The Phases of Warm-Dense Hydrogen and Helium as seen by Quantum Monte Carlo

M. Morales, DMC: *University of Illinois*
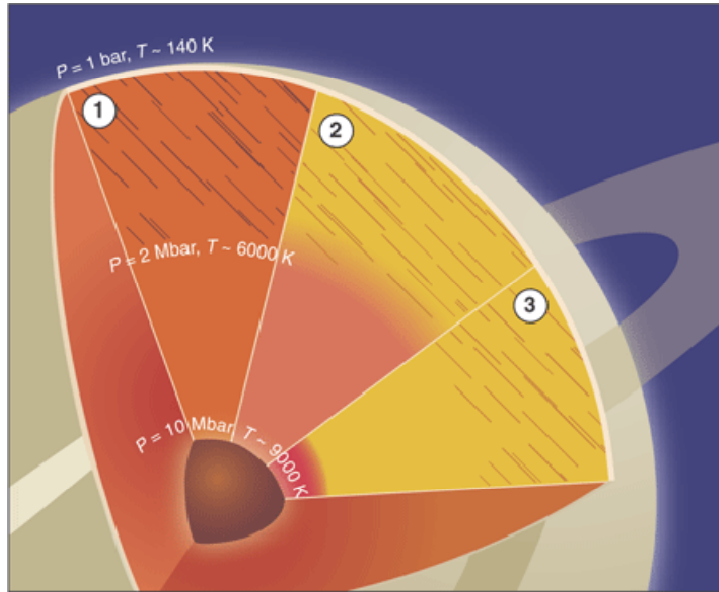
C. Pierleoni: *L'Aquila, ITALY*

Eric Schwegler: *Livermore*

- The coupled electron-ion Monte Carlo method
- Hydrogen and Helium at High Pressure

David Ceperley, UIUC   March 4, 2010   KITP Materials Design

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

- Giant Planets
  - Primary components are H and He
  - $P(\rho, T, x_i)$ closes set of hydrostatic equations
  - Interior models depend very sensitively on EOS and phase diagram
- Saturn's Luminosity
  - Homogeneous evolutionary models do not work for Saturn
  - Additional energy source in planet's interior is needed
  - Does it come from Helium segregation (rain)?

EOS does matter
how big is Jupiter's core?
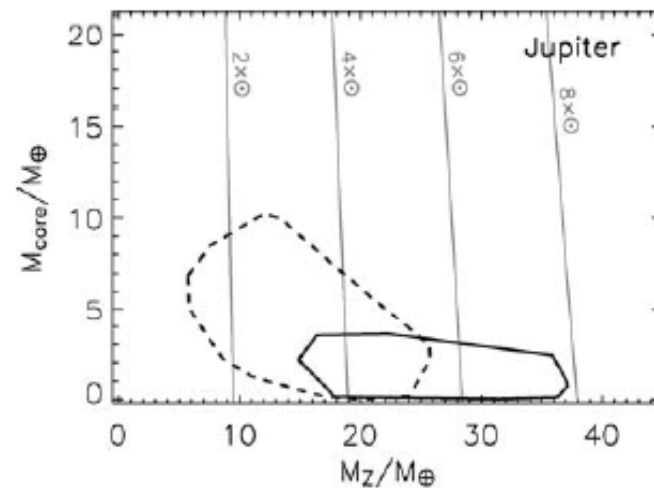
Figure 7 Constraints on Jupiter's interior structure based on Saumon & Guillot (2004). The value of the core mass (M_{core}) is shown in function of the mass of heavy elements in the envelope (M_Z) for models matching all available observational constraints. The dashed region corresponds to models matching the laser compression experiments. The plain box corresponds to models matching the pulsed power and convergent shock compression experiments (see text). Grey lines indicate the values of M_Z that imply uniform enrichments of the envelope in heavy elements by factors of two to eight times the solar value ($Z_\odot = 0.0149$), respectively.

Planet modeling needs P(ρ,T,x) accurate to 1%!
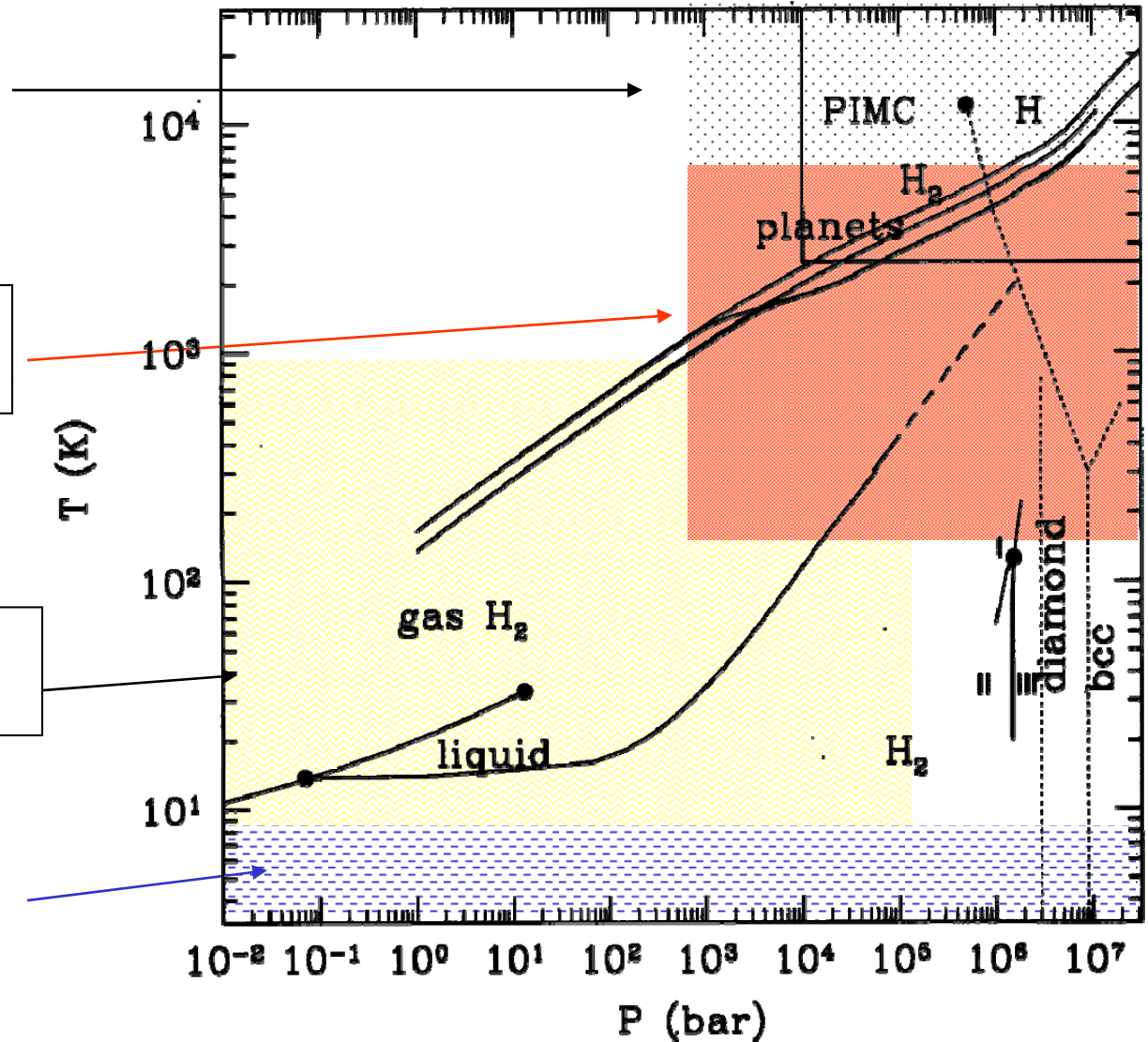Also entropy, compressibility,....

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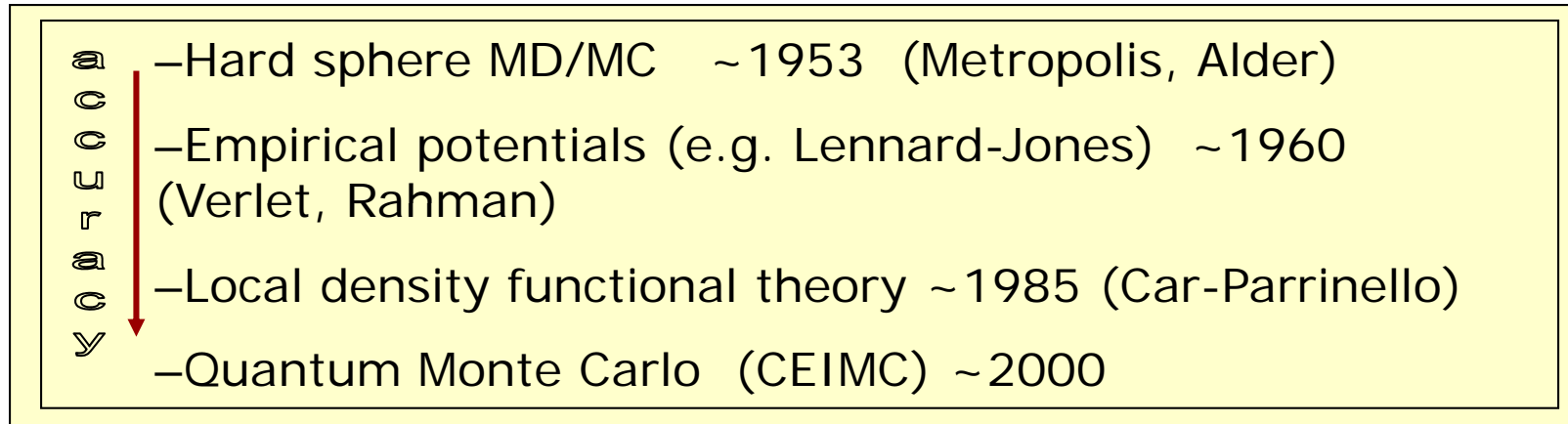# QMC methods for Dense Hydrogen

Path Integral MC for
$T > E_F/10$

Coupled-electron Ion MC

Path Integral MC with an effective potential

Diffusion MC T=0

MD and MC Simulations

<div style="border:1px solid black; background:#ffffcc; padding:10px;">

a c c u r a c y ↓

– Hard sphere MD/MC ~1953 (Metropolis, Alder)

– Empirical potentials (e.g. Lennard-Jones) ~1960 (Verlet, Rahman)

– Local density functional theory ~1985 (Car-Parrinello)

– Quantum Monte Carlo (CEIMC) ~2000

</div>

- Initial simulations used semi-empirical potentials.
- Much progress with "ab initio" molecular dynamics simulations where the effects of electrons are solved for each step.
- However, the potential surface as determined by density functional theory is not always accurate enough
- QMC+MD =CEIMC/MD is a candidate for petascale computing

Quantum Monte Carlo

- Premise: we need to use simulation techniques to "solve" many-body quantum problems just as you need them classically.
- Both the wavefunction and expectation values are determined by the simulations. Correlation built in from the start.
- QMC gives most accurate method for general quantum many-body systems.
- Ceperley-Alder electronic energy is a standard for approximate LDA calculations.
- Path Integral Methods provide a exact way to include effects of ionic zero point motion
- A variety of stochastic QMC methods (we use them all):
  - **Variational Monte Carlo VMC (T=0)**
  - **Projector Monte Carlo (T=0)**
    - **Diffusion MC (DMC)**
    - **Reptation MC (RQMC)**
  - **Path Integral Monte Carlo (PIMC) (T>0)**
  - **Coupled Electron-Ion Monte Carlo (CEIMC)**
- **In the past, QMC has been used for static structures.**

Experiment vs PIMC/DFT simulations

- Older laser (NOVA) shocks are incompatible with microscopic theory.

- Chemical models are not predictive in this regime.

- Z-pinch experiments of *Knudsen et al., PRL 87, 225501 (2001)*

Deuterium Hugoniot

B. Militzer 11–19–01
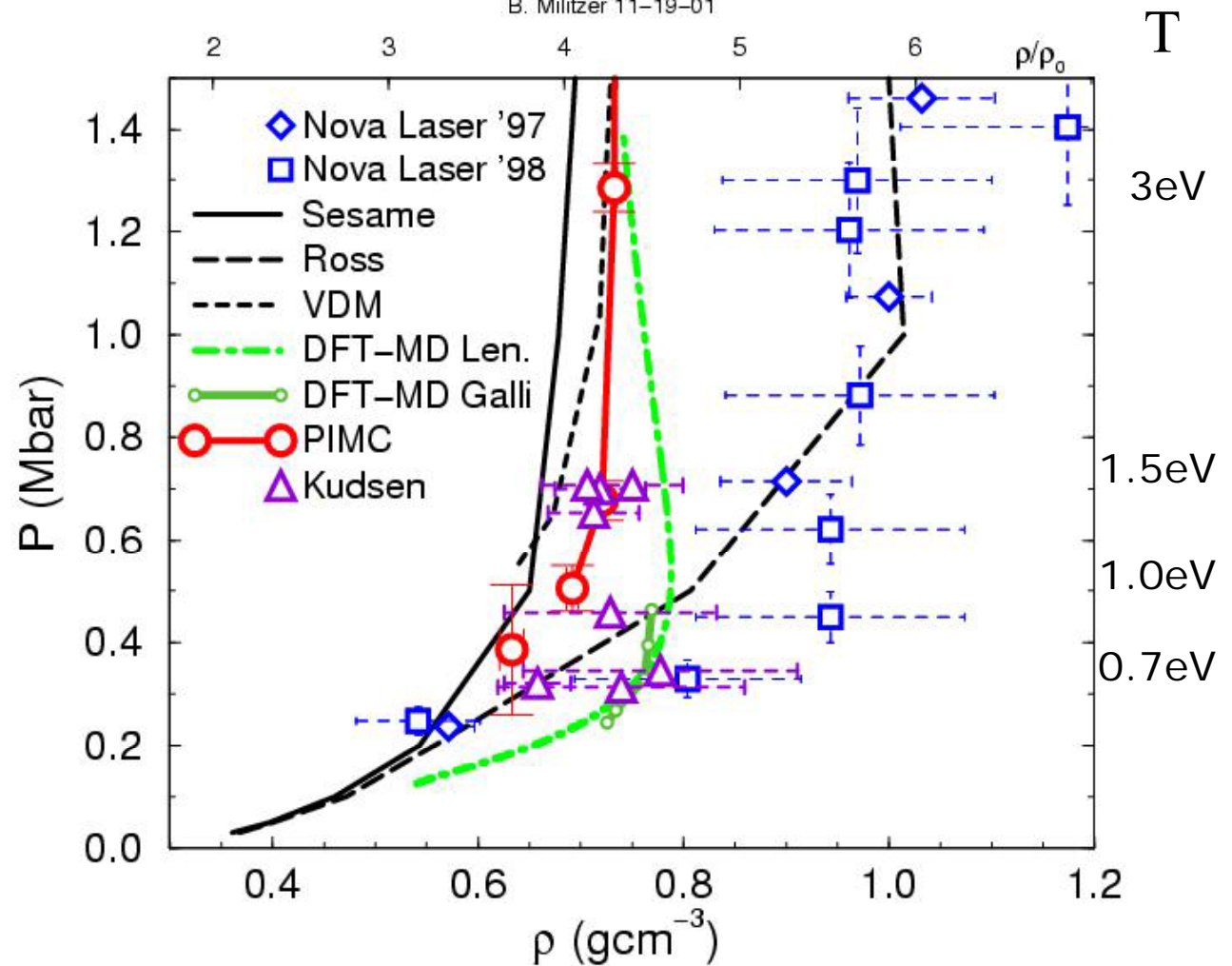
New QMC Techniques

- Better Finite-Size scaling methods
    - Twist averaging for kinetic energy
    - Coulomb correction for potential energy
- Better trial wavefunctions -> better nodes
    - Backflow
    - Iterated backflow
    - Direct coupling to DFT
- Coupled Electron-Ion Monte Carlo
- Optimization
- Computers/parallelization
- Algorithms (e.g. reptation)

Variational Monte Carlo (VMC)
(McMillan 1965)

- Put correlation directly into the wavefunction.
- Integrals are hard to do: need MC.
- Take sequence of increasingly better wavefunctions. Stochastic optimization is important!
- **Can we make arbitrarily accurate functions?** Method of residuals says how to do this.
- Recent progress with "backflow"
- No sign problem, and with classical complexity.

- Posit a wavefunction $\phi(\mathbf{R},\mathbf{a})$
- sample $|\phi(\mathbf{R},\mathbf{a})|^2$ with random walk.
- minimize energy or variance of $\phi(\mathbf{R},\mathbf{a})$ with respect to $\mathbf{a}$

$$R \equiv (\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = \text{"walker"}$$

$$\Psi_2(R) = Det\{\phi_i(\mathbf{r}_j)\}e^{-\sum_{i<j} u_{ij}(r_{ij})}$$

$$\Psi_{n+1}(R) \approx \Psi_n(R)e^{-<\phi_n^{-1}H\phi_n>}$$

smoothing

Trial functions for dense hydrogen

- Slater-Jastrow function:

$$\Psi_2(R) = Det\{\phi_k(r_j)\}e^{-\sum_{i<j}u_{ij}(r_{ij})}$$

  with the orbital from a rescaled LDA calculation.
    - Reoptimization of trial functions during the CEIMC run is a major difficulty in time and reliability.
    - We want trial function with no parameters (i.e. those dependant on precise protonic configuration)
- Trial functions used:
    - Standard LDA requires a lengthy calculation for each structure.
    - Fast band structure solver by removing e-p cusp and putting it into the Jastrow factor. Use plane wave basis and iterative methods. PW cutoff is minimized. Works in intermediate H-H_2 phase.
    - backflow + three body trial function are very successful for homogeneous systems. we generalized them to many-body hydrogen: no free parameters, but only works well for the atomic phase.

Wavefunctions beyond Jastrow

$$\phi_{n+1}(R) \approx \phi_n(R)e^{-\tau<\phi_n^{-1}H\phi_n>}$$

smoothing

- Use method of residuals construct a sequence of increasingly better trial wave functions.
  - Zeroth order is Hartree-Fock wavefunction
  - First order is Slater-Jastrow pair wavefunction (RPA for electrons gives an analytic formula)
  - Second order is "3-body backflow "wavefunction
- Three-body form is like a squared force. It is a bosonic term that does not change the nodes.

$$\Psi_2(R)\exp\{\sum_i[\sum_j \xi_{ij}(r_{ij})(\mathbf{r}_i - \mathbf{r}_j)]^2\}$$

- Backflow means change the coordinates to quasi- coordinates.

$$Det\{e^{i\mathbf{k}_i\mathbf{r}_j}\} \Rightarrow Det\{e^{i\mathbf{k}_i\mathbf{x}_j}\} \qquad \mathbf{x}_i = \mathbf{r}_i + \sum_j \eta_{ij}(r_{ij})(\mathbf{r}_i - \mathbf{r}_j)$$

^{3}He moving in liquid ^{4}He: Feynman 1955.

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Projector Monte Carlo
e.g. Diffusion Monte Carlo (DMC)

- Automatic way to get better wavefunctions.
- Project single state using the Hamiltonian

$$\phi(t) = e^{-(H-E)t}\phi(0)$$

- This is a diffusion + branching operator.
- Very scalable: each walker gets a processor.
- **But is this a probability?**
- **Yes!** for bosons since ground state can be made real and non-negative. **But** all <u>excited states</u> must have sign changes.
- In exact methods one carries along the sign as a weight and samples the modulus. This leads to the famous sign problem

$$\phi(t) = e^{-(H-E)t}\,\text{sign}(\phi(R,0))\,|\,\phi(R,0)\,|$$

Fixed-node method

- Initial distribution is a pdf. It comes from a VMC simulation. $f(R,0) = |\psi_T(R)|^2$

- Impose the condition: $\phi(R) = 0$ when $\psi_T(R) = 0.$
- This is the fixed-node BC

- Will give an upper bound to the exact energy, the best upper bound consistent with the FNBC.

  $E_{FN} \geq E_0$

  $E_{FN} = E_0$ if $\phi_0(R)\psi(R) \geq 0$ all R

- f(R,t) has a discontinuous gradient at the nodal location.
- Accurate method because Bose correlations are done exactly.
- Scales like the VMC method, as N³ or better.

How good is trial function?
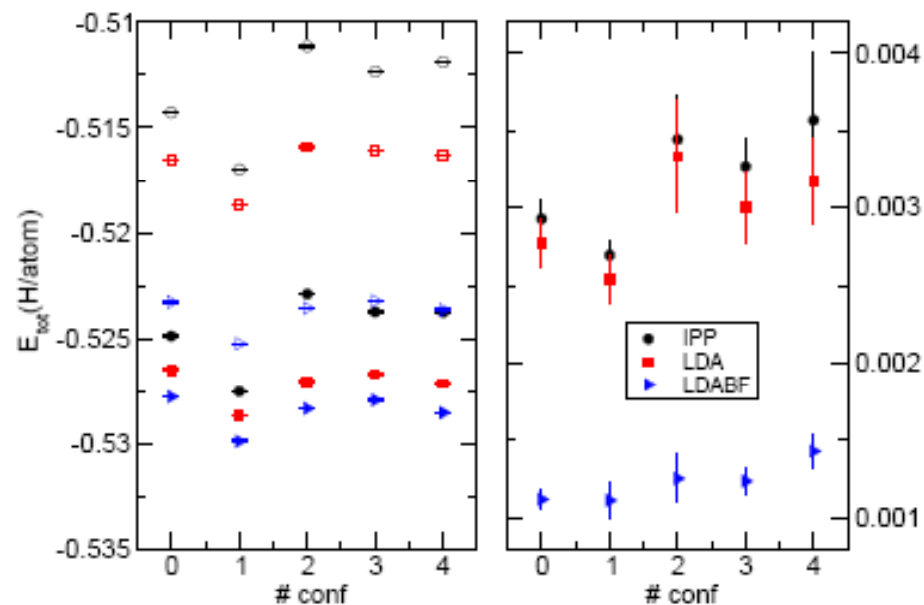
Fig. 4. Total energy (left panel) and quality parameter (right panel) for a number of static proton configurations as obtained with the metallic and the LDABF trial functions at $r_s = 1.40$. TABC with a 6x6x6 fixed grid in the twist space is performed. Energies are in h/atom. In the right panel open symbol represent VMC energies for IPP (circles), LDA (squares) and LDABF (triangles), respectively. RQMC energies for the same trial functions are represented by closed symbols.

Dependence of energy on wavefunction

3d Electron fluid at a density $r_s = 10$

*Kwon, Ceperley, Martin, Phys. Rev. **B58**,6800, 1998*

- Wavefunctions
  - Slater-Jastrow (SJ)
  - three-body (3)
  - backflow (BF)
  - fixed-node (FN)
- Energy $<\phi |H| \phi>$ converges to ground state
- Variance $<\phi [H-E]^2 \phi>$ to zero.
- Using 3B-BF gains a factor of 4.
- Using PMC gains a factor of 4.
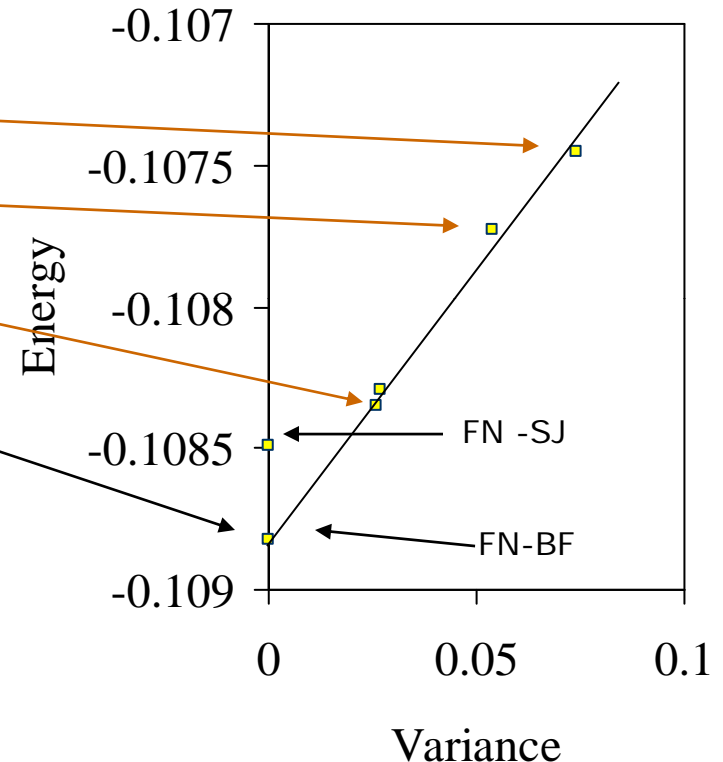
Reptation Monte Carlo (or VPI)
good for energy differences and properties

$$\Psi(\beta) = e^{-\frac{\beta}{2}H} \Psi$$

$$Z(\beta) = \langle \Psi(\beta)\Psi(\beta) \rangle = \langle \Psi e^{-\beta H} \Psi \rangle = \int dR_0...dR_p \Psi(R_0) \langle R_0 e^{-\tau H} R_1 \rangle .... \langle R_{p-1} e^{-\tau H} R_p \rangle \Psi(R_p)$$

$$E(\beta) = \frac{\langle \Psi(\beta) H \Psi(\beta) \rangle}{\langle \Psi(\beta)\Psi(\beta) \rangle} = \langle E_L(R_0) \rangle_\beta \qquad \tau = \frac{\beta}{p}$$

- $\psi(\beta)$ converges to the exact ground state as a function of imaginary time.
- E is an upper bound converging to the exact answer monotonically
- Do Trotter break-up into a path of p steps a la PIMC.
  - Bosonic action for the links
  - Trial function at the end points.
- For fixed-phase: add a potential to avoid the sign problem. Exact answer if potential is correct.
- Typical error is ~100K/atom
- Reptate the path: move it like a snake.

$$\boxed{\left(\mathrm{Im} \nabla \ln \Psi \right)^2}$$
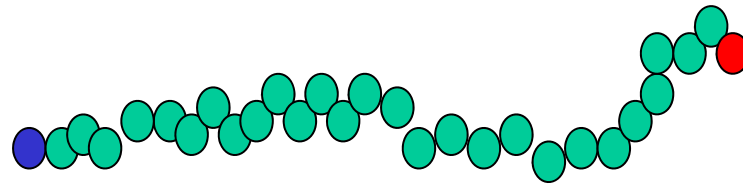
Coupled Electron-Ionic Monte Carlo:CEIMC

1. Do Path Integrals for the ions at T>0.

2. Let electrons be at zero temperature, a reasonable approximation for room temperature simulations.

3. Use Metropolis MC to accept/reject moves based on QMC computation of electronic energy
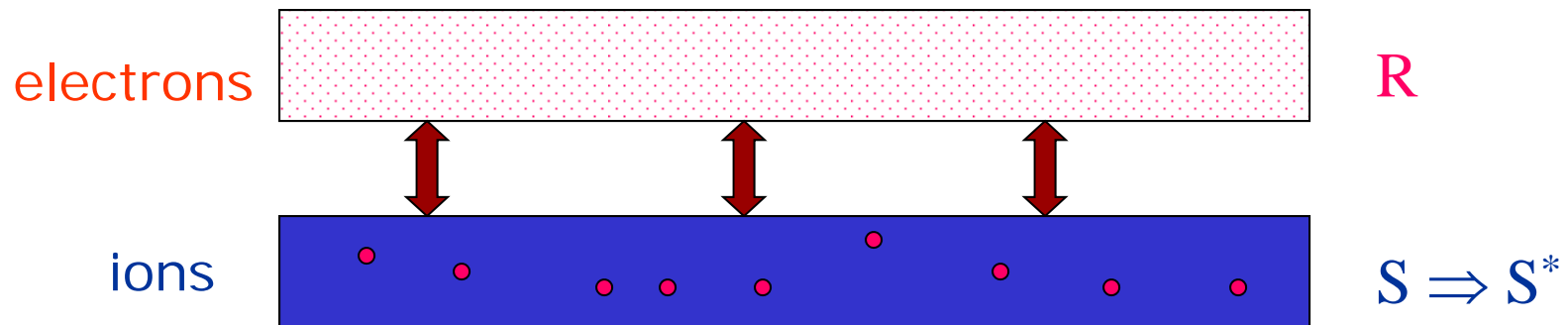
The "noise" coming from electronic energy can be treated without approximation: the penalty method.

Twist averaged boundary conditions

- In periodic boundary conditions, the wavefunction is periodic⇒Large finite size effects for metals because of fermi surface.

- In twist averaged BC, we use an arbitrary phase θ as r →r+L

- Integrate over all phases, i.e. Brillouin zone integration.

- Momentum distribution changes from a lattice of k-vectors to a fermi sea.

- Eliminates single-particle finite-size effects.

$$\Psi(x + L) = e^{i\theta}\Psi(x)$$

$$\bar{A} = \frac{1}{(2\pi)^3} \int_{-\pi}^{\pi} d^3\theta \langle \Psi_\theta A \Psi_\theta \rangle$$

Error with PBC

Error with TABC

Error is zero in the grand canonical ensemble at the mean field level.

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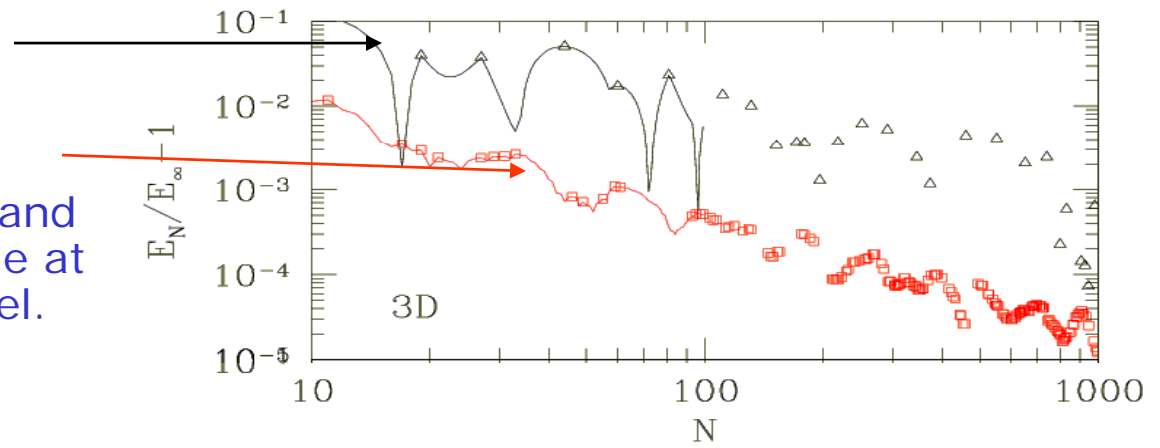
Types of averaging in CEIMC:

1. Path Integrals for ions (for protons or light ions)
   (M_1 time slices to average over.)

2. k-point sampling (integrate over Brillouin zone of supercell). Twist averaged boundary conditions converge much faster than periodic boundary conditions for metals.
   (M_2 k-points)

- In explicit methods such as CP-MD these extra variables will increase the CPU time by $M_1 M_2$.

- With QMC there will be little increase in time if imaginary time and/or k are simply new variables to <u>average over</u>.

The result is a code scaling well to thousands of nodes and competitive with Car-Parrinello MD.

- Make a move of the protonic paths
- Partition the 4D lattice of boundary conditions (θ_x θ_y θ_z) and imaginary time (τ) in such a way that each variable is uniformly sampled (stratified)
- Send them all out to M separate processes
- Do RQMC to get energy differences and variances
- Combine to get global difference and variance.

$$R_\tau \rightarrow R_\tau'$$

$$\Delta E_{BO} = \frac{1}{M} \sum E_{\theta,\tau}$$

$$\sigma^2 = \frac{1}{M^2} \sum \sigma_{\theta,\tau}^2$$

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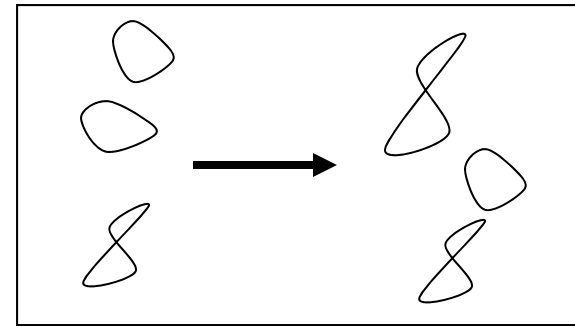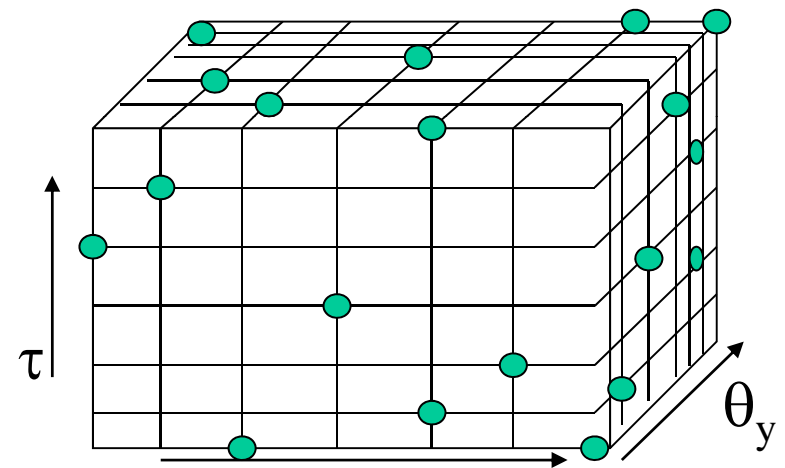
Experimentally-known High Pressure Phase Diagram of H
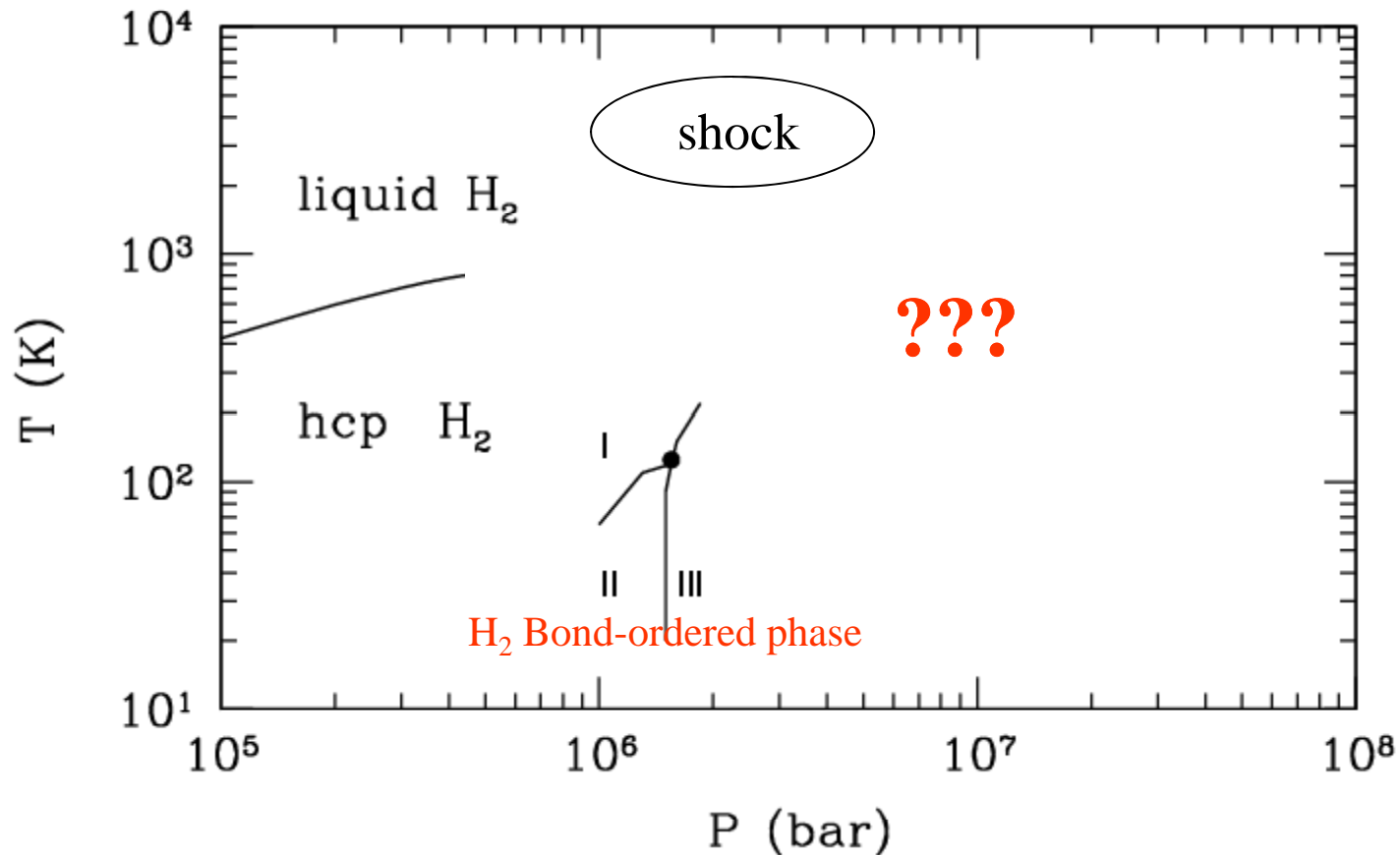
• Wigner-Huntington (1935) predicted that at high enough pressure hydrogen will become a metal.
• Experiments have not reached (definitively) that pressure.

Possible Phase Diagrams
for high pressure hydrogen
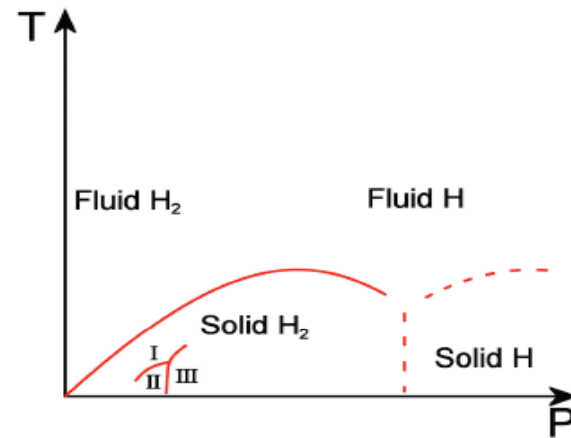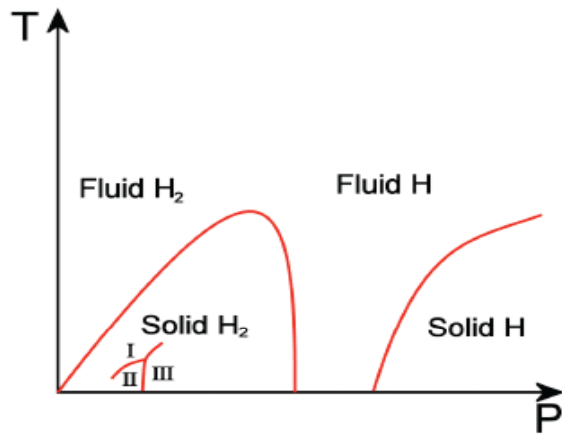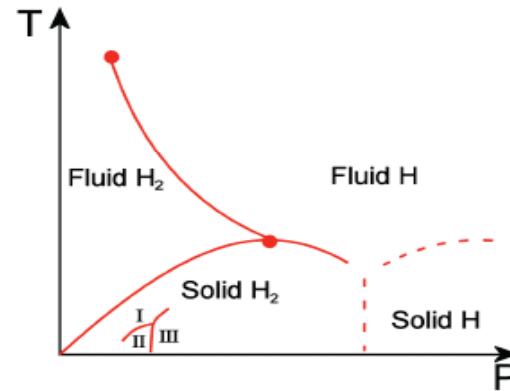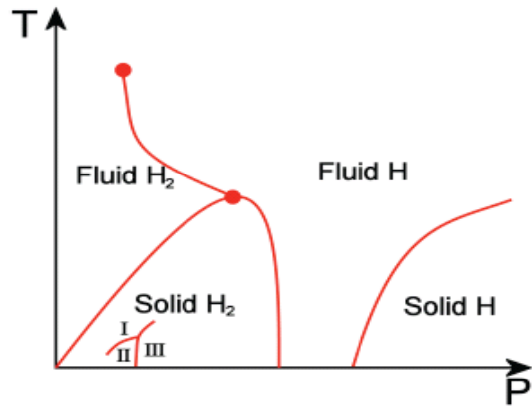
EOS Comparison
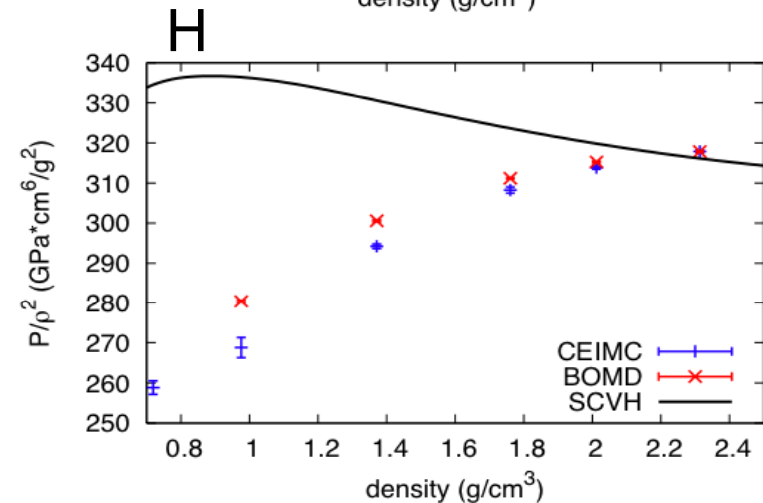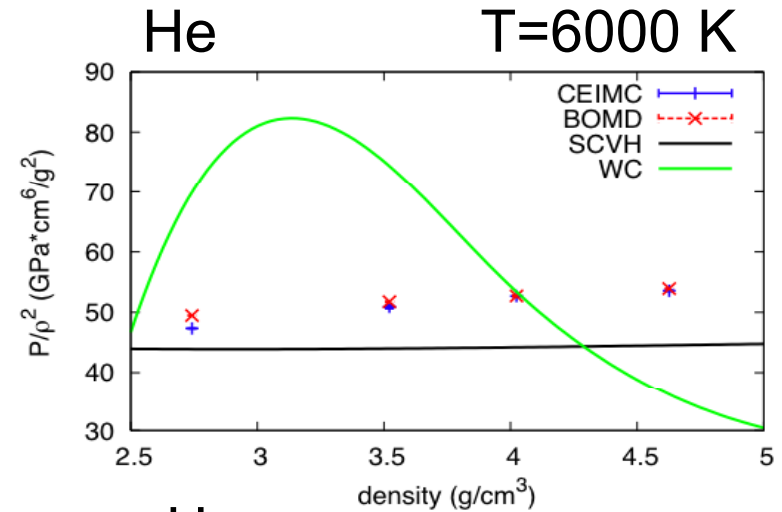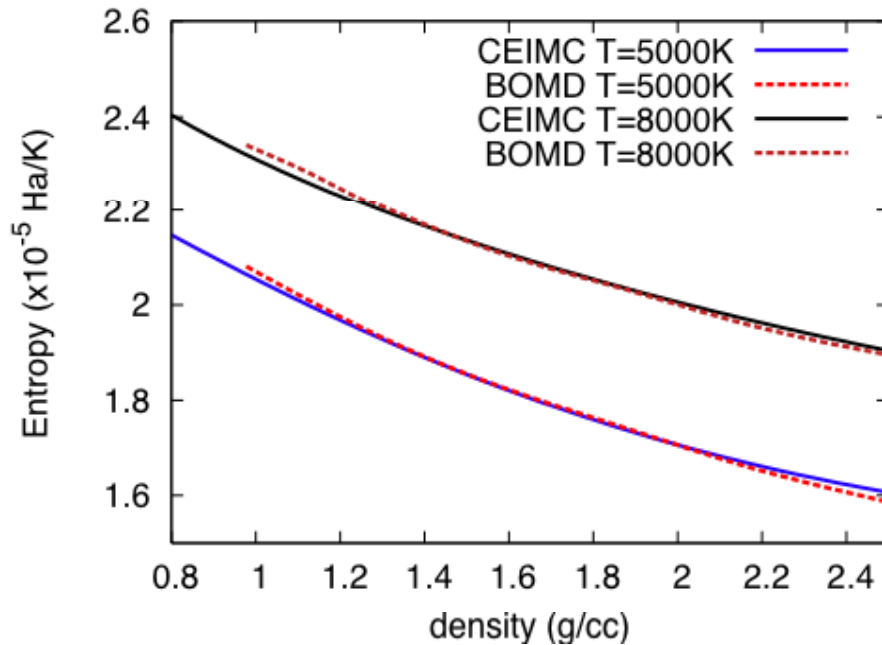
- Excellent agreement with DFT

- Poor agreement with chemical models (near PPT)

"Plasma Phase" Transition

- Pressure plateau at low temperatures (T<2000K)
- Plateau is a signature of a 1st order phase transition
- Seen in CEIMC and BOMD at different densities
- Many previous results!
  - Chemical models always give it
  - K point sampling very important
  - Narrow transition at low T
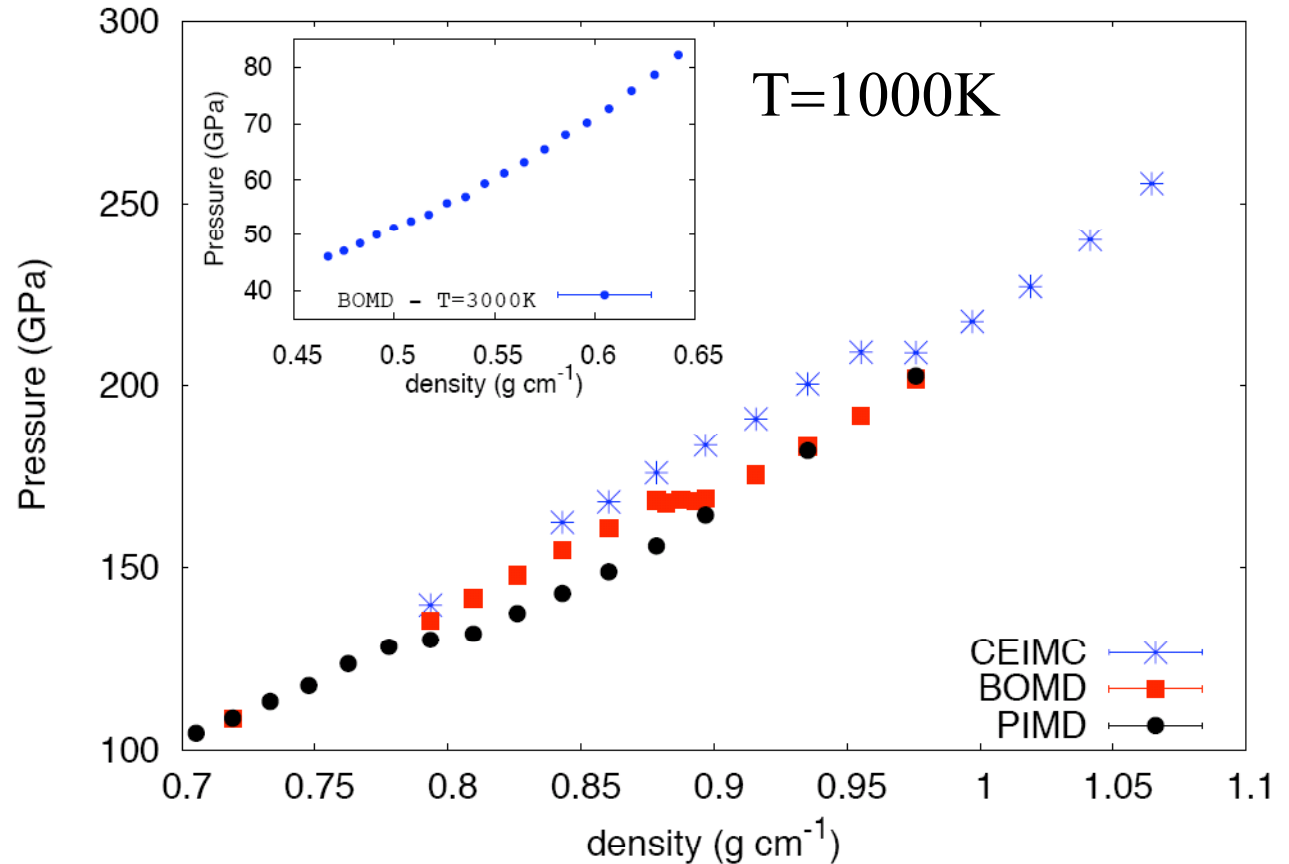
Electronic Conductivity at transition
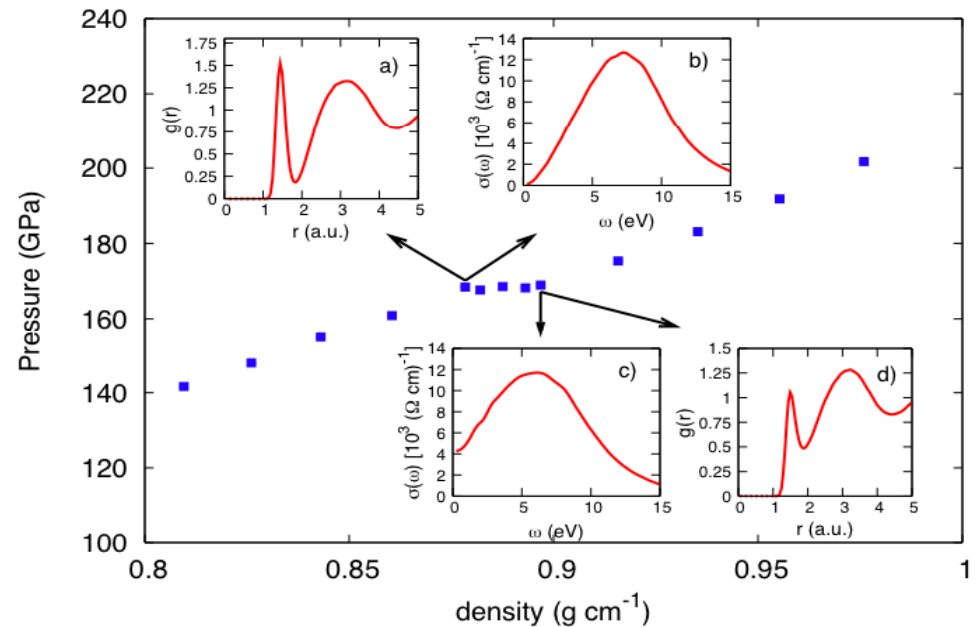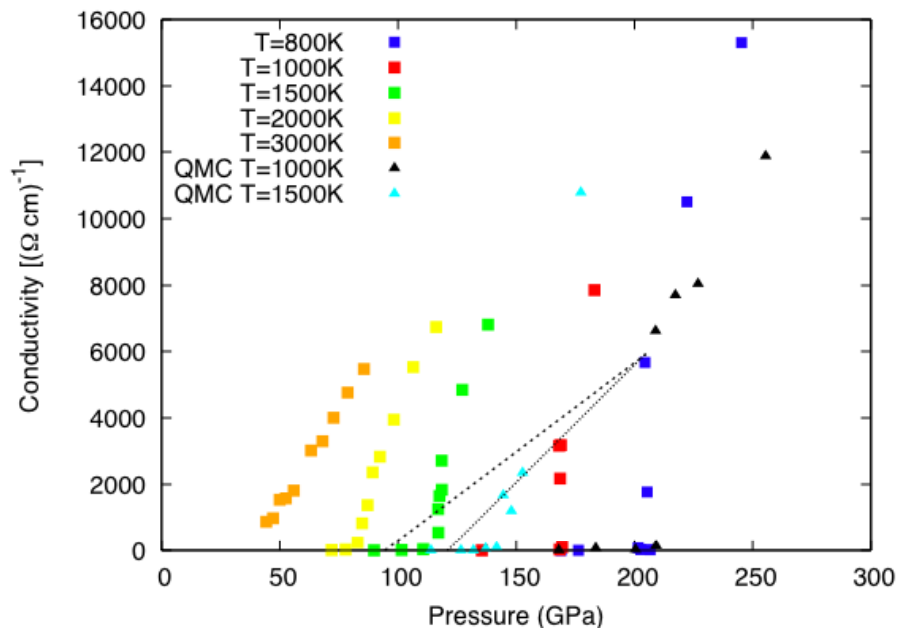
- sharp metallization across the transition
- Atomic-molecular transition more continuous
- Extrapolate discontinuity to find critical point

Revised Hydrogen Phase Diagram
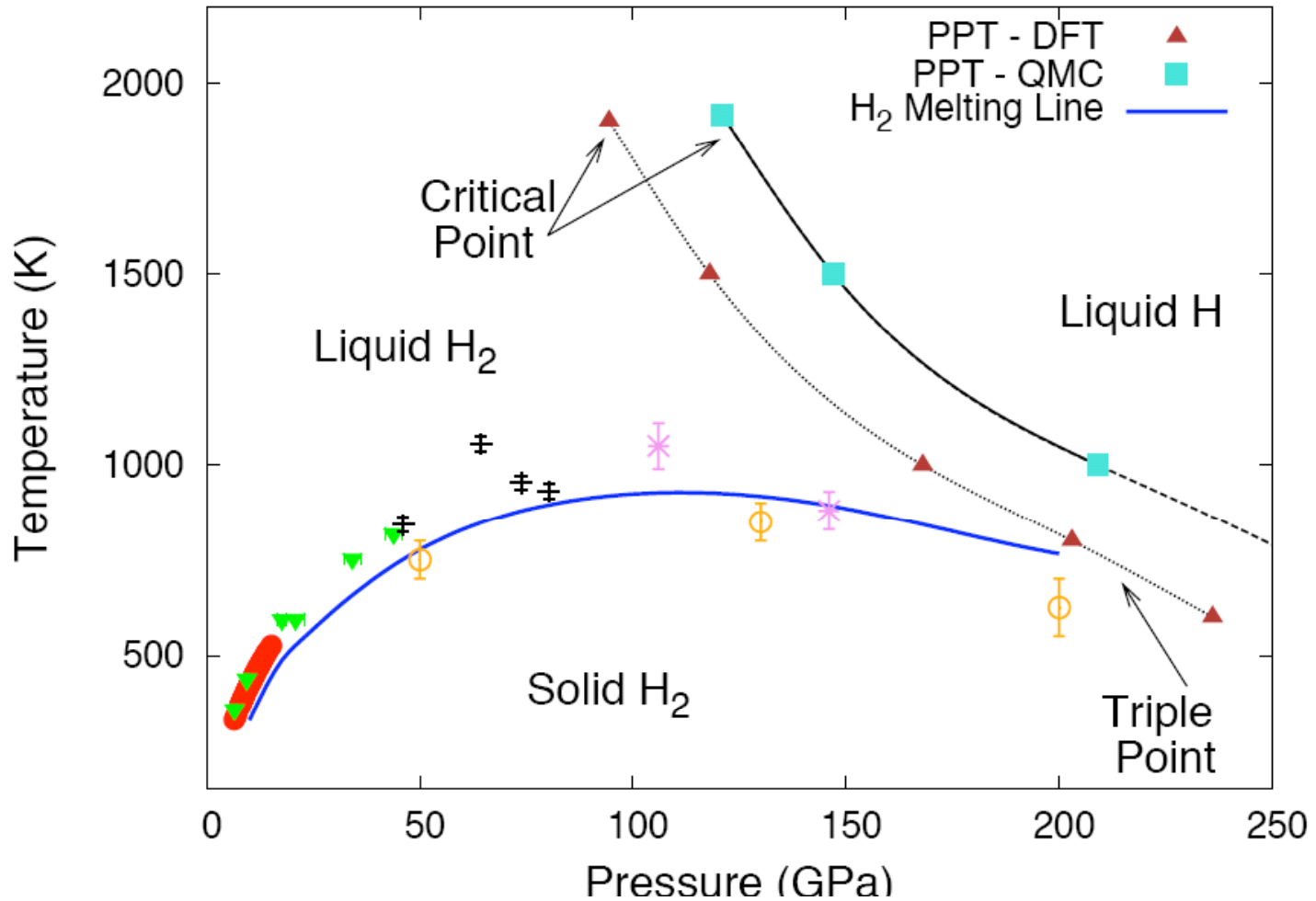
Two Possible Phase Diagrams

for high pressure hydrogen
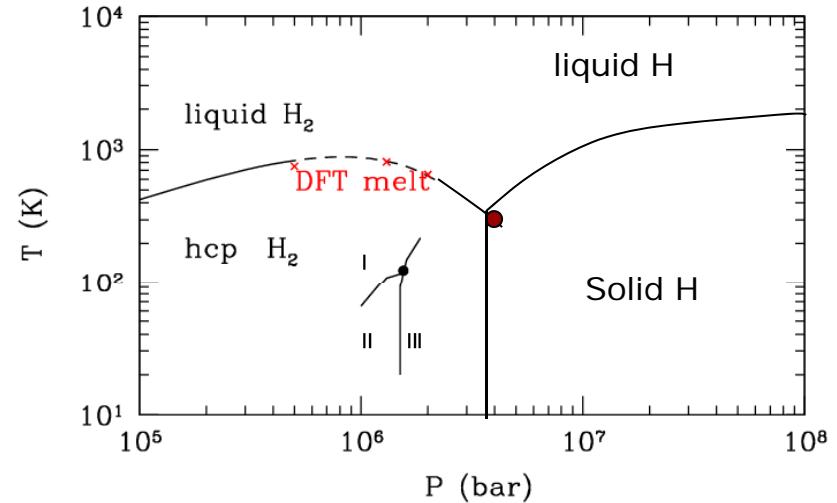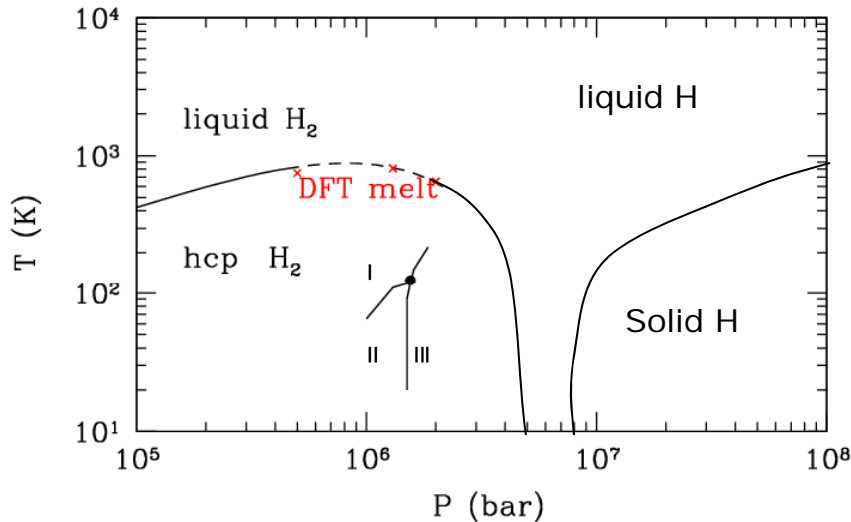
Ashcroft suggested a low temperature liquid metallic ground state.
•Is there a T=0K liquid?

•What temperature is needed to see quantum protonic transitions?
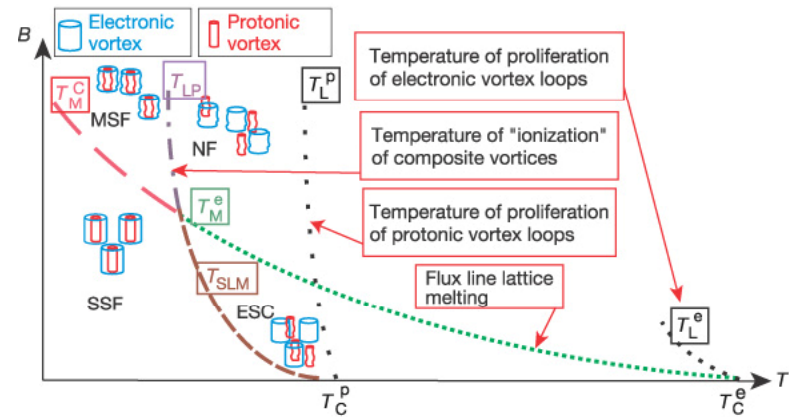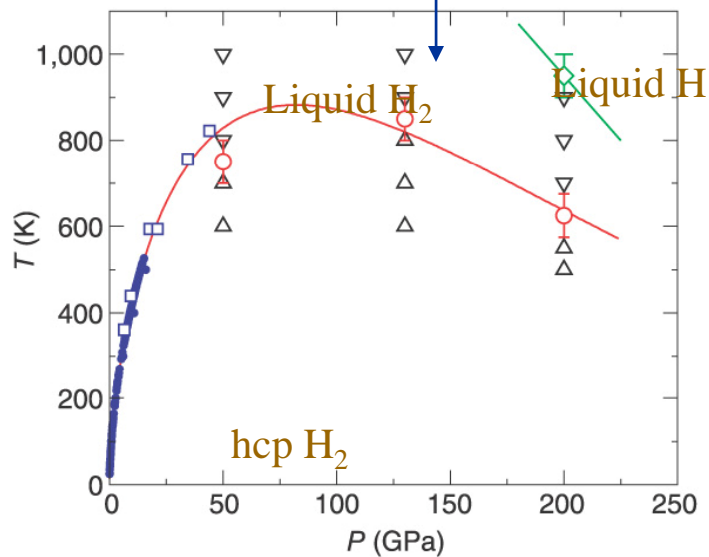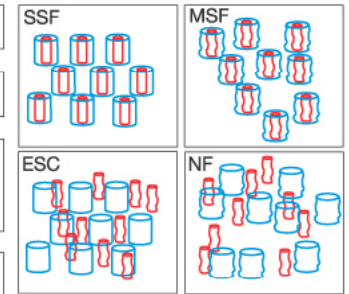•How about electronic superconductivity?

A quantum fluid of metallic hydrogen suggested by first-principles calculations   S. A. BONEV, E. SCHWEGLER, T. OGITSU & G. GALLI

A superconductor to superfluid phase transition in metallic hydrogen   E. BABAEV, A. SUDBØ & N. W. ASHCROFT
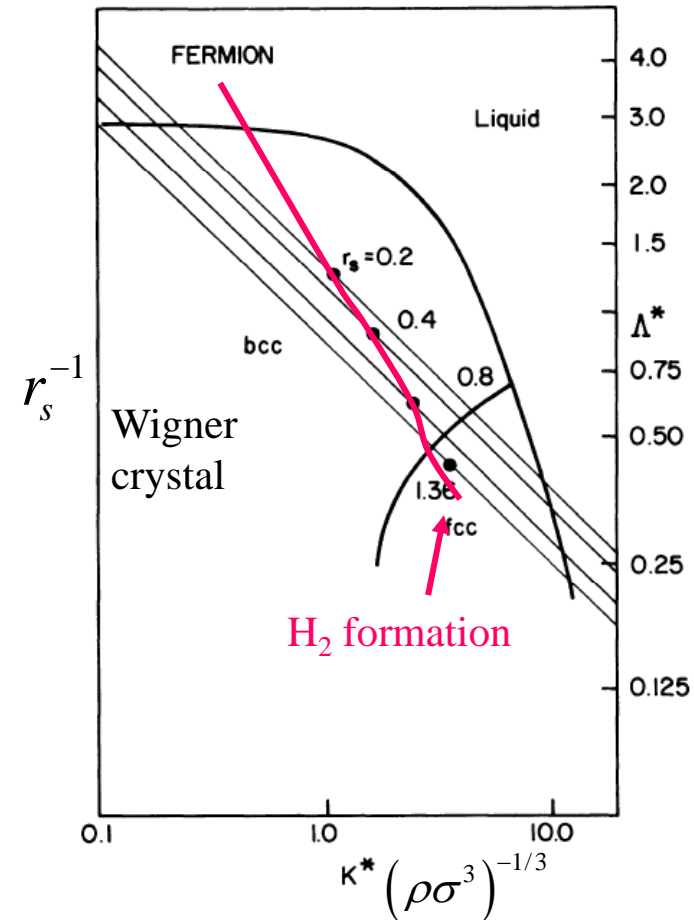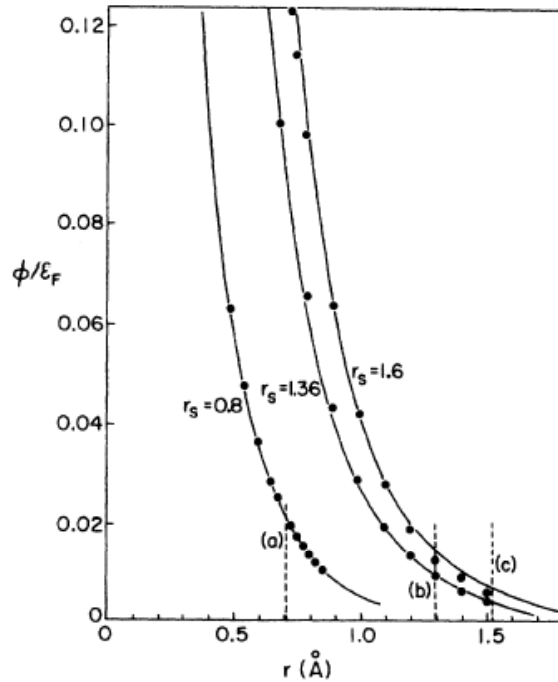
liquid

07 October 2004

Could hydrogen be a quantum fluid like helium?
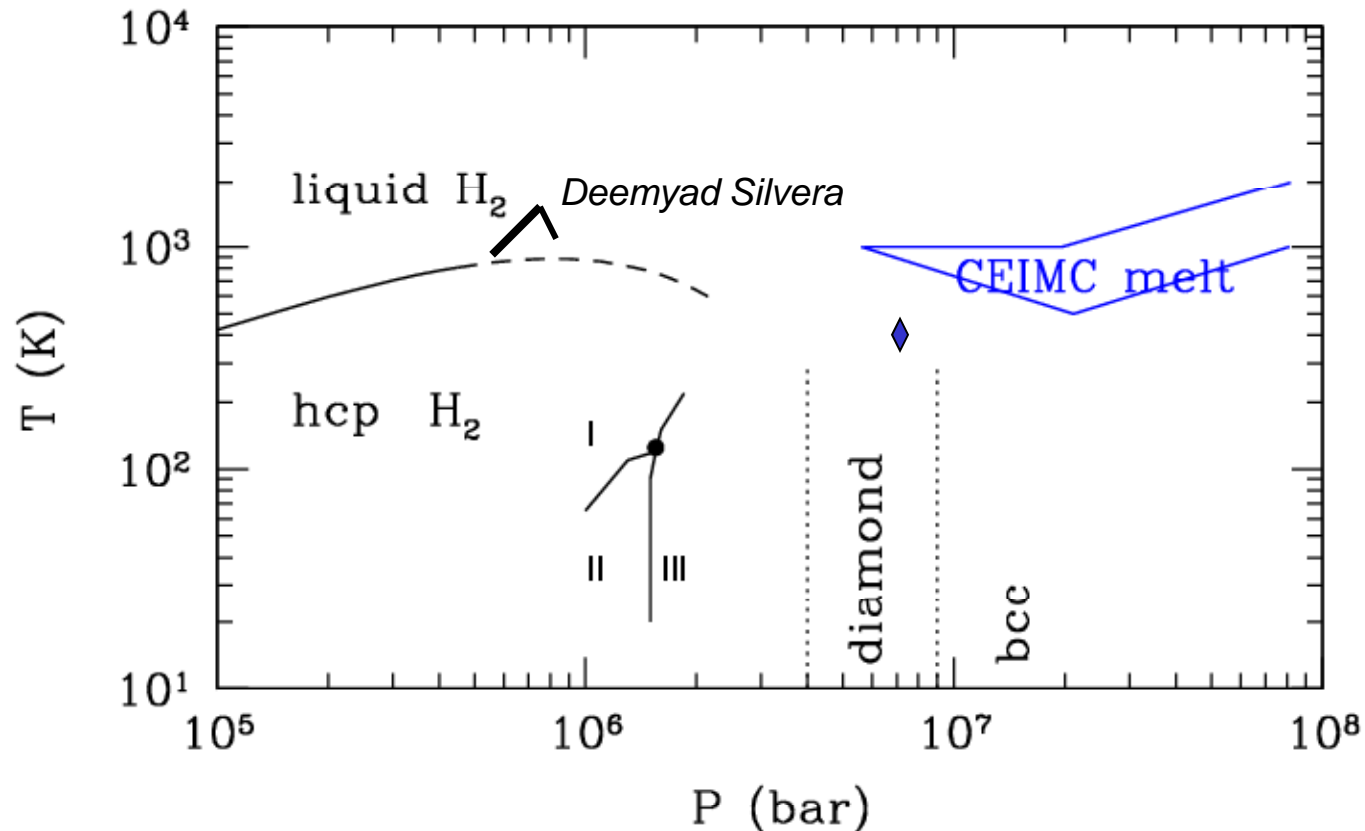
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Why liquid?
Screened Coulomb potential

Electrons screen p-p
interaction

$$H_{pp} = -\sum_i \frac{\hbar^2}{2m}\nabla^2 + \sum_{i<j} v(r_{ij}) \qquad v(r) = \frac{\varepsilon\sigma e^{-r/\sigma}}{r} \qquad \sigma \propto r_s^{-1/2}$$

K.K. Mon et al, Phys. Rev. B 21, 2641 (1980)
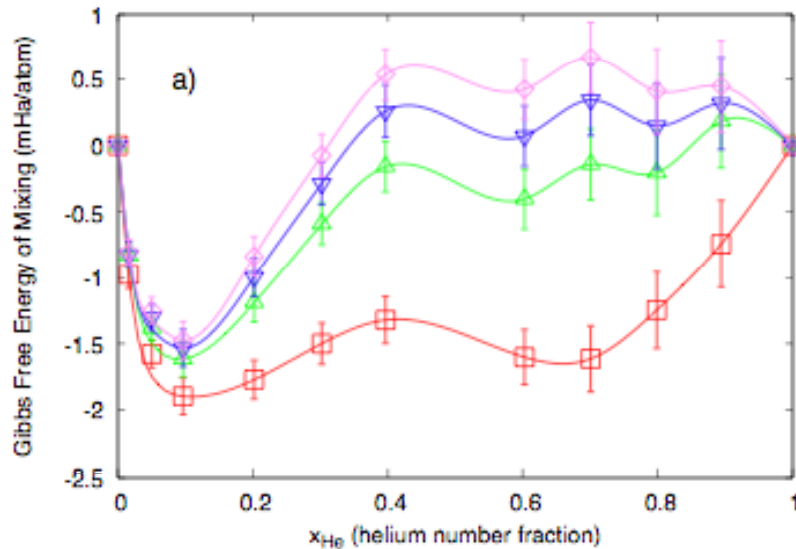*DMC et al. Phys. Rev. B 16, 3081 (1976)*

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Melting of atomic solid using CEIMC

CEIMC predicts $T_{melt} > 500K$ (but hysteresis)
Quantum effects stabilize the solid by 150 (30)K .

Pierleoni, Holtzmann, DMC, PRL 93,146402 (2005).
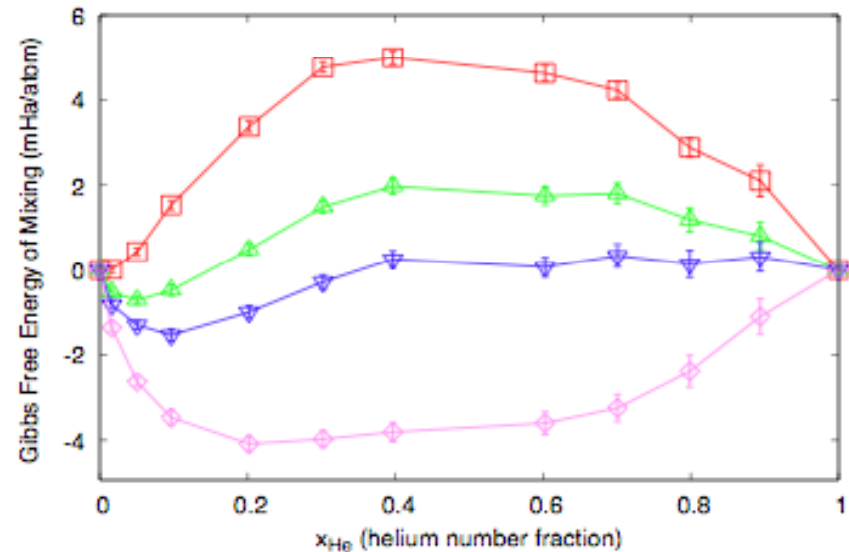
Mixing Free Energy for He in H

T=8000 K   P=10 Mbar

| — 4 Mbar | — 8 Mbar |
| — 10 Mbar | — 12 Mbar |

| — 4000 K | — 7000 K |
| — 9000 K | — 10000 K |

■ Clear minimum at low helium fraction.

■ Very strong temperature dependence, fairly insensitive to pressure.

H-He Demixing Temperature

Klepeis - 10.5 Mbar

Redmer

10 Mbar

4 Mbar

10 Mbar

8 Mbar

Pfaffenzeller

x_He (helium number fraction)

Demixing Temperature (10^3 K)
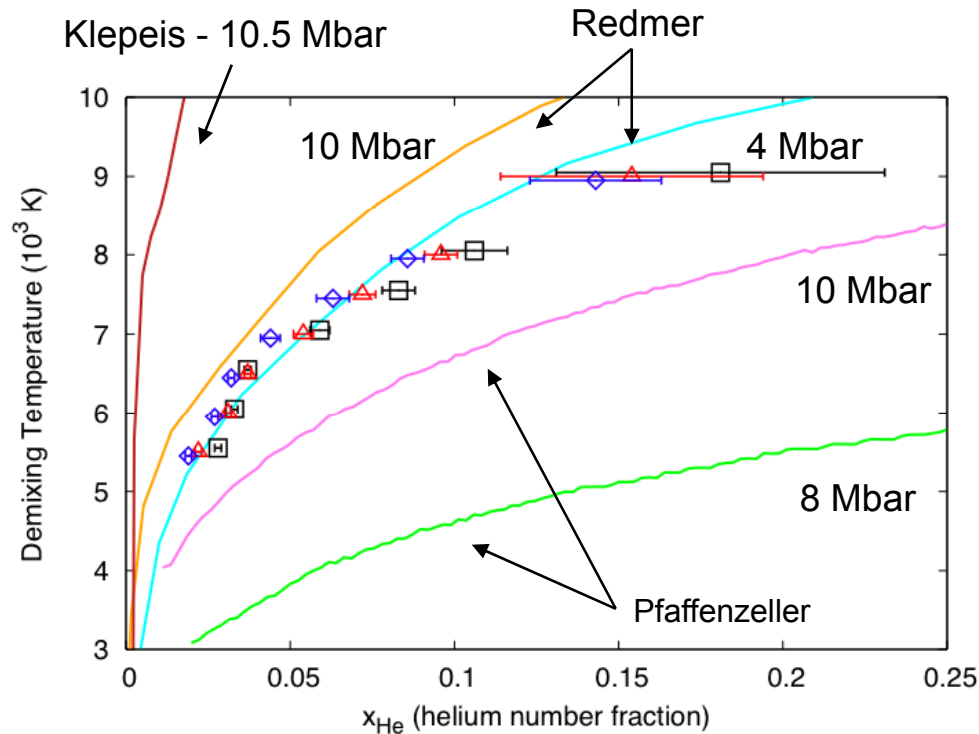
$\square$ 4 Mbar
$\triangle$ 8 Mbar
$\Diamond$ 12 Mbar
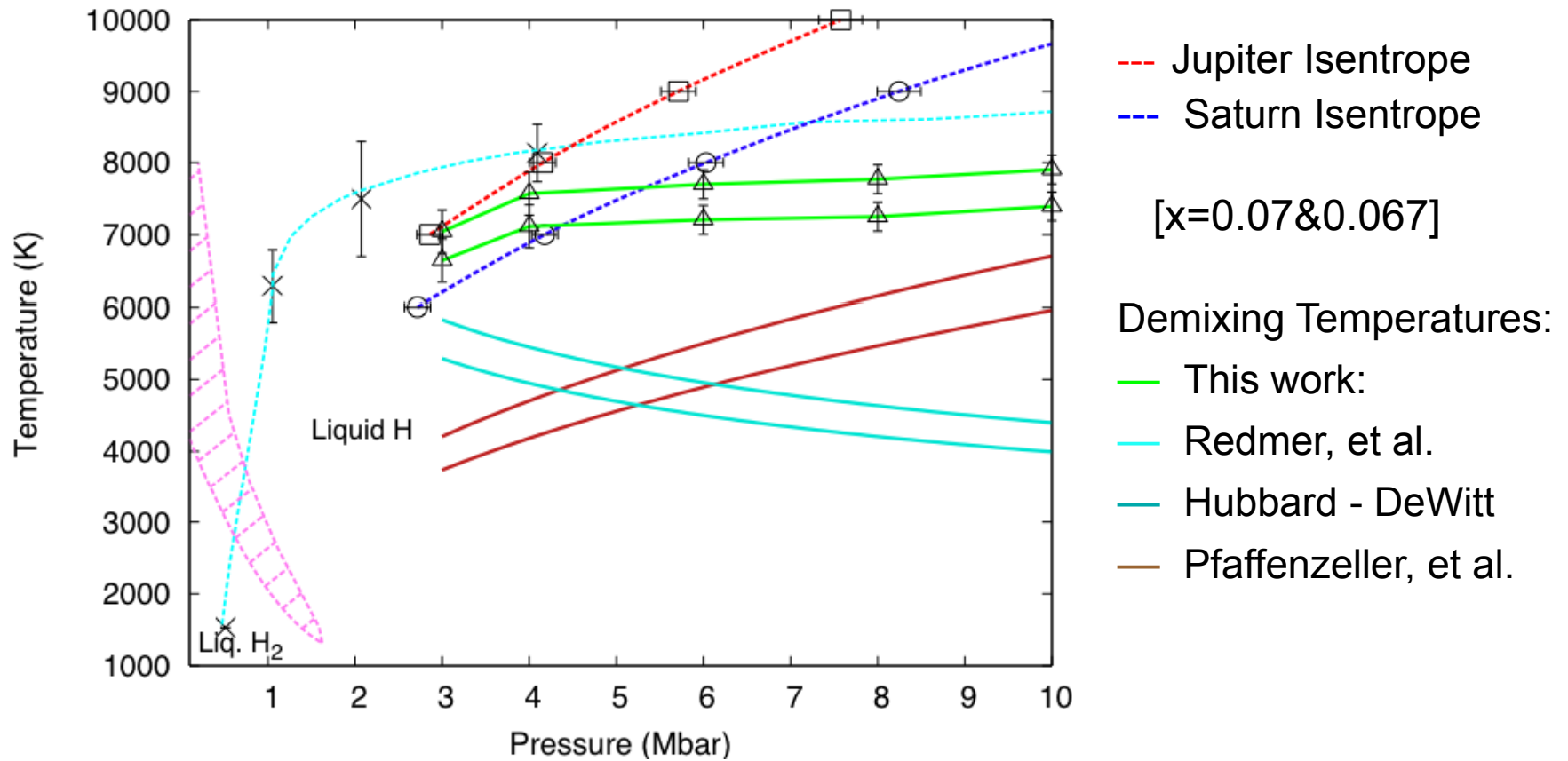
Demixing transition temperatures as a function of helium number fraction, for several pressures

- Previous CPMD simulations underestimate demixing temperature.

- Good agreement with Redmer et.al.

- Differences come from non-ideal effects

Mixing Phase Diagram

Conclusions

- PPT predicted in pure hydrogen
  - Critical point at T~2000K
  - Intersects melting line below T~800K, above 200 GPa.
- helium immiscibility at high pressure and in Saturn.
- QMC today is competitive with other methods for dense hydrogen and potentially much more accurate.
- Progress in these simulations in last 40 years from:
  - Computer power: this method scales with processors
  - Algorithmic power: better trial functions, QMC methods
- We are now in position to do much more accurate simulation of hydrogen, helium, mixtures…
- More work needed in algorithms to get higher accuracy, treat larger systems, and heavier elements.