First Principles Simulations of Hydrogen and Helium at High Pressure

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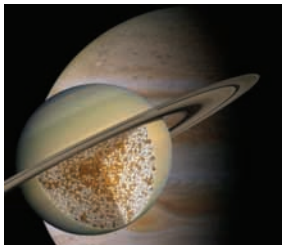
Outline



- Introduction and Motivation
- Simulation Methods
- CEIMC Simulations
  - Metallic hydrogen EOS
  - DFT benchmark
- Hydrogen-Helium Mixtures
  - Equation of state
  - Phase separation
- Molecular Dissociation
  - 1st order liquid-liquid phase transition
  - H_2 melting line

- Collaborators:
  - UIUC
    - David M. Ceperley
    - Fei Lin
  - LLNL
    - Eric Schwegler
    - Sebastien Hamel
    - Kyle Caspersen
  - U. L'Aquila, Italy
    - Carlo Pierleoni
    - Elisa Liberatore

First-Principles Simulations:
direct solution of electronic problem

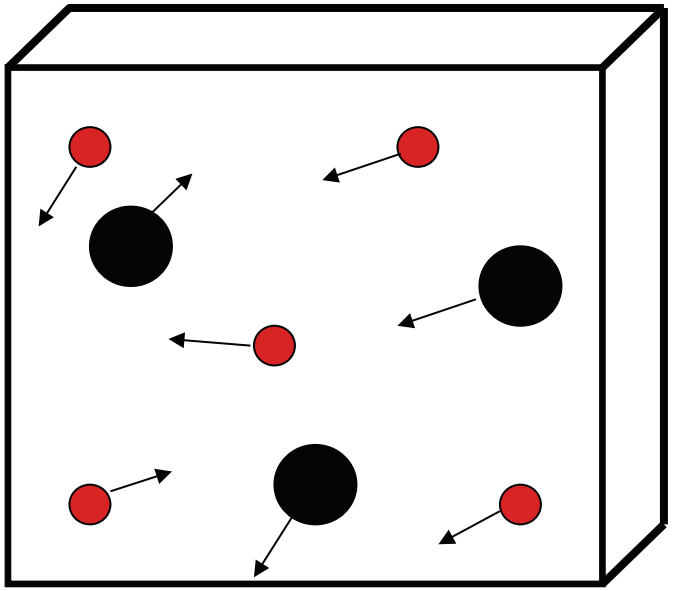
- Fix the position of the nuclei, solve the Schrödinger eqn. for the electrons (BO approximation):

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

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

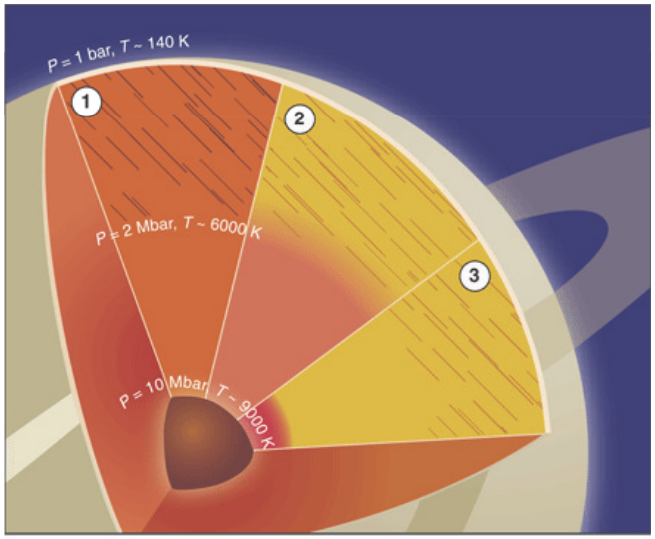
- Electronic Structure Methods:
  - Tight-binding, non-SCF DFT
  - Density Functional Theory (DFT)
    - Semi-local functionals
    - Hybrids
  - Quantum Monte Carlo (QMC)
  - Quantum Chemistry

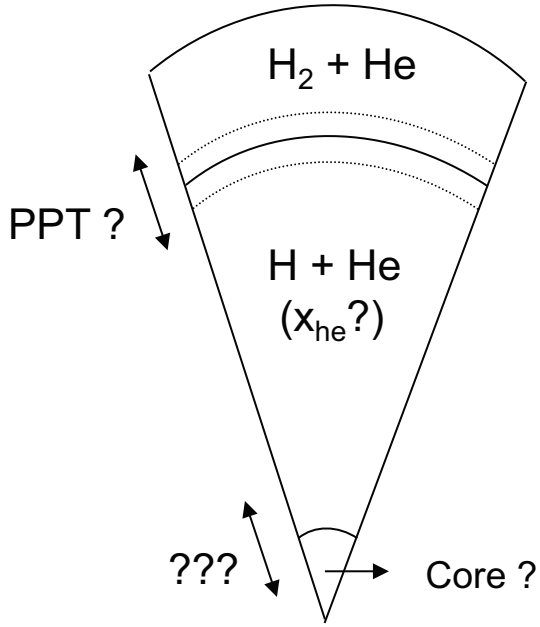
Accuracy ↓



- Nuclei represent an external potential in the electronic problem

Motivation





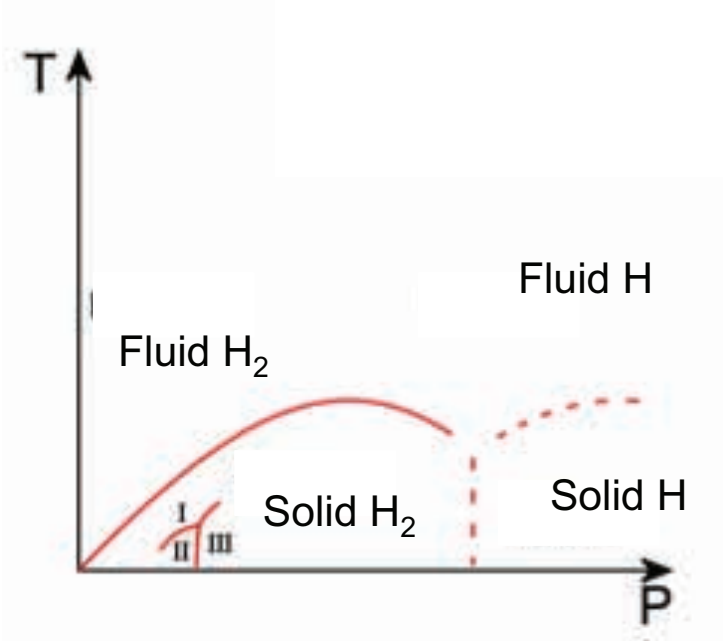
- **Saturn's Luminosity**
  - Homogeneous evolutionary models do not work for Saturn
    - Predicted age: ~2-2.7 Gyr
  - Additional energy source in planet's interior is needed
    - Helium segregation
    - Gravitational differentiation

- **Giant Planets**
  - Primary components
  - $P(\rho, T, x_i)$ closes set of hydrostatic equations
  - Interior models depend very strongly on EOS and phase diagram

Figure taken from: Fortney J. J., *Science* **305**, 1414 (2004).

Hydrogen Phase Diagram

- Interesting physics:
  - Molecular dissociation
  - Metal-Insulator transition
  - Melting



CEIMC simulations

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 / QMC.
  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

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

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

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

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

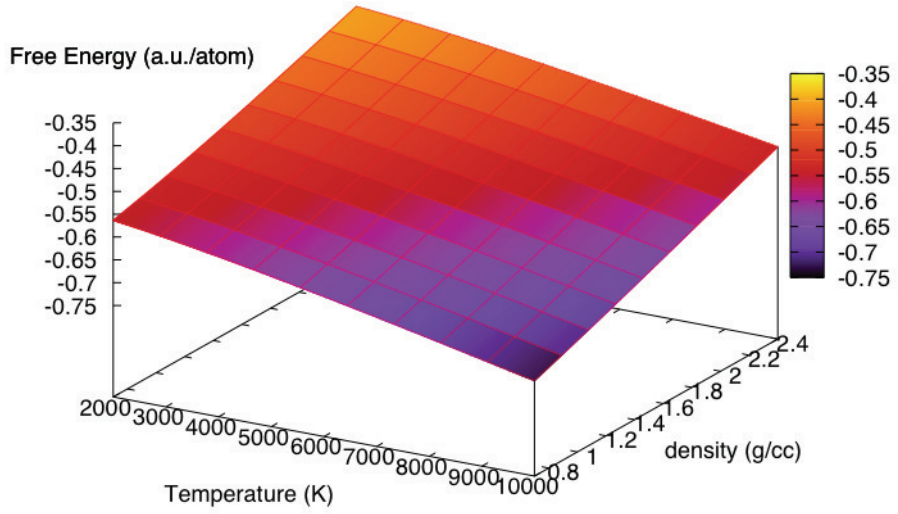
$$= \int_0^1 d\lambda\left\langle (V_1 - V_0)\right\rangle_{T,V,N,\lambda}$$

Very efficient method for simple systems

Free Energy Fits

- Free energy integration with CEIMC
- χ^2 fit to QMC results:

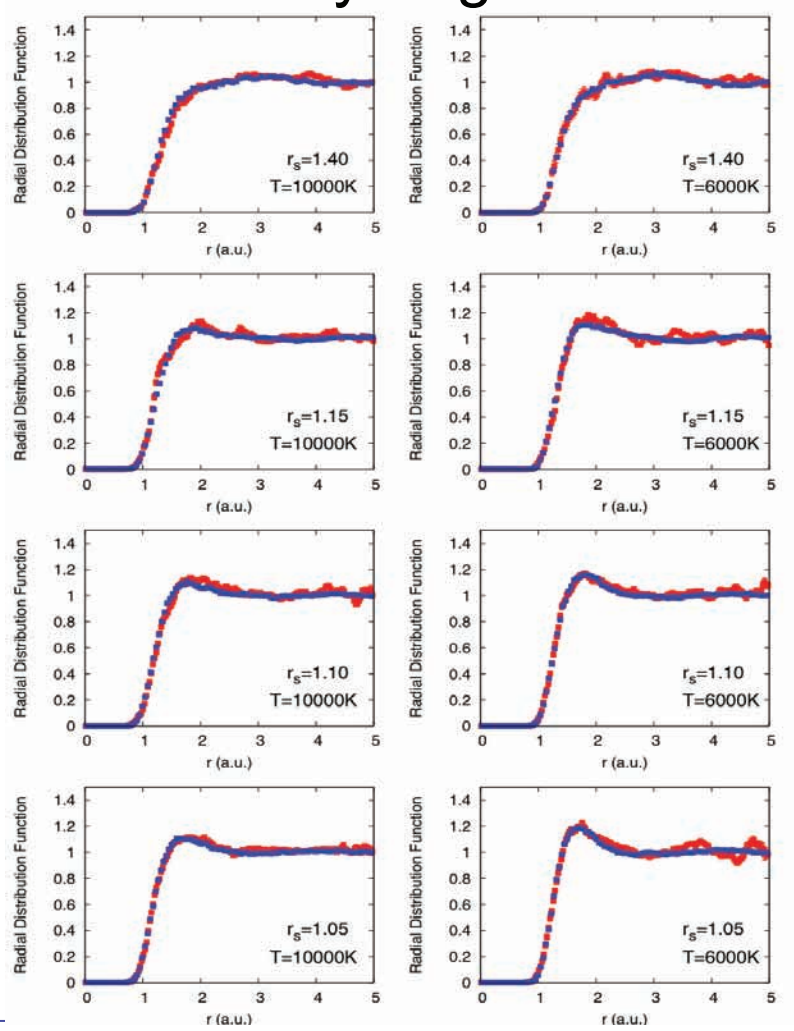
$$F(T,\rho) = \sum_{i,k} c_{i,k} g_i(T) g_k(\rho)$$



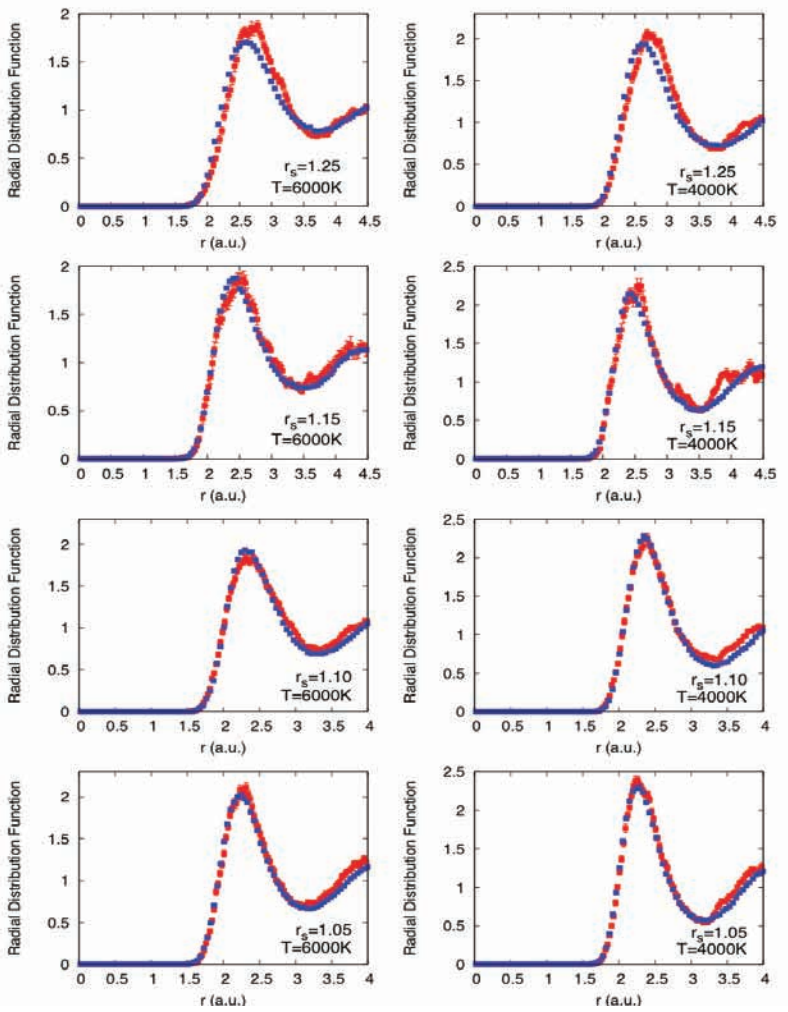
Details in: Phys. Rev. E **81**, 021202 (2010)

Radial Distribution Functions Agree

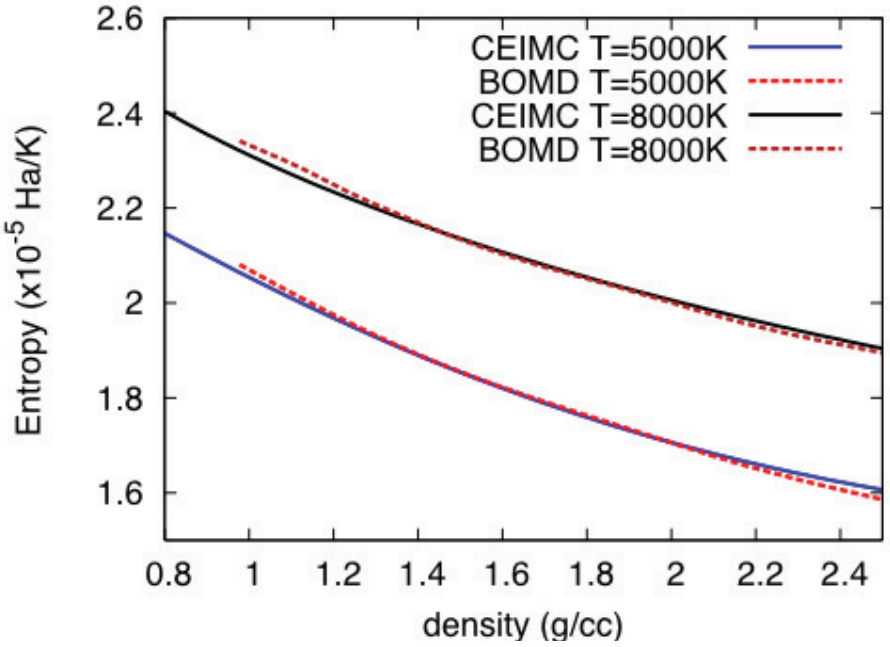
Hydrogen



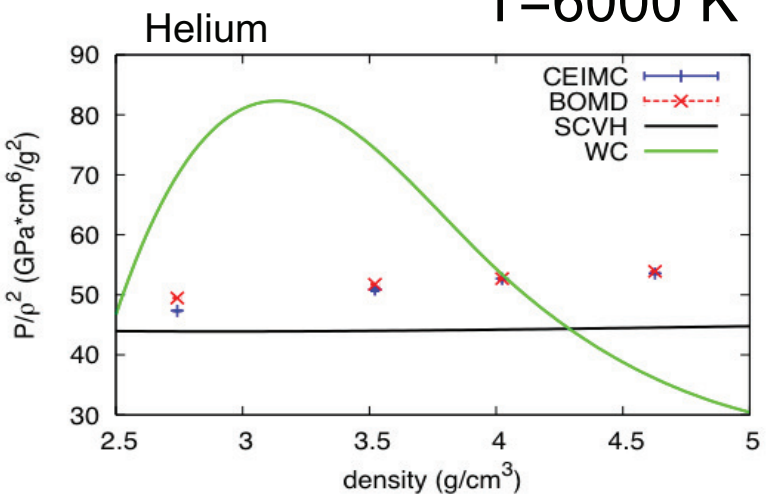
Helium

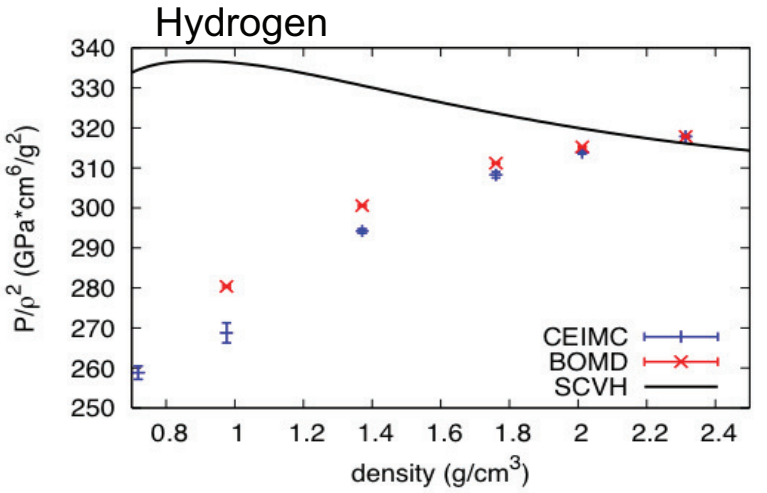


EOS Comparison



T=6000 K





- Excellent agreement with DFT
- Poor agreement with chemical models

H-He mixtures

Previous work

Fully ionized models

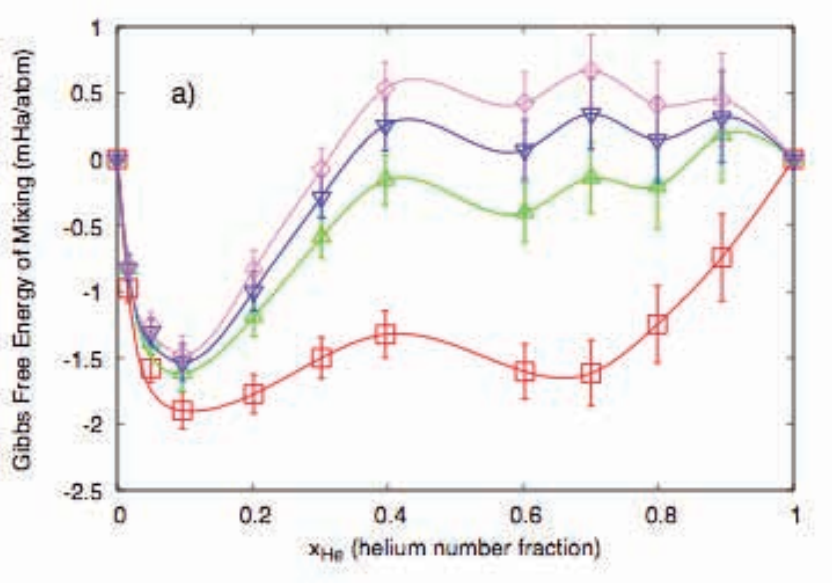
- Stevenson 1975, Hubbard-DeWitt 1985, Pollock-Alder 1976, etc.
  - Protons + Alpha particles in a uniform compensating negative background
  - Low demixing temperatures ➞ no phase separation in planets
  - Predict $T_m(P)$ with negative slope

First Principles

- Ideal mixing approximation
  - Klepeis, *et al.* - 1990: T_m~15,000 K ➞ major differentiation
    - Mixing Enthalpy from calculations on alloys of H-HE
  - Pfaffenzeller, *et al.* - 1994: T_m ~ 4000 – 6000 K ➞ no phase separation
    - Improved over Klepeis, *et al.* by allowing structural relaxation
  - Redmer, *et al.* - 2009: T_m ~ 8000 – 9000 K
    - Composition dependence of enthalpy by BOMD.

Mixing Free Energy

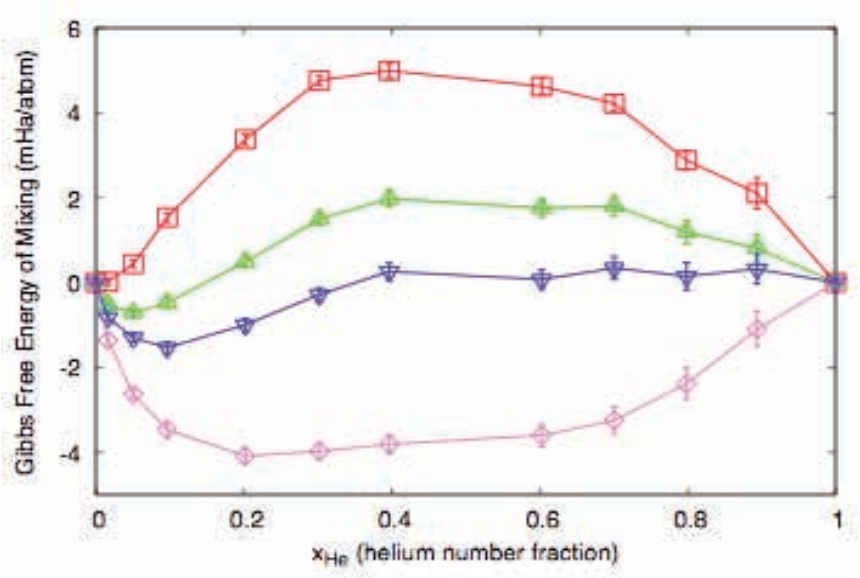
T=8000 K



4 Mbar
8 Mbar
10 Mbar
12 Mbar

- Clear minimum at low helium fraction.

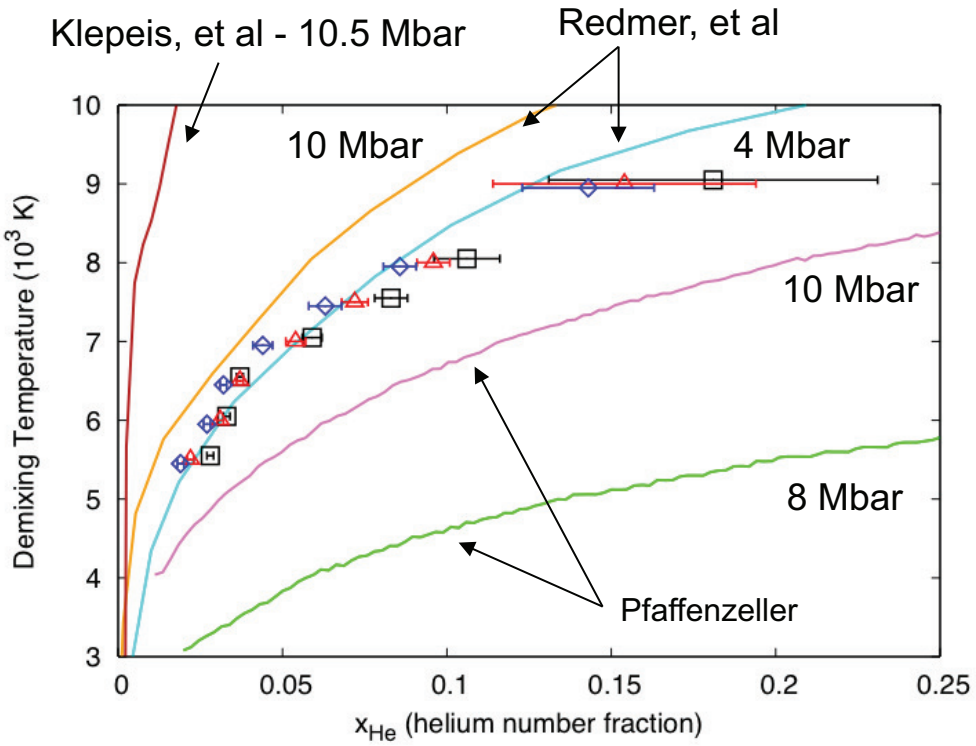
P=10 Mbar



4000 K
7000 K
9000 K
10000 K

- Very strong temperature dependence, fairly insensitive to pressure.

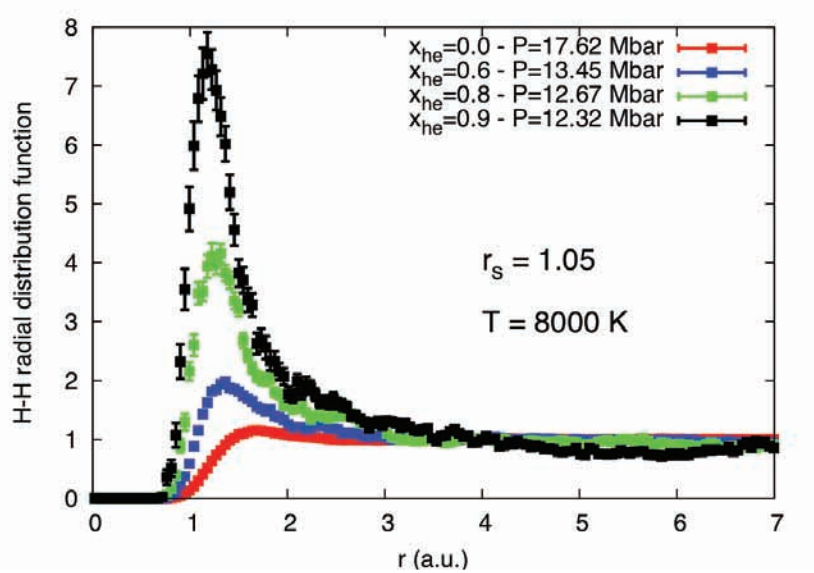
Demixing Temperature



- 4 Mbar
- 8 Mbar
- 12 Mbar

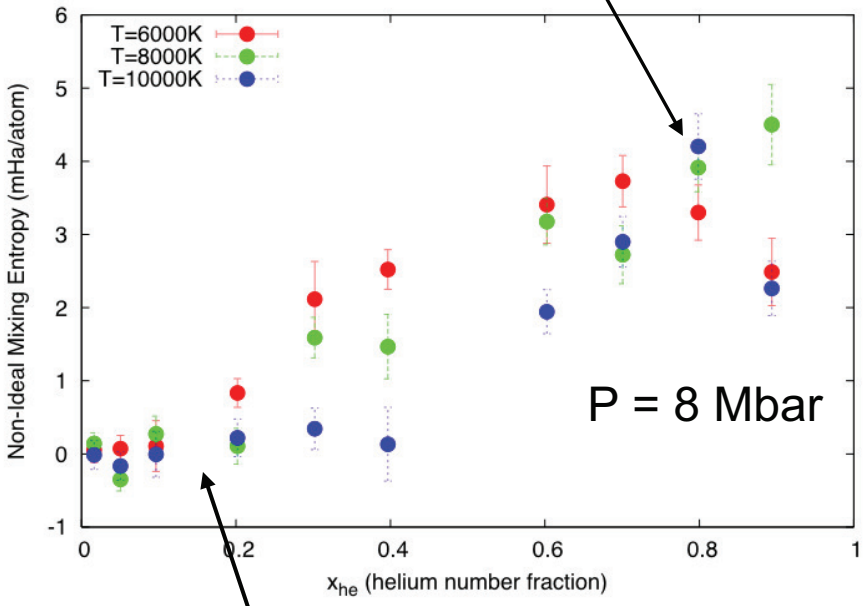
- Previous CPMD simulations underestimate demixing temperature.
- Good agreement with Redmer *et al.*
  - Differences come from non-ideal effects

Molecular-like Correlations



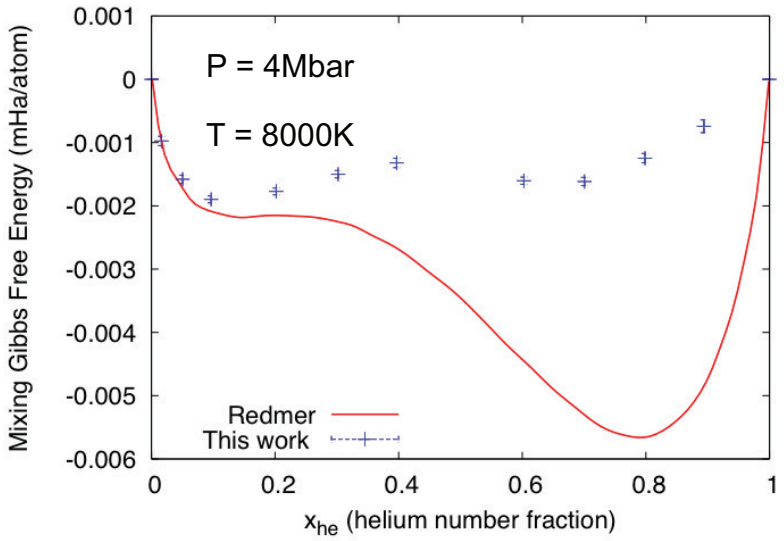
- Weak attraction even at very high pressures
- Induces molecular-like correlations
  - Pseudo-molecular state has smaller entropy compared to atomic state.

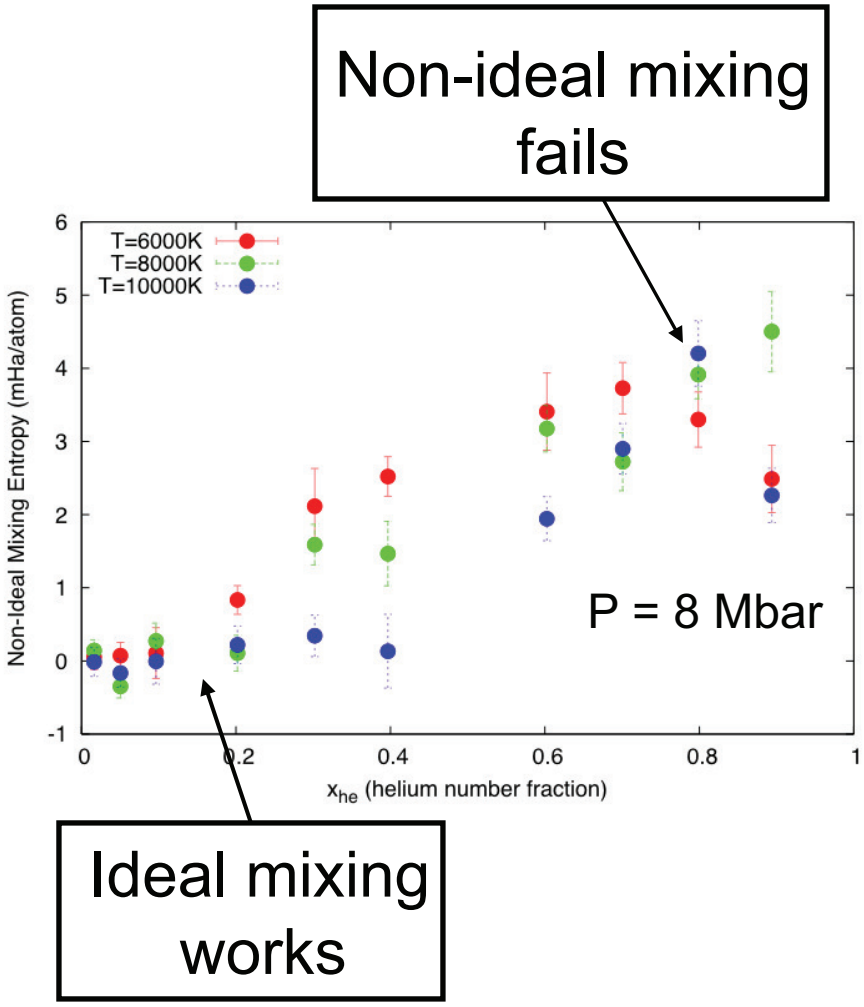
Non-ideal mixing fails



Ideal mixing works

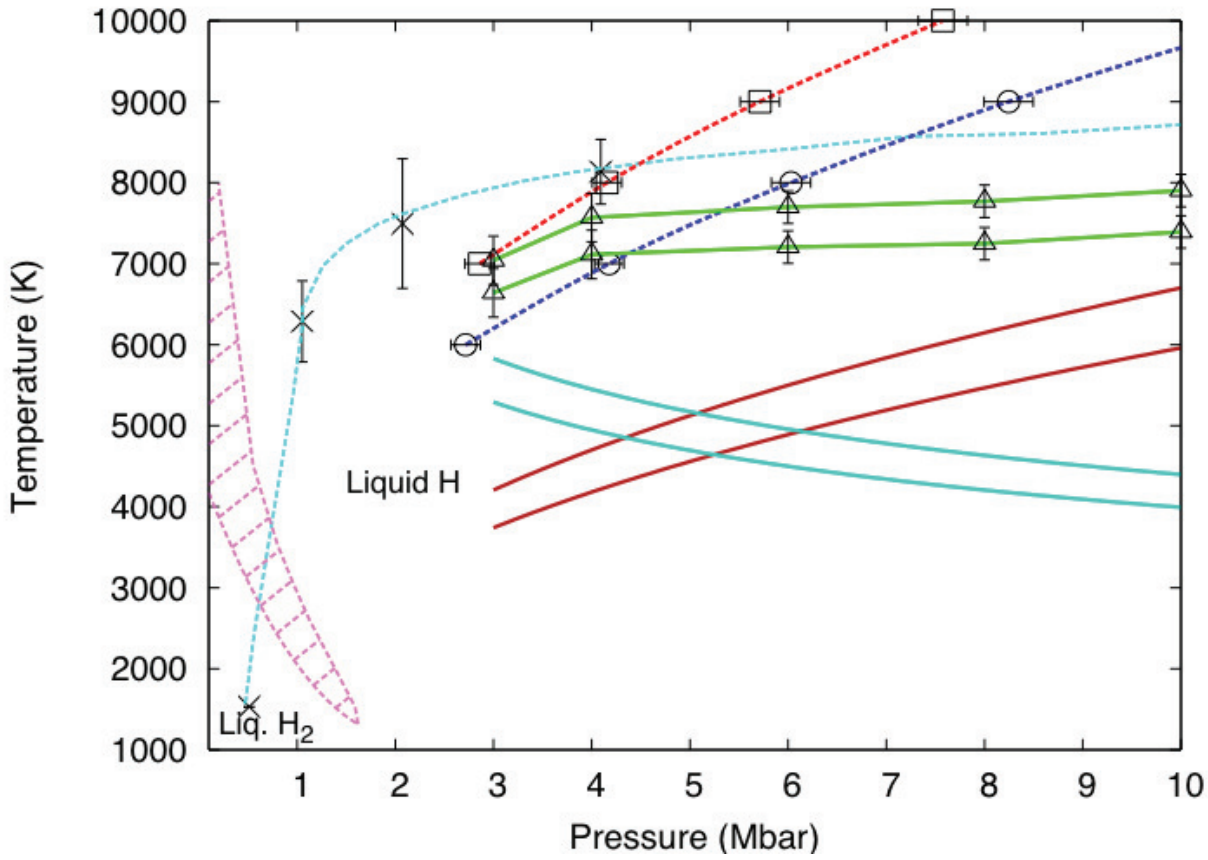
Molecular-like Correlations





- Weak attraction even at very high pressures
- Induces molecular-like correlations
  - Pseudo-molecular state has smaller entropy compared to atomic state.

Phase Diagram



--- Jupiter Isentrope

--- Saturn Isentrope

Demixing Temperatures:

— This work:

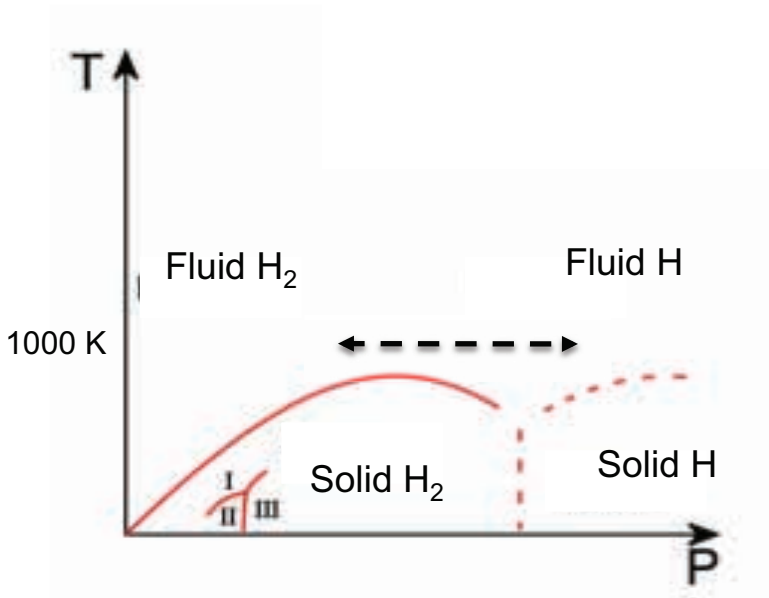
— Redmer, *et al.*

— Hubbard - DeWitt

— Pfaffenzeller, *et al.*

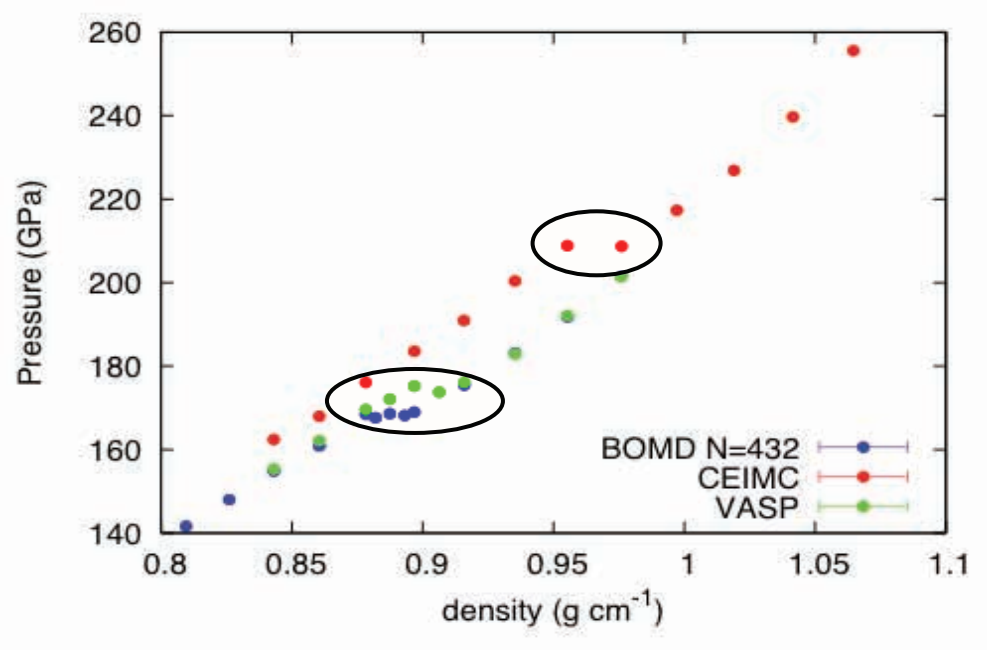
Morales M., *et al.*: PNAS 106:1324-1329 (2009)

Molecular Dissociation

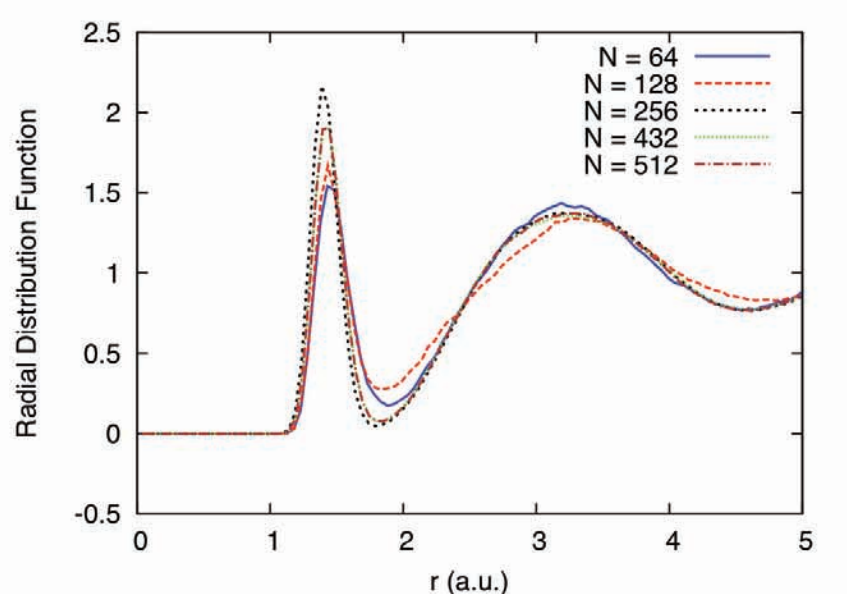


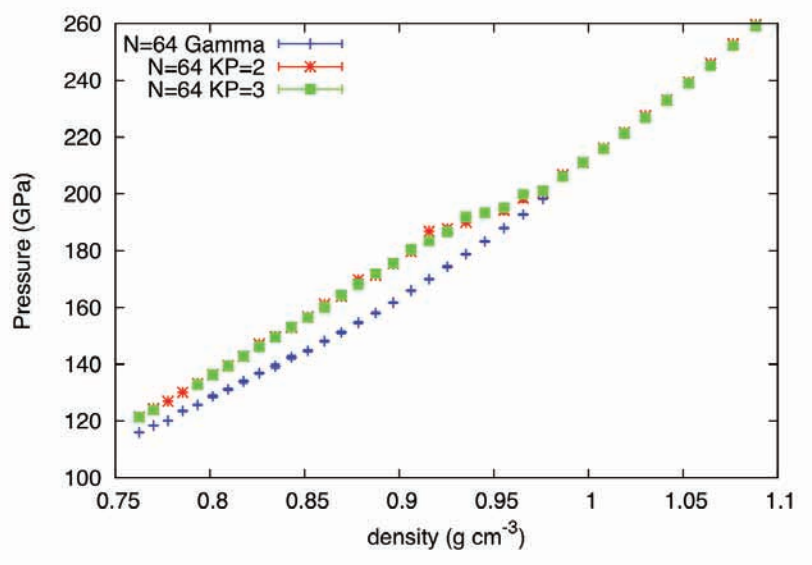
Liquid-liquid Phase Transition

- Pressure plateau at low temperatures
  - Clear signature of 1st order transition
  - Both CEIMC and BOMD simulations show signature
- Similar behavior observed at 2000 K, 1500 K and all the way down to 600 K.



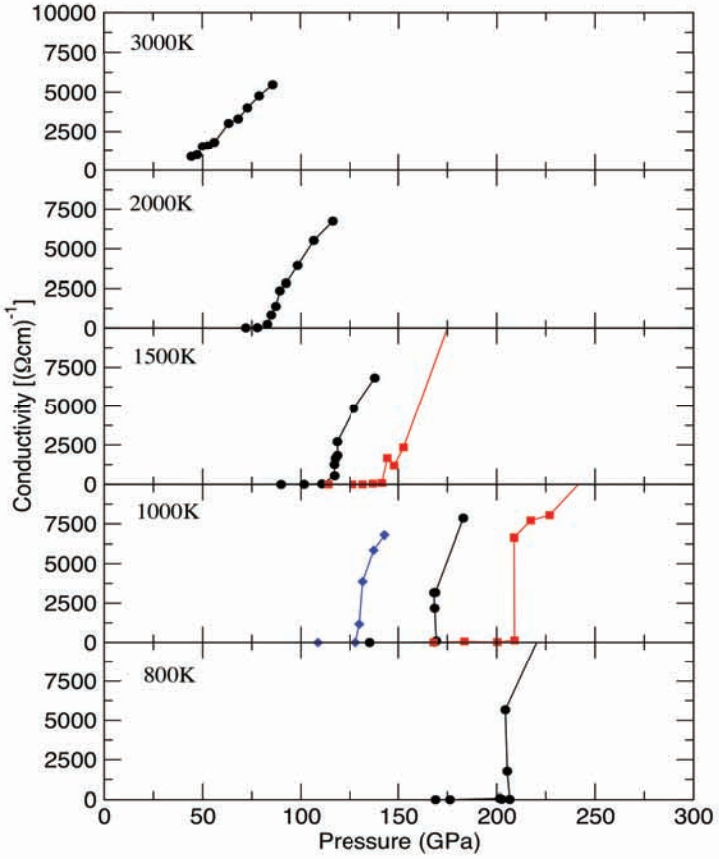
LLT - Size Effects

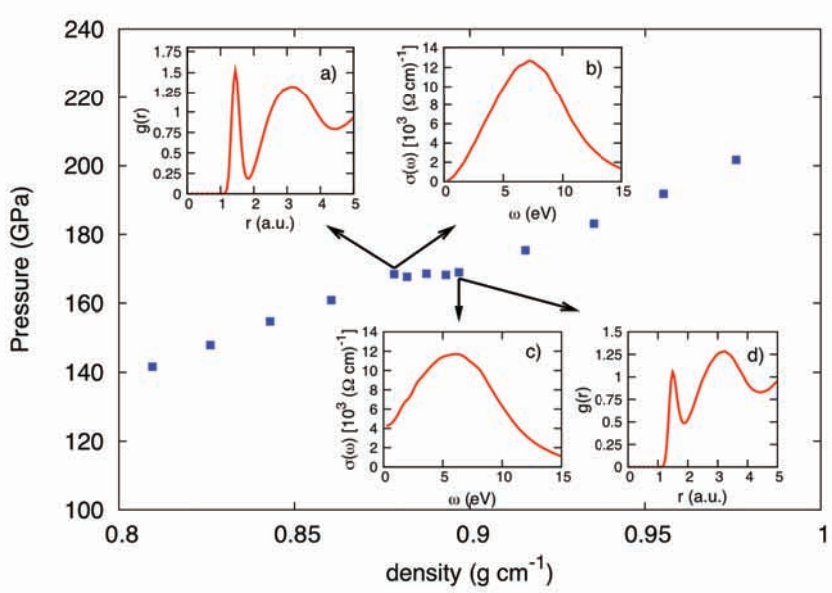




- Electronic size effects are very important in bonding
  - 64 atoms at Γ-point do not show transition at 1000 K
  - Transition appears with k-point integration

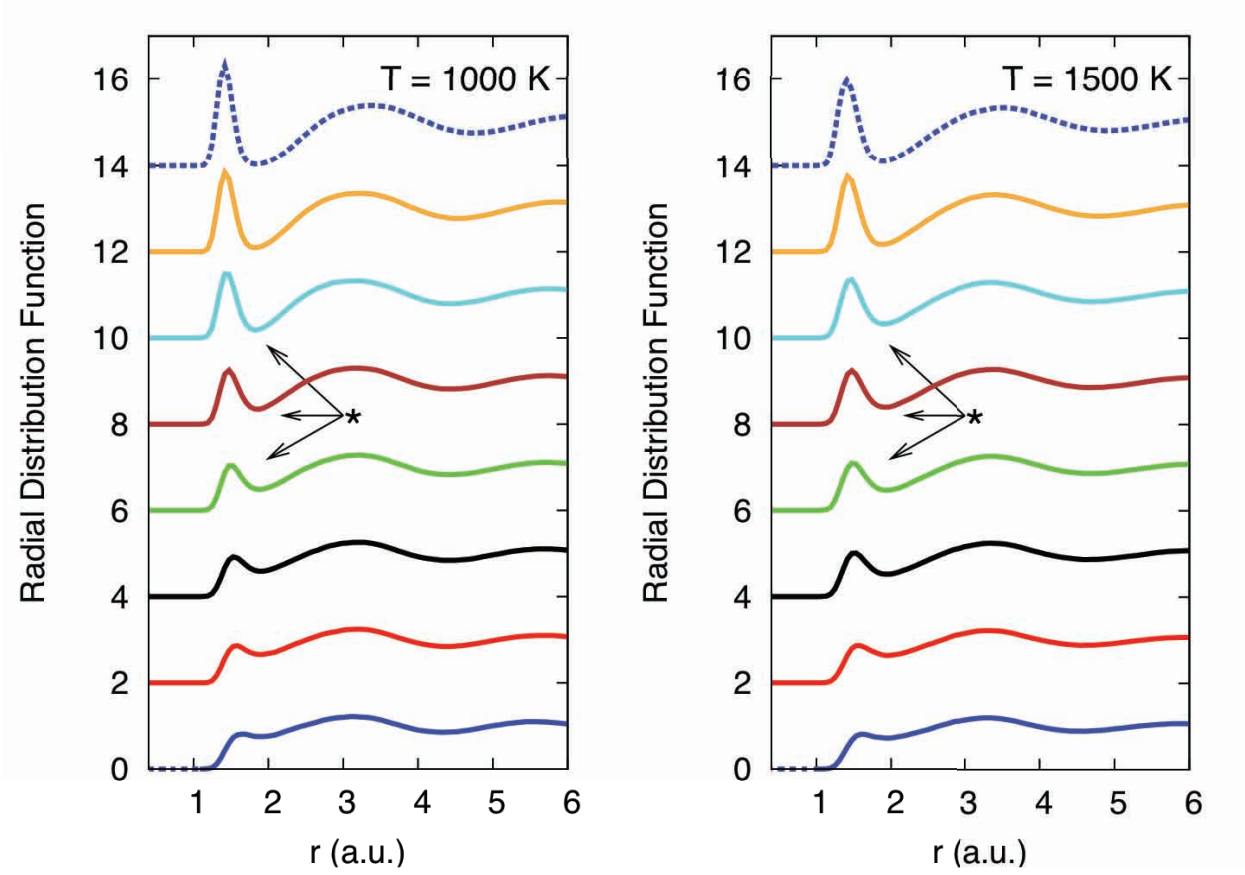
LLT - Electronic Conductivity





- Clear signs of sharp metallization across the transition
- Extrapolate discontinuity to find critical point

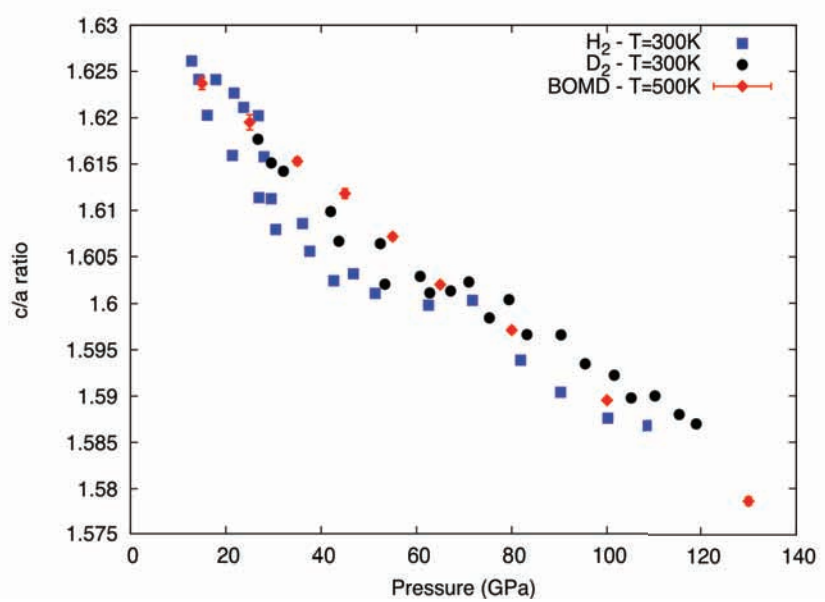
LLT – Molecular Structure



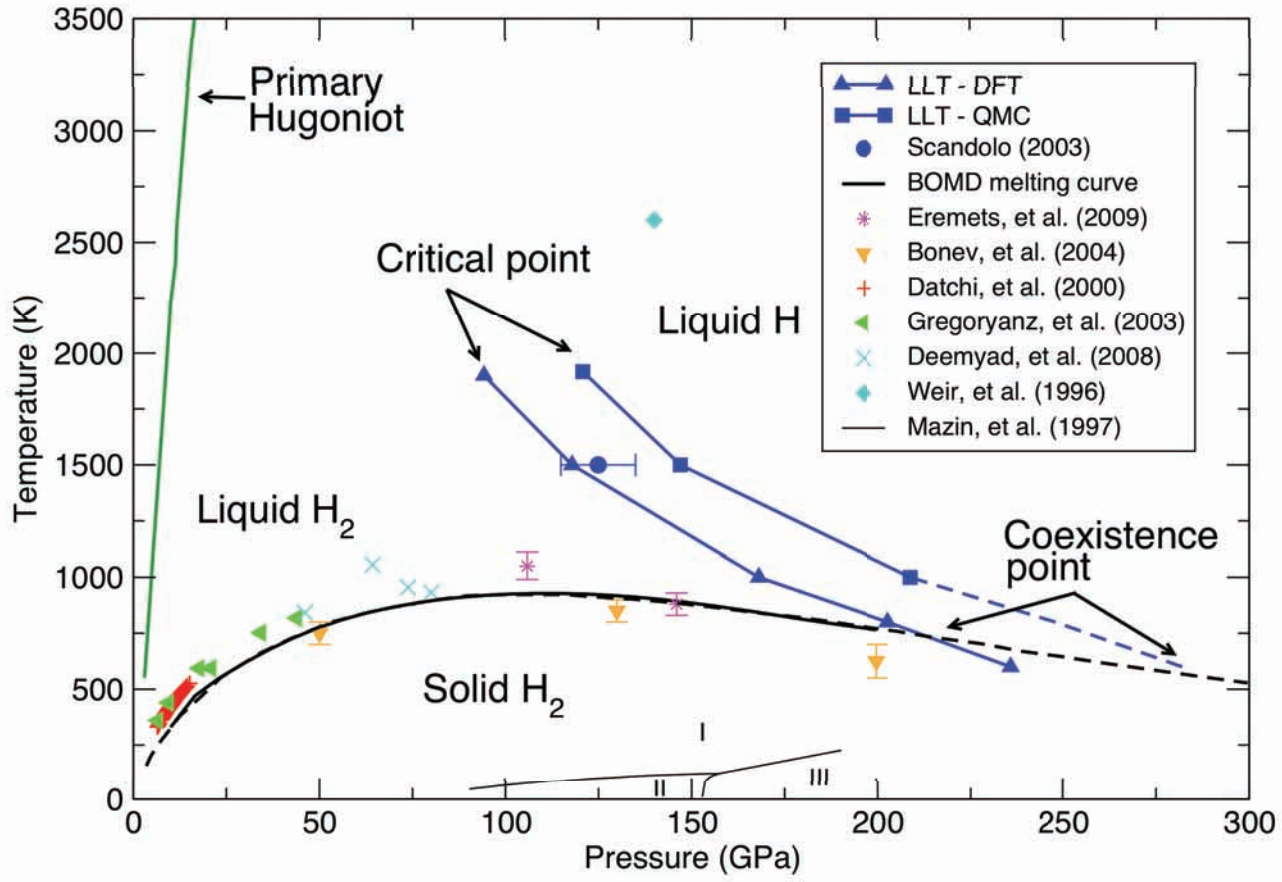
Strong short range correlations in atomic state

H_2 Melting Line

- Independent free energy calculation for liquid and solid phases
  - 10 GPa < P < 200 GPa
  - 500 K < T < 1500 K
- Solid Molecular phase
  - Assume Phase-I, hcp lattice without orientational order
  - NPT simulation to determine equilibrium lattice
  - Coupling constant integration using Einstein crystal method.



Revised Hydrogen Phase Diagram



Morales M. A., *et al.*, accepted for publication in PNAS.

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Summary

- First principles EOS for metallic hydrogen from QMC
  - Good agreement with DFT-based simulations.
- Clear signature of helium immiscibility at high pressure.
  - Strong evidence for helium condensation in Saturn.
- Clear evidence for 1st order LLT in hydrogen
  - Critical point at T~2000 K
  - Intersects melting line below T~800 K, above 200 GPa.

Acknowledgements

- We acknowledge support from:
  - Department of Energy Stewardship Science Graduate Fellowship (SSGF) program
  - DOE
  - LLNL
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  - CINECA (Italy)