First-Principles simulations of hydrogen and helium at high pressure

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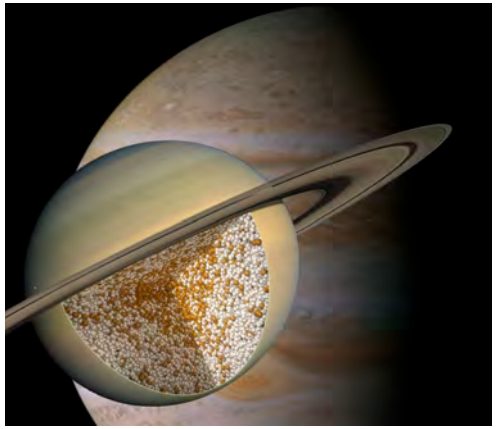
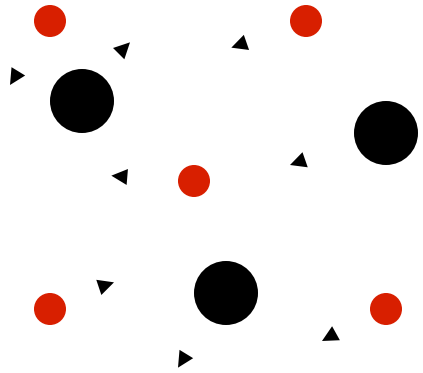
Outline

- First-Principles Simulations
- Planetary Interiors
- Hydrogen-Helium Mixtures



Basic Problem



with pbc.

$$V(\vec{R}) = \sum_{i,j} \phi(R_{ij}) + \ldots$$

Basic problem: solve Newton's equation of motion for a collection of atoms in a "box".

$$\vec{F}_i = \vec{\nabla}_i V(\vec{R}) = m\vec{a}_i$$

Empirical potentials

- determined from "empirical data": experimental EOS, dynamic properties, correlation functions, etc.
- pair potentials + corrections (3-body, embedded atom, polarization, etc)

First-Principles Simulations:
direct solution of electronic problem

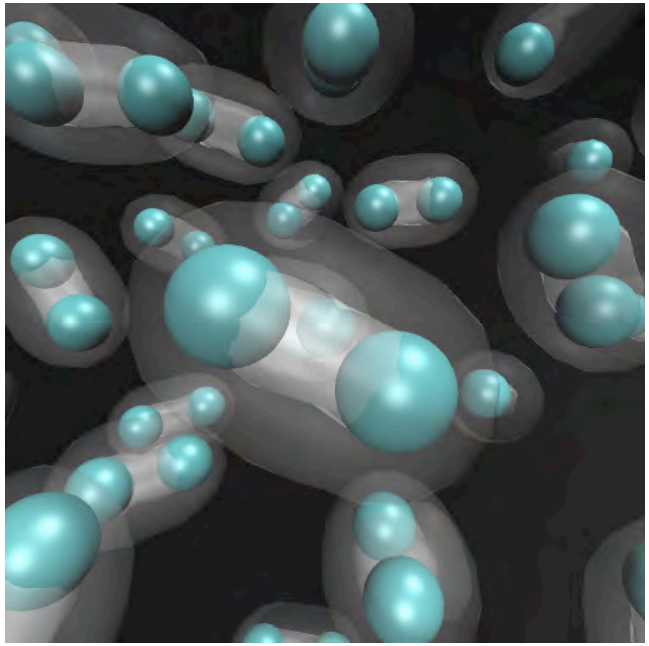
- Fix the position of the nuclei, solve the Schrodinger eqn. for the electrons (BO approximation):

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r},\{\vec{R}\}) - E_{BO}\right]\Psi(\vec{r}) = 0$$

$$\hat{V}(\vec{r},\{\vec{R}\}) = \hat{V}_{e-e} + \hat{V}_{e-n} + \hat{V}_{n-n}$$

- Electronic Structure Methods:
  - Tight-binding, non-SCF DFT
  - Density Functional Theory (DFT)
    - Semi-local functionals
    - Hybrids
  - Quantum Monte Carlo (QMC)
  - Quantum Chemistry

Accuracy ▼

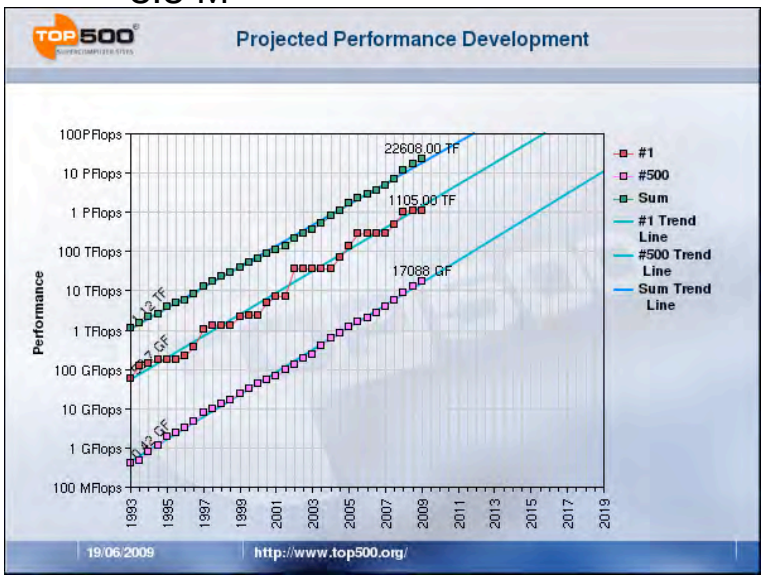


- Nuclei represent an external potential in the electronic problem

First-Principles = HPC

- 1K-10K CPU hours for a medium-size simulation
- Large scale simulations > 100K CPU hours.
- H-He practicum work:

  ~3.5 M



- Good News!!!
  - Computers continue getting faster
  - HPC on the rise !!!
    - Jaguar,Road Runner, Blue Waters, etc

computing.llnl.gov
www.top500.org

Planetary Science

- Known properties (experiments,observation):
  - mass, radius, shape
  - gravitational moments
  - surface temperature, luminosity, etc

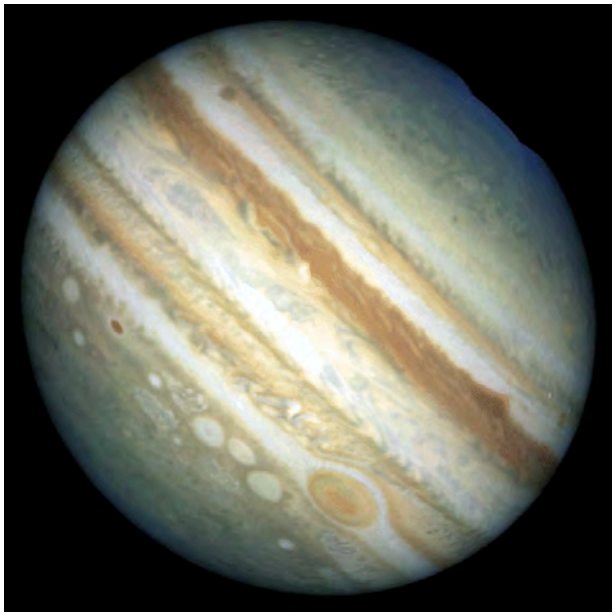
- The challenge to the theorist is to produce a model for the structure and evolution of the planet that reproduces observations

Each planets is a small mystery

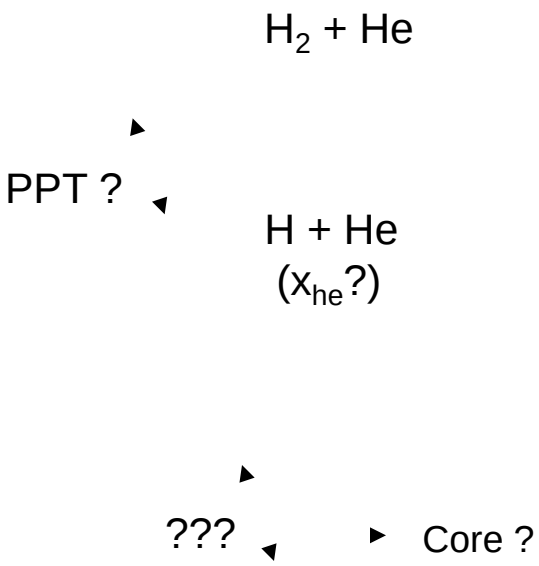
http://jpl.nasa.gov/

Giant Planets

- Giant planets:
  - Jupiter, Saturn
- The simplest and better known objects in the universe (except Earth)
- Some common properties:
  - Made mostly of hydrogen and helium (~97% Jupiter).
  - Radiate more energy than what they take from the sun.
  - Believed to be formed at the same time as the sun: ~4.55 Gyr ago.



Jupiter

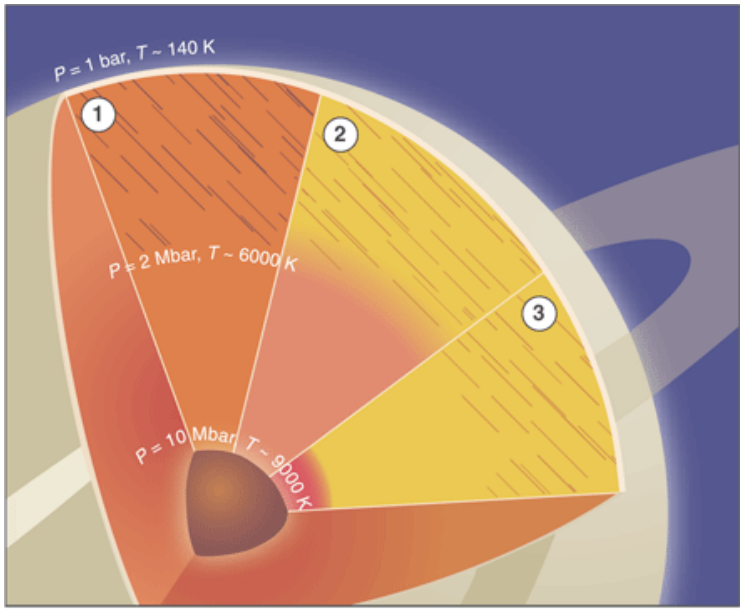


- Uncertainties from:
  - Accurate EOS
    - size of the core
    - distribution of helium
  - PPT

- Simple 3-layer structure
  1. Outer layer: H_2+He, insulating
  2. Inner layer: H+He, metallic
  3. Core: Ices and heavy elements

- Homogeneous Evolutionary Model
  - Planet irradiates energy left over from initial gravitational collapse (+ small contribution from sun)
  - Predicted age in good agreement with estimated age of galaxy

Saturn



- Homogeneous evolutionary models do not work for Saturn:

  Predicted age **~2-2.7 Gyr**

  - Saturn was created about 2 Gyrs after Jupiter? Highly unlikely…
  - Additional energy source within the planet's interior
    - Helium segregation
    - Gravitational differentiation

Problem: Very poor understanding of helium miscibility in metallic hydrogen

Fortney J. J., *Science* **305**, 1414 (2004).

Hydrogen-Helium Mixtures

- **Goal**: Calculate demixing temperature of helium in metallic hydrogen as a function of pressure and composition: $\mathbf{T_{crit}(P,x_{he})}$

- **Long history**:
  - ***Fully ionized models***: Stevenson (1975), Stevenson-Salpeter (1977), Straus-Ashcroft-Beck (1977), Hansen-Torrie-Vieillefosse (1977), Pollock-Alder (1977), Hubbard-DeWitt (1985)
  - ***Density Functional Theory***: Klepeis-Schafer-Barbee-Ross (1990), Pfaffenzeller-Hohl-Ballone(1995), Lorenzen-Holst-Redmer (2009)

Free Energy Calculations

- Free energies are hard to calculate !!!
  - Not ensemble averages, they are related to the available phase space
- Direct evaluation using first-principles is too expensive
  1. Build simple effective potential that resembles DFT.
  2. Do complicated calculations on the simple system
  3. Calculate free energy difference using Coupling Constant Integration
  4. Expand free energy using EOS from regular simulation

$$\frac{F(V,T_2,x)}{T_2} - \frac{F(V,T_1,x)}{T_1} = -\int_{T_1}^{T_2}\left(\frac{E(V,T,x)}{T}\right)\frac{dT}{T}$$

$$F(V_2,T,x) - F(V_1,T,x) = -\int_{V_1}^{V_2} P(V,T,x)dV$$

$$V(\lambda) = \lambda V_1 + (1-\lambda)V_0$$

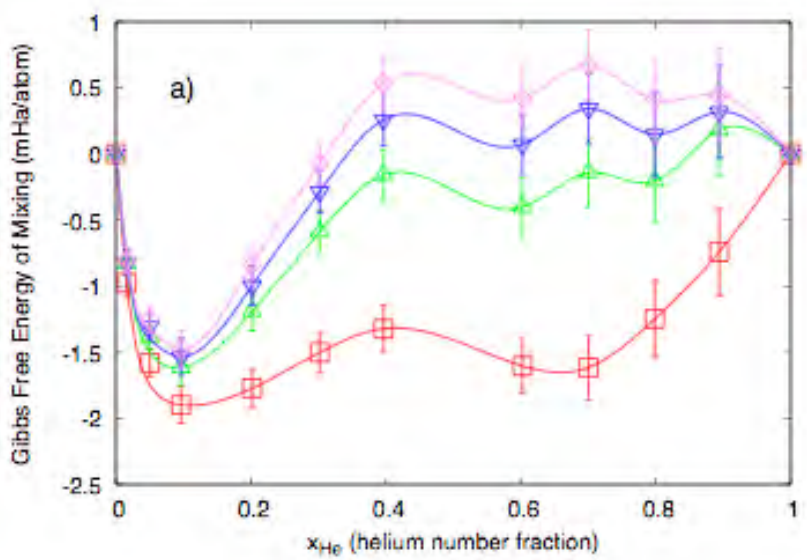
$$F_1(T,V,N) - F_0(T,V,N) = \int_0^1 d\lambda\left(\frac{dF(\lambda)}{d\lambda}\right)$$

$$= \int_0^1 d\lambda\left\langle (V_1 - V_0)\right\rangle_{T,V,N,\lambda}$$

Very efficient method for simple systems

Mixing Functions

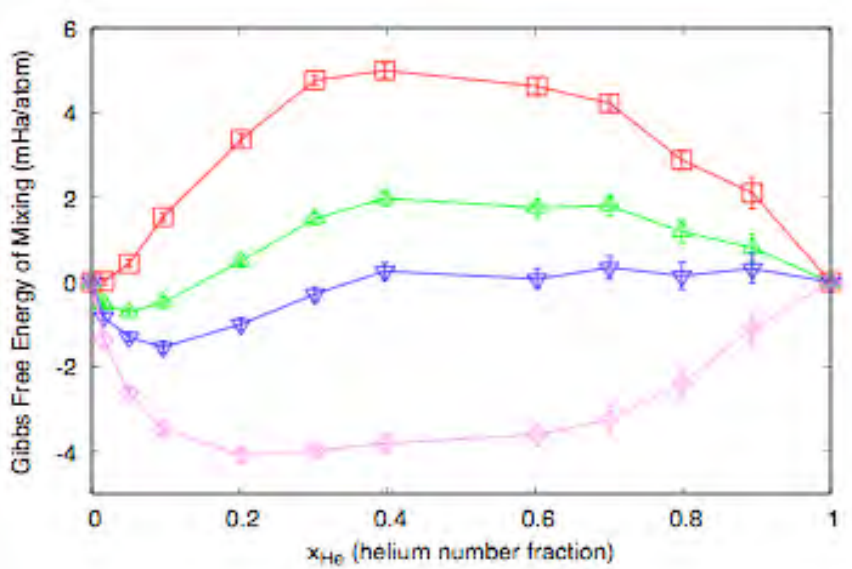
T=8000 K



4 Mbar
8 Mbar
10 Mbar
12 Mbar

- Clear minimum at low helium fraction.

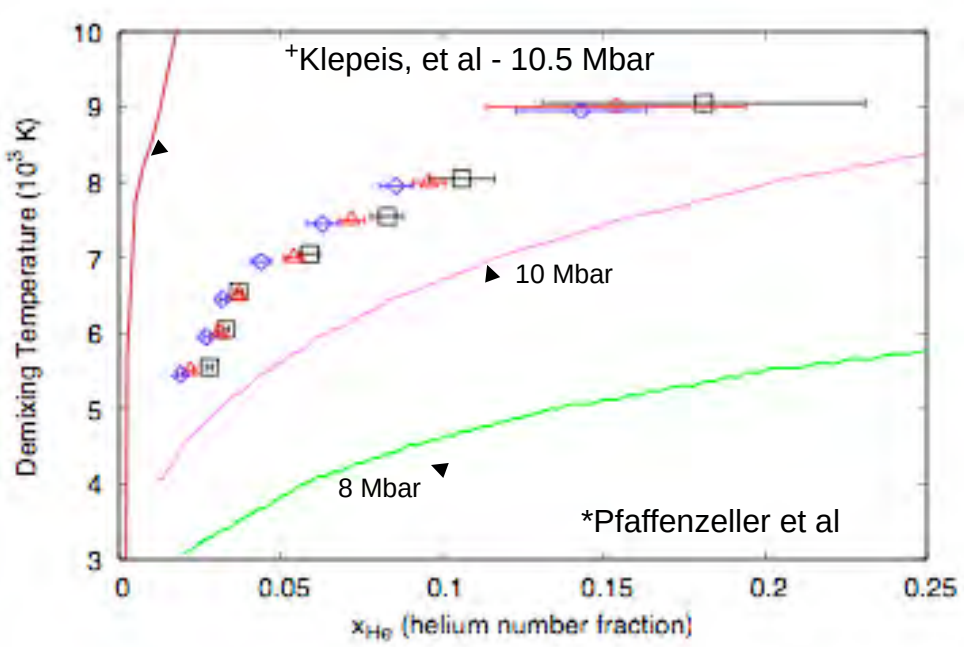
P=10 Mbar



4000 K
7000 K
9000 K
10000 K

- Very strong temperature dependence, fairly insensitive to pressure.

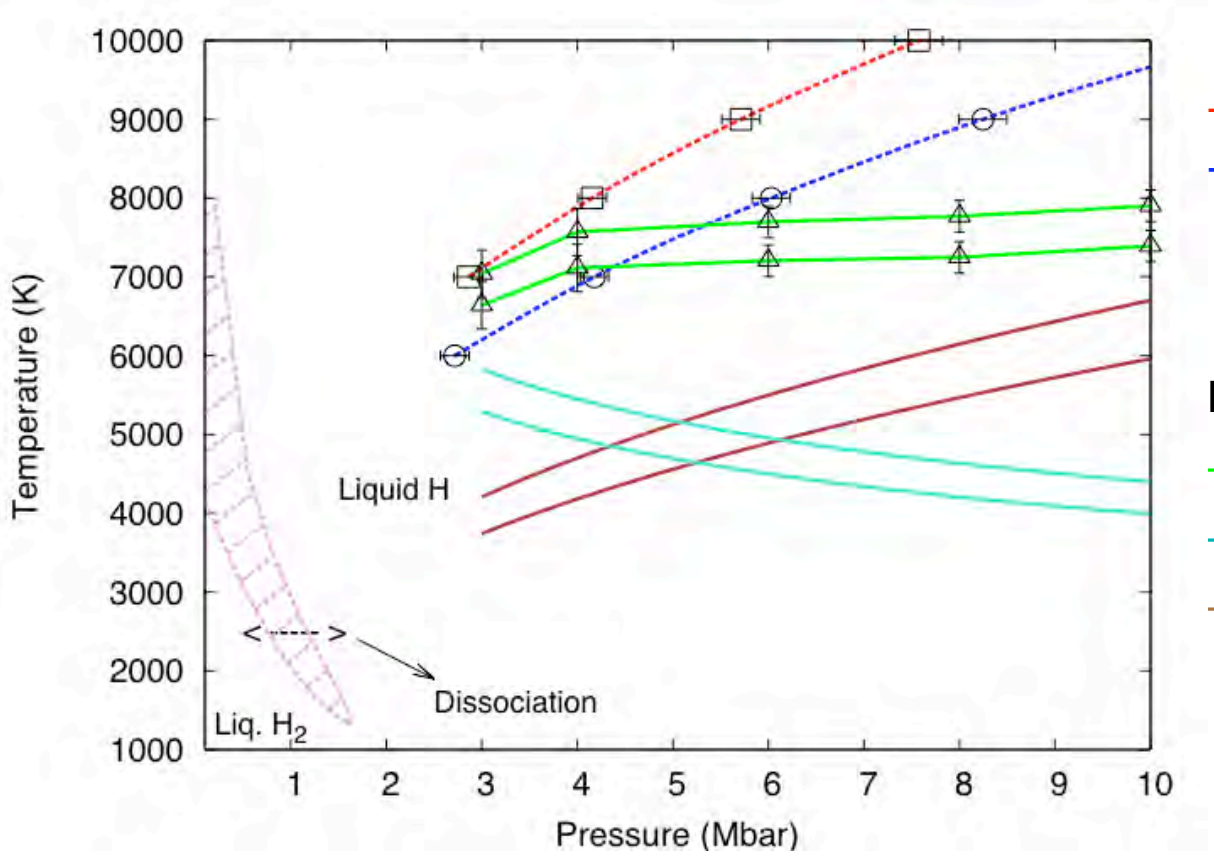
Demixing Temperature



❑ 4 Mbar
△ 8 Mbar
◊ 12 Mbar

- Previous CPMD simulations underestimate demixing temperature.

Phase Diagram



--- Jupiter Isentrope

--- Saturn Isentrope

Demixing Temperatures:

— This work:

— Hubbard - DeWitt

— Pfaffenzeller, et al.

Conclusions

- First-Principles simulation have predictive capabilities in realistic applications
  - Increase in computer power enable better electronic structure methods
- Clear signature of helium immiscibility at high pressure.
  - Strong evidence for helium condensation in Saturn.
  - PNAS **106,** 1324 (2009).

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