ACKNOWLEDGEMENTS

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OVERVIEW AND MOTIVATION

High pressure
- Solid-solid phase transitions
- Equations of state
- Melting

Warm dense matter
- Temperature ionization
- Pressure ionization
- Shock compression

Planetary Interiors
- Super-Earth interior models
- Core/mantle crystallization
- Element Partitioning
- Solubility / Miscibility
1. **Planetary Interiors**
   - A diluted core in Jupiter
   - Rock/Ice mixtures in water planets

2. **High Pressure Phase Transitions**
   - Be & MgO: melting and anharmonicities
   - Melting of SiO$_2$
   - Ramp compression from DFT

3. **Warm Dense Matter**
   - Warm dense silicates: Mg, MgO & MgSiO$_3$
   - FPEOS
Jupiter’s Interior

P~ 40 Mbar (4000 GPa)
T~ 16000 K

Can metallic H dissolve the rocky core?
Free energy of solvation

\[ \Delta G \equiv G(H_nSiO_2) - [G(H_n) + G(SiO_2)] \]

Free energy of the Dissolved System

\[ \Delta G < 0 \Rightarrow \text{Dissolves} \]

How to calculate \(G(P,T)\)?

Gonzalez & Militzer, APJ (2014)
PLANETARY INTERIORS

A diluted core in Jupiter

Thermodynamic Integration

\[ U_A \rightarrow U_B \]

**\( U_A \):** reference system

**\( F_A \):** known

\[ U(\lambda) = U_A + \lambda(U_B - U_A) \]

\((U(0) = U_A; \ U(1) = U_B)\)

\[ \Delta F = \int_A^B dF = \int_0^1 d\lambda \frac{\partial F}{\partial \lambda} = -\int_0^1 d\lambda \frac{k_B T}{Z} \frac{\partial Z}{\partial \lambda} \]

\[ = \int_0^1 d\lambda \frac{k_B T}{Z} \sum_s e^{-\frac{U(\lambda)}{k_BT}} \frac{1}{k_B T} \frac{\partial U(\lambda)}{\partial \lambda} \]

\[ = \int_0^1 d\lambda \left( \frac{\partial U(\lambda)}{\partial \lambda} \right)_\lambda = \int_0^1 d\lambda (U_B - U_A)_\lambda \]

\[ F_B = F_A + \Delta F \]

\[ G_B = F_B + PV \]

\[ F = -kT \ln Z \]

\[ Z = \sum_s e^{\frac{U(\lambda)}{k_BT}} \]
**Planetary Interiors**

A diluted core in Jupiter

### Liquids
- **Ideal Gas**
  
  \[ U = 0 \]

### Two-Steps TDI
- **Pair Potential**
  
  \[ U = U_{PP} \]

- **DFT**
  
  \[ U = U_{KS} \]

### Solids
- **Einstein Crystal**
  
  \[ \frac{1}{2} m \omega r^2 \text{ (one body)} \]

  \[ U = U_{Einstein} \]

- **Pair Potential + Einstein**
  
  \[ (\text{one body} + \text{two body}) \]

  \[ U = U_{Einstein} + U_{PP} \]

- **DFT**
  
  \[ U = U_{KS} \]

- **Classical MD**
- **VASP**

- **VASP**

  - GGA-PBE
  - \( \text{Ecut} = 900 \text{ eV} \)
  - 144 atoms
  - \( \Gamma \) - point
  - 14 val. elect.

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*S. Izvekov & Parrinello, JCP (2004)*
PLANETARY INTERIORS

A diluted core in Jupiter

\[ \Delta G \equiv G(H_nSiO_2) - [G(H_n) + G(SiO_2)] \]

\[ \Delta G < 0 \text{ at CMB} \]

- SiO\textsubscript{2} gets dissolved
- At SiO\textsubscript{2}:H < 1:100

- SiO\textsubscript{2} more soluble than MgO
- Fe, H\textsubscript{2}O also soluble in H

\[ \Delta G > 0 \]

Wahl+, APJ (2013)
Wilson+ & Militzer APJ (2012)
Gonzalez & Militzer, APJ (2014)
Gravitational Moments

\[ J_n = -\frac{2\pi}{Ma^n} \int dr \, d\mu \, \rho(r) \, r^{n+2} \, P_n(\mu) \]
Jupiter’s Interior

- Diluted core
- He rain
- Metallic H
- H + He mix

Compact core (Solid/Liquid?)
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Liquid core?
Water Ice
Rocks (silicates)
Mixture (rocks+H$_2$O)
Rocks (silicates)
Solid core?

Do water and silicates mix?

Super-Earths $\rightarrow$ Sub-Neptunes

Do water and silicates mix?

PLANETARY INTERIORS

H₂O

MgSiO₃


WATER WORLDS
1. **Planetary Interiors**
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HIGH PRESSURE

Beryllium

- Laser Heated DAC
- No signature of bcc
HIGH PRESSURE Beryllium

- QHA (quasi-harmonic approximation)
- No signature of bcc in experiments
- Two-phase simulations of melting

Benedict+ PRB (2009)
HIGH PRESSURE Beryllium

Thermodynamic Integration

- DFT-MD
- hcp/bcc/liquid

Wu, Gonzalez, Militzer, PRB (2021)
HIGH PRESSURE Beryllium

Thermodynamic Integration

\[ \Delta G = G_{\text{hcp}} - G_{\text{bcc}} \]

Wu, Gonzalez, Militzer, PRB (2021)
\[ \Delta G = G_{liq} - G_{sol} \]

Melting lines Be & MgO

- 2x2x2 k-points in Be in ~100-atoms cells

- Strong anharmonicities:
  - QHA does not work well.
  - B1-B2 / hcp-bcc needs higher P.

Wu, Gonzalez, Soubiran, Militzer, JPCM (2022)
Double Shock compression

- **MgO**
  - Liquid phase

- **Be**
  - Liquid phase
  - Initial condition of 2\(^{nd}\) shock
  - Re-emerging in liquid
  - Intersection with melting line

**Phase Diagrams**

- **B1**
- **B2**

**Labels**

- Principal Hugoniots
- Secondary Hugoniots
- Double shock experiments

**References**

Wu, Gonzalez, Soubiran, Militzer, JPCM (2022)
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$\Delta G = G_{\text{liq}} - G_{\text{sol}}$

Coexistence (Two phase)

Alfe, PRB (2009)

Z method
HIGH PRESSURE

Melting SiO$_2$

Z method

NVE heat until it melts


SiO$_2$ is solid at CMB of
• Super-Earths
• Gas Giants

HIGH PRESSURE

Z method

NVE heat until it melts

SiO$_2$


SiO$_2$ is solid at CMB of

• Super-Earths
• Gas Giants

Millot $+$, Science (2015)

Z method agreement with

• Two-phase simulations
• Experiments

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Ramp compression model from ab initio simulations

Gonzalez+, PRB (2021)

5000 GPa

Lazicki+, Nature (2021)

2000 GPa

No signature of bc8

Smith+ Nature (2014)
Ramp compression model

from ab initio simulations

Gonzalez+, PRB (2021)

Smith+ Nature (2014)

\[ T > 20,000 \text{ K} \]

If liquid
Ramp $\sim$ multishocks

\[ E - E_0 = \frac{1}{2}(P + P_0)(V_0 - V) \]
Ramp ~ multishocks

\[ E - E_0 = \frac{1}{2}(P + P_0)(V_0 - V) \]

1. Initial state
2. Uniaxial compression
3. Ediff → Kinetic energy

\( \Delta E \rightarrow K \)
OUR MODEL OF RAMP COMPRESSION

for ramp compression from ab initio simulations

\[ (\rho_c = \rho_b, T_c) \]

\[ E_c = E_b - E_b^* \]

\[ (\rho_a, T_a) \rightarrow E_a \]

\[ (\rho_b, T_a = T_b) \rightarrow E_b \]

\[ \rho_a \rightarrow \rho_b \]

(a) Initial structure
(b) Compress at fix T
(c) Heat hydrostatic

Hydrostatic
Uniaxial

Get energy difference
Relax NVE
Output

Gonzalez+, PRB (2021)
**MULTISHOCKS / OUR MODEL**

$P_{isen} = \sigma_x - \frac{2}{3}Y - \int \beta dW_p - \gamma \rho_H (E_H - E_{isen})$

$\mathbf{TQ} = \beta = 0.25$

* Diamond is weaker than expected
* 3/4 plastic work absorbed by defects!
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WARM DENSE MATTER

Shock compression:
The Hugoniot curve

Temperature (kelvin)

Pressure (GPa)

Density (grams/centimeter$^3$)

ICF capsule at ignition

White Dwarf cores

Solar core

White Dwarf He envelope

Lightning discharges

Imploding ICF capsules

Jupiter core

Earth core

Gas + Liquid

Gas

Solid

Liquid

Plasma

Relativistic effects

Radiation effects

Excitations of K shell electrons

Excitations of L shell electrons

Shock compression ratio $\rho/\rho_0$

Magnesium shock Hugoniot curve

Mg curve with relativistic effects

Mg with K shell excitations

Mg without K shell excitations

Oxygen curve

MgO curve

https://www.lanl.gov
WARM DENSE MATTER

DFT-MD

PIMC

CONSISTENT EOS
WARM DENSE MATTER

$g(r)$ Structural properties

Density (g cm$^{-3}$) vs Temperature (K)

- PIMC
- DFT-MD (LDA)
- DFT-MD (GGA)

Isentrope
- Isobar

Mg Hugoniot curve
- Mg Hugoniot curve radiation effects

$\frac{\partial E}{\partial V}|_T = 0$
WARM DENSE MATTER

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Gonzalez-Cataldo+ PRB (2020)
WARM DENSE MATTER

\[ C_V = \left( \frac{\partial E}{\partial T} \right)_V \]

Heat capacity \( C_V \) in kilo-electronvolts per unit (k\(E\) per f.u.) as a function of temperature (K). Different curves represent different densities, with red lines indicating 0.10\( \rho_0 \) and 0.25\( \rho_0 \), green lines for 1.00\( \rho_0 \), 2.00\( \rho_0 \), and other densities.

For Mg: \([\text{He}]2s^22p^63s^23p^2\)

For O: \([\text{He}]2s^22p^6\)

For Si: \([\text{He}]2s^22p^63s^23p^2\)

MgSiO\(_3\) molecule structure is also shown.
**WARM DENSE MATTER**

**Linear Mixing Approximation:**

\[ V_{mix} = N_1 V_1 + N_2 V_2 + N_3 V_3 \]

\[ m_{mix} = N_1 m_1 + N_2 m_2 + N_3 m_3 \]

\[ E_{mix} = N_1 E_1 + N_2 E_2 + N_3 E_3 \]

(at constant \( P \) and \( T \))

(additive volume rule)

\[ \rho_{mix} = \frac{m_{mix}}{V_{mix}} \]

Militzer, Gonzalez, Zhang, Whitley, Swift, Millot, JCP (2020)
WARM DENSE MATTER

Millot et al. GRL 2020
FIRST PRINCIPLES EQUATION OF STATE (FPEOS)

http://militzer.berkeley.edu/FPEOS

Higher $\rho_{\text{max}}/\rho_0$
1. Planetary interiors: mixing, erosion, crystallization.
2. Thermodynamic Integration: melting, anharmonicity
3. Z method agrees with two-phase and $\Delta G$.
4. Ramp compression: better models needs
5. Validated Linear Mixing for MgO, MgSiO$_3$, and BN plasmas.