Quantum Monte Carlo Methods for Warm Dense Matter

- Computational methods:
  - Coupled Electron Ion Monte Carlo
  - Path Integral Monte Carlo
- Examples:
  - Electron gas
  - Hydrogen

WHO DID THE WORK?

Miguel Morales, Livermore

Carlo Pierleoni: L'Aquila, Italy
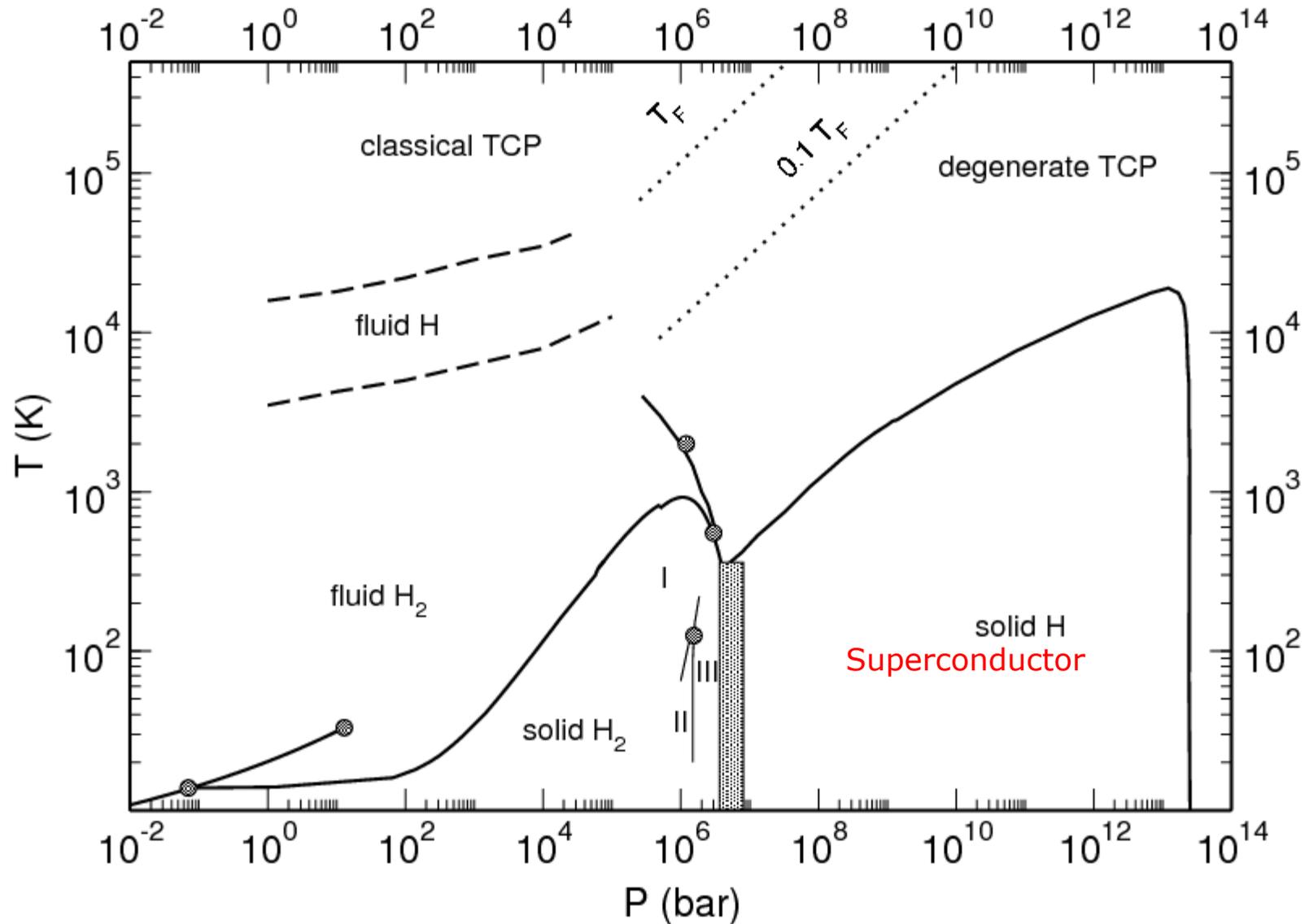
Jeff McMahon   U of Illinois

Ethan Brown   U of Illinois
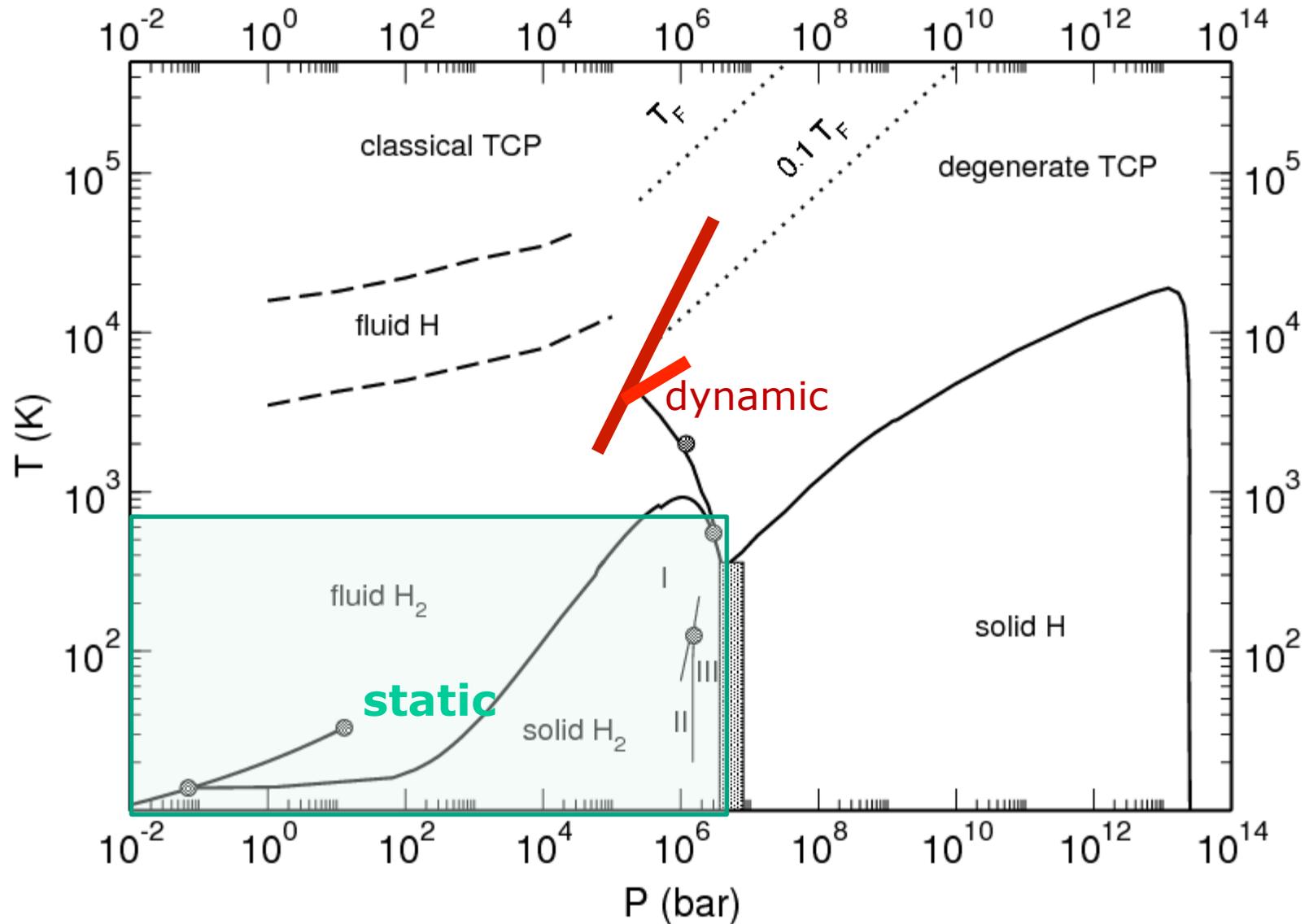
Bryan Clark   Princeton

...many others

Hydrogen Phase Diagram

10^{-2} 10^{0} 10^{2} 10^{4} 10^{6} 10^{8} 10^{10} 10^{12} 10^{14}

T_F

$0.1 T_F$

classical TCP

degenerate TCP

fluid H

10^5

10^4

10^3

10^2

T (K)

fluid H_2

I

solid H

Superconductor

II

III

solid H_2

10^{-2} 10^{0} 10^{2} 10^{4} 10^{6} 10^{8} 10^{10} 10^{12} 10^{14}

P (bar)

Hydrogen Phase Diagram

Atomic/Molecular Simulations

accuracy

- –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

- 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, we do not know if the density functional theory energies are accurate enough--particularly at metallization.

Can we use petascale computers + new algorithms to do better?
Instead of going to bigger systems, try to improve the quality of the calculations for benchmarking.

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.
- QMC determined electronic energy is the standard for approximate LDA calculations. (but fermion sign problem!)
- Path Integral Methods provide a exact way to include effects of ionic zero point motion (include all anharmonic effects)
- A variety of stochastic QMC methods:
  - **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. Can it treat fluids?

New QMC Techniques

- Algorithms (e.g. reptation)
- Better Finite-Size scaling methods
  - Twist averaging for kinetic energy
  - Coulomb corrections for potential energy
- Better trial wavefunctions -> better nodes
  - Backflow
  - Direct coupling to DFT
- Coupled Electron-Ion Monte Carlo
- Optimization of trial function parameters
- Computers/parallelization: huge increase in available resources. Factors of 1000 / decade.

Regimes for Quantum Monte Carlo
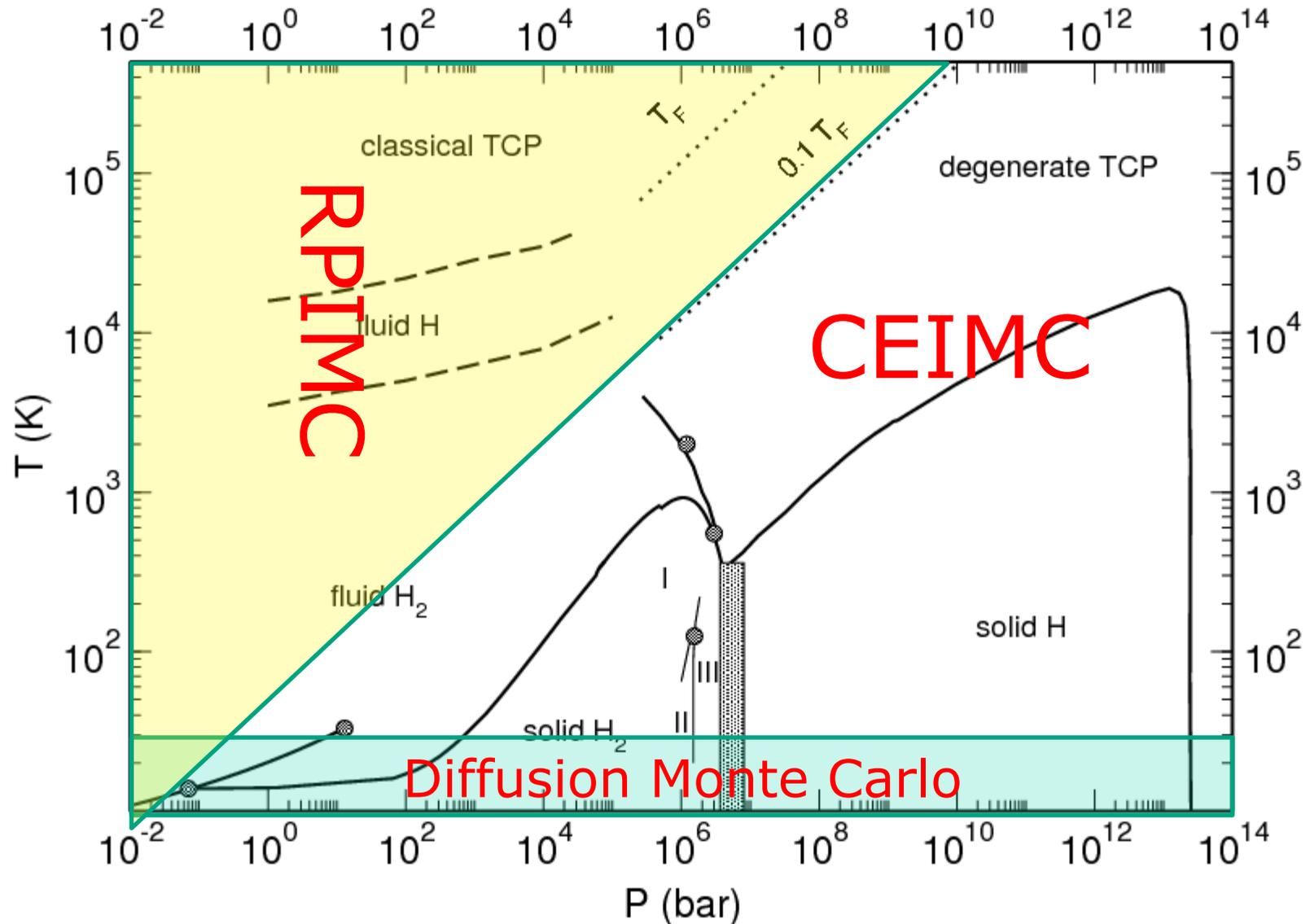
The density matrix

How perform computer simulations at finite T?

- Find exact eigenstates of H.
- Probability of occupying state α is exp(-βE$_α$)
- All equilibrium properties can be calculated in terms of thermal density matrix
- Convolution theorem relates high temperatures to low temperatures.

$$H\phi_\alpha = E_\alpha\phi_\alpha \qquad R \equiv \{r_1, r_2, ...r_N\}$$

$$\rho(R;\beta) = \sum_\alpha |\phi_\alpha(R)|^2 e^{-\beta E_\alpha} \quad \beta = 1/kT$$

off-diagonal density matrix:

$$\rho(R,R';\beta) = \sum_\alpha \phi_\alpha^*(R')\phi_\alpha(R)e^{-\beta E_\alpha}$$

$$\rho(R,R';\beta) \geq 0 \ \text{(without statistics)}$$

$$\rho(R_1, R_2; \beta_1 + \beta_2) =$$

$$= \int dR' \rho(R_1, R';\beta_1)\rho(R', R_2; \beta_2)$$

Imaginary-time path integrals

The density matrix is:

$$\hat{\rho} = e^{-\beta(\hat{T}+\hat{V})}$$

- Trotter's formula (1959):

$$\hat{\rho} = \lim_{M\to\infty} \left[e^{-\tau\hat{T}} e^{-\tau\hat{V}} \right]^M$$

- M is number of time slices. $\quad \tau = \beta / M$

- Then:

$$Z = \int dR_1 ... dR_M\, e^{-\sum_{i=1}^{M} S(R_i, R_{i+1}; \tau)}$$

Where the primitive link action is:

$$S(R_0, R_1; \tau) = \frac{(R_0 - R_1)^2}{4\lambda\tau} + \frac{\tau}{2}\left[V(R_0) + V(R_1) \right]$$

- Exact mapping to a classical problem where each particle turns into a "polymer."
- Trace implies $R_0 = R_M$ ⇨ closed or ring polymers

"Distinguishable" particles within PIMC

- Each atom is a ring polymer; an exact representation of a quantum wavepacket in imaginary time.
- Integrate over all paths
- The dots represent the "start" of the path. (but all points are equivalent)
- The lower the real temperature, the longer the "string" and the more spread out the wavepacket.
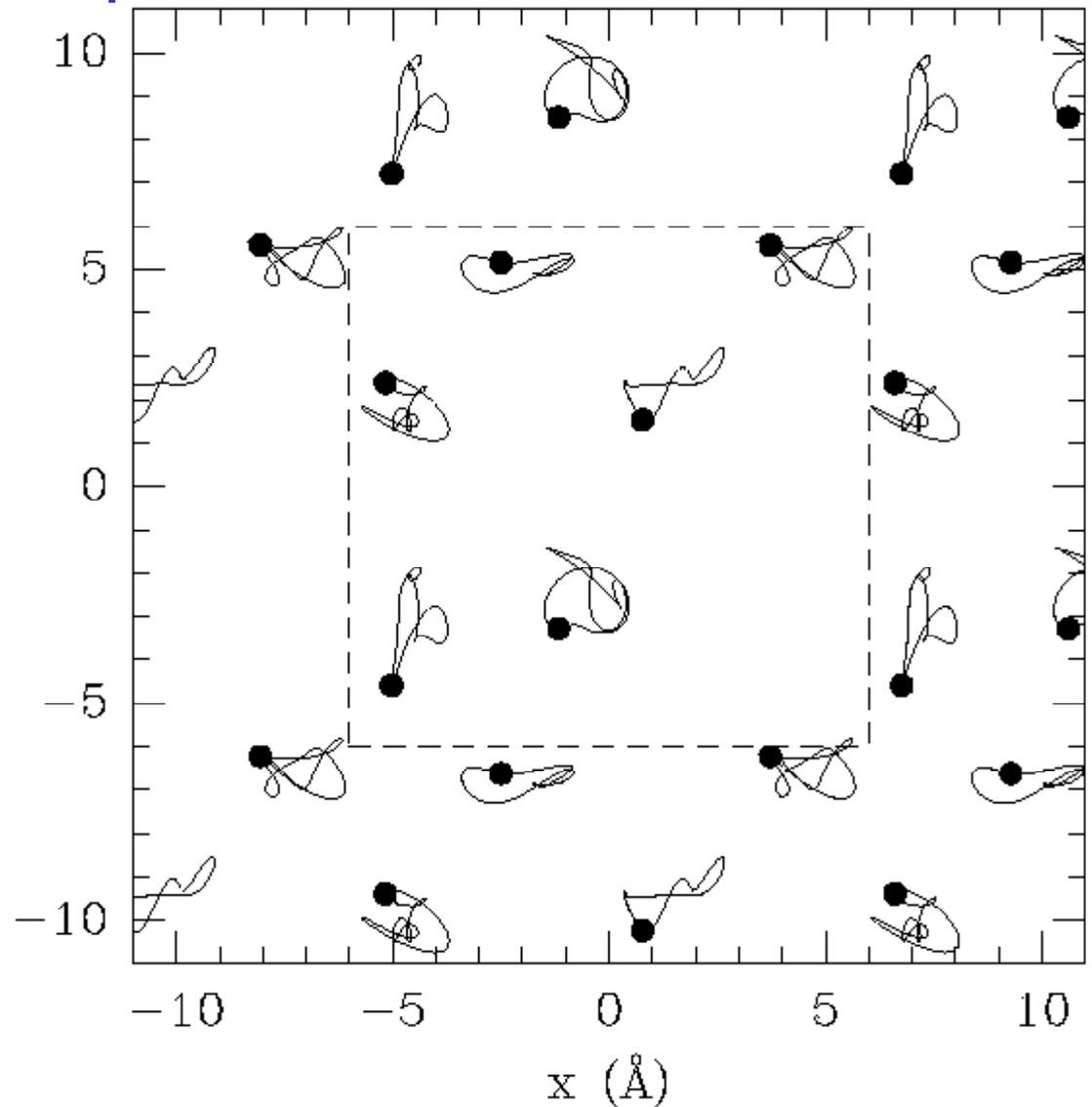
Quantum statistics

- BUT not all states are allowed: only totally symmetric or antisymmetric wavefunctions. Statistics are the origin of BEC, superfluidity, the lambda transition, fermi liquids, superconductivity, chemistry…

- Use the permutation operator to project out the correct states:

$$Pf(R) = \sum_{p=1}^{N!} \frac{(\pm 1)^P}{N!} f(PR) \qquad \begin{array}{l} \text{+ bosons} \\ \\ \text{- fermions} \end{array}$$

$$Z = \sum_{p=1}^{N!} \frac{(\pm 1)^P}{N!} \int dR_1 ... dR_M \, e^{-\sum_{i=1}^{M} S(R_i, R_{i+1})}$$

- For the trace, the path closes on itself with a permutation. **$R_1 = PR_{M+1}$**

- Too many permutations to sum over; we must <u>sample</u> them. This is possible if the integrand is positive (bosons).

- PIMC task: sample path { $R_1, R_2, ... R_M$ and P} with Metropolis Monte Carlo (MCMC) using "action", S, to accept/reject.

- EXACT MAPPING OF QUANTUM MECHANICS TO CLASSICAL MECHANICS --No trial function or bias—only the Hamiltonian

How about Fermions?
"Direct" Fermion Path Integrals

$$Z = \sum_{p=1}^{N!} \frac{(-1)^P}{N!} \int dR_1 ... dR_M \, e^{-\sum_{i=1}^{M} S(R_i, R_{i+1})}$$

$R_0 = PR_M$, **P** permutation,
$S(R_i, R_{i+1})$ is "boltzmannon action"
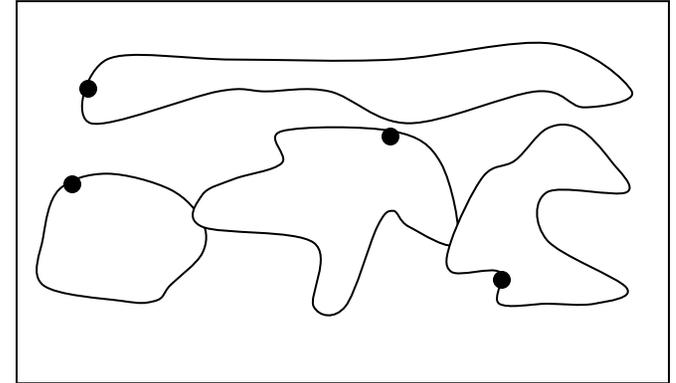
- Fermions: sample the "action" and carry **$(-1)^P$** as a weight.
- Observable is **even P - odd P.**
- **efficiency** scales exponentially in N and T^{-1}!

$$\text{CPUtime} \propto \varepsilon^{-2} e^{2N[\mu_F - \mu_B]/k_B T}$$

$$\varepsilon = \text{error}$$

Fixed-Node method with PIMC

- Get rid of negative walks by canceling them with positive walks. We can do this if we know where the density matrix changes sign. Restrict walks to those that stay on the same side of the node.

- Fixed-node identity. Gives exact solution if we know the places where the density matrix changes sign: the nodes.

$$\rho_F(R_\beta, R_*; \beta) = \frac{1}{N!} \sum_P (-1)^P \int_{\rho_F(R_t, R_*; t)>0} dR_t \, e^{-S(R(t))} \text{ with } R_0 = PR_*$$

- On diagonal, $(-1)^P = 1$, only even permutations
- Classical mapping for fermions exists!!
- Problem: fermion density matrix appears on both sides of the equation. We need nodes to find the density matrix.
- But still useful approach. (In the classical world we don't know V(R).)
- H2 has no nodes!   No approximation

Free particle nodes

- For non-interacting (NI) particles the nodes are the finite temperature version of a Slater determinant:

$$\rho_F^{NI}(R',R;t) = \frac{1}{N!}\det\left[g\left(r'_i,r_j;t\right)\right]$$

where $g\left(r'_i,r_j;t\right)$ is the single particle density matrix.

With no external potential:

$$g\left(r',r;t\right) = \left(2\pi\tau\right)^{-3/2} e^{-\frac{(r-r')^2}{2\tau}} + \text{periodic images}$$

At high $T \gg T_F$, nodes are hyperplanes.
As $T \to 0$, nodes minimize the energy.

- In general we need to minimize the free energy wrt nodes
- Problem: no spin-coupling in nodes needed for superconductivity

Path Integral Picture of Molecular Hydrogen at low density

Pink and blue paths are up and down electrons.
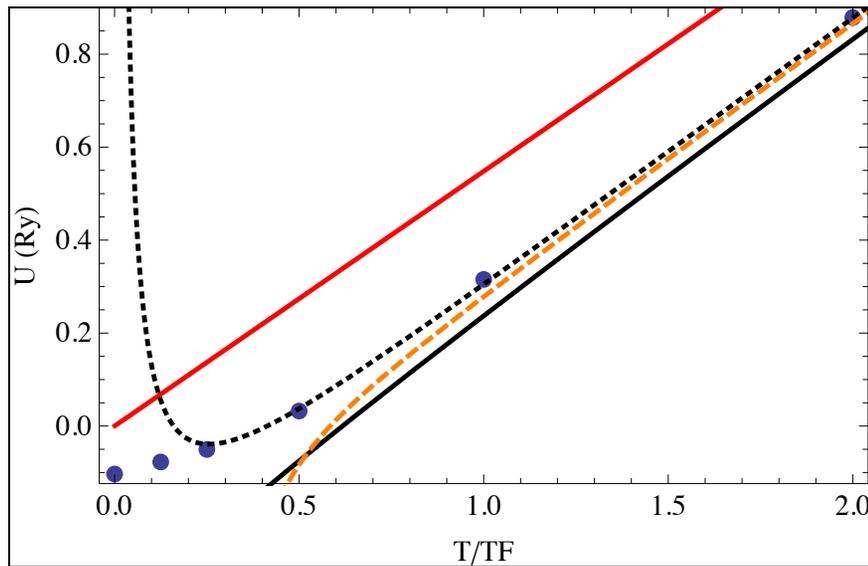
Smaller pink dots are protons

$M_p/M_e=1836$

T=5000K

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 *Knudson et al., PRL 87, 225501 (2001)*

- Working on new Hugoniot now

Deuterium Hugoniot
B. Militzer 11-19-01

Legend:
- ◇ Nova Laser '97
- ☐ Nova Laser '98
- —— Sesame
- – – – Ross
- – – – – VDM
- –·–·– DFT–MD Len.
- —○— DFT–MD Galli
- —○—○— PIMC
- △ **Knudson**

Axes: P (Mbar) vs ρ (gcm^{-3}); top axis ρ/ρ_0; right axis T with markers 3eV, 1.5eV, 1.0eV, 0.7eV

OCP calculations with R–PIMC
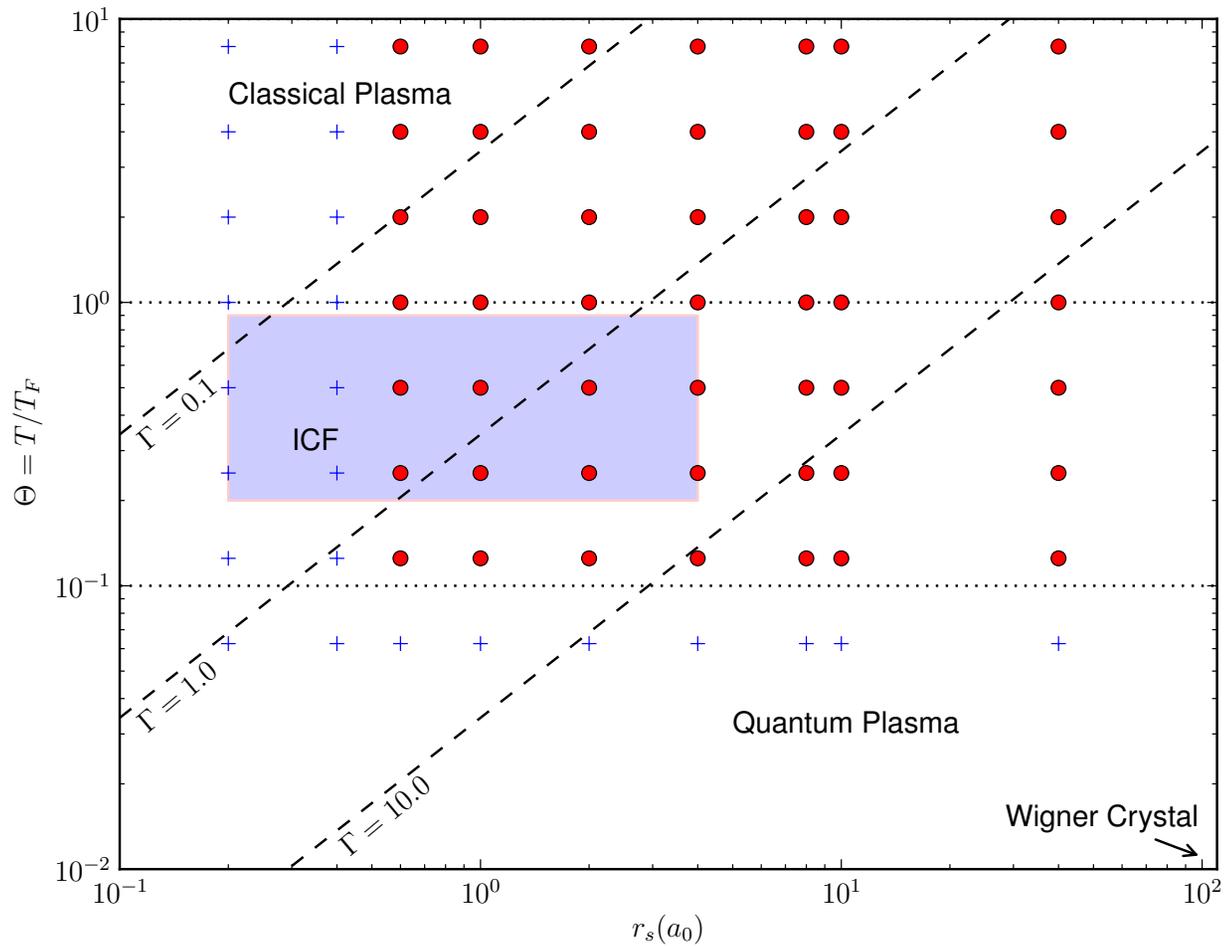
talk to Ethan Brown or Bryan Clark

(QOCP) Electron gas at $r_s=4$

Legend:
- **Ideal Gas** (red solid line)
- **Purely Classical Semi−Empirical** (black solid line)
- **2nd Order Wigner−Kirkwood** (black dashed line)
- **Exchange Correction (Low T)** (orange dashed line)
- **Path Integral Monte Carlo** (blue dots)
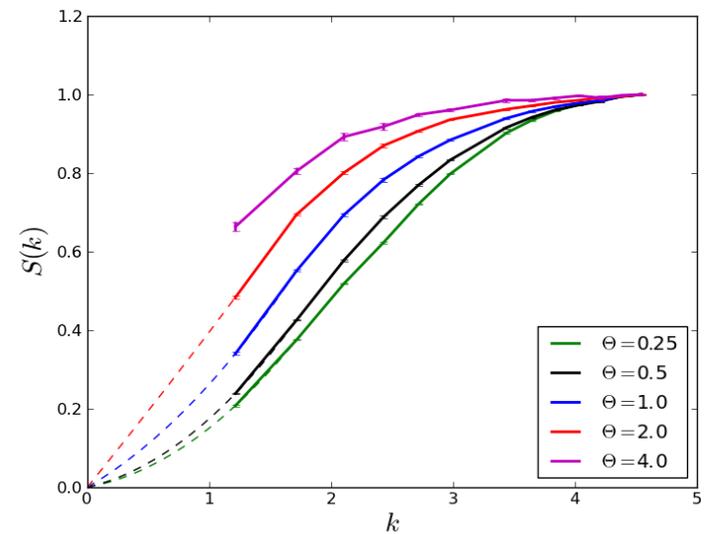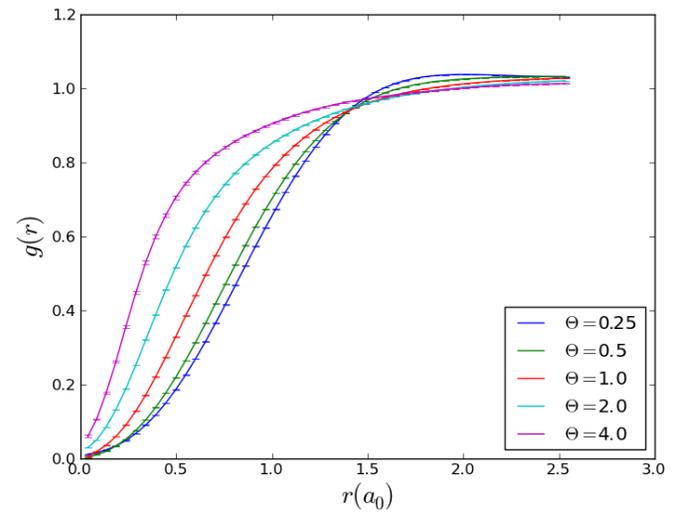
Limitations of PIMC

- Trouble at low temperature
  - Slow down of code (~1/T or worse)
  - What to use for the restriction

- PIMC not reliable under 10,000K (200GPa) with current code

- PIMC limited to about 100 electrons (efficiency)

- None of these problems are fundamental, but…

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
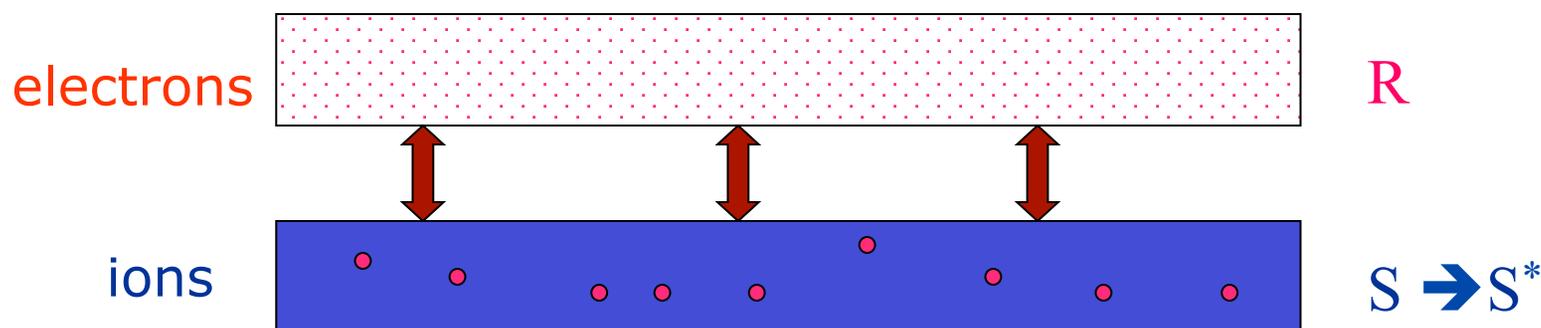
The "noise" coming from electronic energy can be treated without approximation using the penalty method.

Why MC and not MD??

The Penalty method

- **Assume** <u>estimated</u> energy difference Δe is **normally distributed*** with variance σ^2 **and the correct mean**.

$$< \Delta e > = \Delta E$$

$$< [\Delta e - \Delta E]^2 > = \sigma^2$$

*central limit thrm applies since we average over many steps

- $a(\Delta e; \sigma)$ is acceptance ratio.
- average acceptance $A(\Delta E) = < a(\Delta e) >$
- We can achieve detailed balance: $A(\Delta E) = \exp(-\Delta E)A(-\Delta E)$ if we accept using: $a(x, \sigma) = \min[1, \exp(-x - \sigma^2/2)]$
- $\sigma^2/2$ is "penalty". Causes extra rejections.
- Large noise (order k_BT) is more efficient than low noise, because the QMC will then be faster.

Reptation Monte Carlo
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 with
  - 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.

$$\boxed{\left(\mathrm{Im}\,\nabla \ln \Psi\right)^2}$$
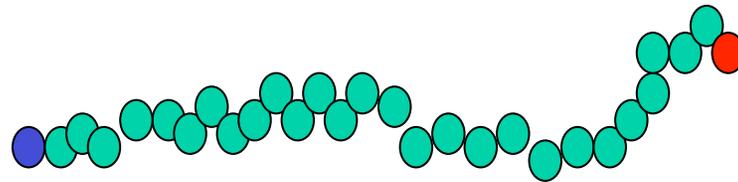
An advantage of Monte Carlo

Extra averaging is free! (almost)

Types of averaging we use:

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 since imaginary time and/or k are simply new variables to <u>average over</u>.

- Increase in parallelization

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

How good are QMC energies for many-body hydrogen?

energy   variance

•QMC energies are accurate to about 100K/atom

•Relative energies between similar bonding structures should be more accurate than this.
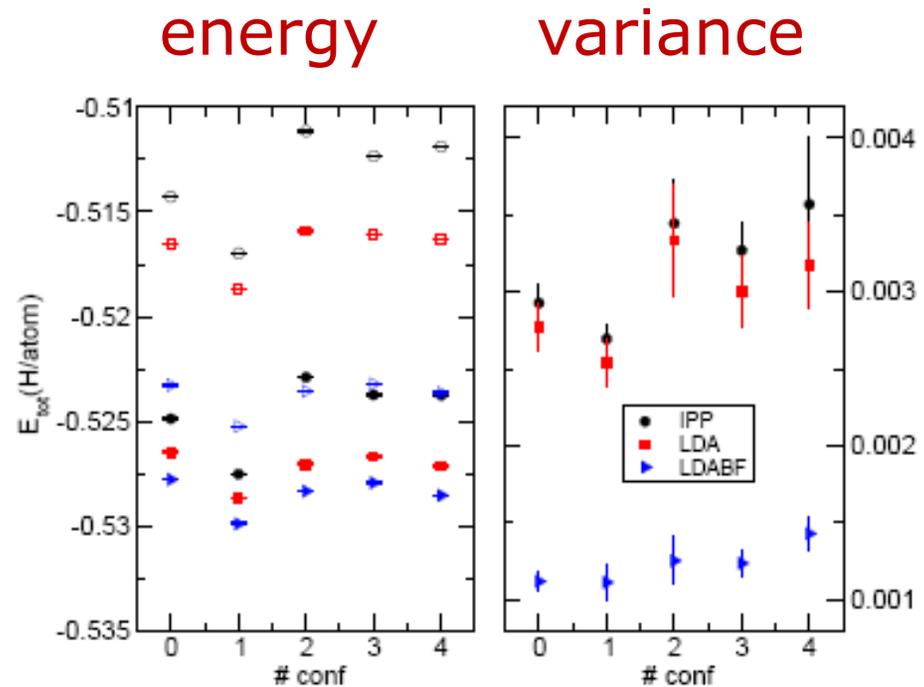
•Lower is better!

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.
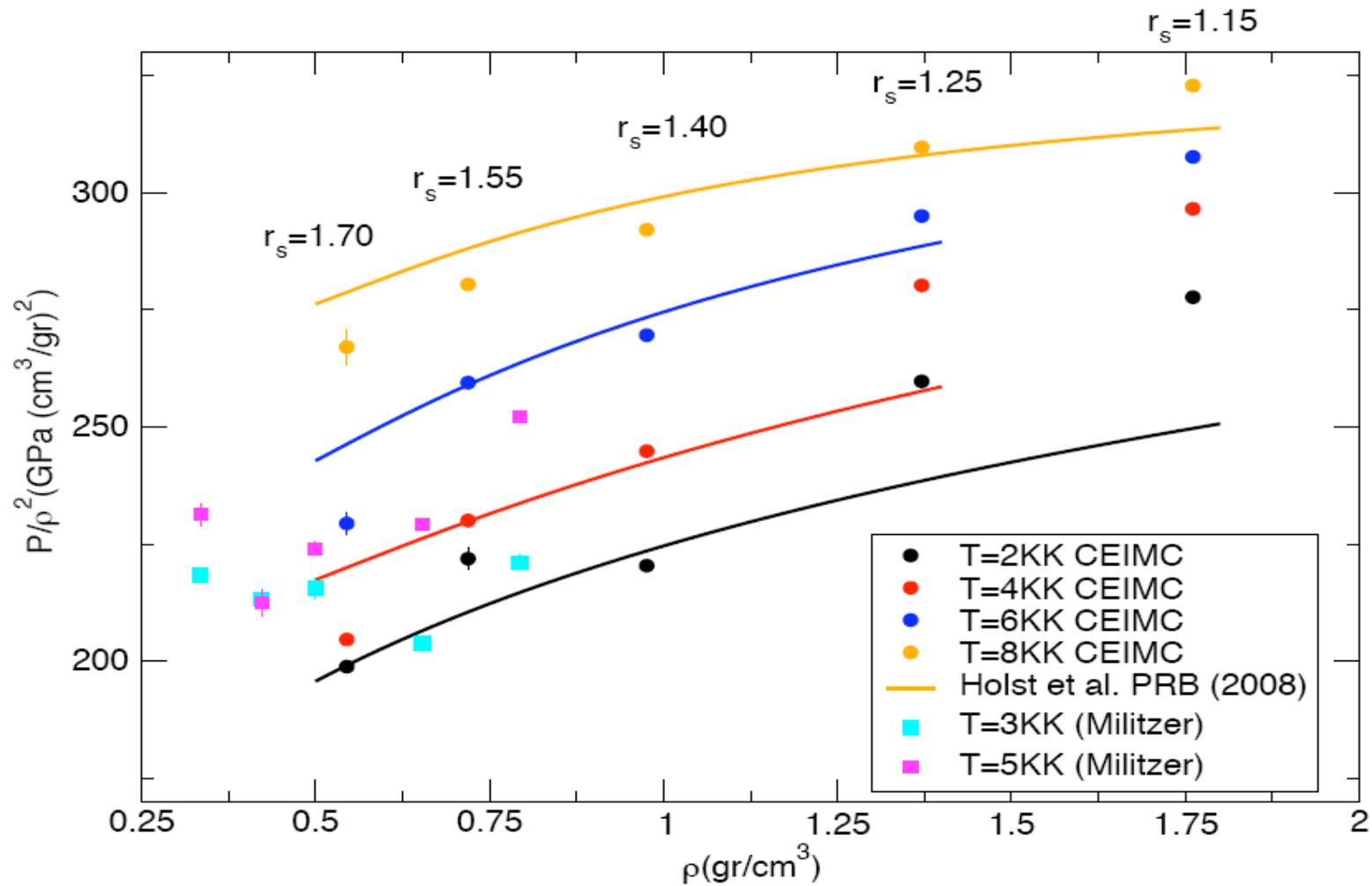
Hydrogen plasma: $r_s=1.0$, T=0.1 a.u.
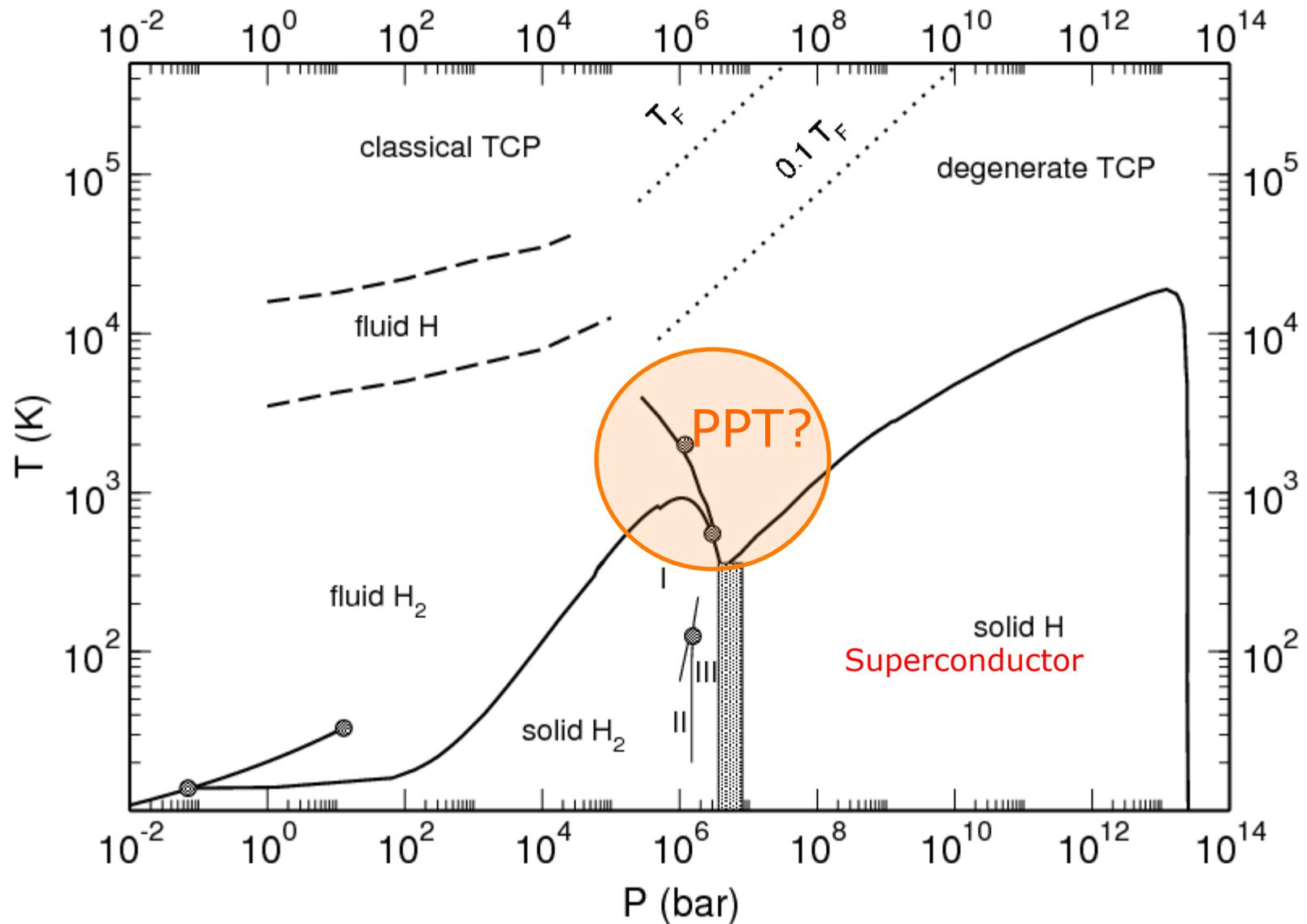
$N_e=N_p=54$, PIMC-GS nodes vs BOMC-pw-single phase

$g_{e-e}(r)$ – like spin

$g_{e-e}(r)$ – unlike spin

$g_{e-p}(r)$

— PIMC
— BOMC

$g_{p-p}(r)$
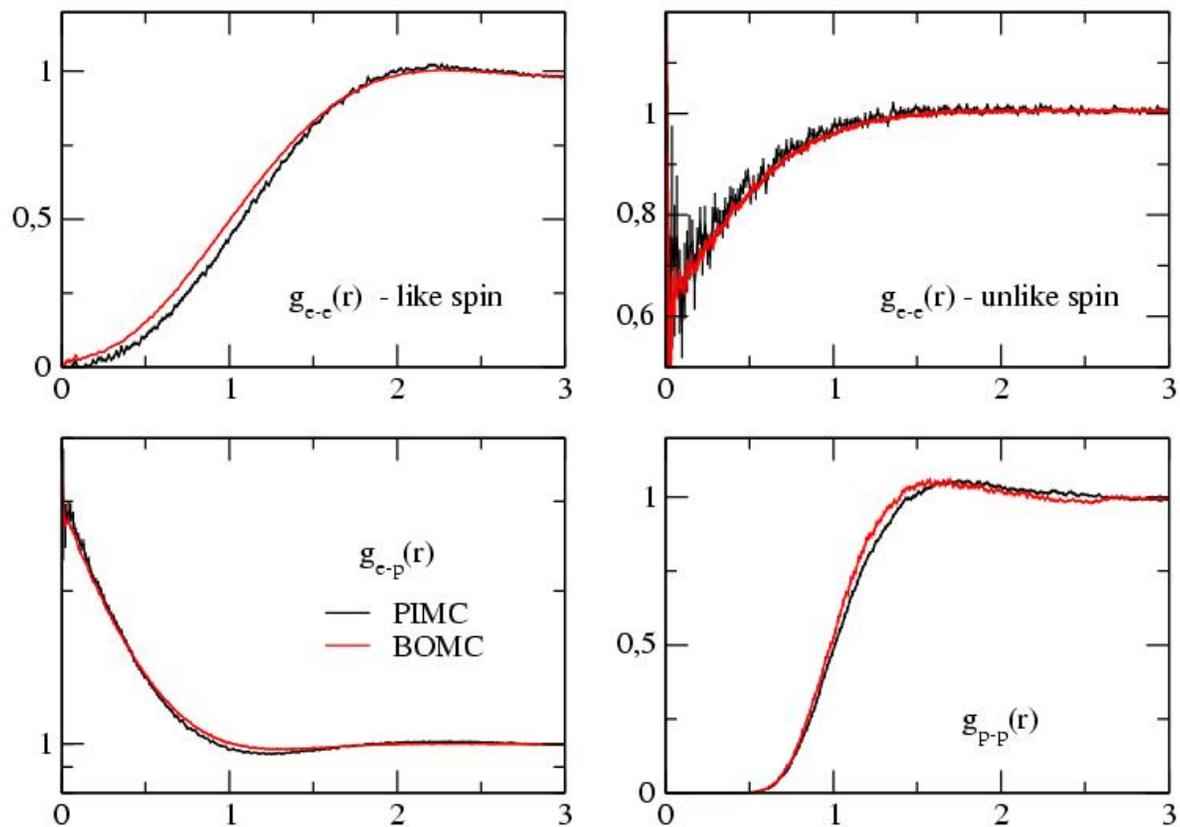
Agreement with the PIMC calculations for metallic hydrogen.

EOS: CEIMC vs BOMD

Planetary calculations will require P to 1% !

Hydrogen Phase Diagram

Liquid-Liquid transition

- How does an insulating molecular liquid become a metallic atomic liquid? Either a
  - Continuous transition or
  - First order transition with a critical point
- Zeldovitch and Landau (1944) *"a phase transition with a discontinuous change of the electrical conductivity, volume and other properties must take place"*

- Chemical models are predisposed to the LLT since it is difficult to have an analytic free energy crossover
  - e.g. Saumon Chabrier hydrogen EOS
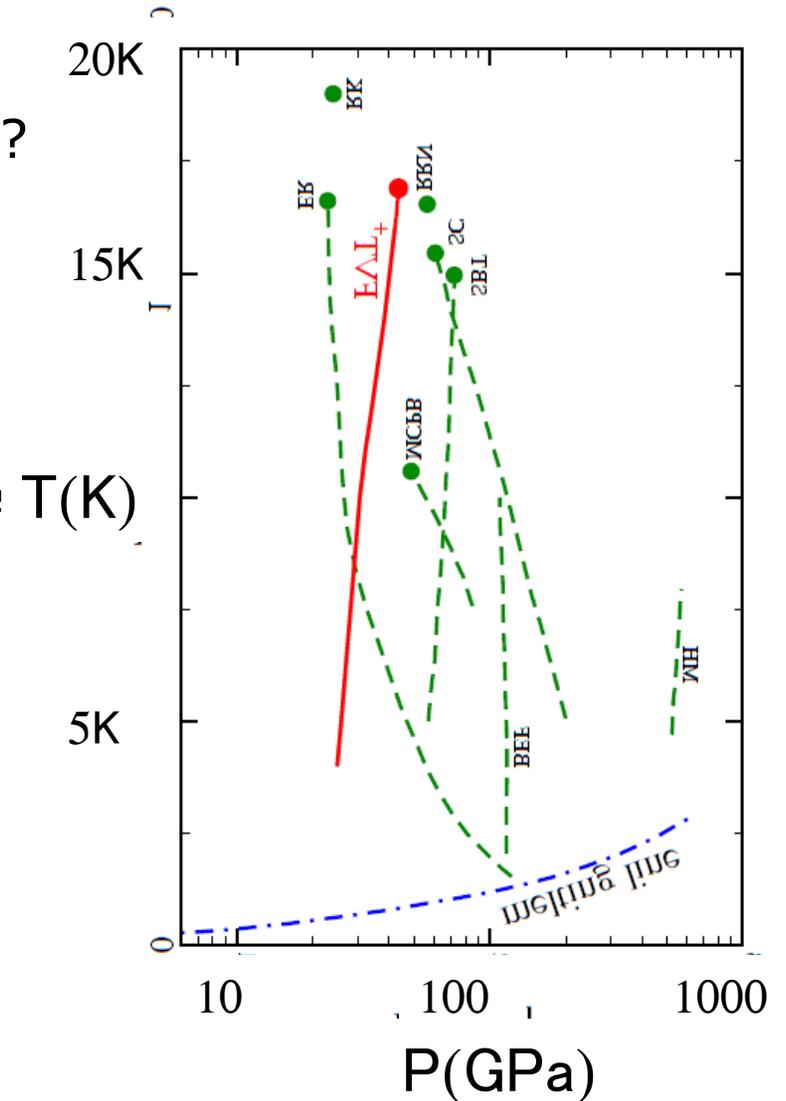
Simulation Methods

Density Functional Theory
Deterministic

- Electron energy is an assumed functional of electron density
- Born-Oppenheimer MD
- Norm-conserving pseudopotentials
- Number of atoms
  - PPT: 432 electrons
 - H-He: 250 electrons

Quantum Monte Carlo
Stochastic

- Coupled Electron-Ion Monte Carlo
- Electrons at T=0K with Reptation Quantum Monte Carlo
- 54/108 electrons
- Correlated trial wave function with backflow.

- No density functional
- No energy cutoff
- No pseudopotential
- Twist Averaged Boundary Conditions: 4x4x4 grids
- quantum protons

Liquid-Liquid Transition

Morales,Pierleoni, Schwegler,DMC, PNAS 2010.

- Pressure plateau at low temperatures (T<2000K)- signature of a 1st order phase transition

- Seen in CEIMC and BOMD at different densities

- Many previous results!
  - Finite size effects are very important
  - Narrow transition (~2% width in V)
  - Low critical temperature
  - Smaller energy differences
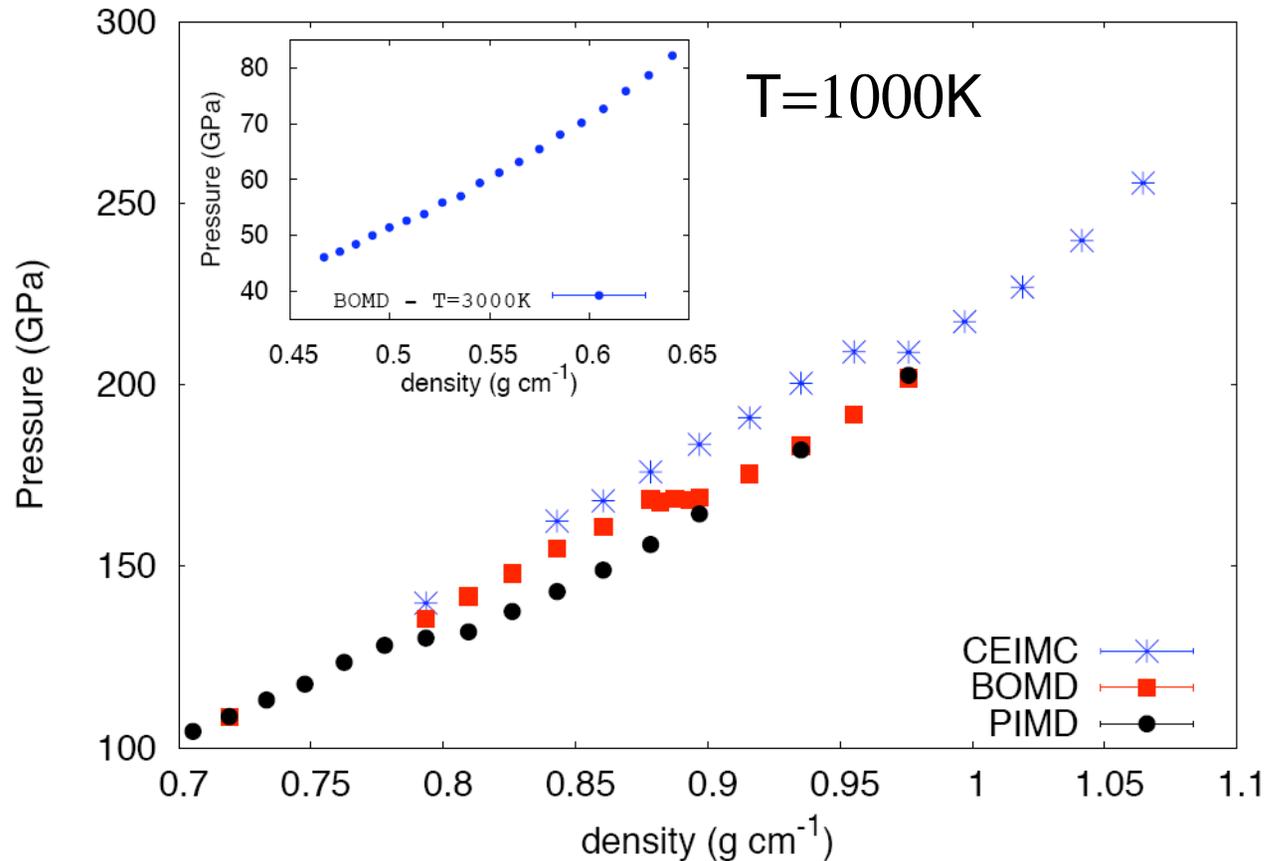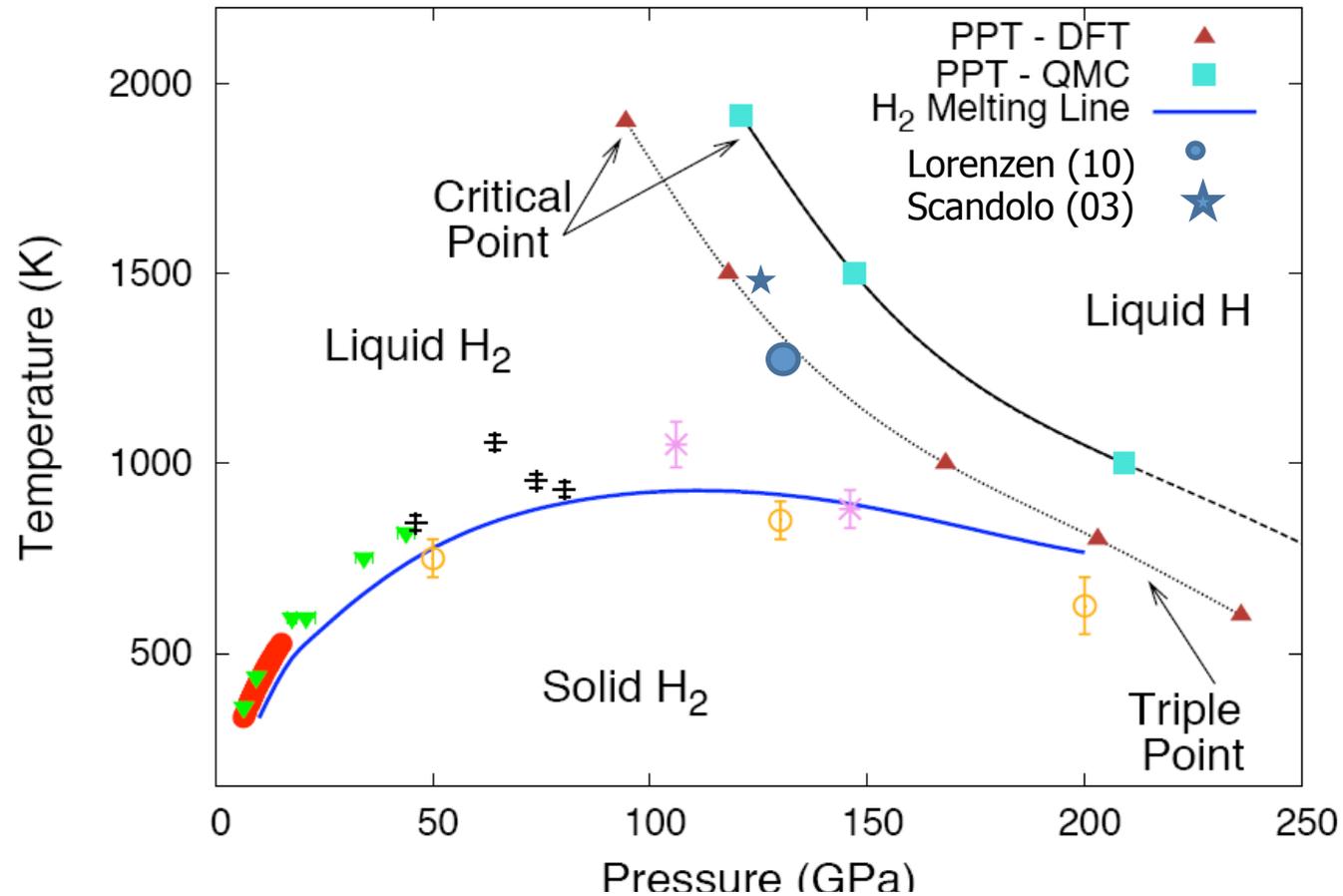
- DFT underestimates band gaps → transition too early.
- Liquid-liquid line for QMC with quantum protons lies near the DFT line.
- quantum protons ~ band gap problem of DFT
- *Can experiment see the triple point on the melting line?*
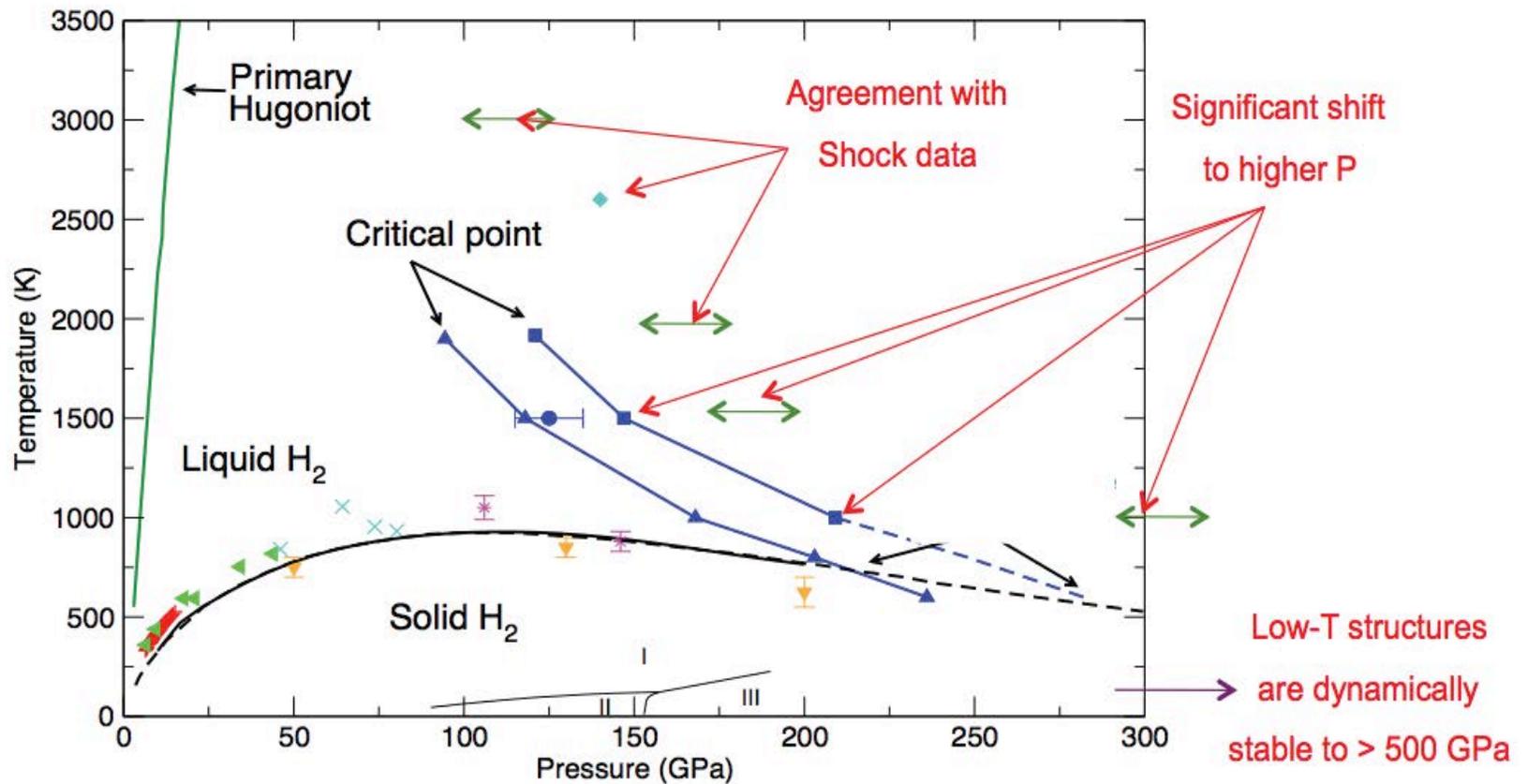
- DFT functional with van der Waals interaction pushes transition to higher pressures—in agreement with shock experiments

Accuracy of QMC

- Technical (programming) issues
- Convergence issues:
  - Iterations of Markov chain
  - Size of supercell
  - Number of time slices
- Nodes (phases) of density matrix or trial function

Some earlier calculations were not converged, but could be done now with better algorithms and computers.

SUMMARY

- Liquid-Liquid transition predicted in pure hydrogen
    - Critical point at T~1700K
    - Intersects melting line T~750K, 220 GPa.
- Simulation methods can now predict properties of dense hydrogen & helium much more accurately because:
    - Computer power is still increasing!
    - Algorithmic power: better trial functions, methods.
- Overall good agreement between DFT and QMC away from critical region. QMC can be used to determine a (n,T) smooth correction to a given functional.
- More work needed to get higher accuracy, more properties, treat larger systems, and heavier elements.