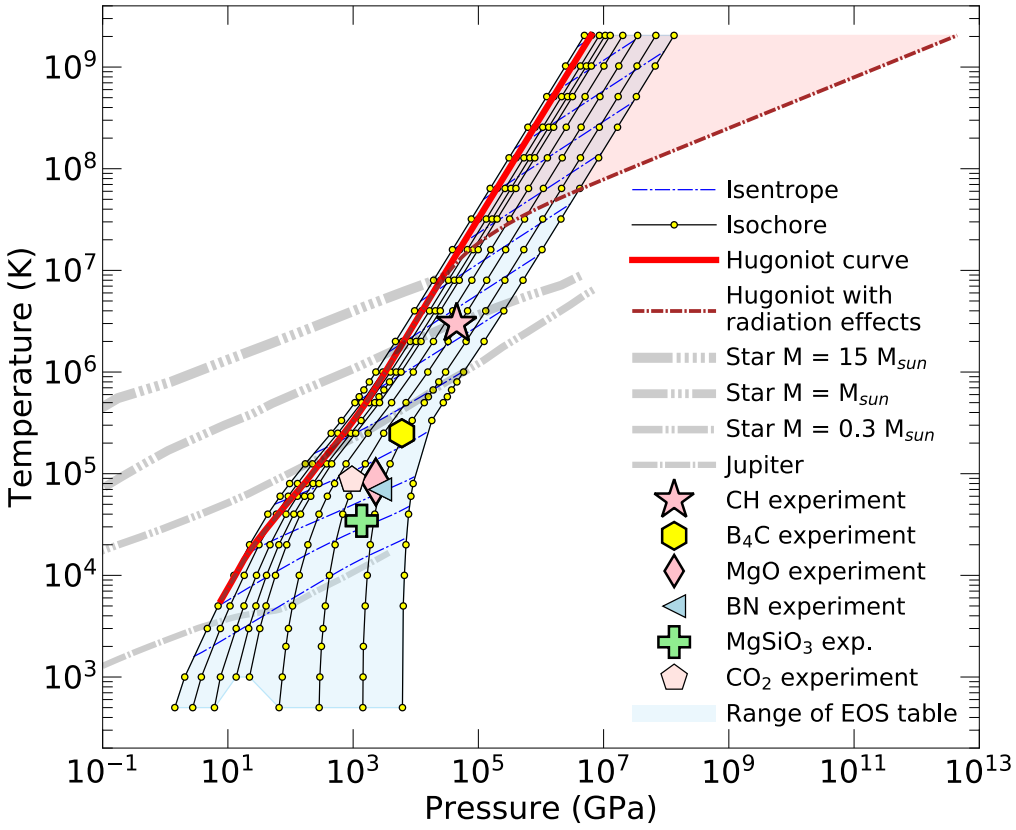


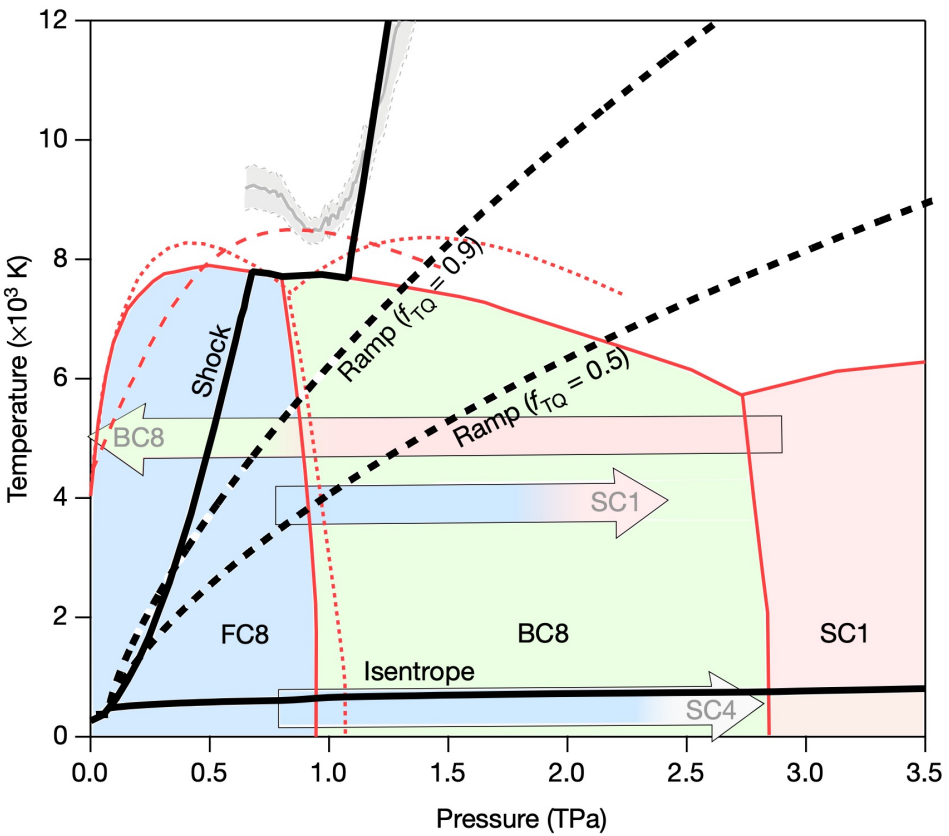
Article

Metastability of diamond ramp-compressed to 2 terapascals

A. Lazicki[1]✉, D. McGonegle[2], J. R. Rygg[3,4,5], D. G. Braun[1], D. C. Swift[1], M. G. Gorman[1], R. F. Smith[1], P. G. Heighway[2], A. Higginbotham[6], M. J. Suggit[2], D. E. Fratanduono[1], F. Coppari[1], C. E. Wehrenberg[1], R. G. Kraus[1], D. Erskine[1], J. V. Bernier[1], J. M. McNaney[1], R. E. Rudd[1], G. W. Collins[3,4,5], J. H. Eggert[1] & J. S. Wark[2]

2 TPa = 2000 GPa = 20 Mbar



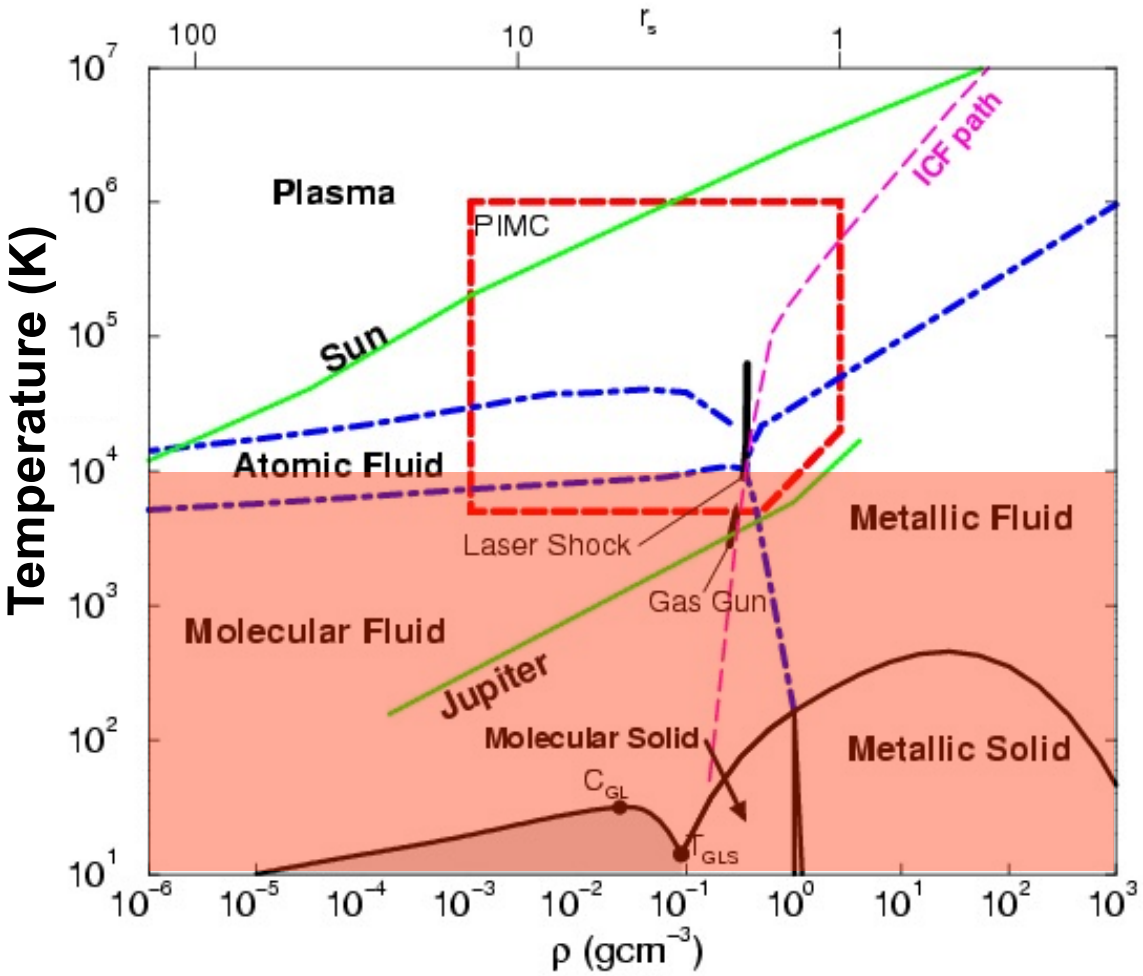


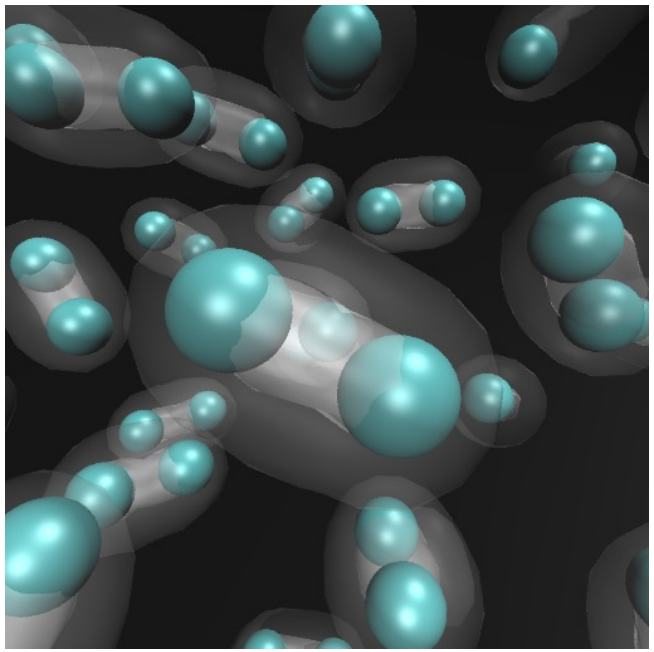
Outline

- Path integral Monte Carlo (PIMC) method
- EOS computation and combination with DFT-MD
- Si and $MgSiO_3$ silicates
- Application to CH plastic
- Linear mixing approximation
- FPEOS database
- Why the EOS of H-He matters for Jupiter

I.
Warm Dense Matter

Density functional molecular dynamics at lower T



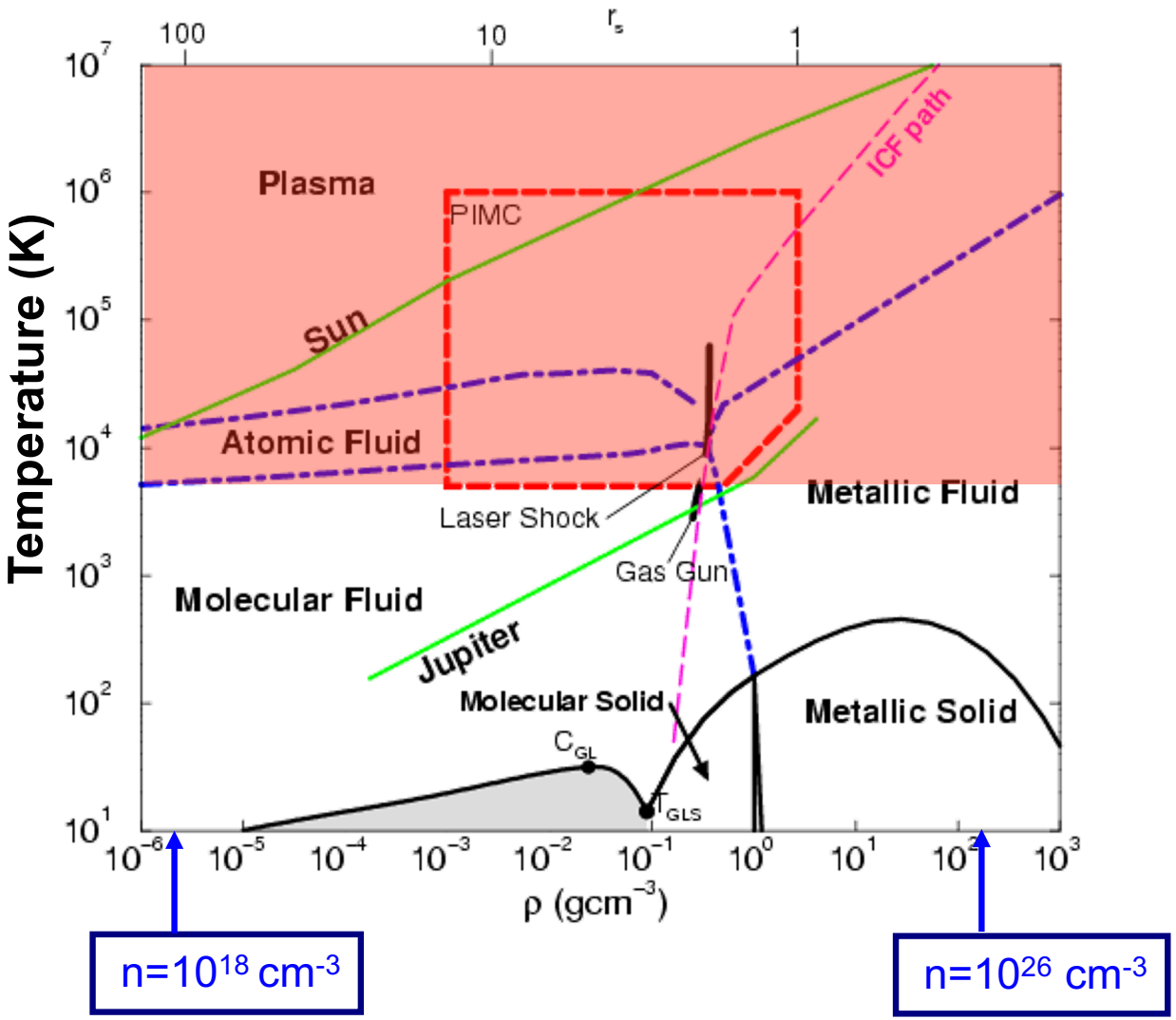


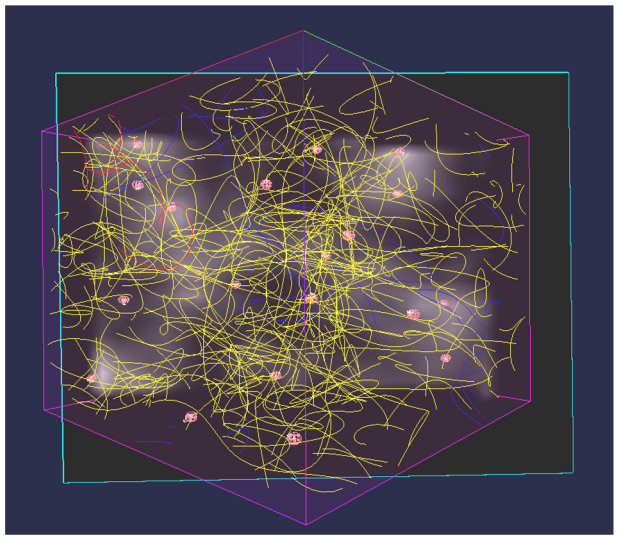
Born-Oppenheimer approx.
MD with classical nuclei:

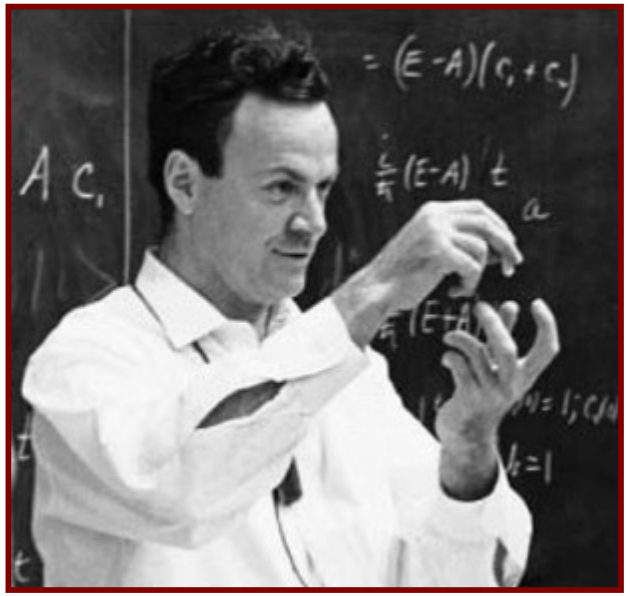
F = m a

Forces derived DFT with electrons in the instantaneous ground state.

Path integral Monte Carlo at high T > 10^4…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]

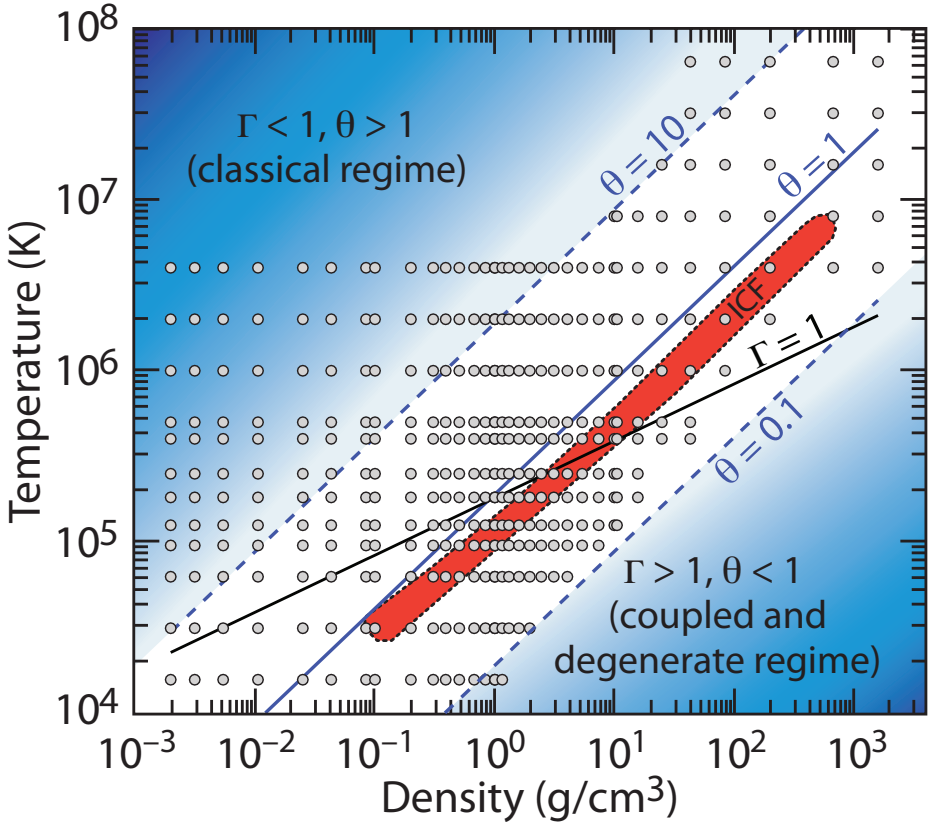
VOLUME 76, NUMBER 8 PHYSICAL REVIEW LETTERS 19 FEBRUARY 1996

Molecular Dissociation in Hot, Dense Hydrogen

W. R. Magro,[1] D. M. Ceperley,[2] C. Pierleoni,[3] and B. Bernu[4]

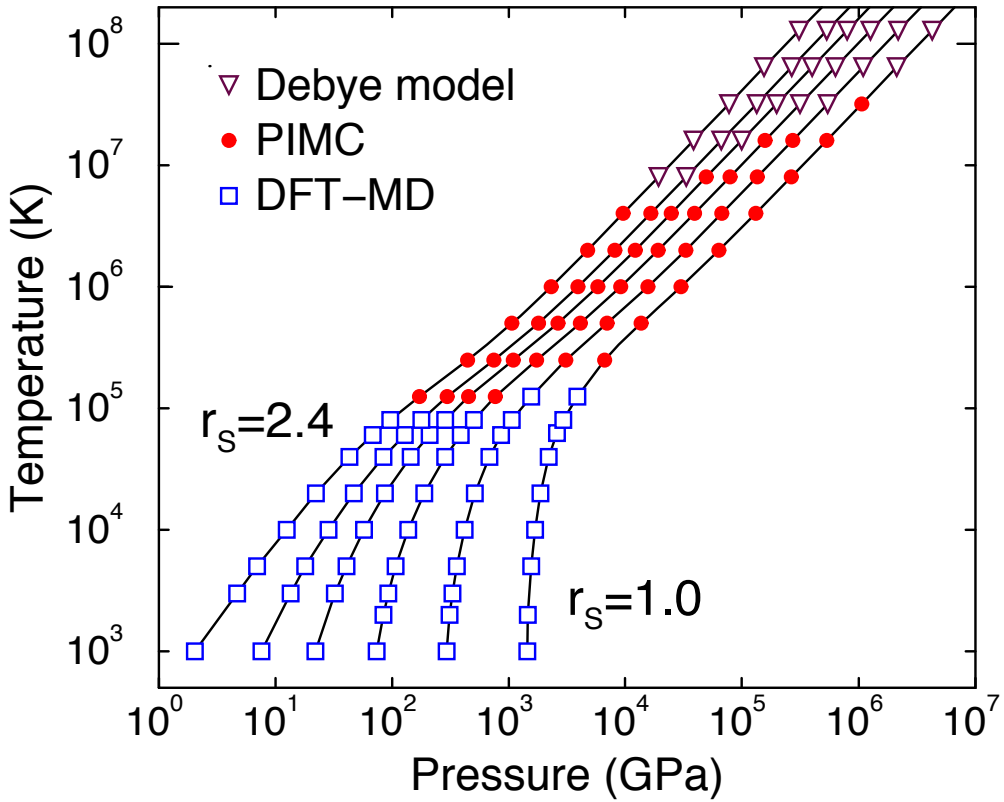
PIMC and DFT-MD Simulations of Hydrogen and Helium

Hydrogen



S. X. Hu, B. Militzer, V. N. Goncharov, S. Skupsky, *Phys. Rev. Lett.*, **104** (2010) 235003
Phys. Rev. B **84** (2011) 224109.

Helium



B. Militzer, *Phys. Rev.* B **79** (2009) 155105
B. Militzer, *Phys. Rev. Lett.* **97** (2006) 175501

Canonical Ensembles:

Classical

Boltzmann factor

$$e^{-E \,/\, k_B T}$$

Quantum

Density matrix

$$\hat{\rho} = e^{-\beta\, \hat{\mathrm{H}}}$$

$$\rho(R,R',\beta) = \left\langle R \middle| e^{-\beta\, \hat{\mathrm{H}}} \middle| R' \right\rangle$$

$$\rho(R,R',\beta) = \sum_S e^{-\beta\, E_S}\ \Psi_S^*(R)\ \Psi_S(R')$$

Thermodynamic averages:

$$Z_{Cl} = \sum_S e^{-\beta\, E_S}$$

$$Z_Q = Tr[\hat{\rho}] = \int dR\ \left\langle R \middle| e^{-\beta\, \hat{\mathrm{H}}} \middle| R \right\rangle$$

$$\left\langle \hat{O} \right\rangle = \frac{Tr[\hat{O}\ \hat{\rho}]}{Tr[\hat{\rho}]}$$

Path Integrals in Imaginary Time

Simplest form for the paths' action: primitive approx.

Density matrix:

$$\hat{\rho} = e^{-\beta \hat{\mathrm{H}}} = \left(e^{-\tau \hat{\mathrm{H}}}\right)^M, \quad \beta = \frac{1}{k_B T}, \quad \tau = \frac{\beta}{M}$$

$$\langle \hat{O} \rangle = \frac{\mathrm{Tr}[\hat{O}\hat{\rho}]}{\mathrm{Tr}[\hat{\rho}]}$$

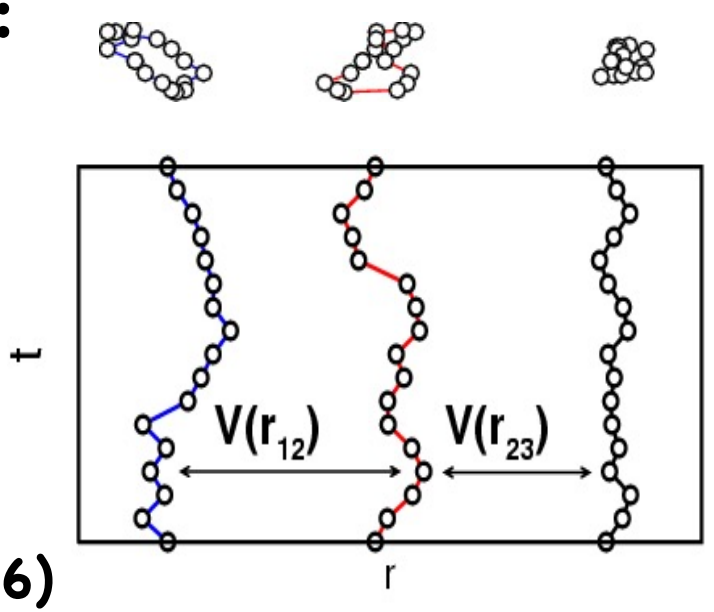
Trotter break-up:

$$\langle R | \hat{\rho} | R' \rangle = \langle R | (e^{-\tau \hat{\mathrm{H}}})^M | R' \rangle = \int dR_1 \ldots \int dR_{M-1} \langle R | e^{-\tau \hat{\mathrm{H}}} | R_1 \rangle \langle R_1 | e^{-\tau \hat{\mathrm{H}}} | R_2 \rangle \ldots \langle R_{M-1} | e^{-\tau \hat{\mathrm{H}}} | R' \rangle$$

Path integral and primitive action S :

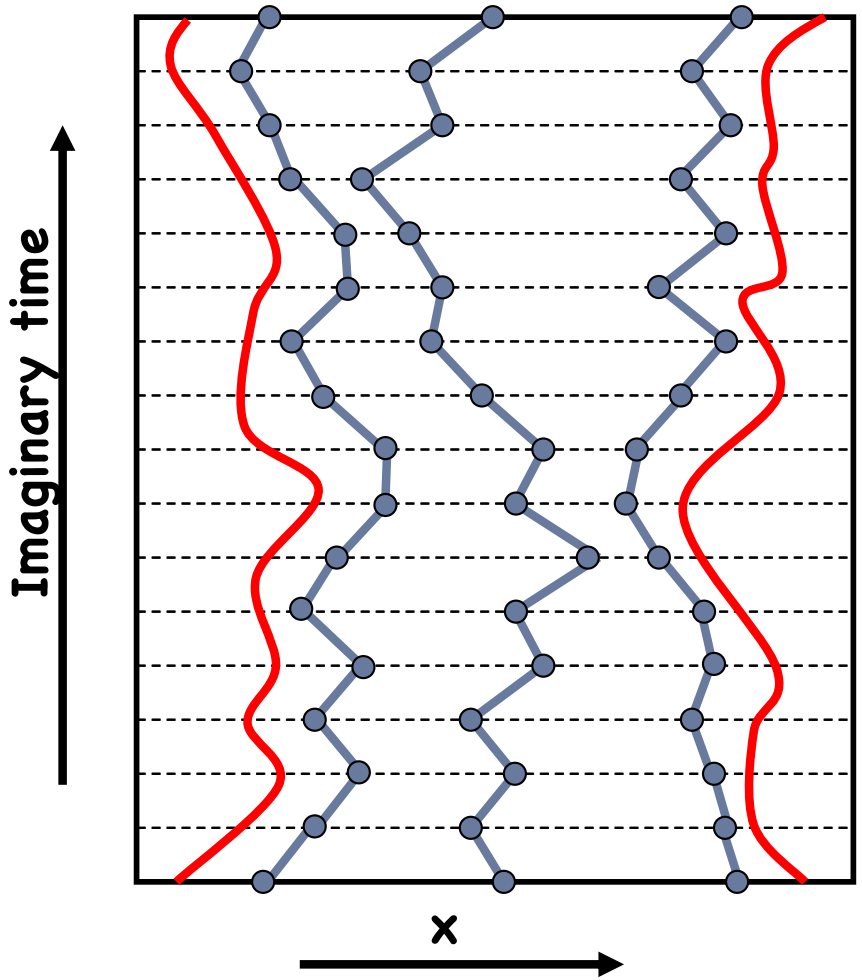
$$\langle R | \hat{\rho} | R' \rangle = \oint_{R \to R'} dR_t e^{-S[R_t]}$$

$$S[R_t] = \sum_{i=1}^{M} \frac{(R_{i+1} - R_i)^2}{4\lambda\tau} + \frac{\tau}{2}\left[V(R_i) + V(R_{i+1})\right]$$



Pair action: Militzer, Comp. Phys. Comm. (2016)

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:

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

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

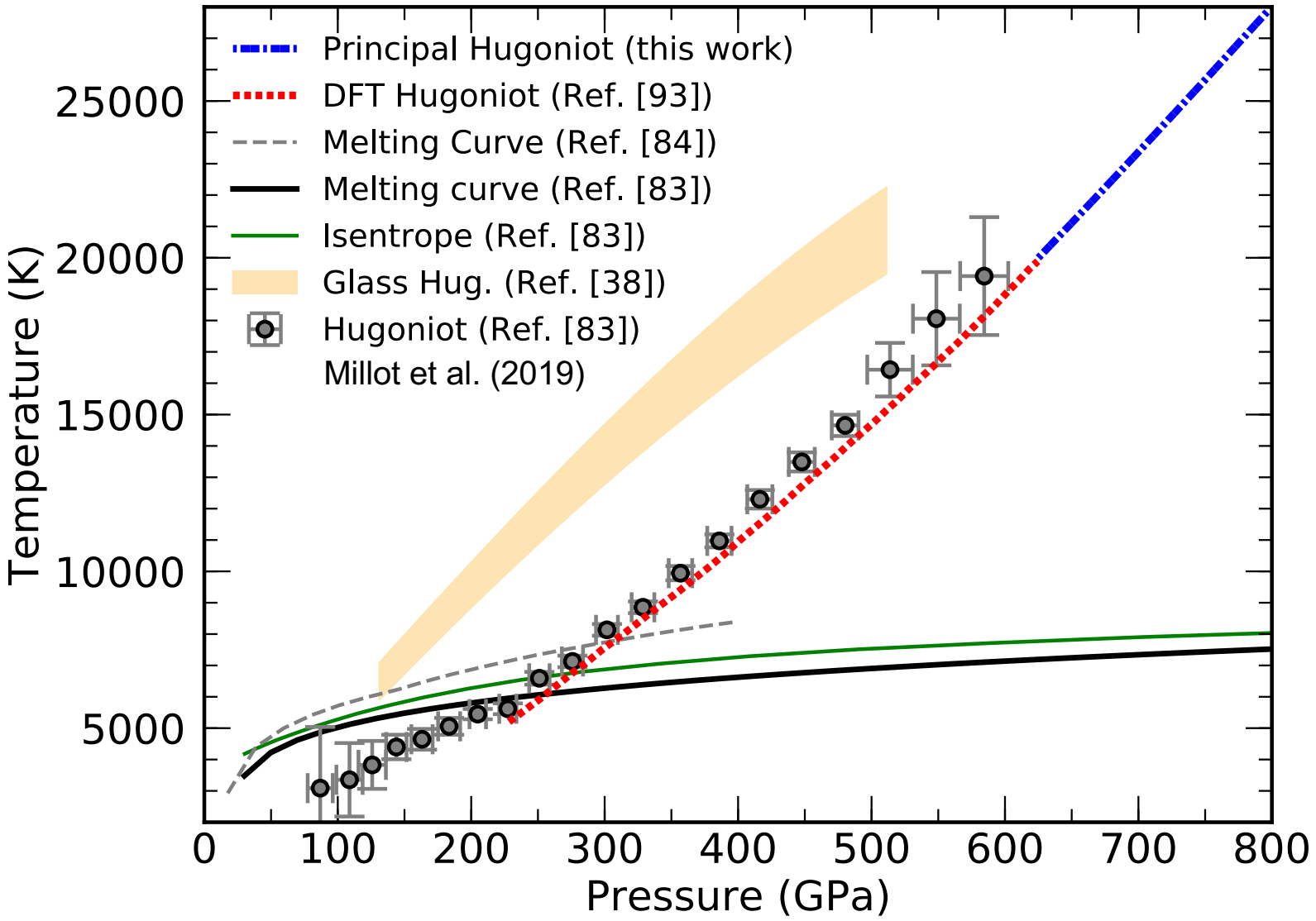
Free-particle nodes:

$$\rho_0^{[1]}(r,r';\beta) = \sum_k e^{-\beta E_k}\,\Psi_k(r)\,\Psi_k^*(r')$$

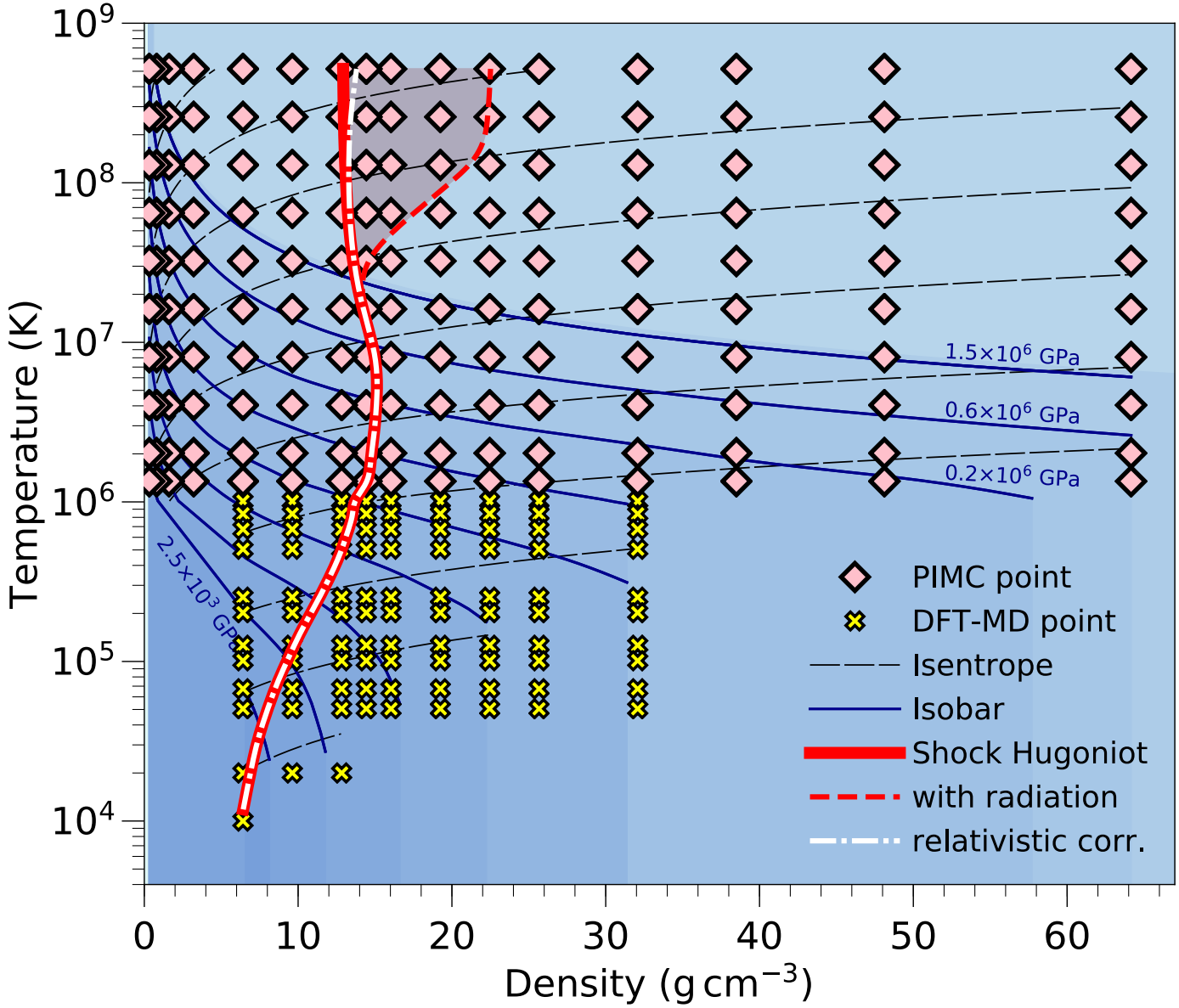
Silicates:

$MgSiO_3$

$MgSiO_3$: Principal Hugoniot Curve

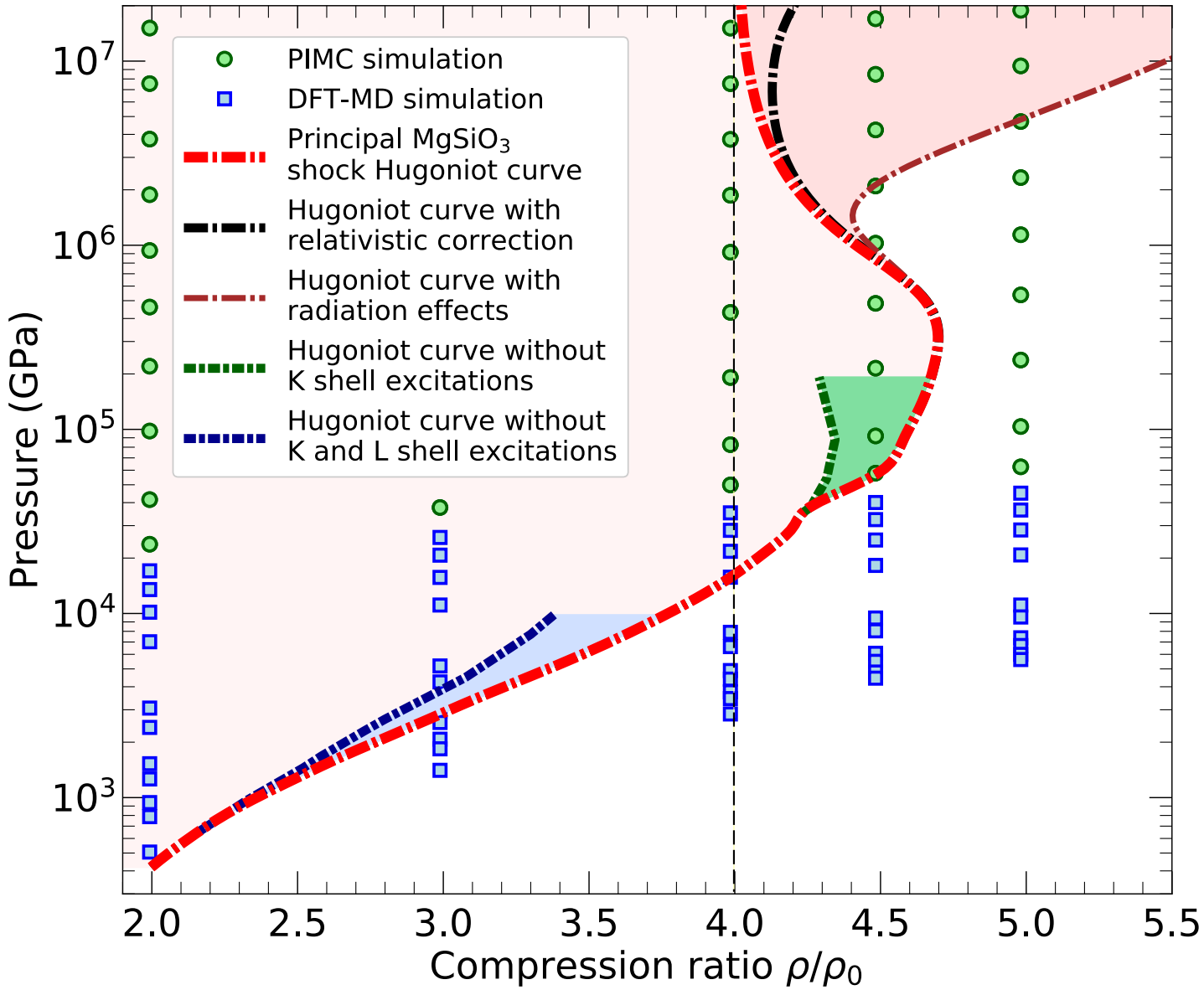


$MgSiO_3$: Principal Hugoniot Curve



Gonzalez, Soubiran, Peterson, Militzer, *Phys. Rev. B* **101** (2020) 024107

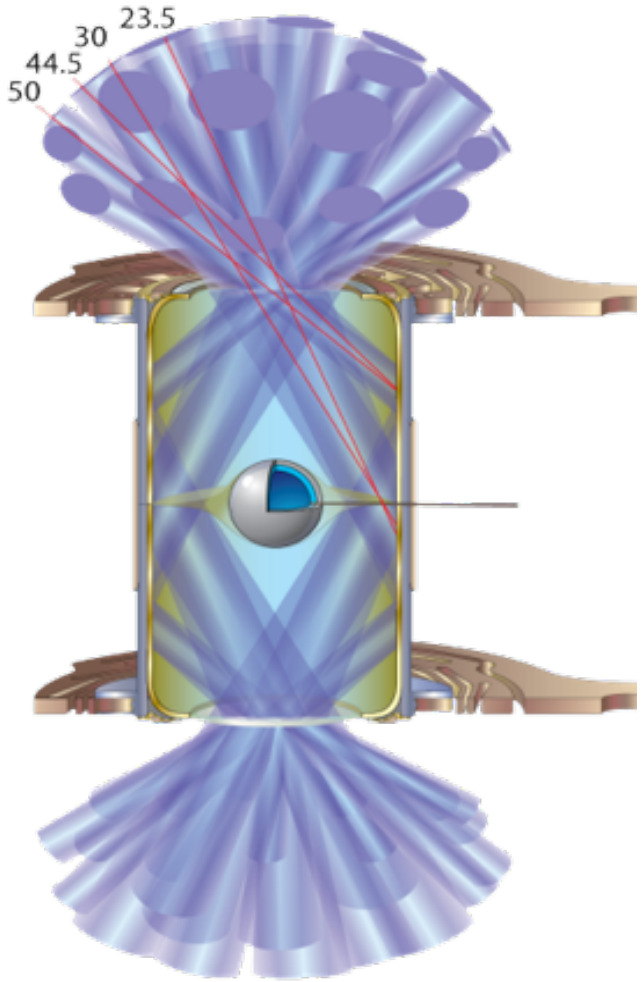
$MgSiO_3$: Principal Hugoniot Curve

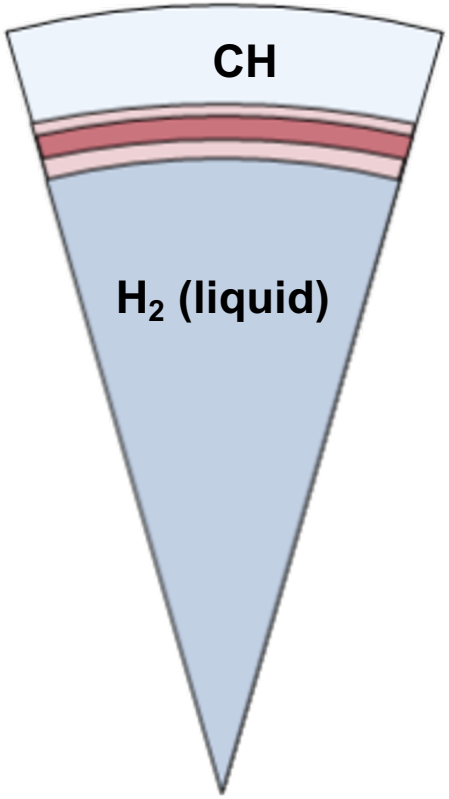


Gonzalez, Soubiran, Peterson, Militzer, *Phys. Rev. B* **101** (2020) 024107

CH plastics

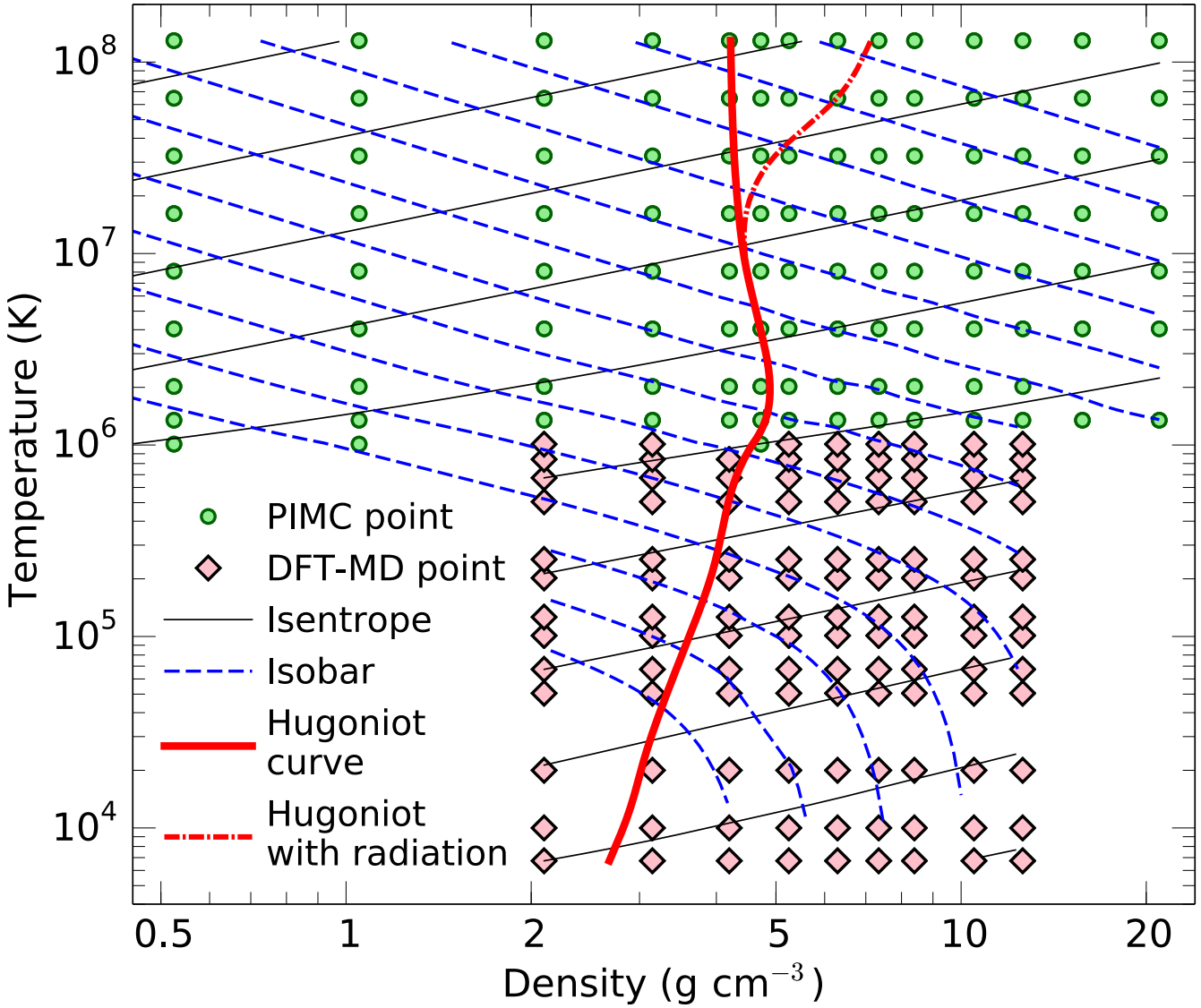
Inertial confinement fusion experiments with plastic coated spheres of liquid H_2





(Graphics: Bachmann et al. LLNL)

PIMC and DFT-MD simulations performed for C_2H, CH, C_2H_3, CH_3 and CH_4.

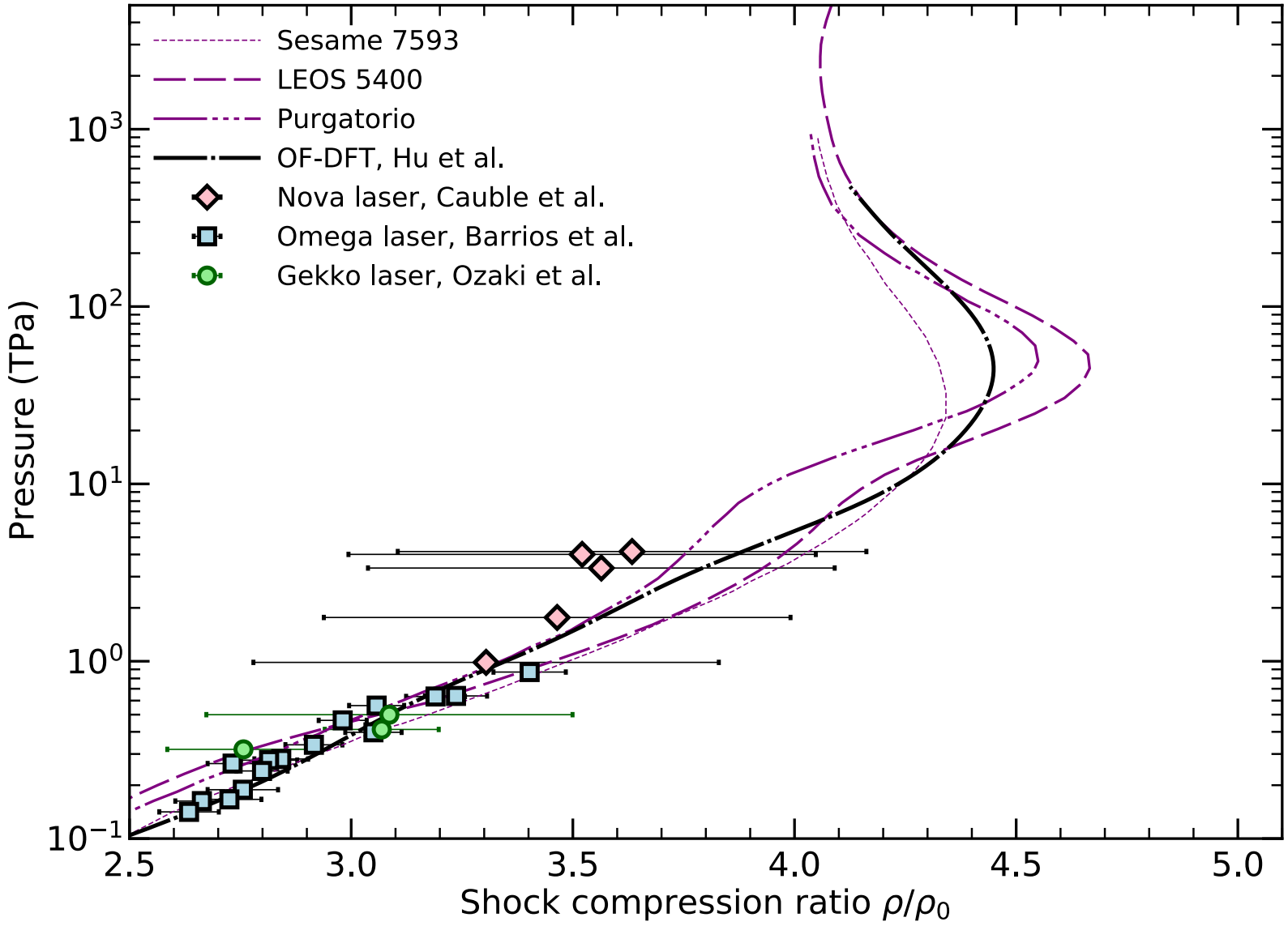


All calculations performed on

BLUE WATERS
SUSTAINED PETASCALE COMPUTING

NCSA

CH Shock Hugoniot Curves: Comparison of Theory and Experiments



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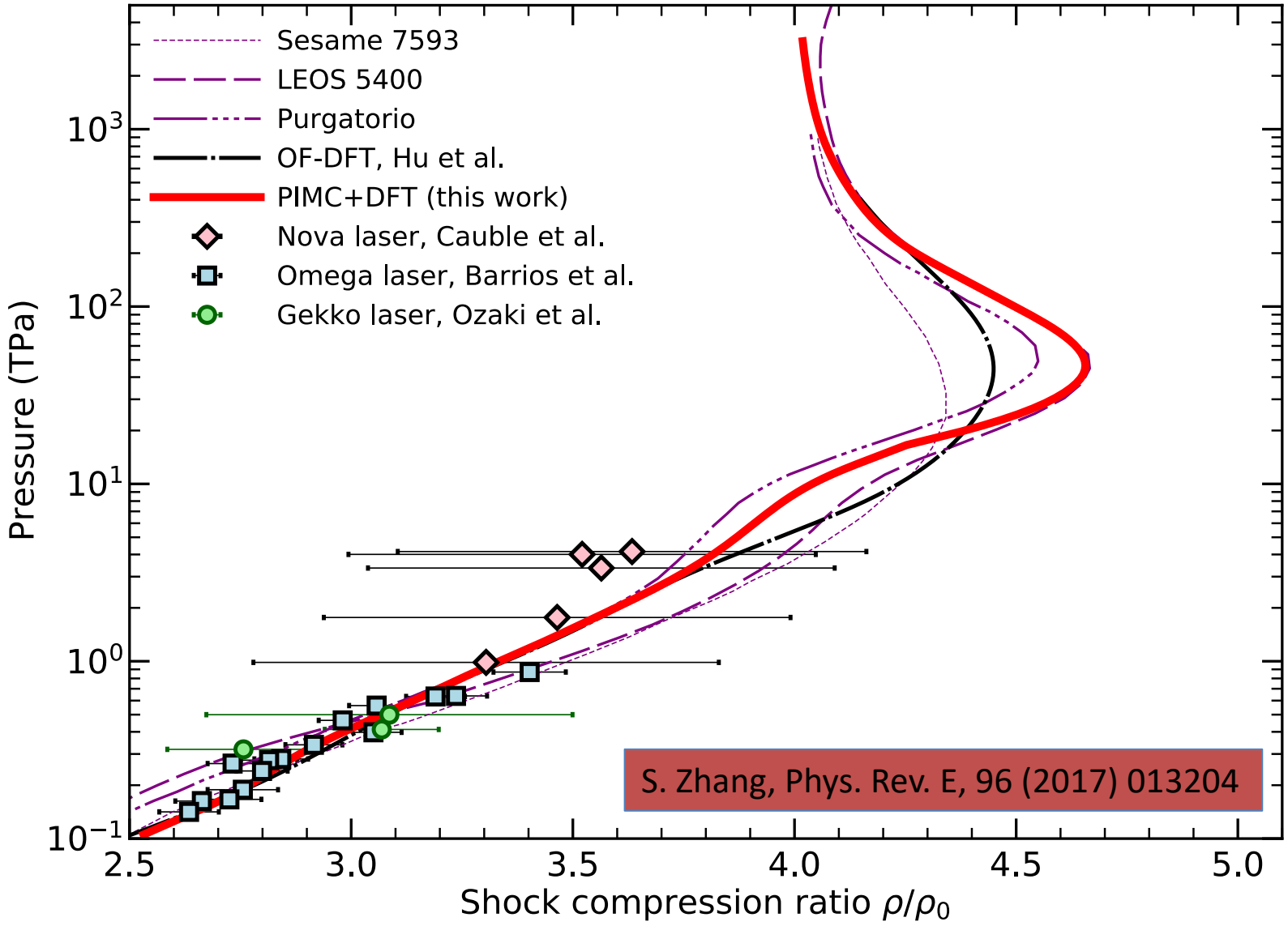

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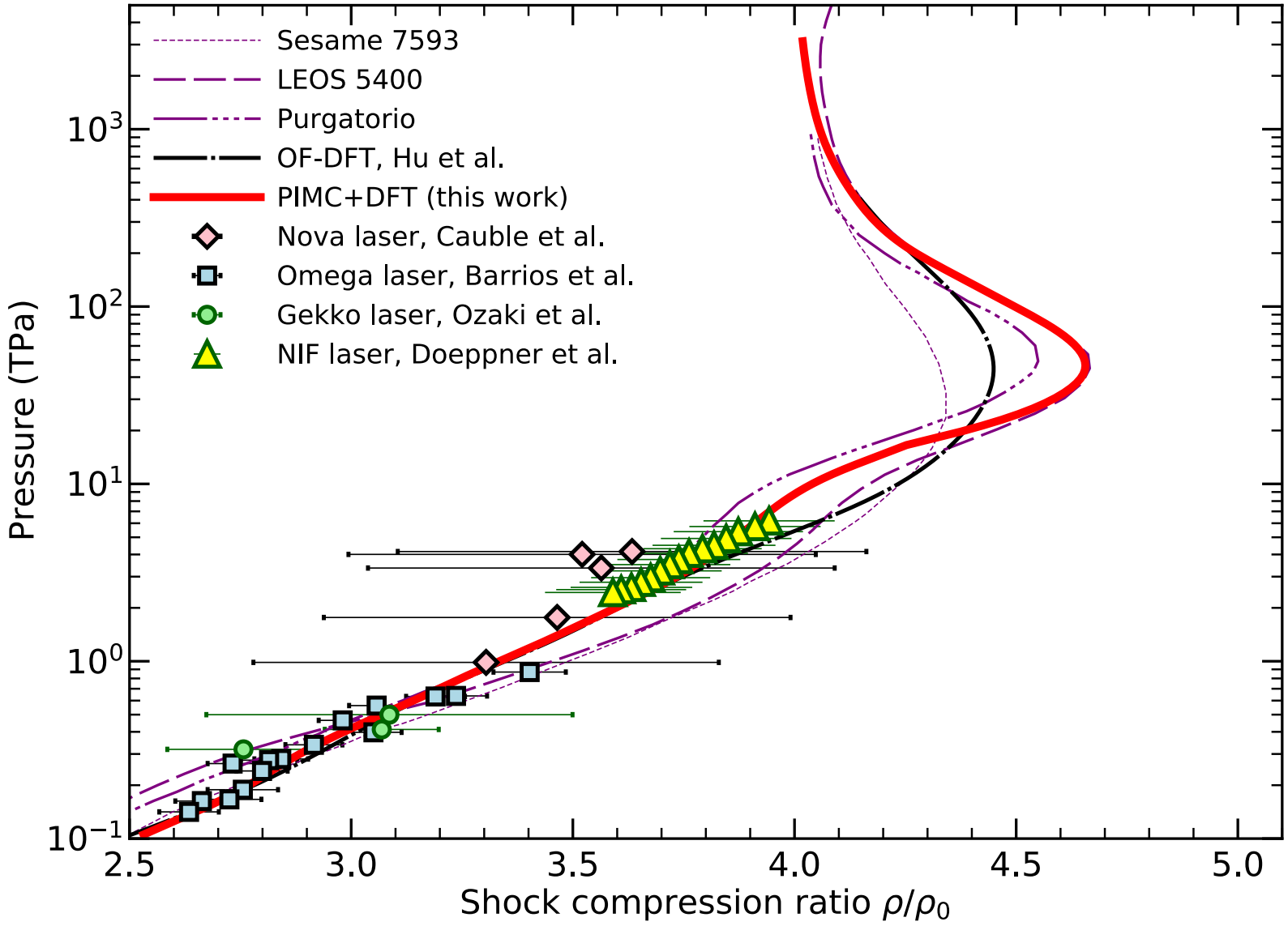

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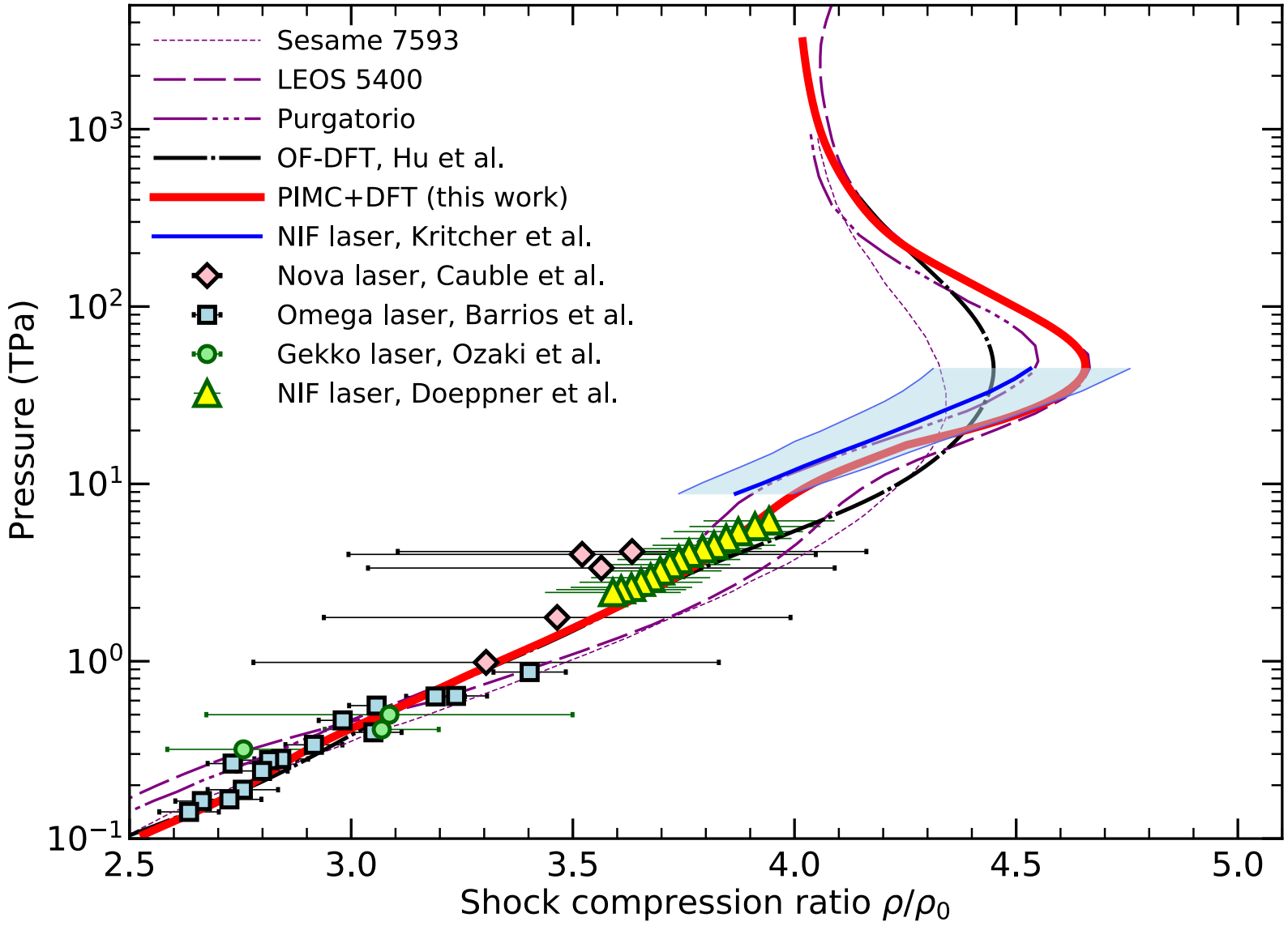
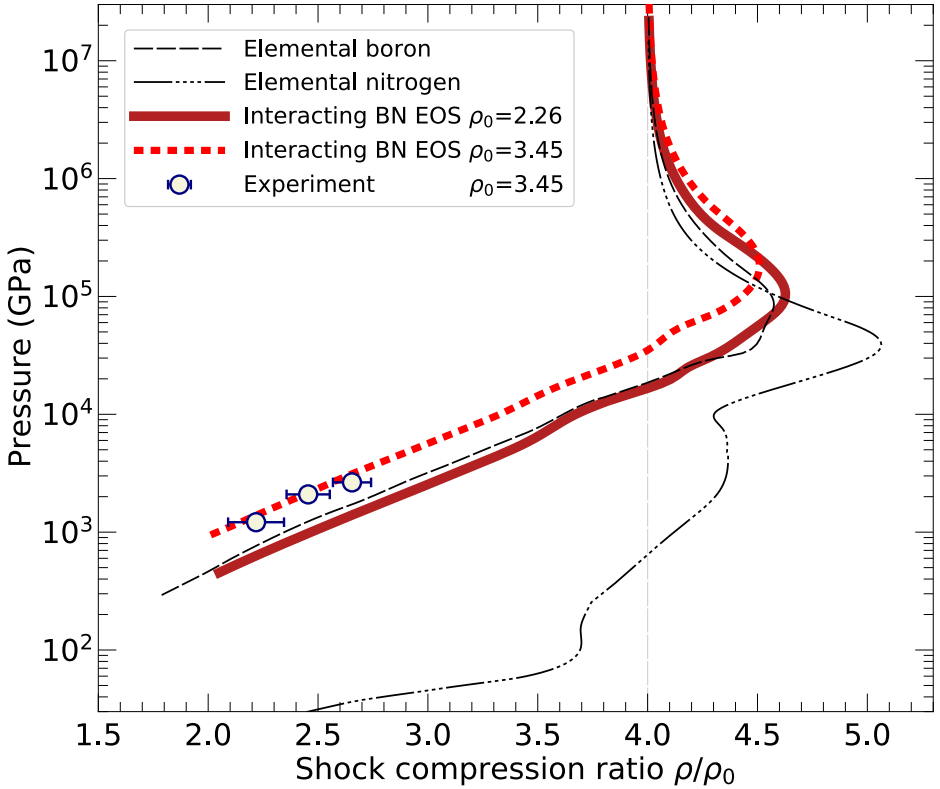


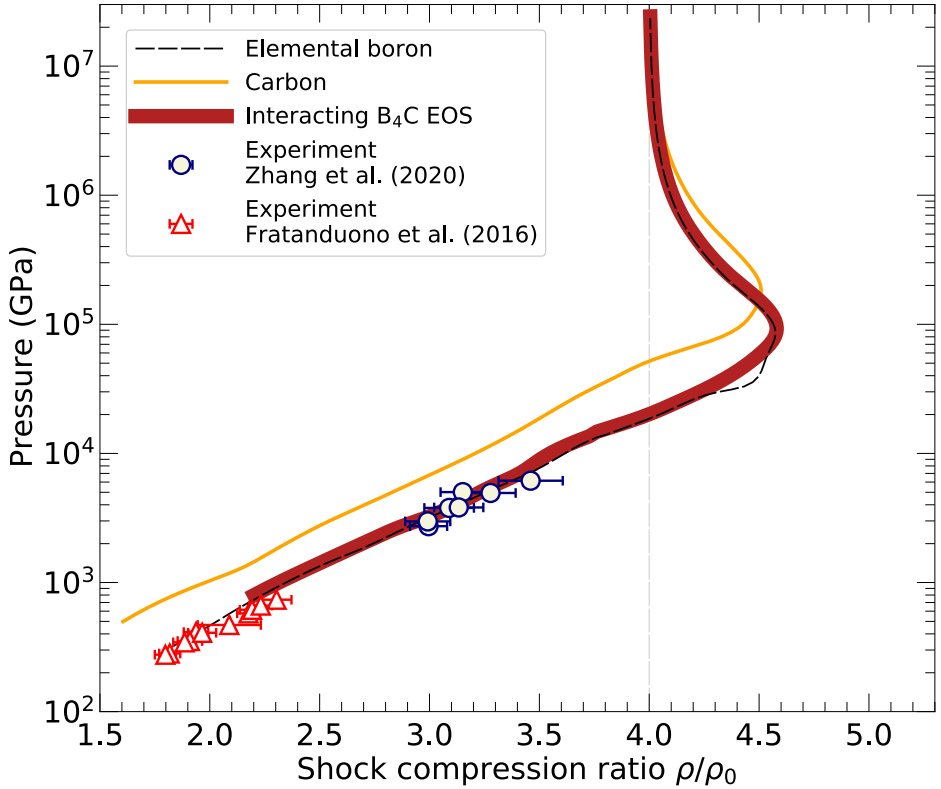
Hugoniot Curves of BN and B_4C

Fully interacting EOS and Linear Mixing agree quite well.

Boron nitride
Zhang et al. PRB 2019



Boron carbide
Zhang et al. PRE 2020



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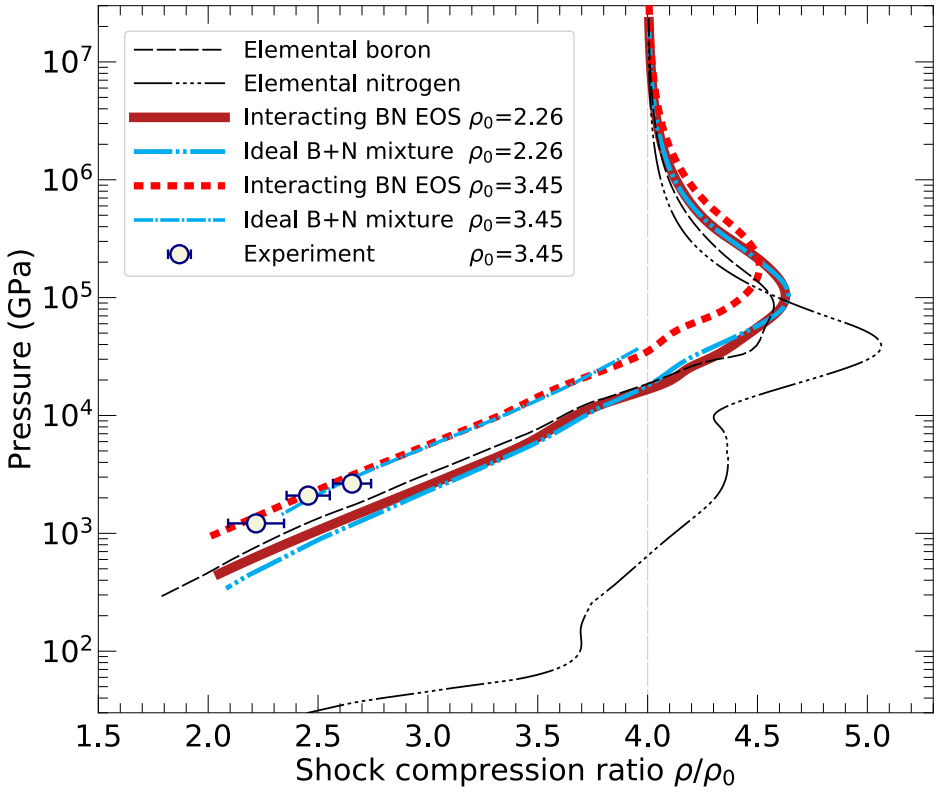

Boron carbide
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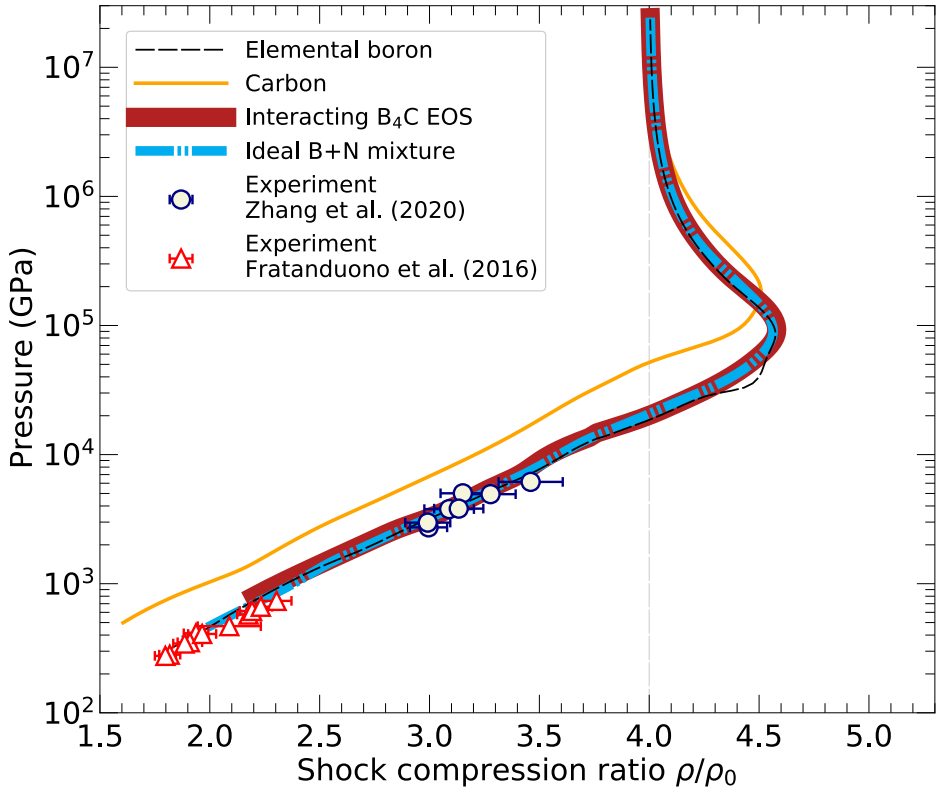
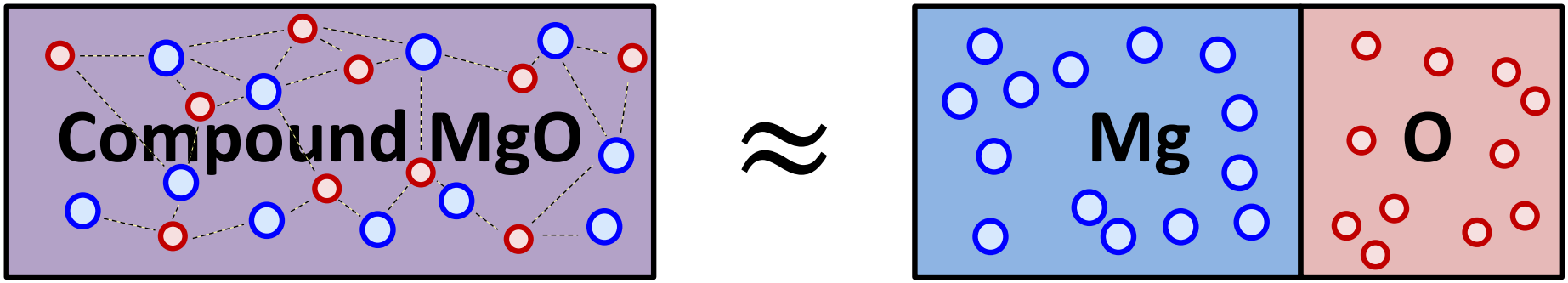


Linear Mixing at Constant P and T

(Also called additive volume rule)



$$V_{\mathrm{mix}} = N_1 V_1 + N_2 V_2 \ ,$$

$$m_{\mathrm{mix}} = N_1 m_1 + N_2 m_2 \ ,$$

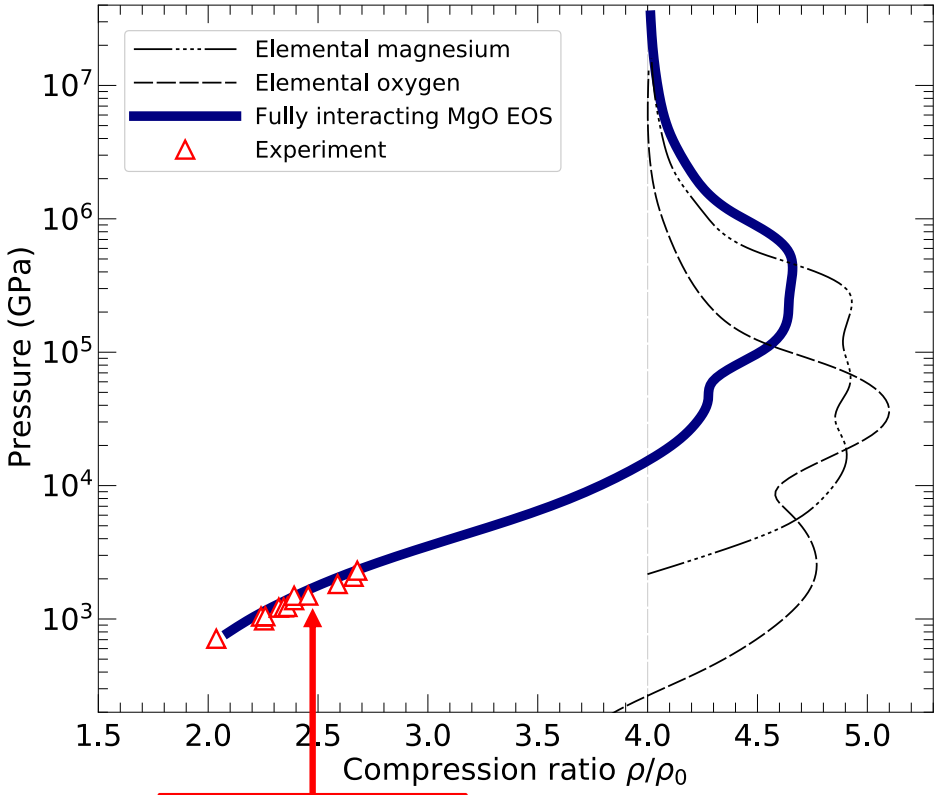
$$E_{\mathrm{mix}} = N_1 E_1 + N_2 E_2 \ ,$$

$$\rho_{\mathrm{mix}} = m_{\mathrm{mix}} / V_{\mathrm{mix}}$$

Hugoniot Curves of MgO and $MgSiO_3$

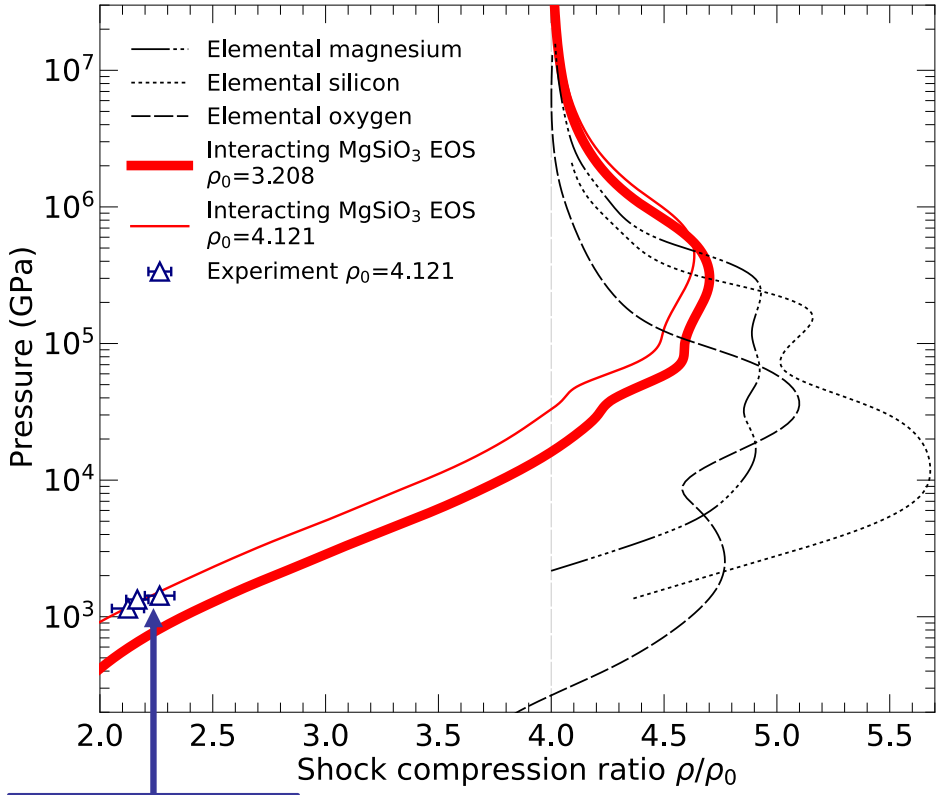
Results from fully interacting EOS and experiment.

Soubiran et al. JCP 2019



McCoy et al. PRB 2019

Gonzalez et al. PRB 2020

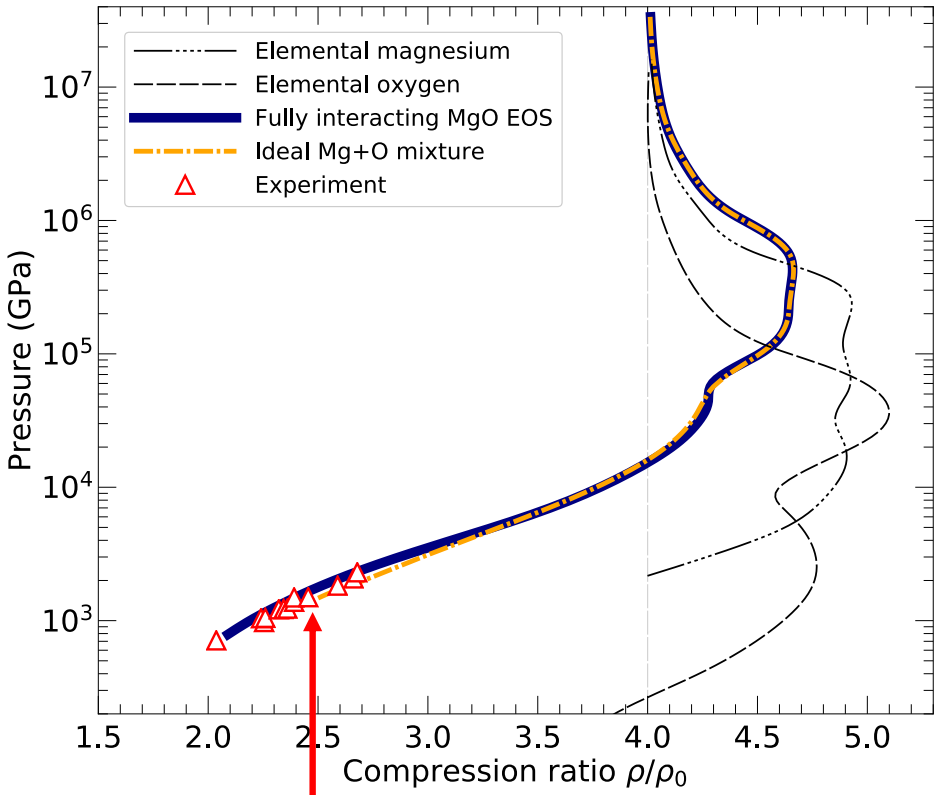


Millot et al. GRL 2020

Hugoniot Curves of MgO and $MgSiO_3$

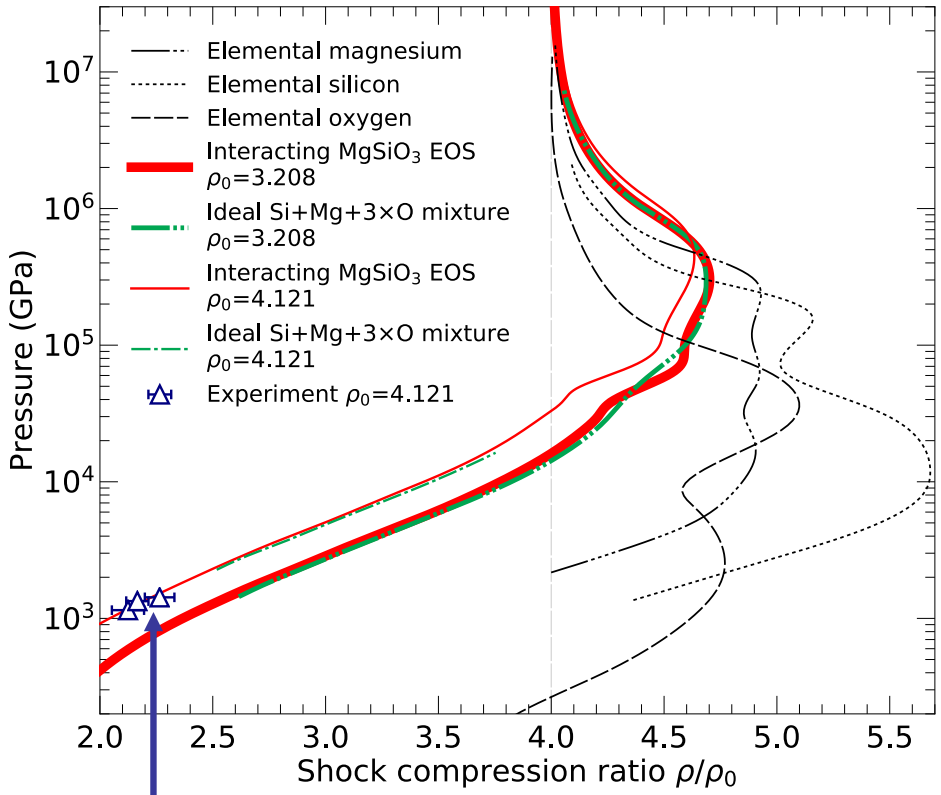
Fully interacting EOS and Linear Mixing agree quite well.

Soubiran et al. JCP 2019



McCoy et al. PRB 2019

Gonzalez et al. PRB 2020



Millot et al. GRL 2020

Linear mixing works well for $T \gtrsim 2\times10^5\mathrm{K}$ and $\varrho/\varrho_0 \gtrsim 3.2$

The Journal of Chemical Physics

Nonideal mixing effects in warm dense matter studied with first-principles computer simulations

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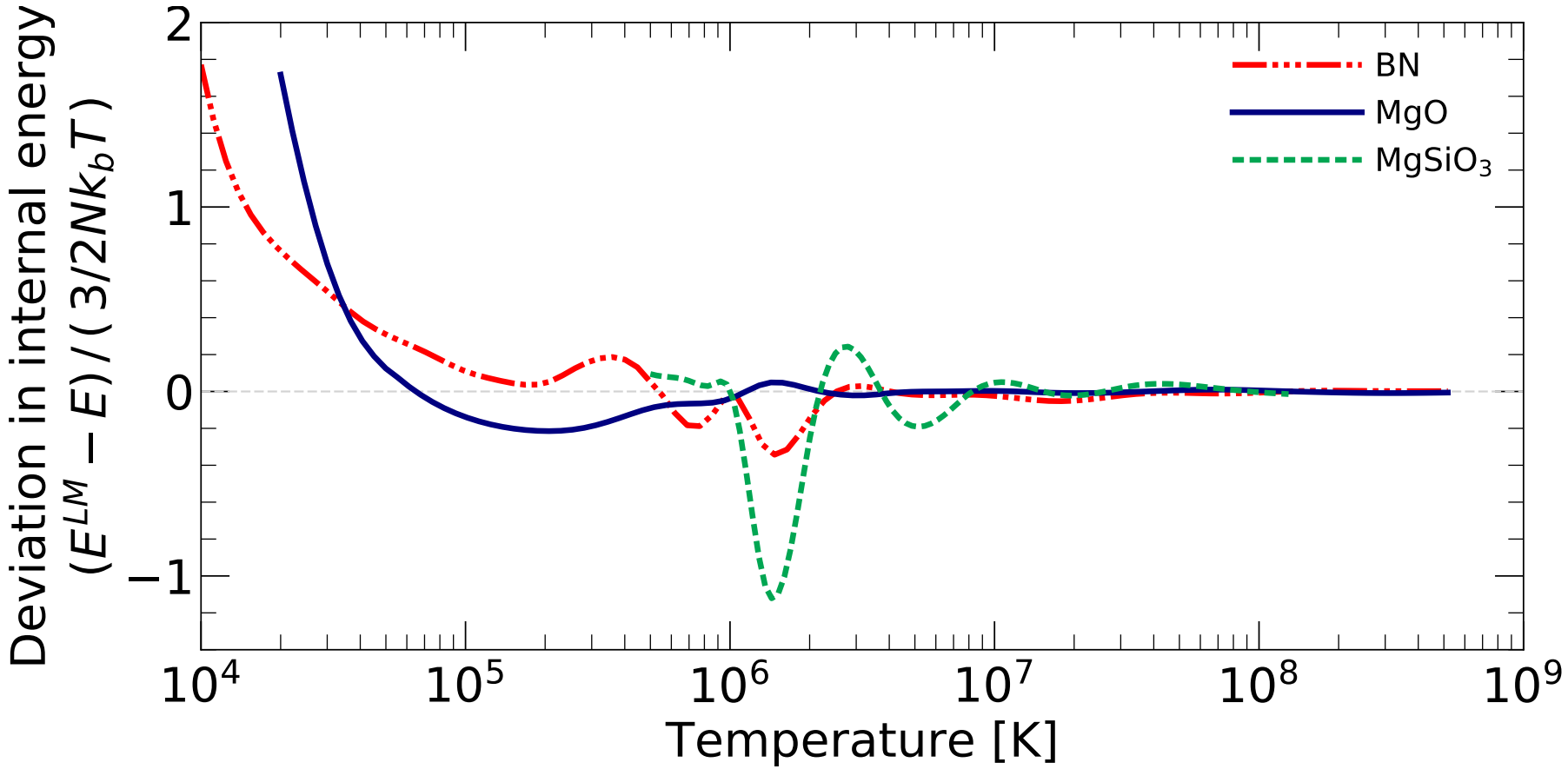
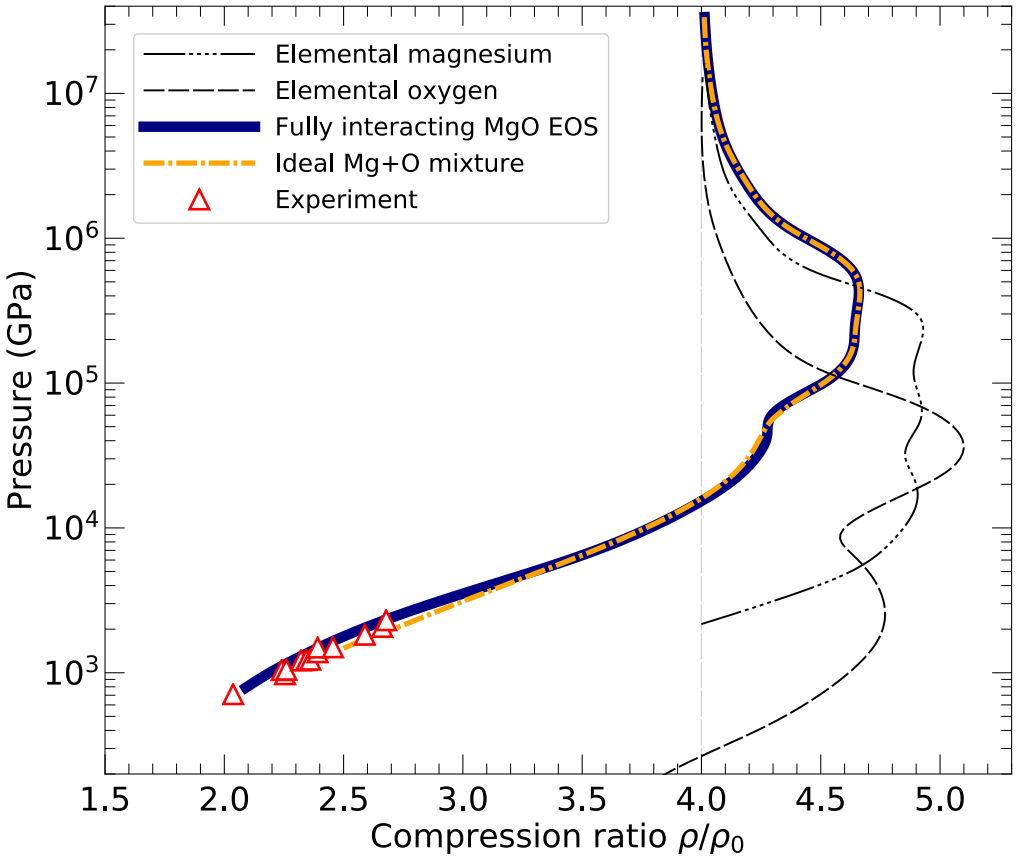
Nonlinear Mixing Effects in $MgSiO_3$

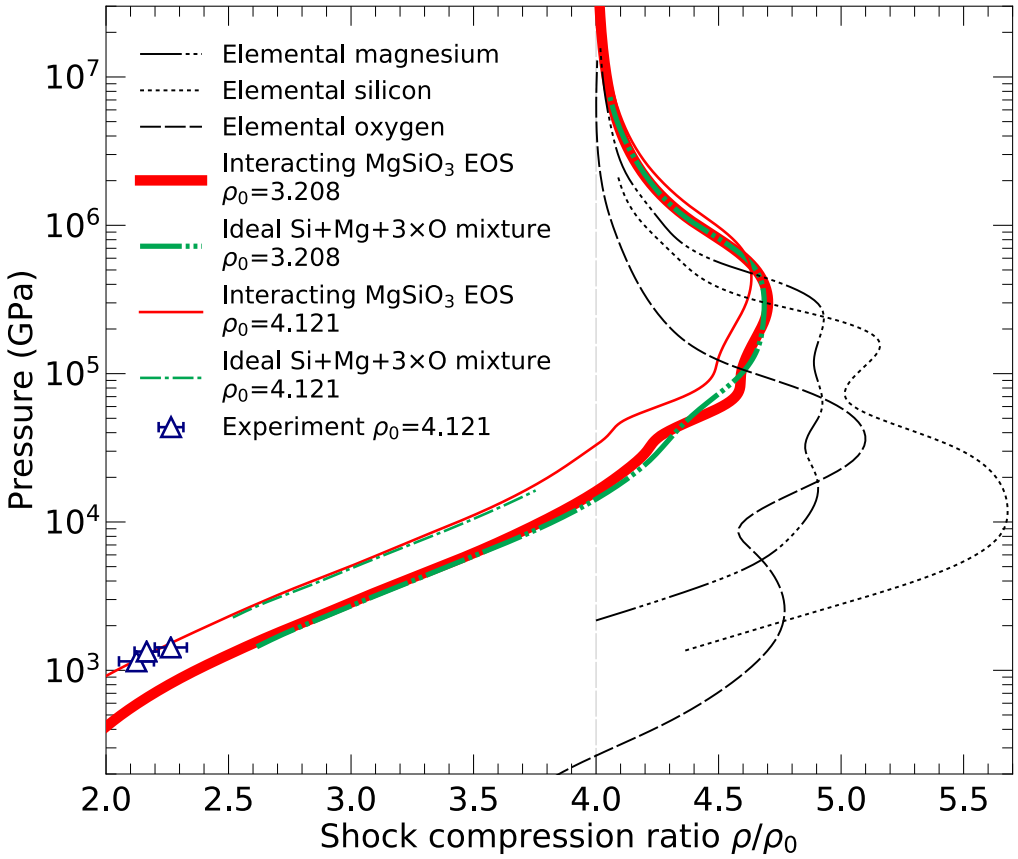
Fully interacting EOS and Linear Mixing agree quite well.



Linear mixing works well for $T \gtrsim 2\times10^5\mathrm{K}$ and $\varrho/\varrho_0 \gtrsim 3.2$

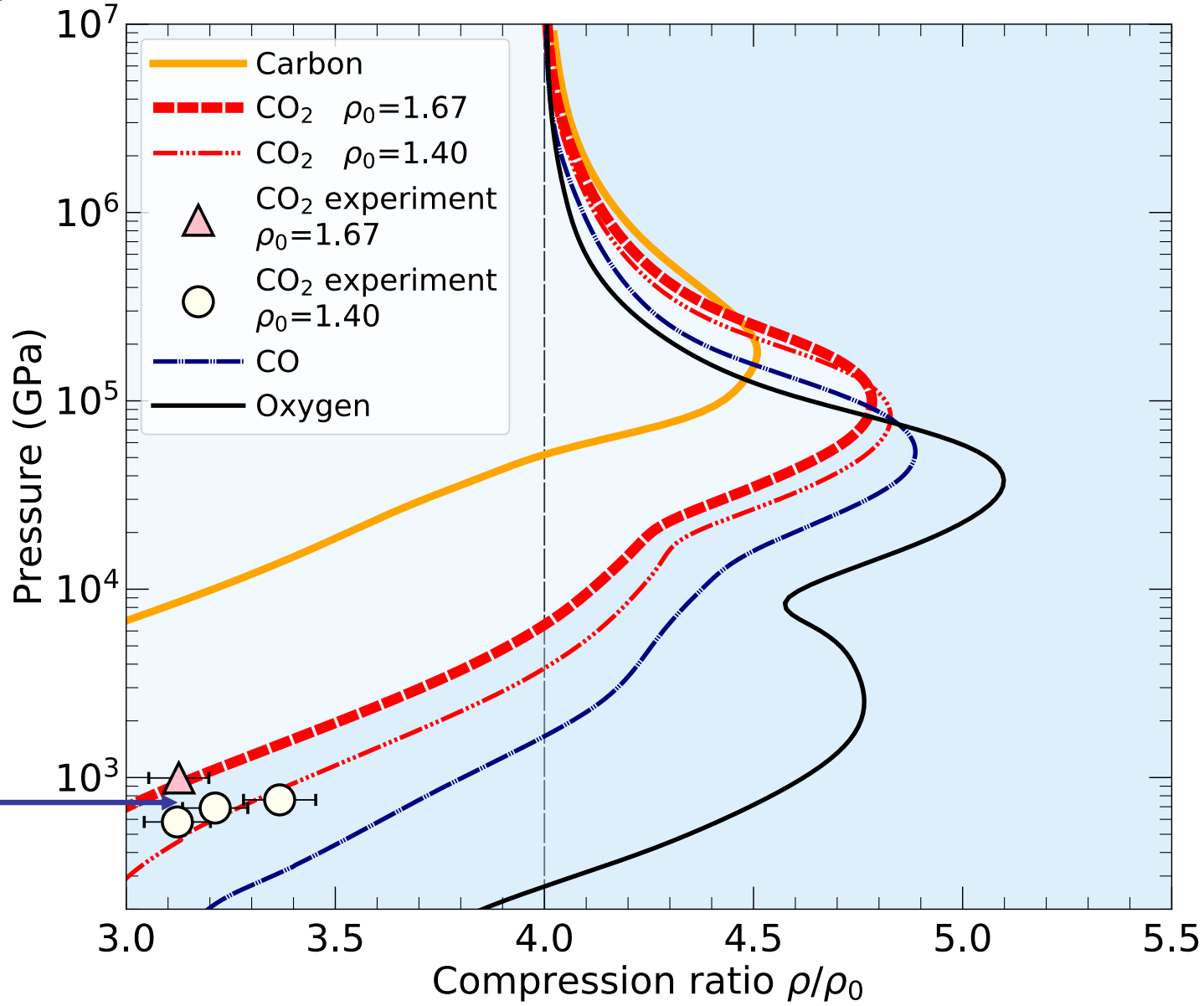
Hugoniot Curves of MgO and $MgSiO_3$





Hugoniot Curves of CO and CO_2

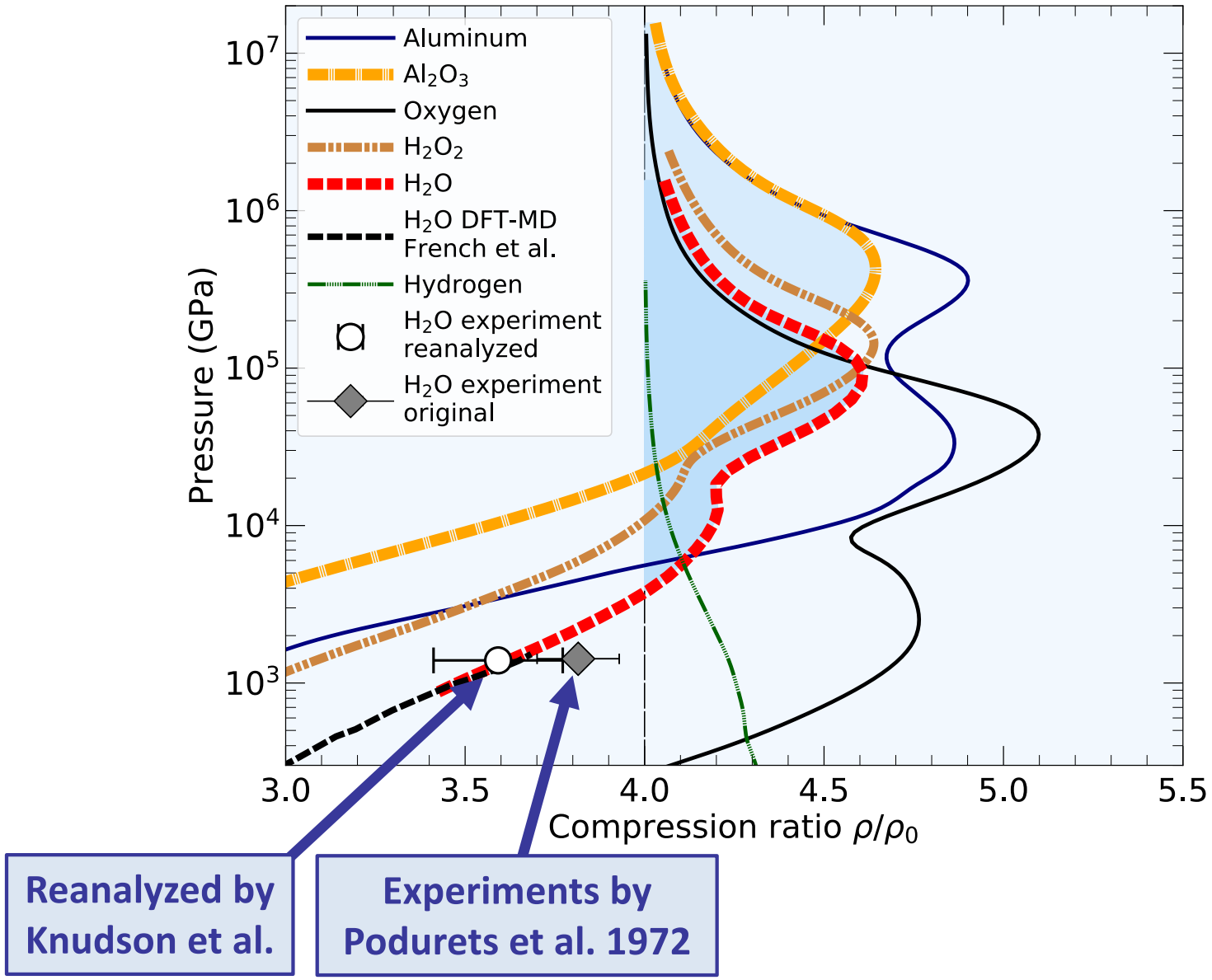
Experimental CO_2 Hugoniot agree with Linear Mixing result



Crandall et al. PRL 2020

Hugoniot Curves of H_2O, H_2O_2, and Al_2O_3

Experimental H_2O Hugoniot agree with Linear Mixing result



FPEOS: 11+10 Available Tables

Material	Number of isochores	Minimum density [g cm^{-3}]	Maximum density [g cm^{-3}]	Minimum temperature [K]	Maximum temperature [K]	Number of EOS points	References
Hydrogen	33	0.001	798.913	15625	6.400×10^{7}	401	[69–74]
Helium	9	0.387	10.457	500	2.048×10^{9}	228	[75, 76]
Boron	16	0.247	49.303	2000	5.174×10^{8}	314	[77]
Carbon	9	0.100	25.832	5000	1.035×10^{9}	162	[78, 79]
Nitrogen	17	1.500	13.946	1000	1.035×10^{9}	234	[80]
Oxygen	6	2.486	100.019	10000	1.035×10^{9}	76	[81]
Neon	4	0.895	15.026	1000	1.035×10^{9}	67	[82]
Sodium	9	1.933	11.600	1000	1.293×10^{8}	193	[83, 84]
Magnesium	23	0.431	86.110	20000	5.174×10^{8}	371	[85]
Aluminum	15	0.270	32.383	10000	2.156×10^{8}	240	[86]
Silicon	7	2.329	18.632	50000	1.293×10^{8}	85	[87, 88]
LiF	8	2.082	15.701	10000	1.035×10^{9}	91	[89]
B_4C	16	0.251	50.174	2000	5.174×10^{8}	291	[90]
BN	16	0.226	45.161	2000	5.174×10^{8}	311	[91]
CH_4	16	0.072	14.376	6736	1.293×10^{8}	247	[92, 93]
CH_2	16	0.088	17.598	6736	1.293×10^{8}	248	[92, 93]
C_2H_3	16	0.097	19.389	6736	1.293×10^{8}	247	[92, 93]
CH	16	0.105	21.000	6736	1.293×10^{8}	248	[92, 93]
C_2H	16	0.112	22.430	6736	1.293×10^{8}	245	[92, 93]
MgO	19	0.357	71.397	20000	5.174×10^{8}	286	[94]
$MgSiO_3$	16	0.321	64.158	6736	5.174×10^{8}	284	[95, 96]

First-Principles Equation of State Database online http://militzer.berkeley.edu/FPEOS

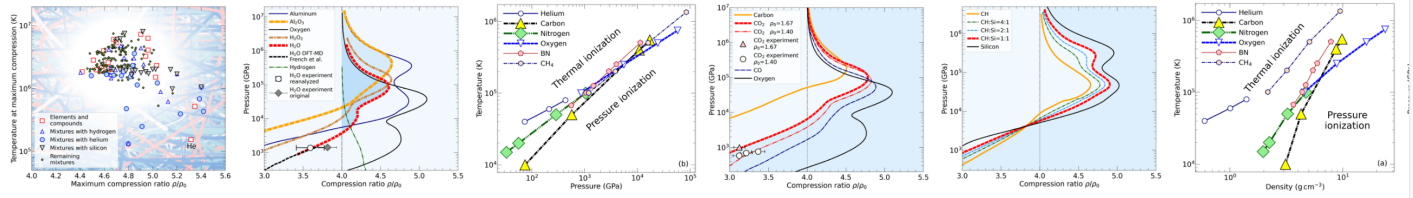
militzer.berkeley.edu

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 isotherms 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, B_4C, BN, CH_4, CH_2, C_2H_3, CH, C_2H, MgO, and $MgSiO_3$. 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.

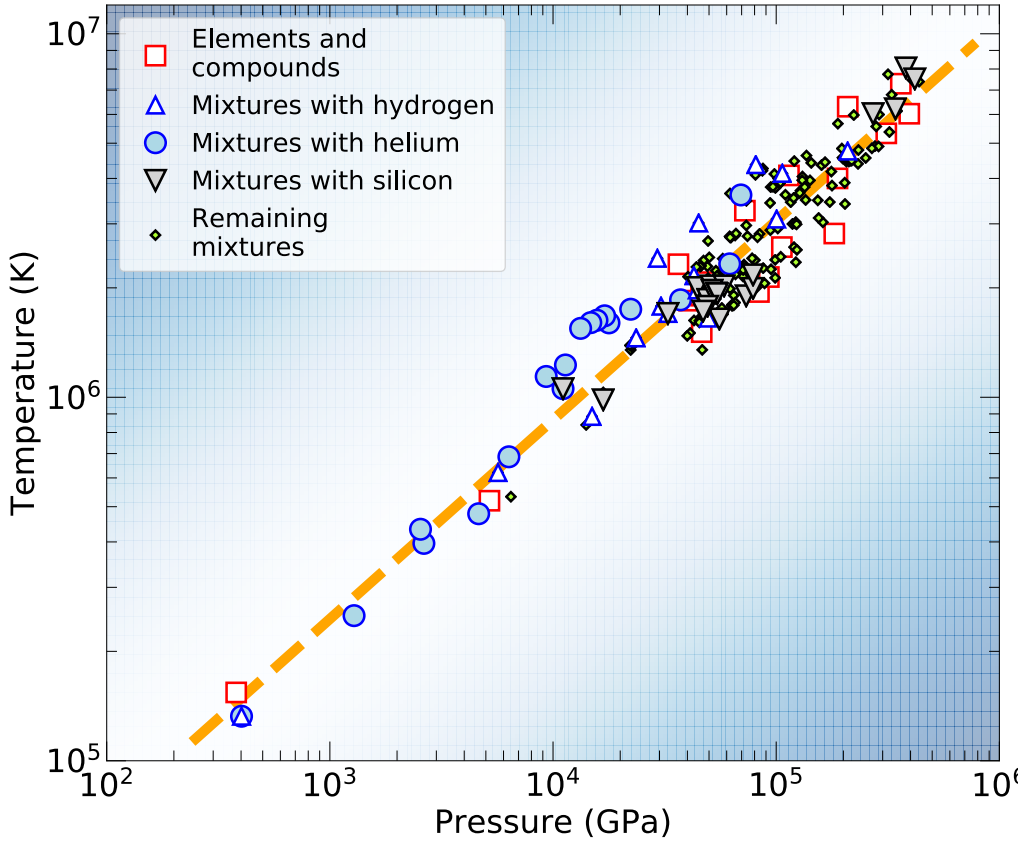
Recommended citation: B. Militzer, F. Gonzalez-Cataldo, S. Zhang, K. P. Driver, F. Soubiran, "First-Principles Equation of State Database for Warm Dense Matter Computation", *Physical Review E* **103** (2021) 013203.

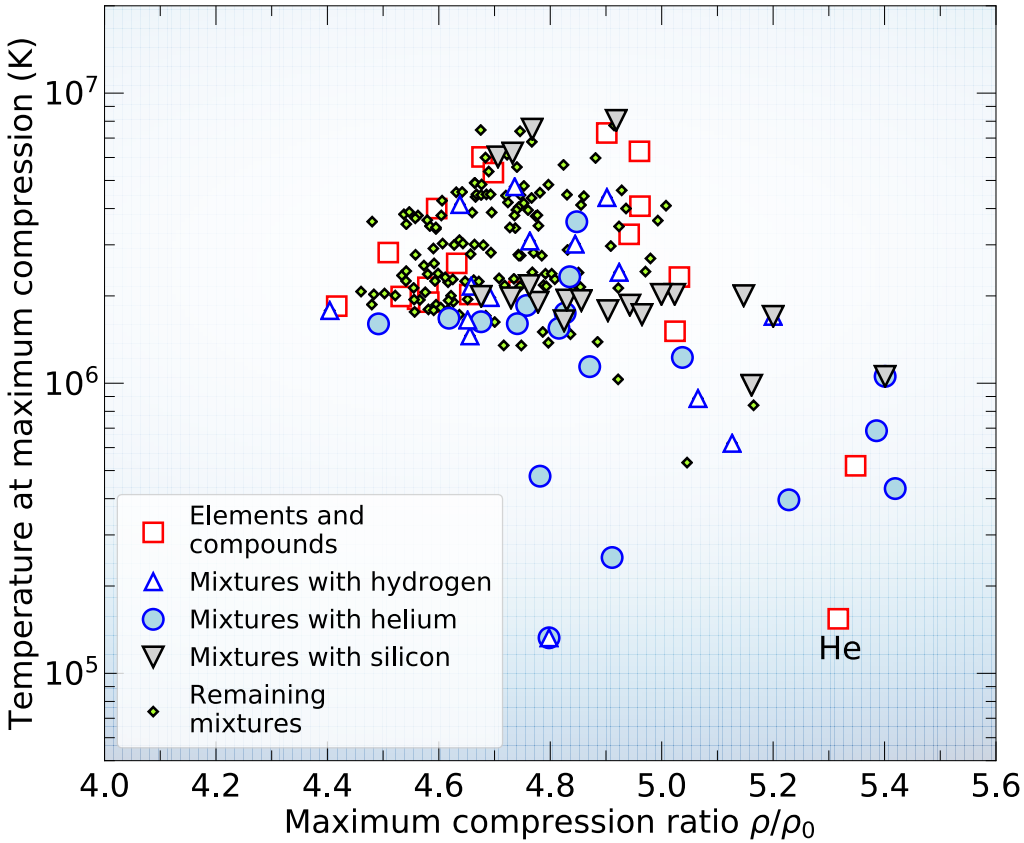


5000 first-principles calculations have been combined into our FPEOS database. So anyone can predict shock Hugoniot curves for a variety of compounds and mixtures. This will make warm dense matter calculations more reliable and efficient.

FPEOS demo

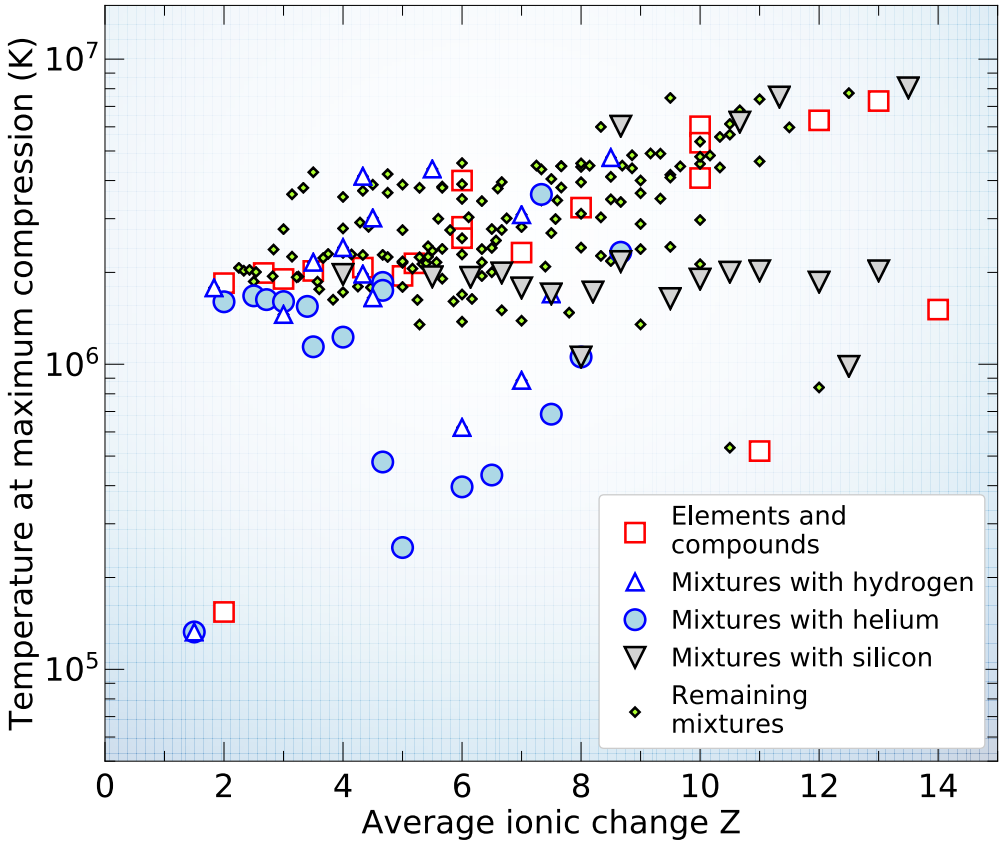
Database Application: Study Maximal Compression States of 194 Binary Mixtures

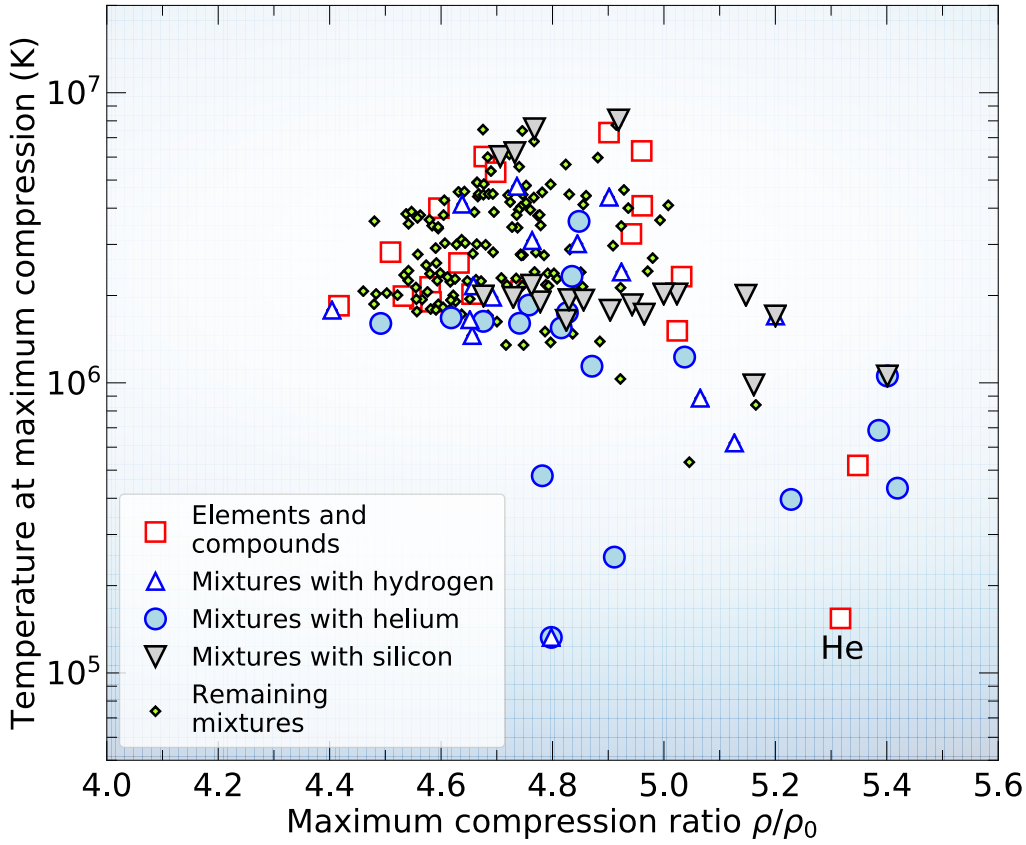




FPEOS codes and tables submitted for publication in PRE (2020)

Database Application: Study Maximal Compression States of 194 Binary Mixtures





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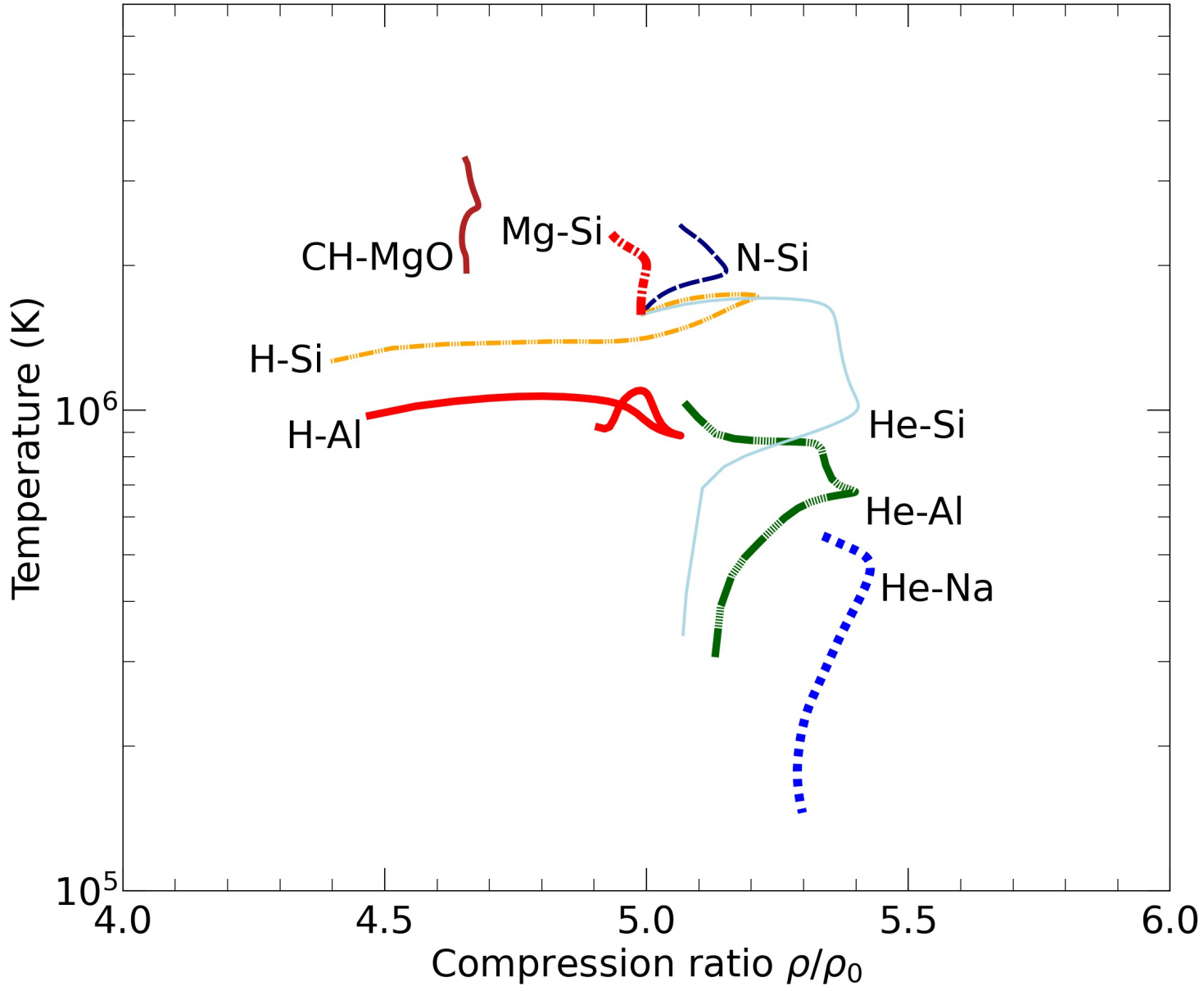
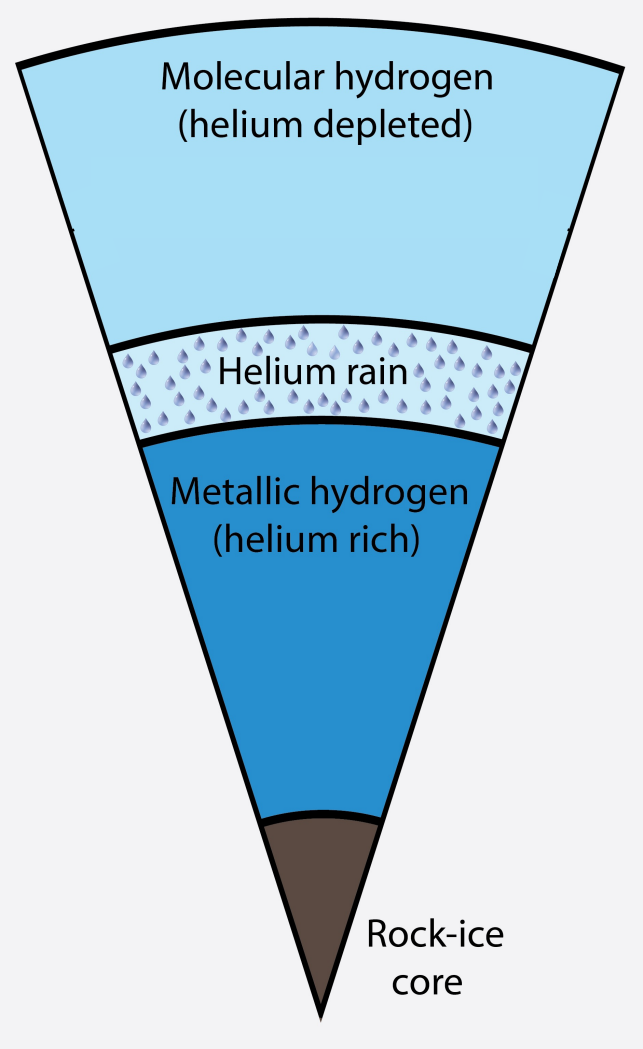
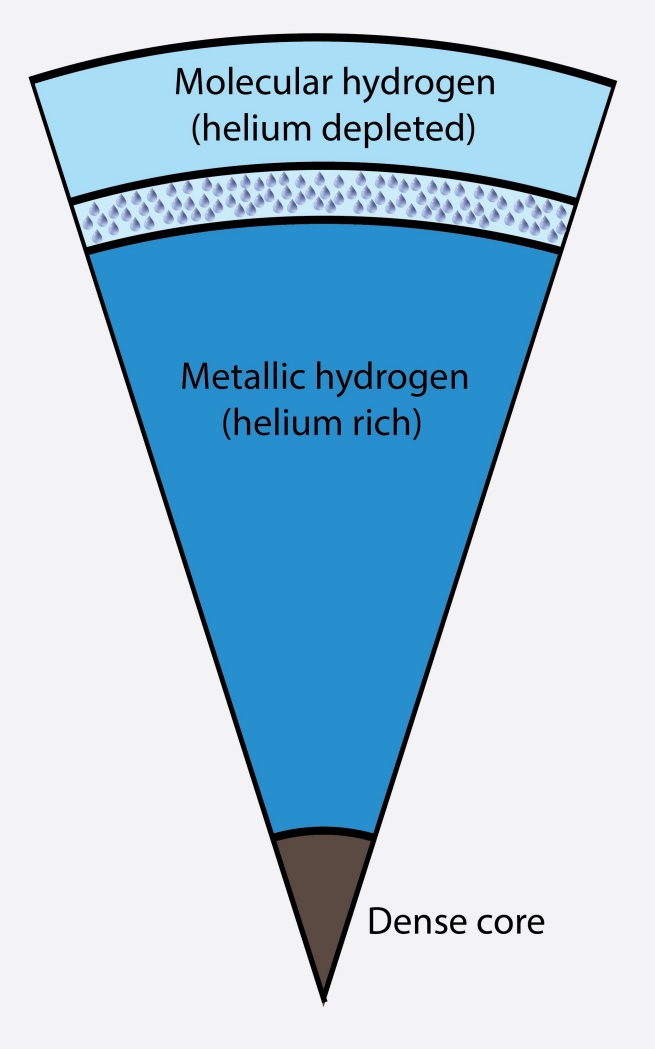


II.
Giant Planet Interiors

Typical 4-layer Models for the Interiors of Saturn and Jupiter

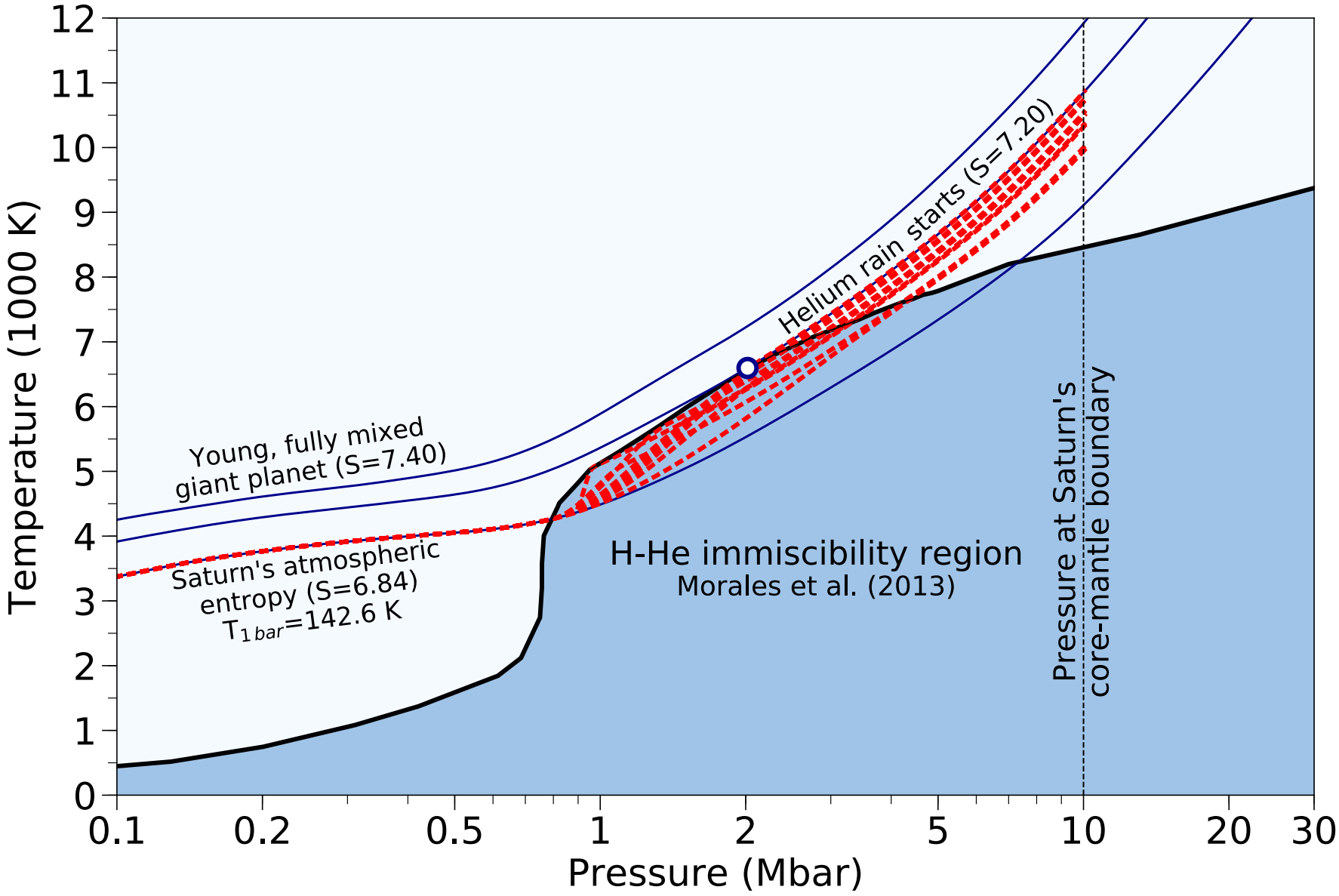


Saturn's interior



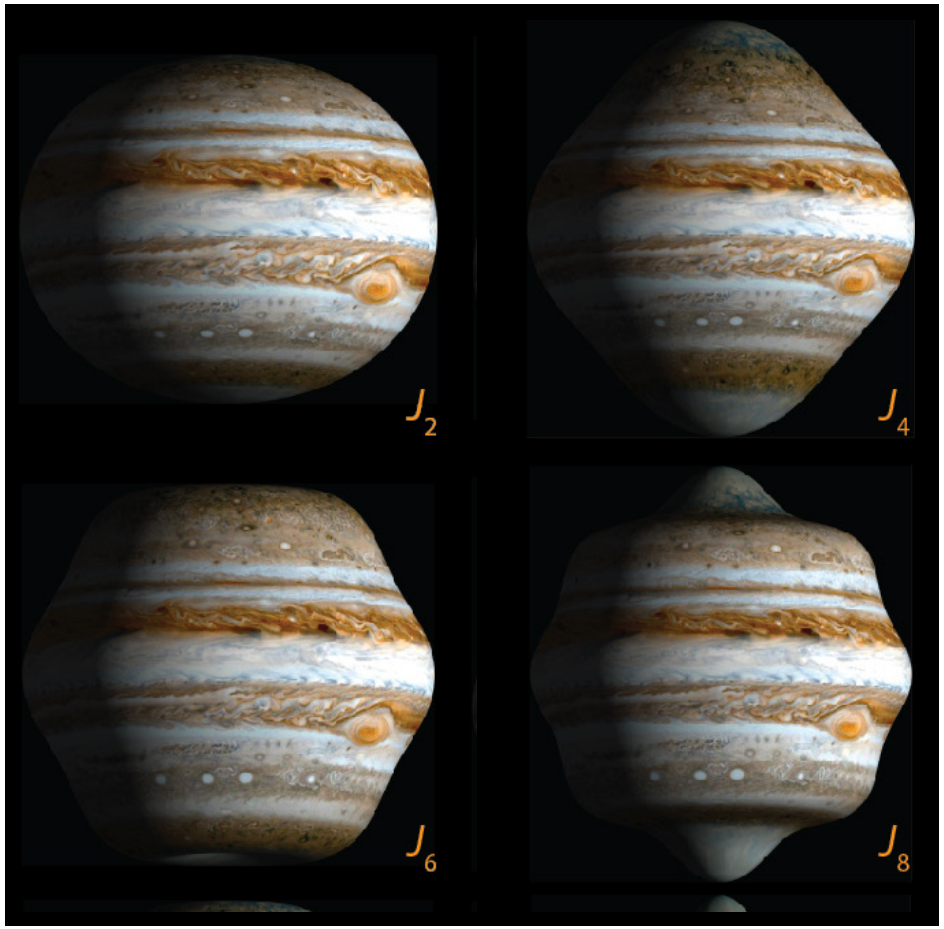
Jupiter's interior

Adiabats in our Saturn Models with Differential Rotation



Measured Gravity Field

$$V(r,\,\mu) = \frac{GM}{r}\left[1 - \sum_{n=1}^{\infty}\left(\frac{a}{r}\right)^{2n} J_{2n} P_{2n}(\mu)\right]$$



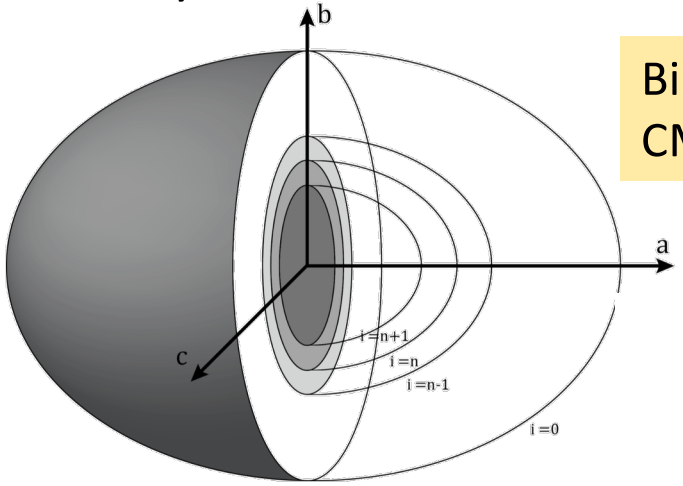
Interior Models

Match: M, R, gravity moments J_{2n}

$$J_n = -\frac{2\pi}{Ma^n}\int_{-1}^{1} d\mu \int_{0}^{a} r^{n+2} P_n(\mu)\,\rho\,(r,\mu)\,dr$$

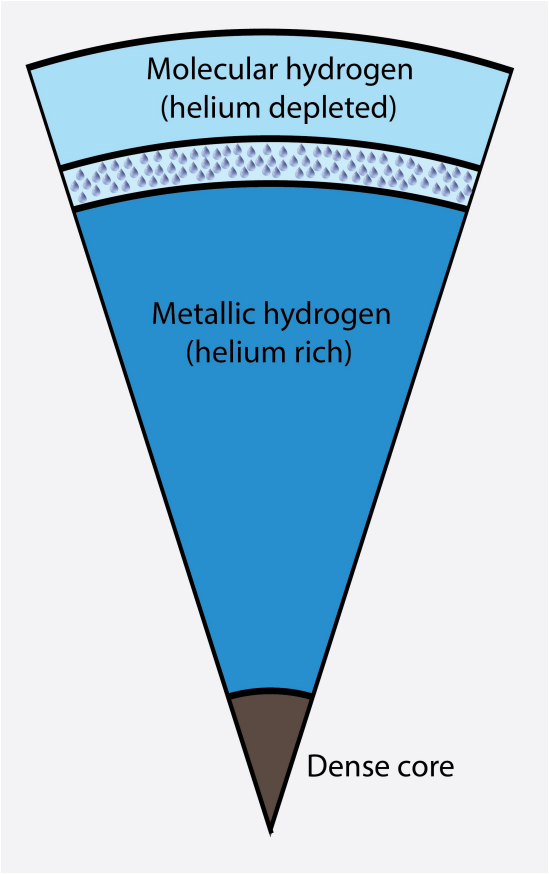
Model parameters:

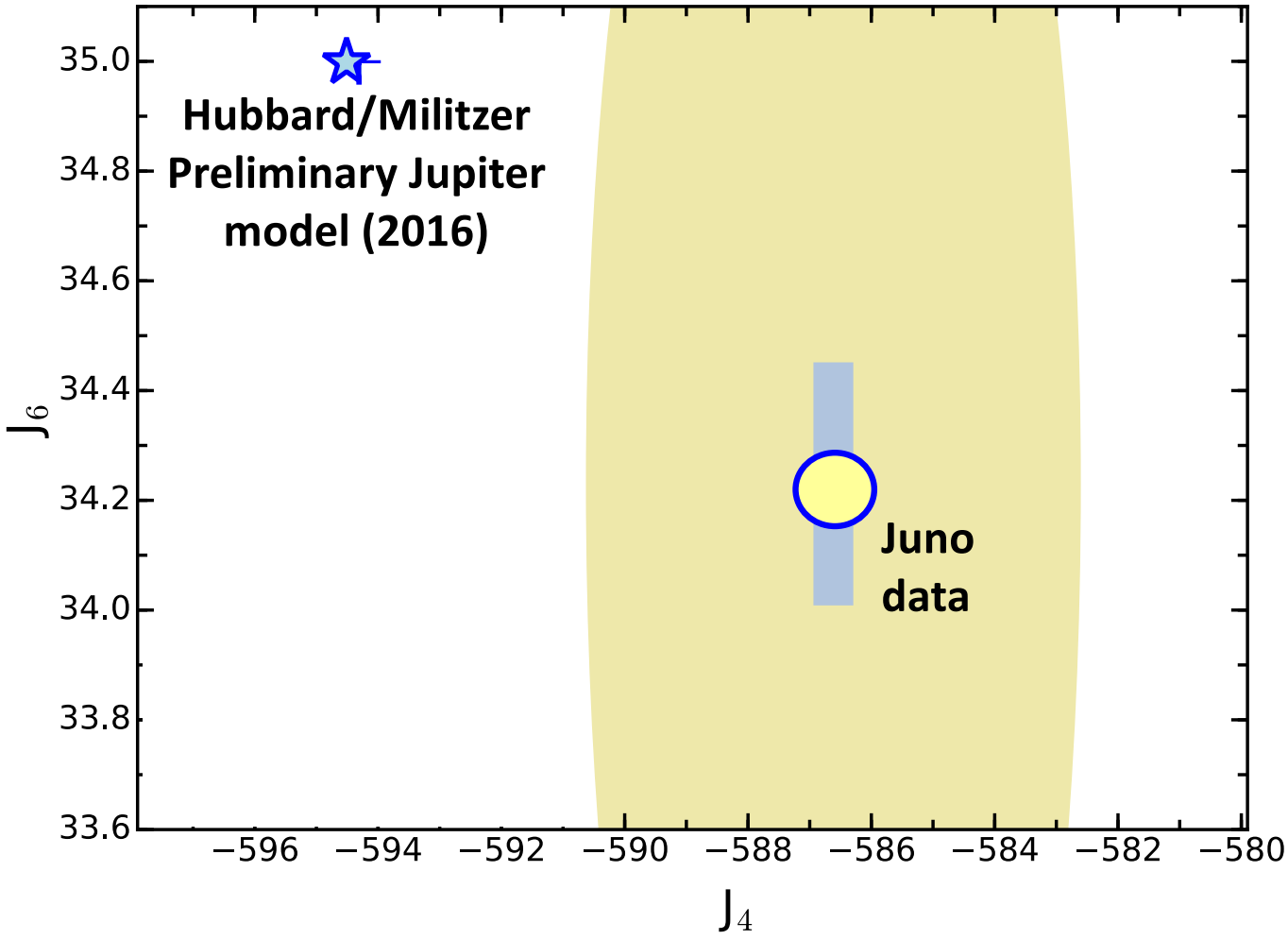
- EOS of H, He, Z (from *ab initio* simulations)
- Size of the core
- How much helium was sequestered
- Interior entropy
- Heavy Z elements in metallic H
- Heavy Z elements in molecular H



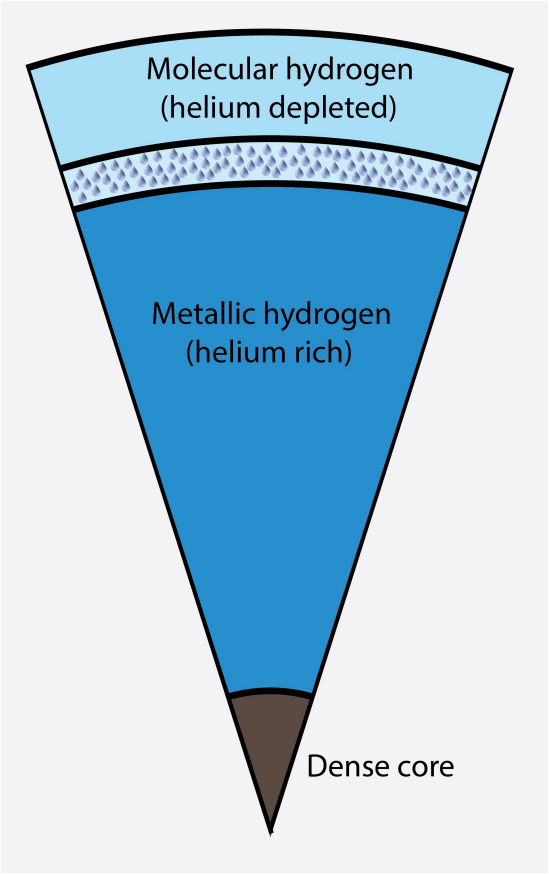
Bill Hubbard's CMS method.

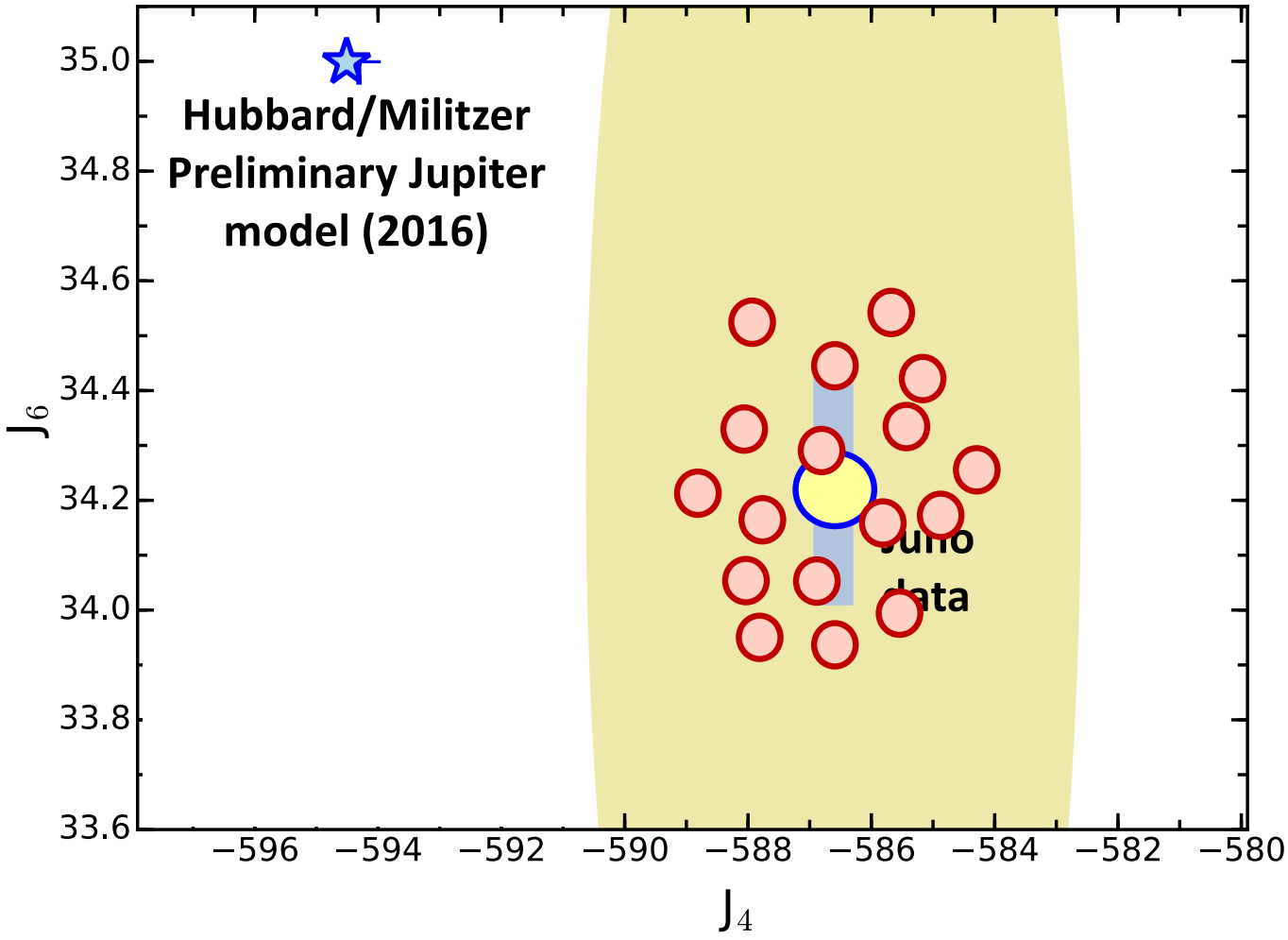
The Challenge of Fitting Jupiter's even Gravity Coefficients with Four-Layer Interior Models





The Challenge of Fitting Jupiter's even Gravity Coefficients with Four-Layer Interior Models





The End