Quantum Simulations

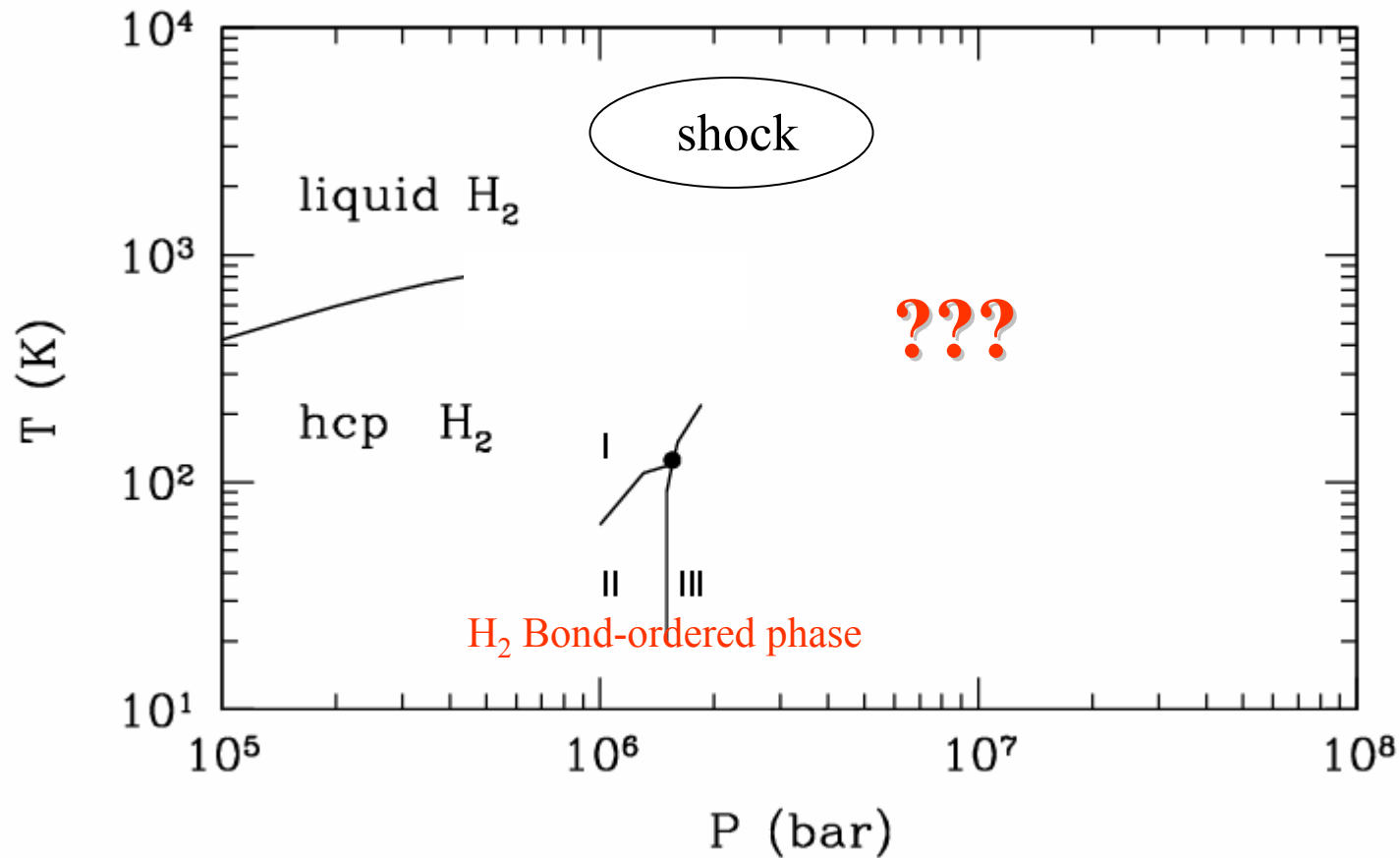## of warm dense hydrogen

C. Pierleoni, L'Aquila
M. Morales and DMC, Illinois
M. Holzmann, Paris
K. Delaney, UCSB

- Why quantum Monte Carlo?
- Various QMC methods
- Some results in hydrogenic physics

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.

MD and MC 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, the potential surface as determined by density functional theory is not always accurate enough
- How can we use the power of today's processors to enhance accuracy of simulations of real materials?

nature

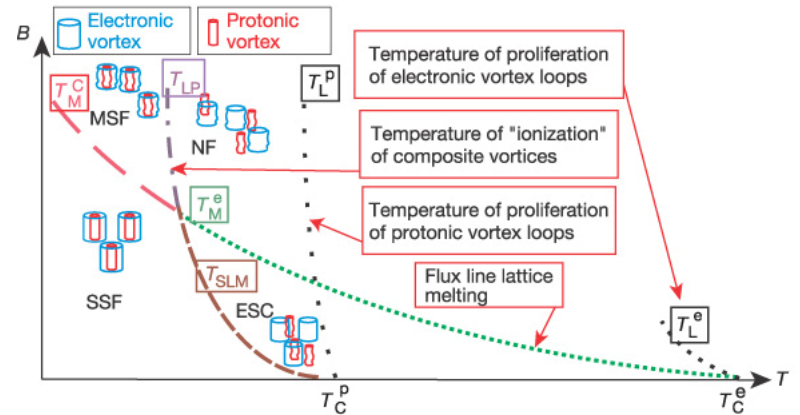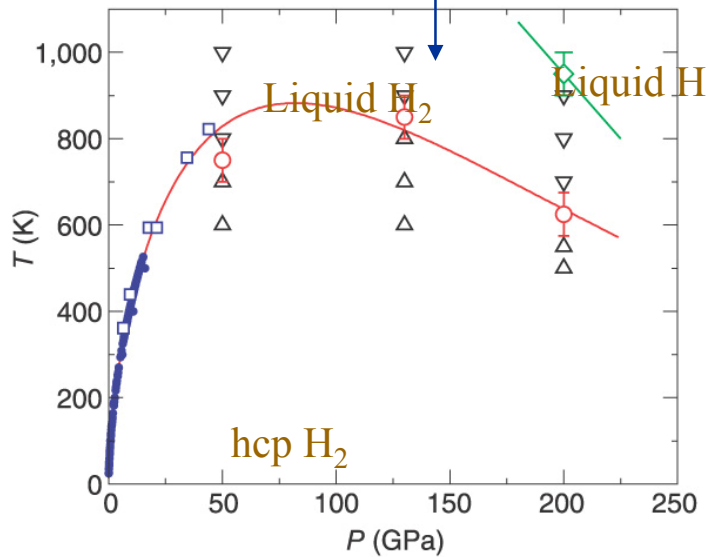**Melting hydrogen**
A new superfluid awaits discovery

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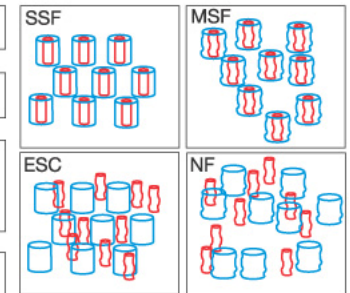
liquid

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

Liquid H_2

Liquid H

hcp H_2

Could hydrogen be a quantum fluid like helium?

Hydrogen simulations

- Early MD work of Young 60's
- Band structure calculations of lattices
- Ceperley & Alder 1985 using QMC
- Natoli et al 1990
- Magro, Pierleoni, Militizer: PIMC 1995-2000
- Kohanof   1990
- Bonev, Galli, Gygi, Militzer : AIMD 2005
- CEIMC: Dewing, Pierleoni: 2004-2006

Short history of Quantum Computations

- Early days before computers:
  - Hartree, Slater, Hylleraas , Fock, Wigner, Seitz, Bardeen, Hellmann
- First scientific computer in Los Alamos (1950).
- QM scattering among first calculations in 1950
- Quantum chemistry actively developed in 50's
- Gaussian* programs started in 60's
- Density Functional Theory: * 1960-present
- Quantum Monte Carlo : McMillan(1965) and Kalos
- Car-Parrinello ab initio dynamics, 1985-realistic simulations

*Noble prize in chemistry to Pople and Kohn

Quantum Monte Carlo

- 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 new understanding of superfluidity <u>and</u> a practical tool
- A continuum of stochastic methods:
  - Variational Monte Carlo
  - Projector Monte Carlo such as diffusion, reptation MC
  - Path Integral Monte Carlo for T>0
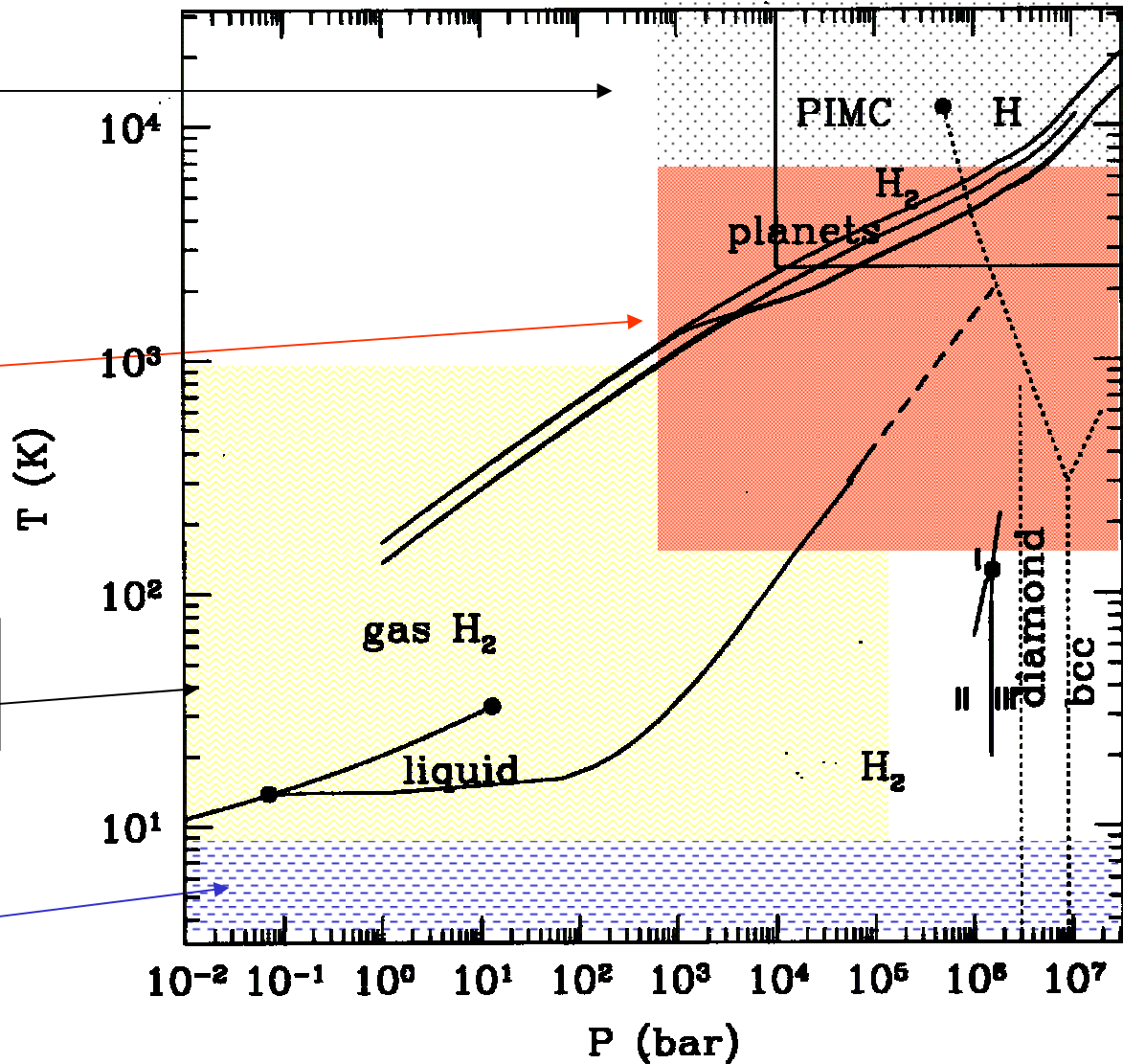 - Coupled electron-ion Monte Carlo

QMC methods for Hydrogen

Path Integral MC for
$T > E_F/10$

Coupled-electron Ion
MC

Path Integral MC with
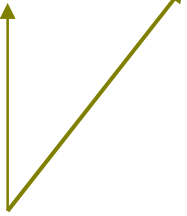an effective potential

Diffusion MC T=0

Variational Monte Carlo
(McMillan 1965)

- Put correlation directly into the wavefunction.
- Integrals are hard to do need MC.
- Take sequence of increasingly better wavefunctions.
- **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.
- Method for learning about the true trial function.

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

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

smoothing

Slater-Jastrow trial functions.

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

- Orbital from a rescaled LDA calculation.
  - Reoptimization of trial functions is a major difficulty in time and reliability.
  - Requires a lengthy LDA calculation after each proton move.
- Trial functions used:
  - backflow + three body trial function are very successful for homogeneous systems. we generalized them to many-body hydrogen: no free parameters,
  - A single gaussian orbital/molecule works well in H_2 phase.
  - 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.

Trial functions.

- 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.
  - Requires a lengthy LDA calculation after each proton move.
- Trial functions used:
  - 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.
  - A single gaussian orbital/molecule works well in H_2 phase.
  - 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.

Generalized Feynman-Kac expression for wavefunction

- Suppose we start with the free particle function.
- Using method of residuals we can construct a sequence of increasingly better trial wave functions.

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

Smoothing by random walks

Linearized Feynman-Kac formula

- First order is Slater-Jastrow pair wavefunction.
- Second order is 3-body / backflow wavefunction
- Backflow improves the nodal surfaces, important for fixed-node methods.

*Holzmann, DMC, Pierleoni & Esler, Phys. Rev. **E 68**, 046707:1-15(2003).*

Backflow- 3B Wave functions

Backflow means change the coordinates to quasi-coordinates.

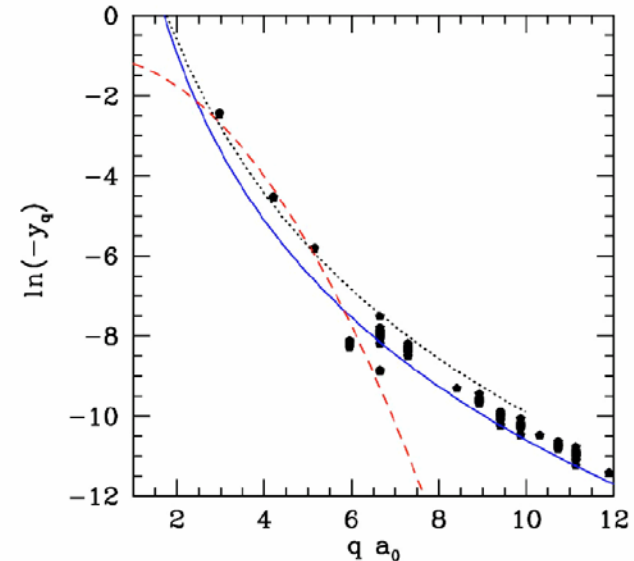$$Det\{e^{i\mathbf{k}_i\mathbf{r}_j}\} \Rightarrow Det\{e^{i\mathbf{k}_i\mathbf{x}_j}\}$$

$$\mathbf{x}_i = \mathbf{r}_i + \sum_j \eta_{ij}(r_{ij})(\mathbf{r}_i - \mathbf{r}_j)$$

Three-body form is like a squared force.

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

Consider a single electron in a lattice of protons. With exact diagonalization find: $\varphi_\mathbf{k}(\mathbf{r})$

Then relate to the backflow function.

$$\eta(r) = -\frac{1}{r}\frac{dy(r)}{dr} \qquad -i\mathbf{k}\cdot\mathbf{q}\,y_\mathbf{q} = FT\left\{\frac{\ln[\varphi_\mathbf{k}(\mathbf{r})]}{\ln[\varphi_0(\mathbf{r})]}\right\}$$

Band energy with BF trial function

- Error in band energy goes as k^4 instead of k^2
- Very accurate wavefunction near the Γ point.
- Bad near the zone boundary because it doesn't know about the lattice symmetry.

Backflow functions are parameter-free, derived from many-body perturbation theory.

Almost as accurate as band-theory based orbitals for liquid metallic H (accurate to 100K).
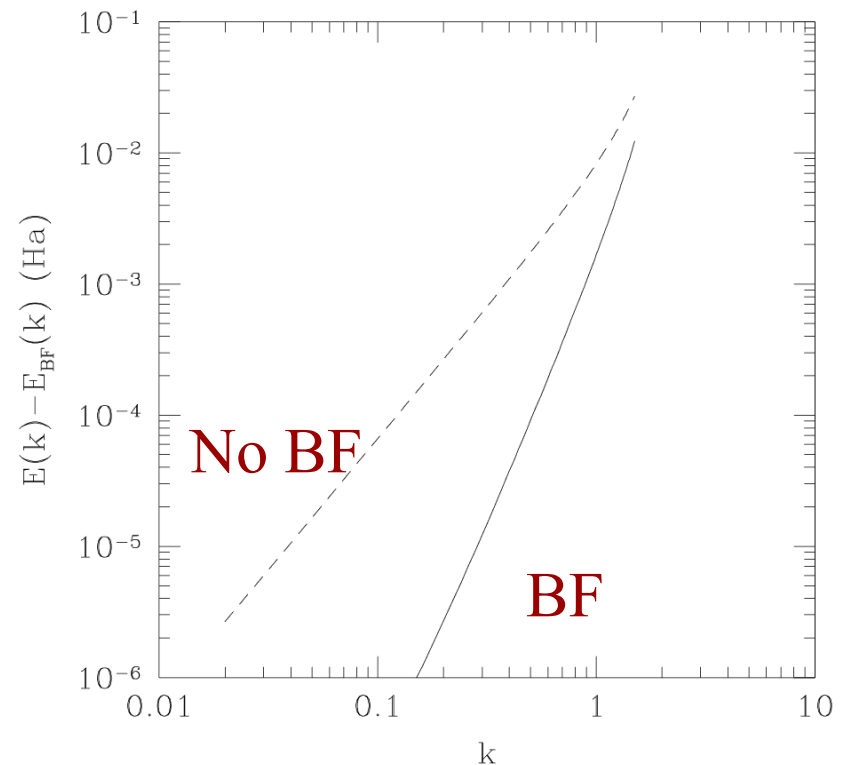
Analytic 3Body-backflow

- Start with analytic Slater-Jastrow using Gaskell trial function
- Apply Bohm-Pines collective coordinate transformation and express Hamiltonian in new coordinates
- Diagonalize resulting hamiltonian.
- Long-range part is Harmonic oscillator which can be solved
- Expand about k=0 to get backflow and 3body forms.
- Significant long-range component to BF

OPTIMIZED BF   ANALYTIC BF

$r_s=1,5,10,20$
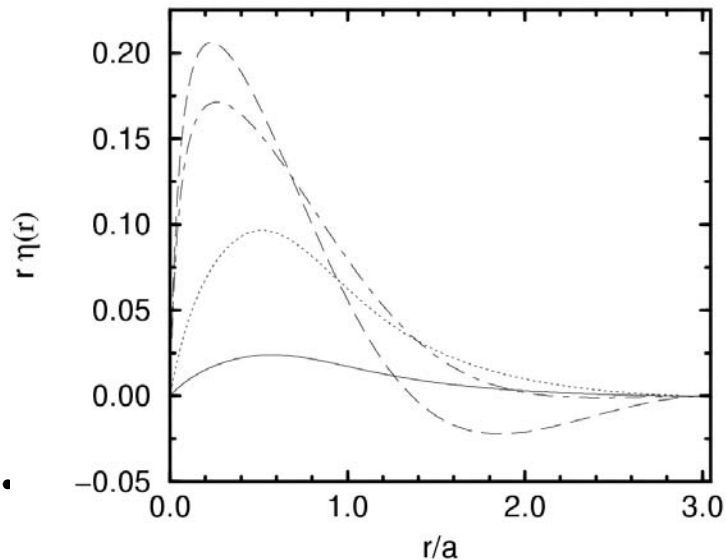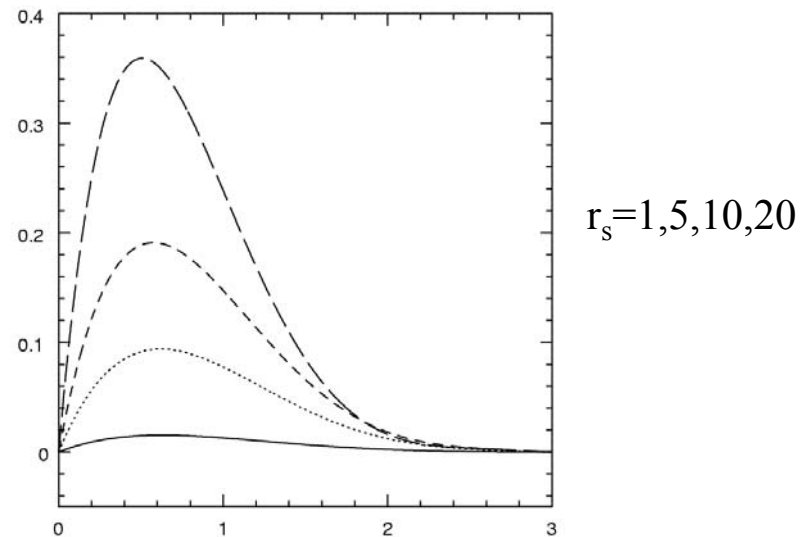
$$\Psi_2(R)\exp\{\sum_i \vec{\nabla}_i W_y(R)\vec{\nabla}_i W_u(R)\}$$

# Projector Monte Carlo
aka Green's function MC, Diffusion MC

- 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

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

Fixed-node method

- Initial distribution is a pdf.
  It comes from a VMC simulation.

  $$f(R,0) = \left|\psi_T(R)\right|^2$$

- Drift term pushes walks away from the nodes.

- Impose the condition:

- This is the fixed-node BC

  $$\phi(R) = 0 \ \text{ when } \ \psi_T(R) = 0.$$

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

  $$E_{FN} \geq E_0$$

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

- f(R,t) has a discontinuous gradient at the nodal location.

- Accurate method because Bose correlations are done exactly.

- Scales well, like the VMC method, as N³. *Classical complexity.*

DMC predictions of T=0 structures
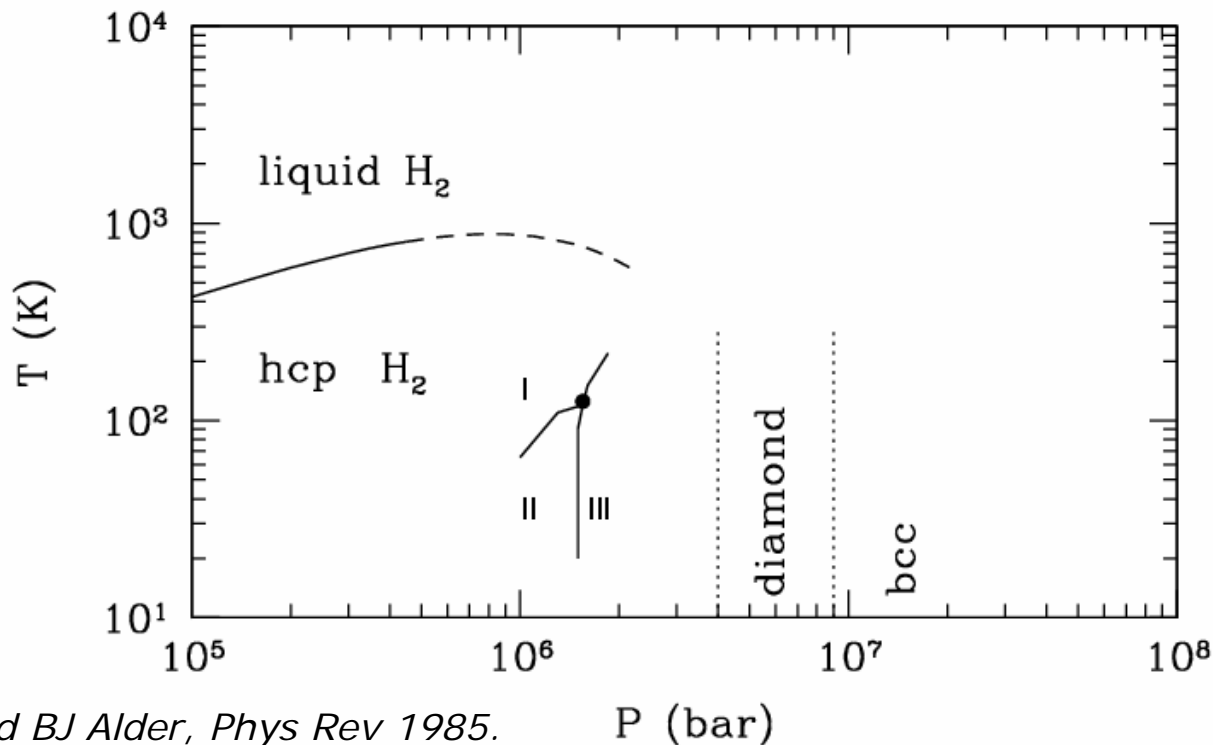
DMC and BJ Alder, Phys Rev 1985.
*Natoli, V., Martin, R. M. and DMC, Phys. Rev. Lett. **70**, 1952 (1993).*

- Predicted I-II transition
- Problem with p-e "timescales"
- What about T>0?

PIMC: Imaginary-time path integrals

The density matrix is:

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

- Trotter's theorem (1959):

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

- n is number of time slices.

$$\tau = \beta / M$$

- Then:

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

Where the primitive link action is:

$$S(R_0, R_1; \tau) = -\frac{3N}{2}\ln(4\pi\lambda\tau) + \frac{(R_0 - R_1)^2}{4\lambda\tau} + \frac{\tau}{2}\left[V(R_0) + V(R_1)\right]$$

- Analogous to a classical problem where each particle turns into a "polymer."
- Trace implies $R_0 = R_M$ $\Rightarrow$ 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 with Monte Carlo

- Trace picture: The dots represent the "start" of the path.

- The lower the real temperature, the longer the "string" and the more spread out the wavepacket.

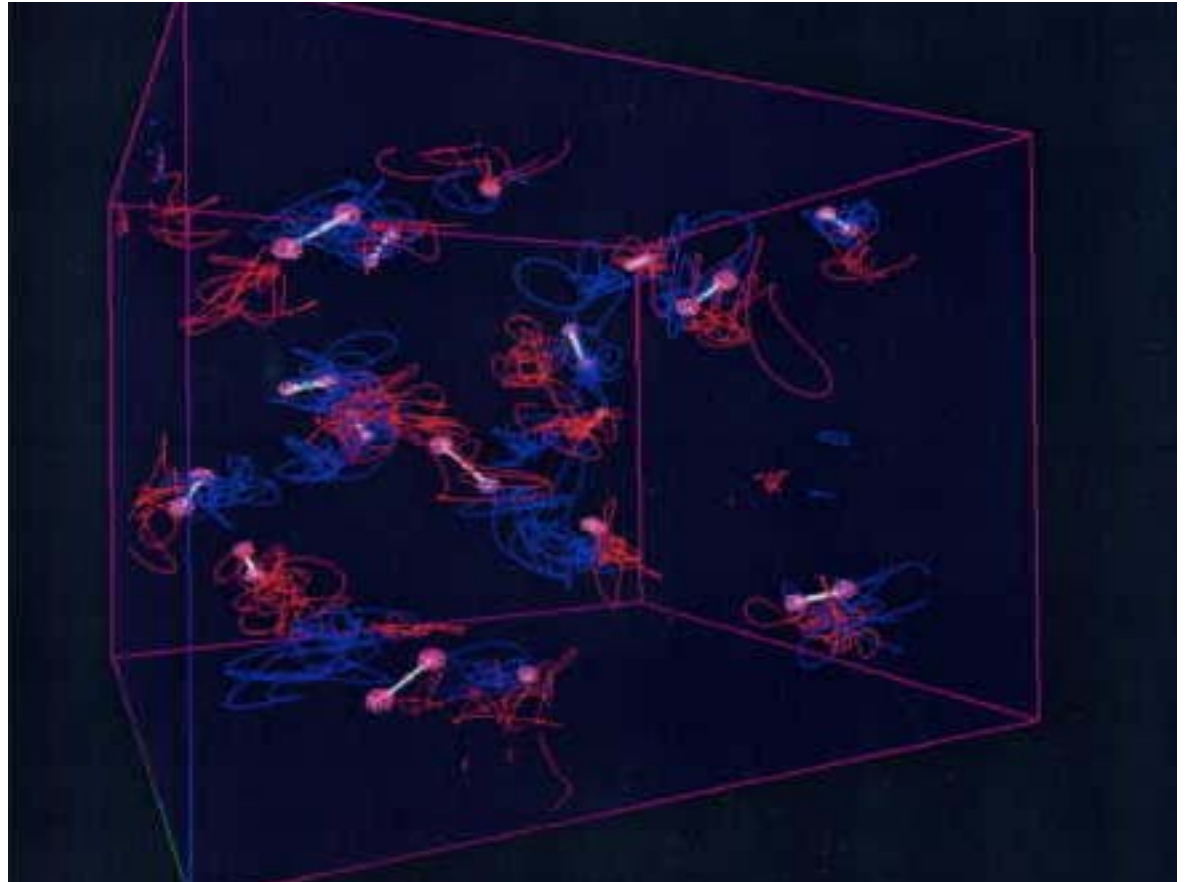- Difficulty getting down to "low" temperatures
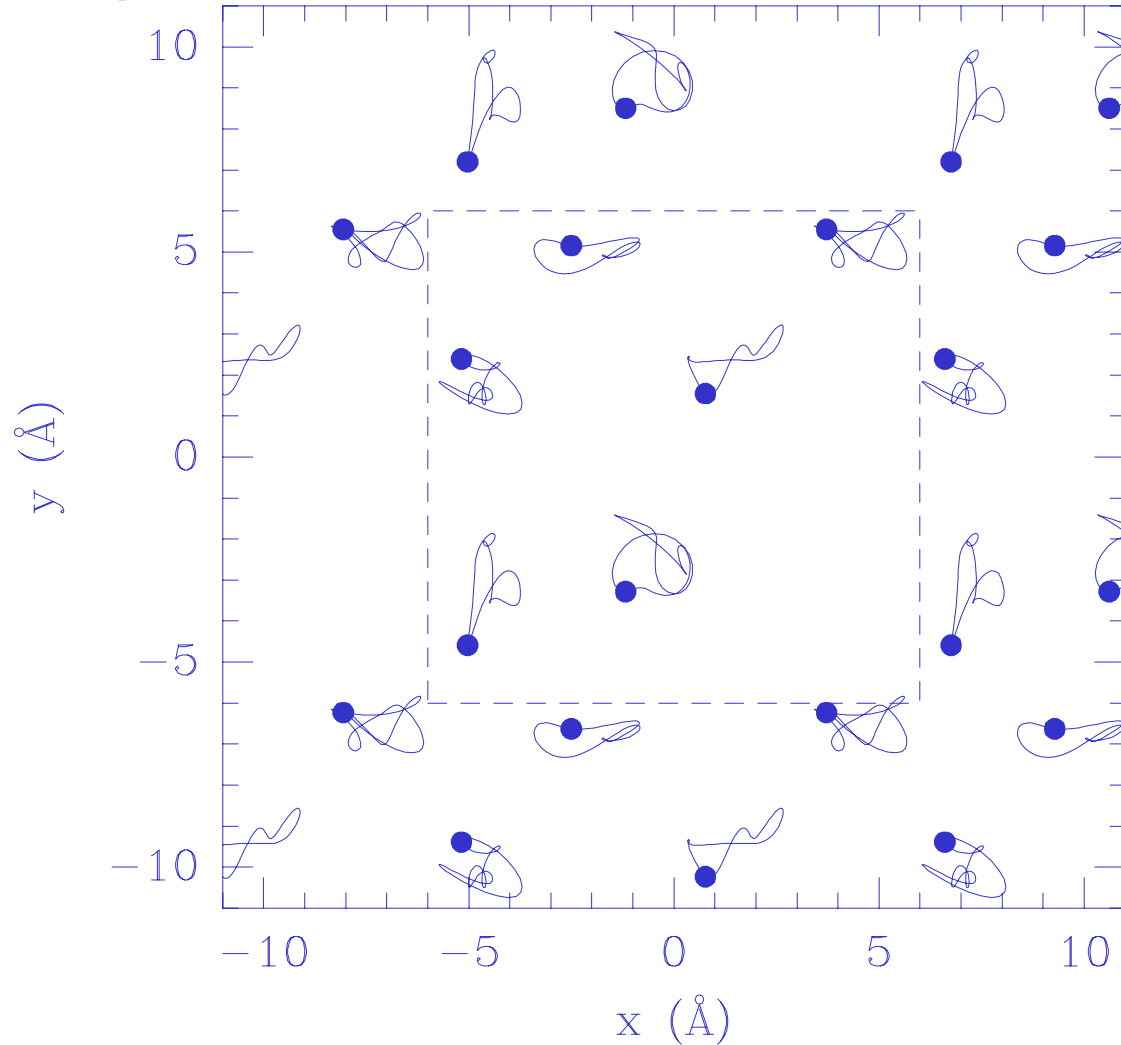
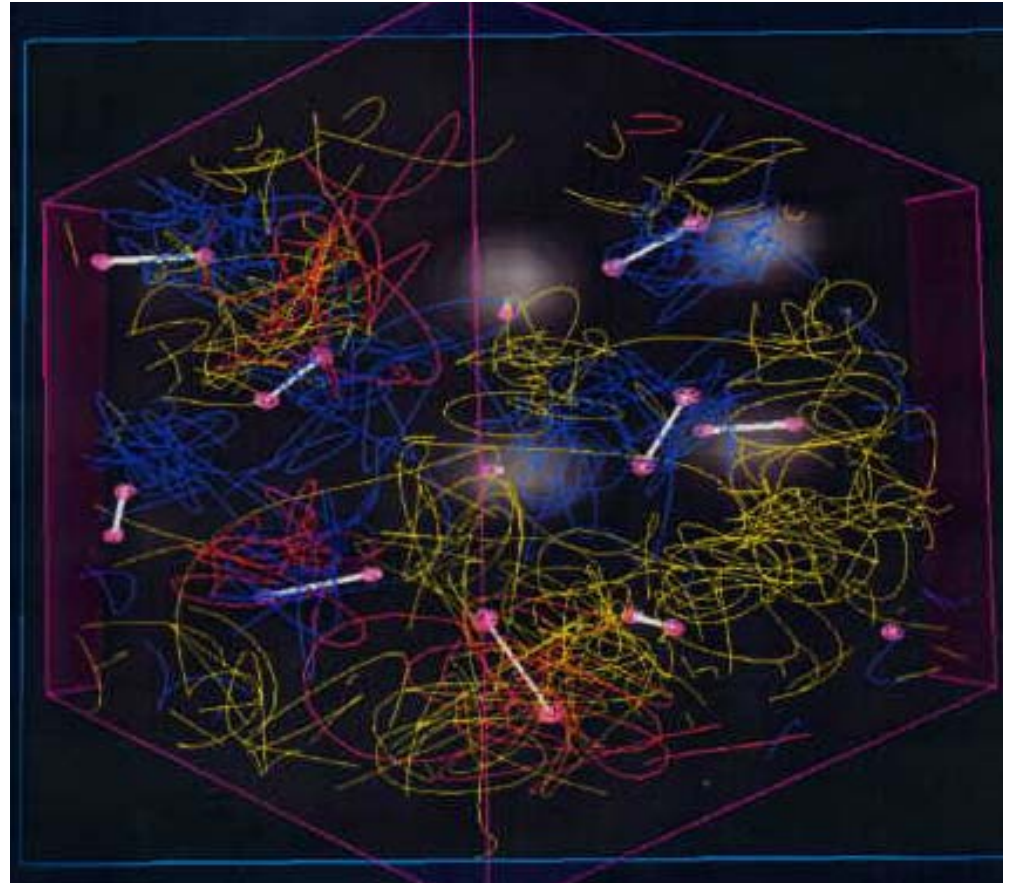# Low Density Molecular Fluid

Hydrogen

T=5000K

r_s=4.0

Molecular Metallic liquid

Deuterium

T=5000K

r_s=1.86

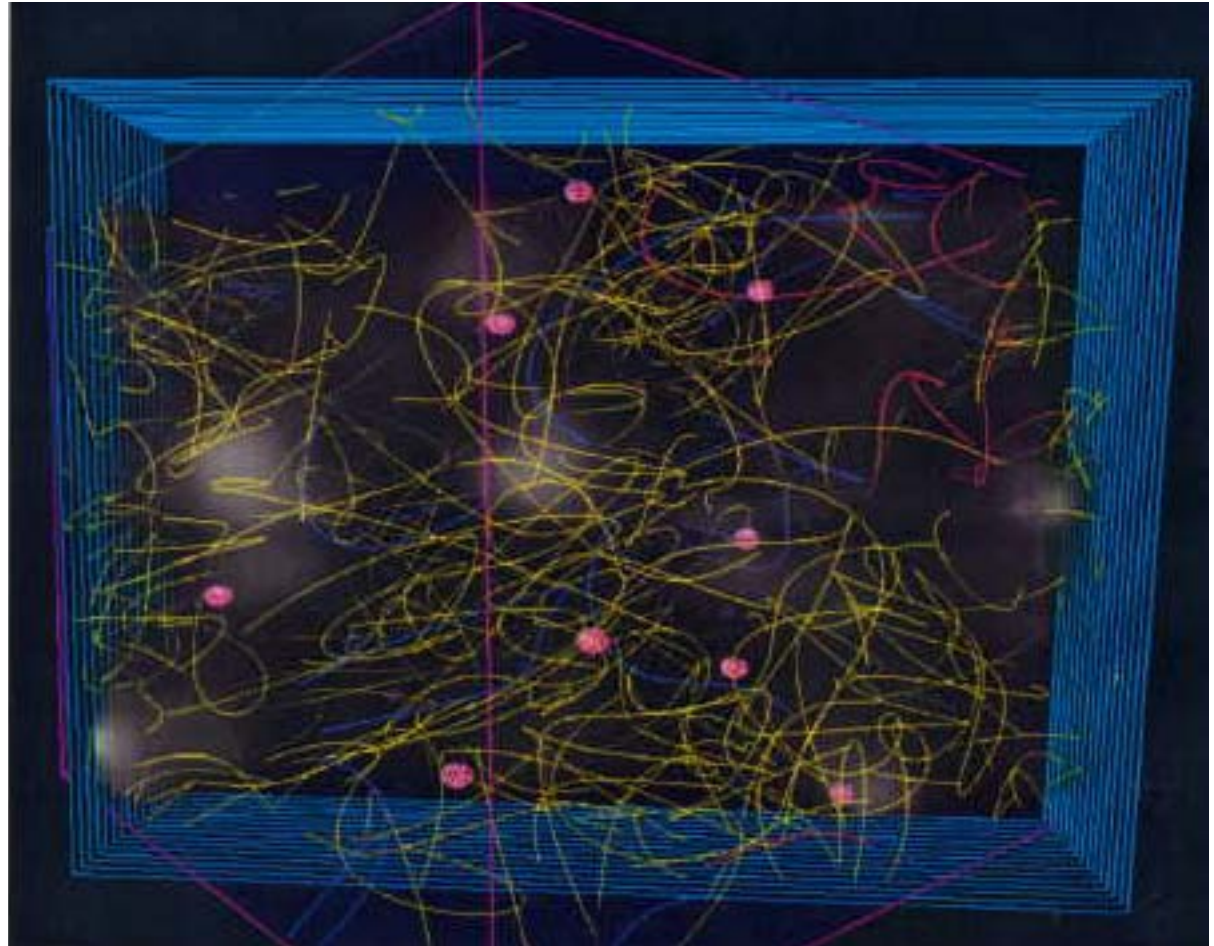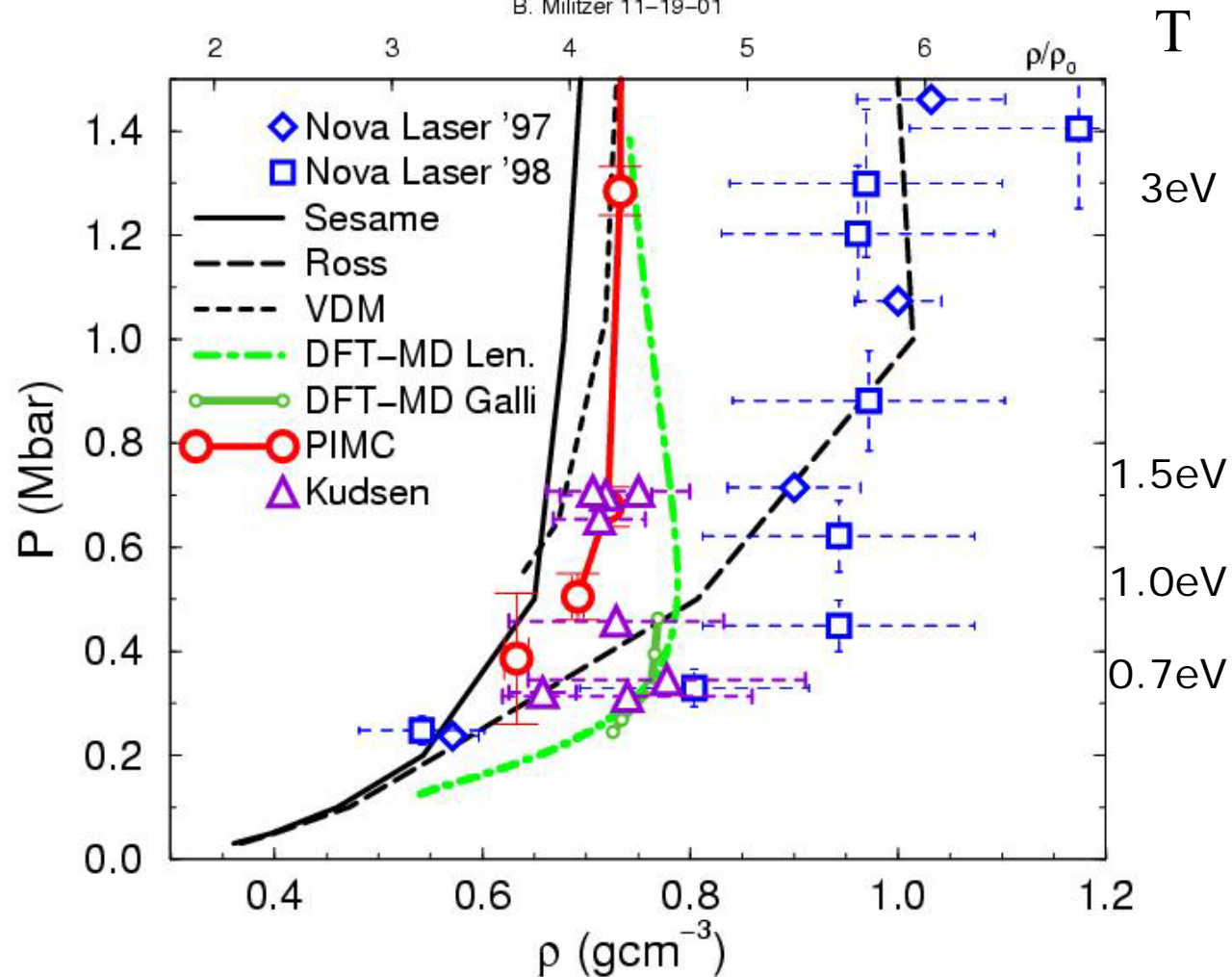# Ionized Fermi Liquid

Deuterium

T=6250K

r_s=1.60

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

T

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

electrons R

ions $S \Rightarrow S^*$
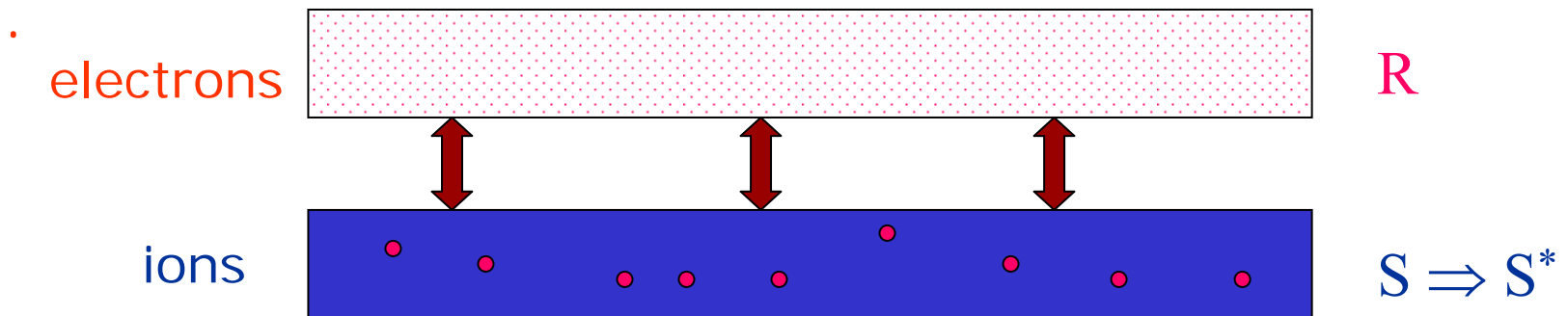
- What about the "noise" coming from electronic energy?

The Penalty method

DMC & Dewing, J. Chem. Phys. 110, 9812(1998).

- **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 theorem for $\sigma < \infty$

- $a(\Delta e; \sigma)$ is acceptance ratio.
- average acceptance $A(\Delta E) = < a(\Delta e) >$
- detailed balance: $A(\Delta E) = \exp(-\Delta E) \, A(-\Delta E)$
- An **<u>exact solution</u>** is: $a(x, \sigma) = \min[1, \exp(-x - \sigma^2/2)]$
- $\sigma^2/2$ is "penalty"
- Large noise (order $k_B T$) is more efficient than low noise, because the QMC is so much faster.

An advantage of Monte Carlo:

Averages are almost free.

$$E(s) = \tfrac{1}{M} \sum_{i=1}^{M} E(s; q_i)$$

1. Path Integrals for ions (particularly for protons or light ions) (M 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 k-points)

- In explicit methods such as LDA, these extra variables will increase the CPU time by a factor M.

- With QMC there will be little increase in time if imaginary time and/or k are simply new variables to <u>average over</u>. Except for startup time, it just increases dimensionality of integral.

- We assign different values of phases and imaginary time to different processors.

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.
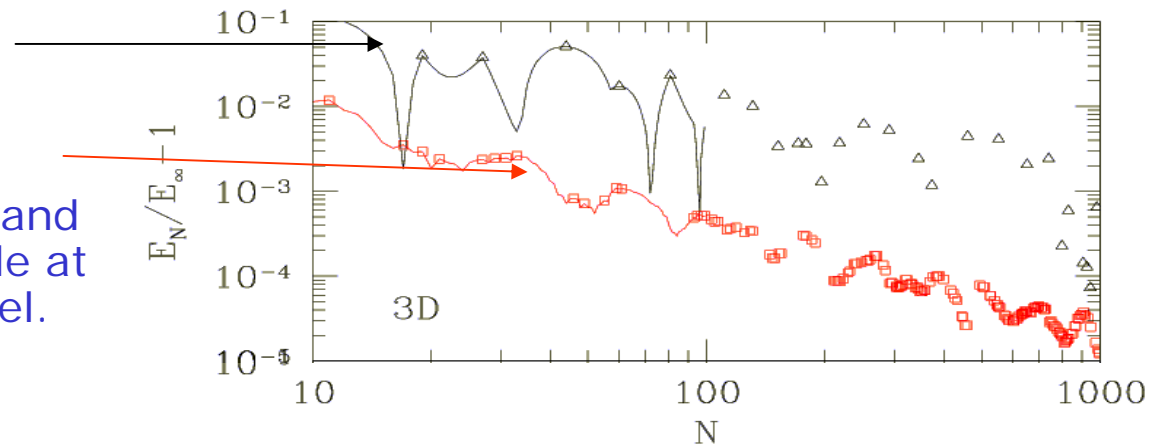- Makes 54 atoms much closer to thermodynamic limit.

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

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

Error with PBC

Error with TABC

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

- 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)
- Budge twist angles
- Send them all out to M separate processes
- Do reptation QMC to get energy differences and variances
- Combine to get global difference and variance.
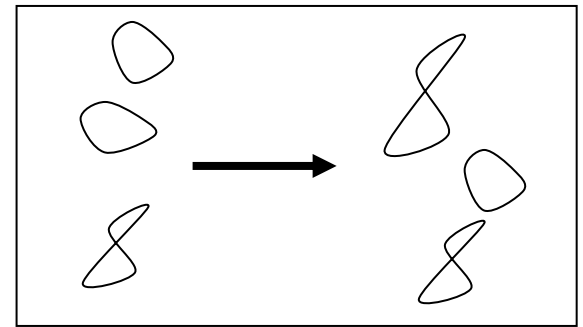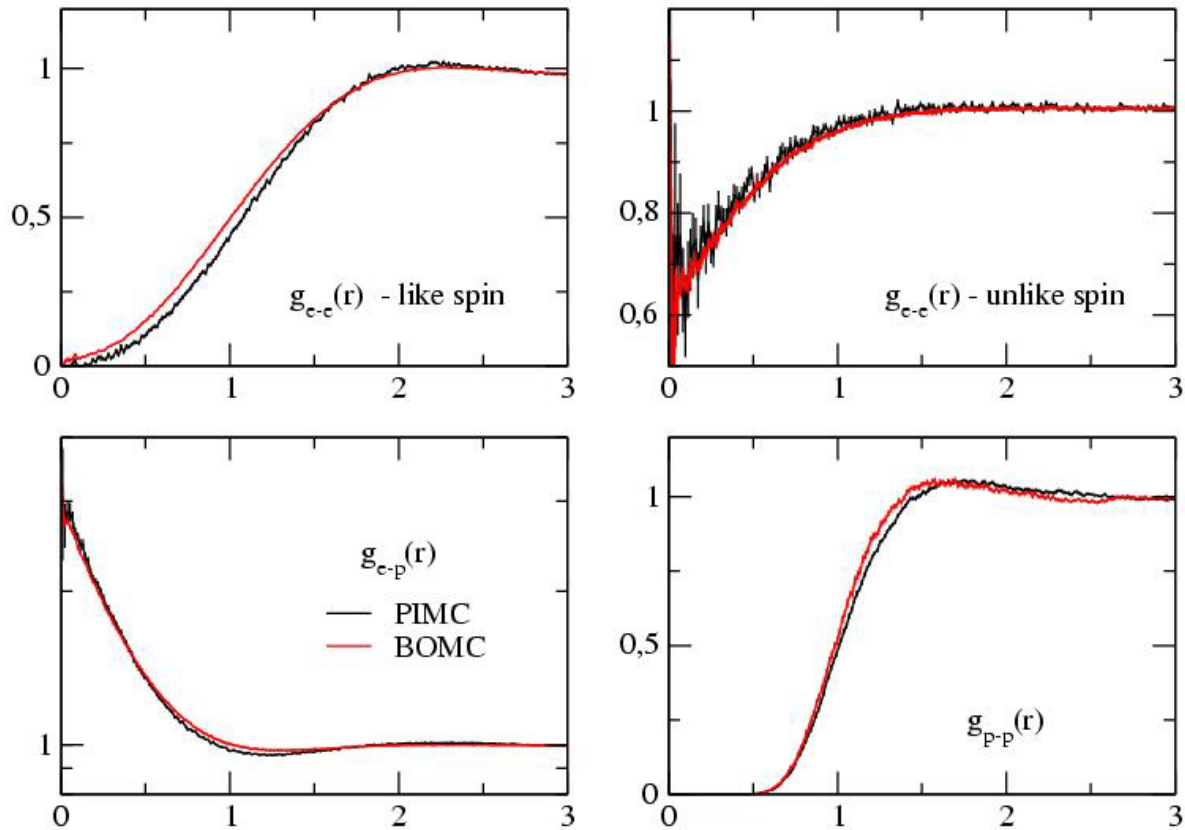
$$R_\tau \rightarrow R'_\tau$$
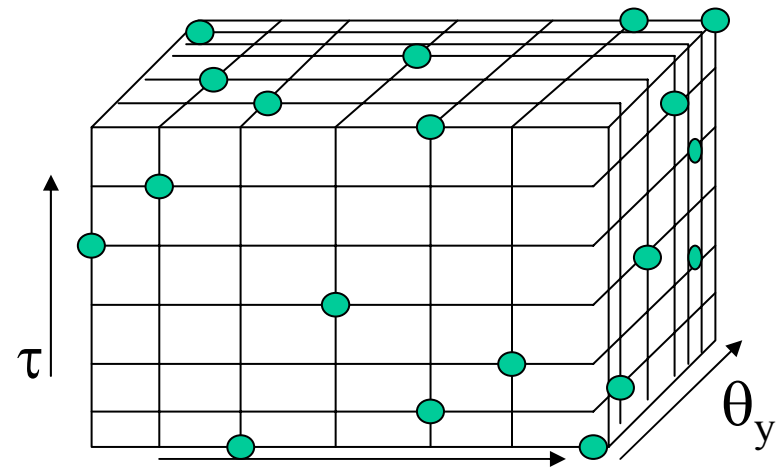
$$\Delta E_{BO} = \frac{1}{M} \sum E_{\theta,\tau}$$

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

Hydrogen plasma: $r_s=1.0$, T=0.1 a.u.

$N_e=N_p=54$, PIMC-GS nodes vs BOMC-pw-single phase

$g_{e\text{-}e}(r)$ - like spin

$g_{e\text{-}e}(r)$ - unlike spin

$g_{e\text{-}p}(r)$

—— PIMC
—— BOMC

$g_{p\text{-}p}(r)$

Agreement with the PIMC calculations for metallic hydrogen.

r_s	V(cc/mol)	T(K)	Pressure (Mbar)				
			Gasgun	S-C	S-G	CEIMC-VMC	CEIMC-DMC
2.100	6.92	4530	0.234	0.213	0.201	0.226(4)	0.225(3)
2.202	7.98	2820	0.120	0.125	0.116	0.105(6)	0.10(5)
1.800	4.36	3000	-	-	0.528	-	0.433(4)

Results for
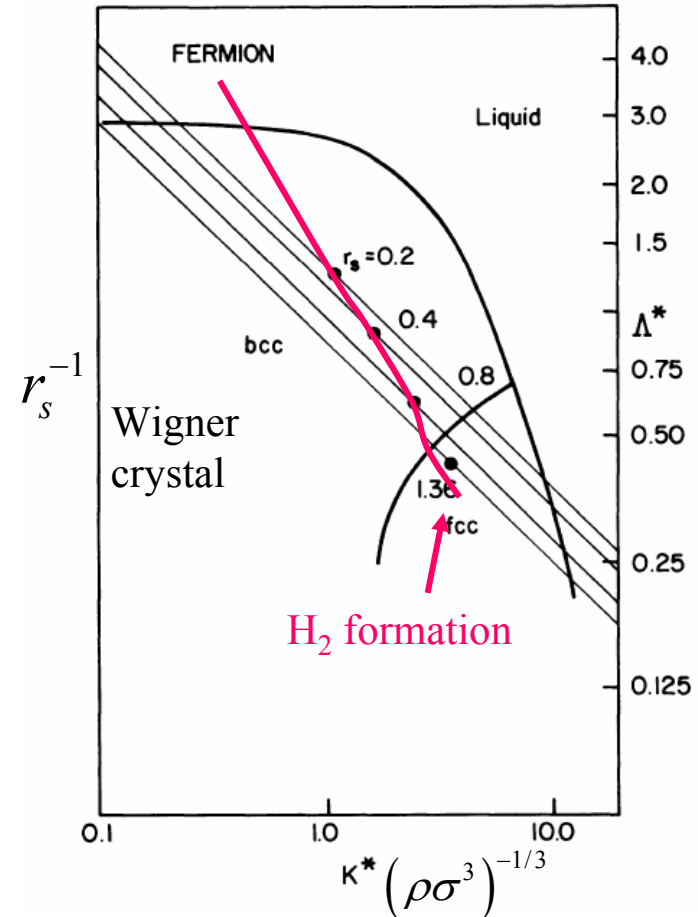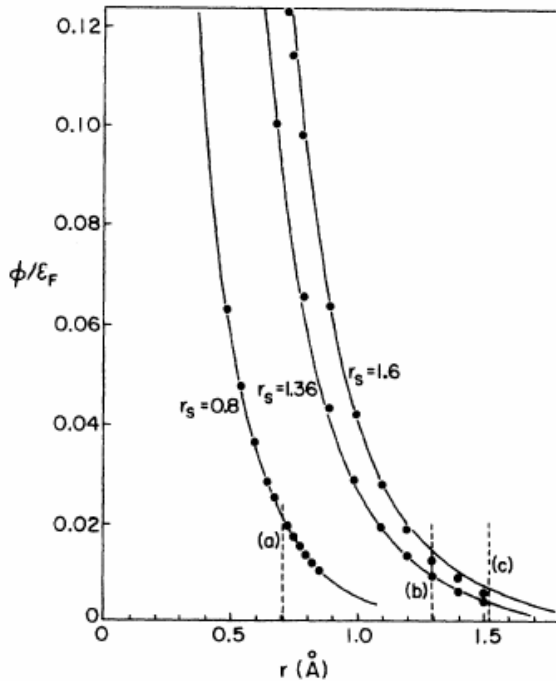
Molecular H_2

M. Dewing's
thesis (2000)
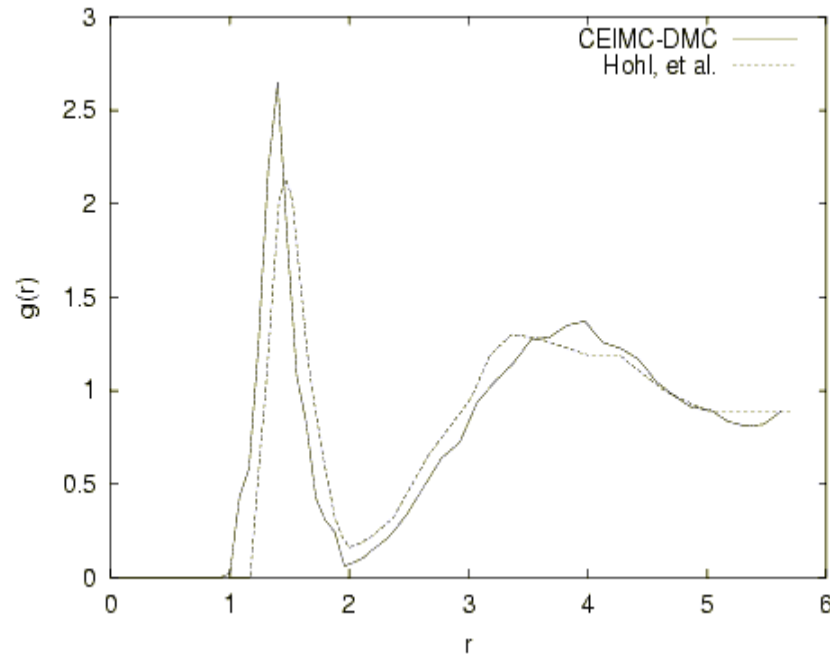
•Comparison of g(r) between CEIMC and Car-Parrinello MD.

•Reasonable agreement between methods.

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)

Zero temperature QMC calculations

$$E_{liquid} - E_{solid}$$

Calculations show T=0 energy to liquify

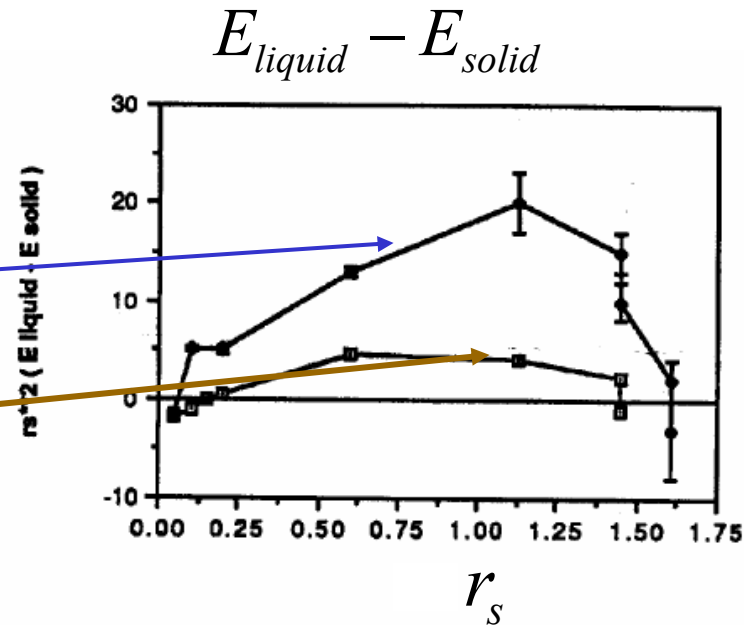- e-p system

- Effective p-p potential

Figure 4. The energy difference between an atomic liquid and an atomic crystal (times $1000 r_s^2$). The upper curve with error bars is from a GFMC calculation of a two component system of electron and protons while the lower curve is from a GFMC calculation of proton system where the electrons screen the bare proton-proton coulomb interaction.
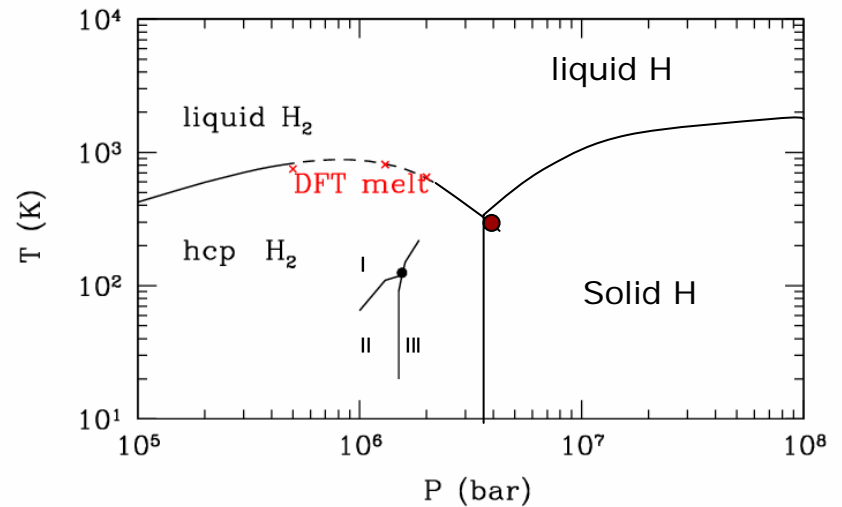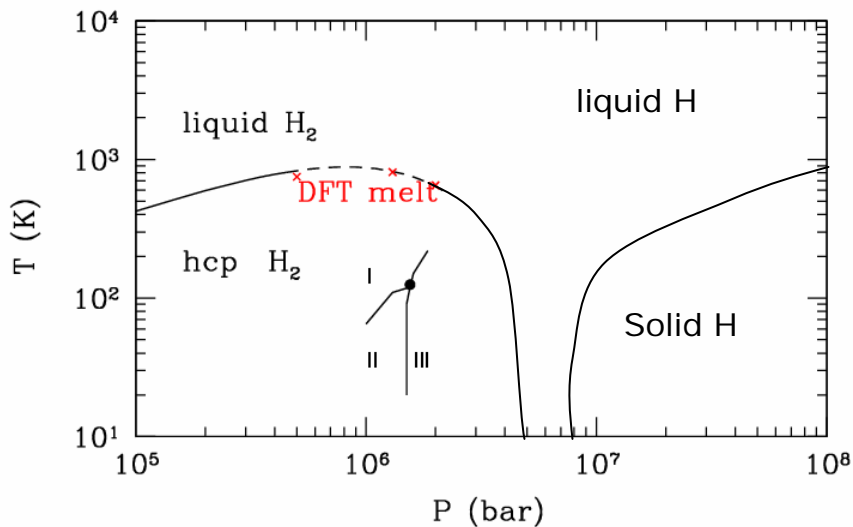
The linear response p-p potential misses a lot!

K.K. Mon et al, Phys. Rev. B 21,2641 (1980)
DMC et al. Phys. Rev. B 16, 3081 (1976)
DMC and B.J. Alder, Phys. Rev. B 36, 2092 (1987).
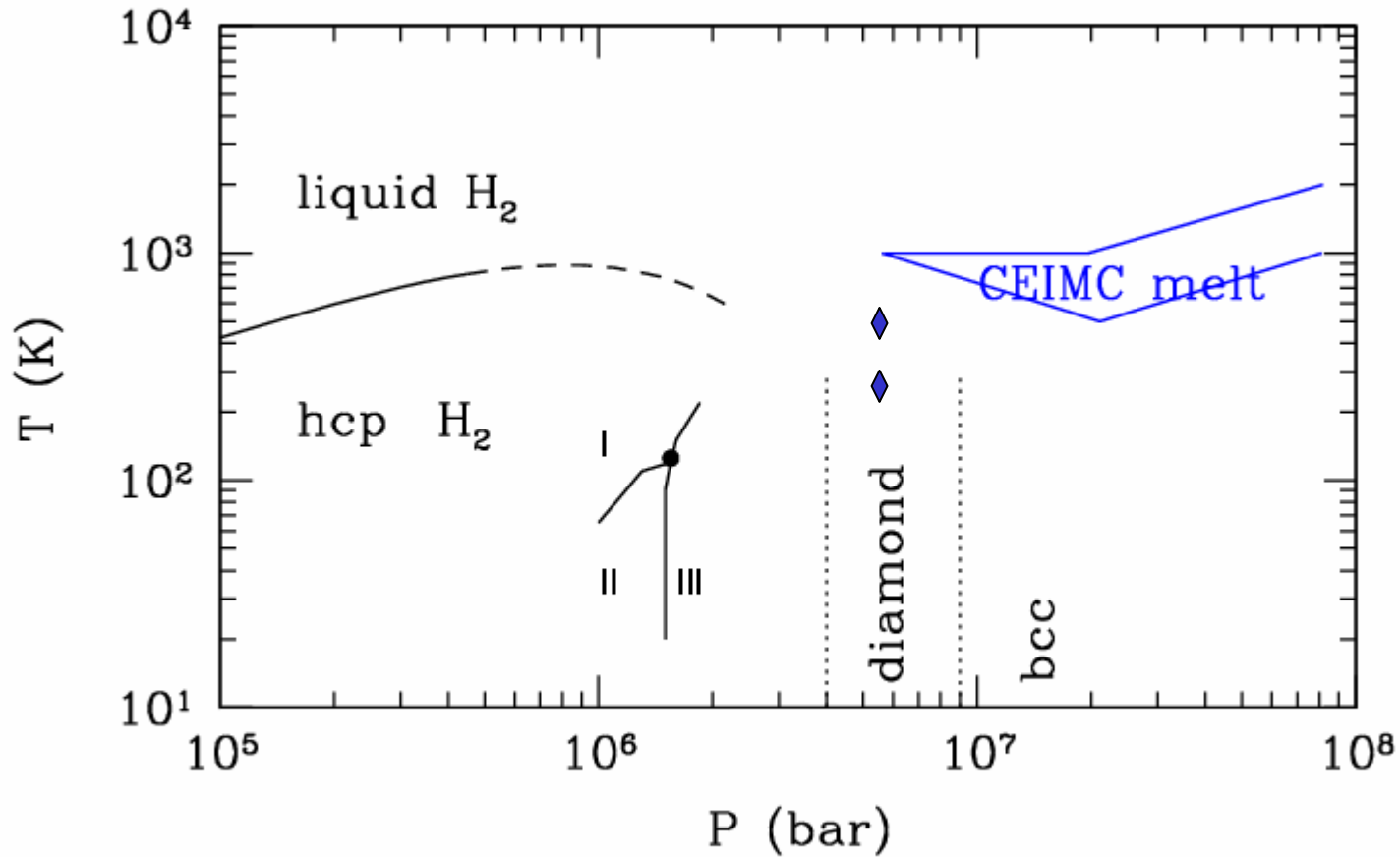DMC in" Simple Molecular Systems at Very High Density", ed. A. Polian, et al.,1989.

Two Possible Phase Diagrams

Ashcroft suggested a low temperature liquid metallic ground state.
•Does the liquid go to T=0K?

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

Melting of atomic solid using CEIMC

**CEIMC predicts T$_{melt}$>500K.**

*Pierleoni, Holtzmann, DMC, PRL **93**,146402 (2005).*

- Temperature dependence in LDA is off by 100%.

- This effect also seen in Natoli et al. calculation of various metallic hydrogen crystal structures and for liquid H_2 structures.

- In LDA (and some other functionals) energy landscape is too flat!
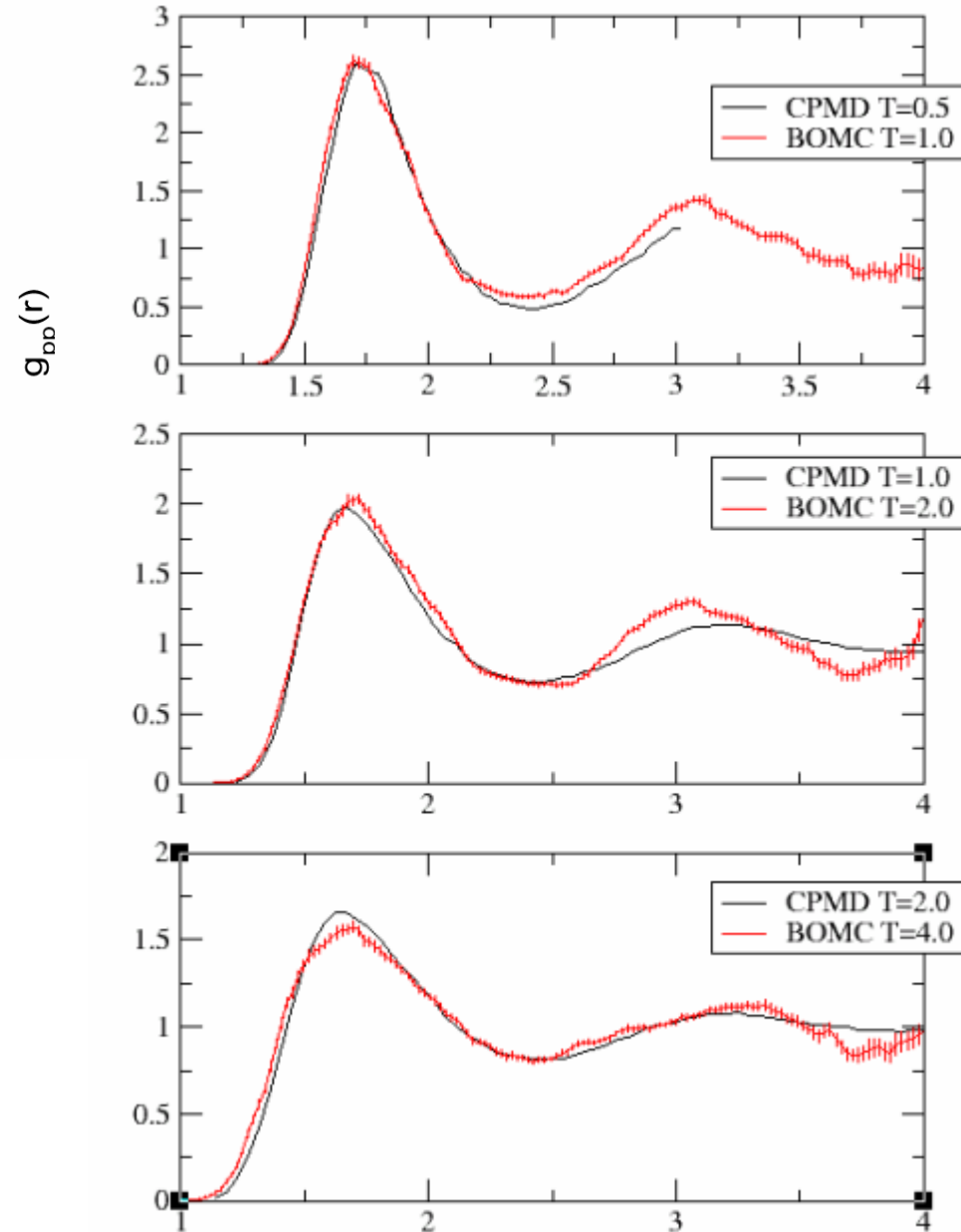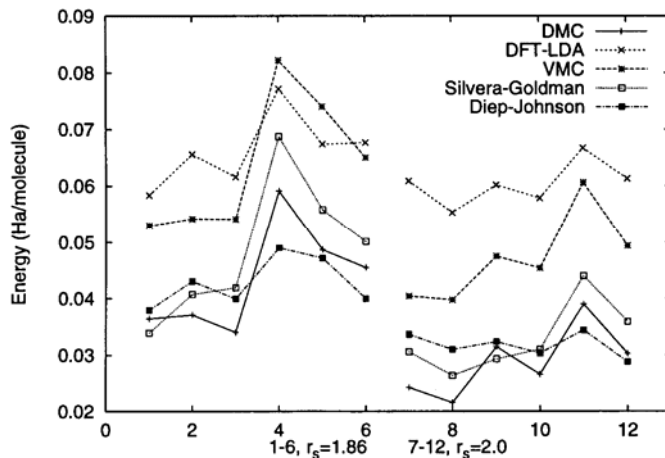
Plasma Phase Transition

- Study nature of transition from molecular to non-molecular fluid using CEIMC
- Simulations at $T=2000K$ with $P=50\text{-}200GPa$
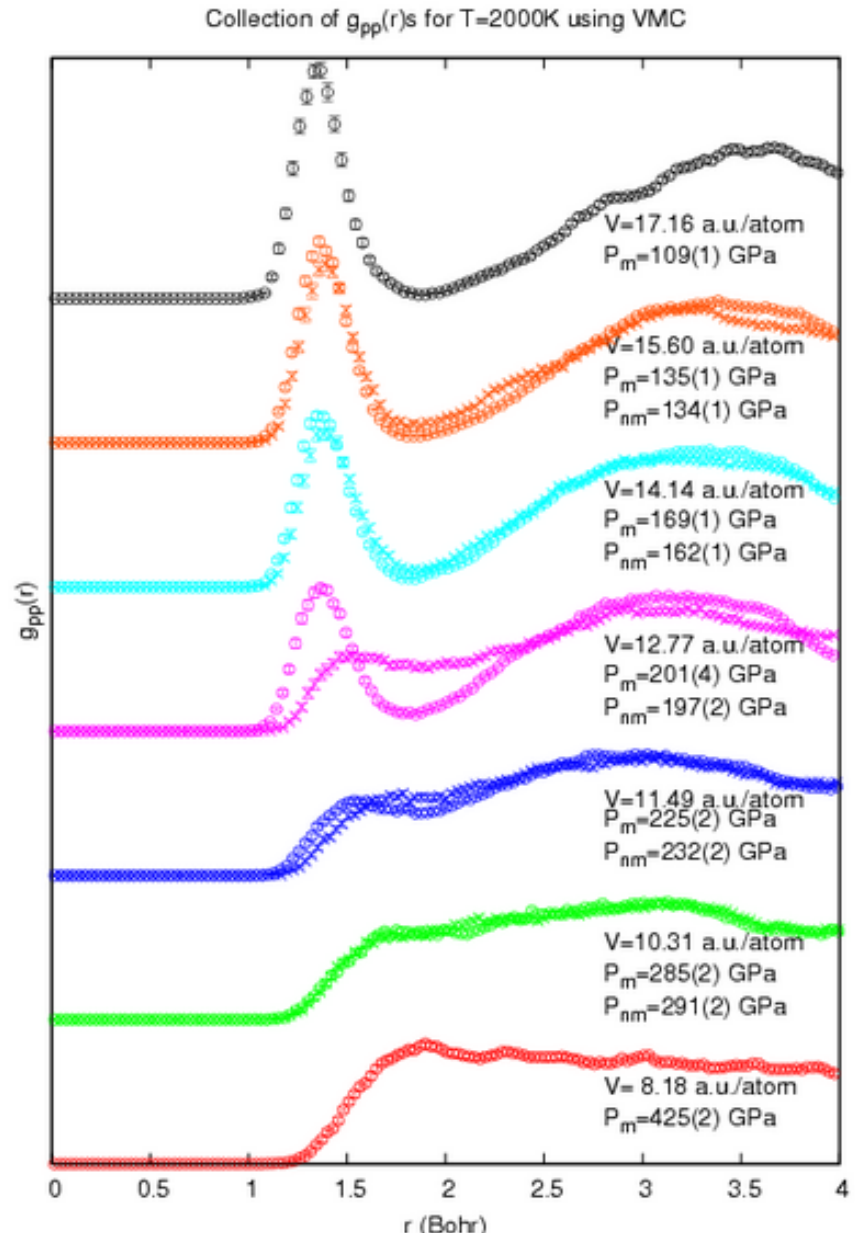

Hydrogen Phase Diagram
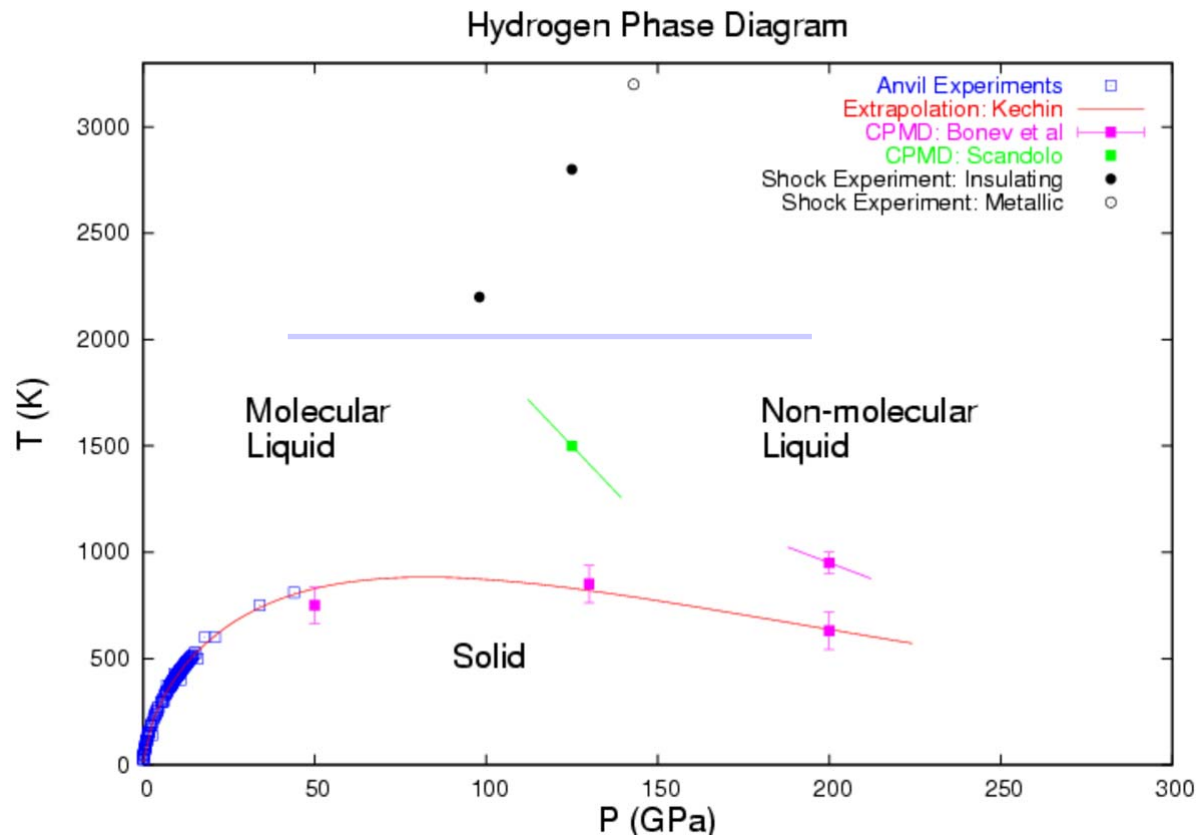
CEIMC(VMC) Simulations

- Look at proton-proton correlation function
- Clear bonding peak.

- Circles: simulations started from molecular fluid
- Crosses: from non-molecular fluid

  Hysteresis in H-H$_2$ transition.

Energy from VMC

- 32 atoms
- 216 twist angles

Collection of g$_{pp}$(r)s for T=2000K using VMC

g$_{pp}$(r)

V=17.16 a.u./atom
P$_m$=109(1) GPa

V=15.60 a.u./atom
P$_m$=135(1) GPa
P$_{nm}$=134(1) GPa

V=14.14 a.u./atom
P$_m$=169(1) GPa
P$_{nm}$=162(1) GPa

V=12.77 a.u./atom
P$_m$=201(4) GPa
P$_{nm}$=197(2) GPa

V=11.49 a.u./atom
P$_m$=225(2) GPa
P$_{nm}$=232(2) GPa

V=10.31 a.u./atom
P$_m$=285(2) GPa
P$_{nm}$=291(2) GPa

V= 8.18 a.u./atom
P$_m$=425(2) GPa

r (Bohr)
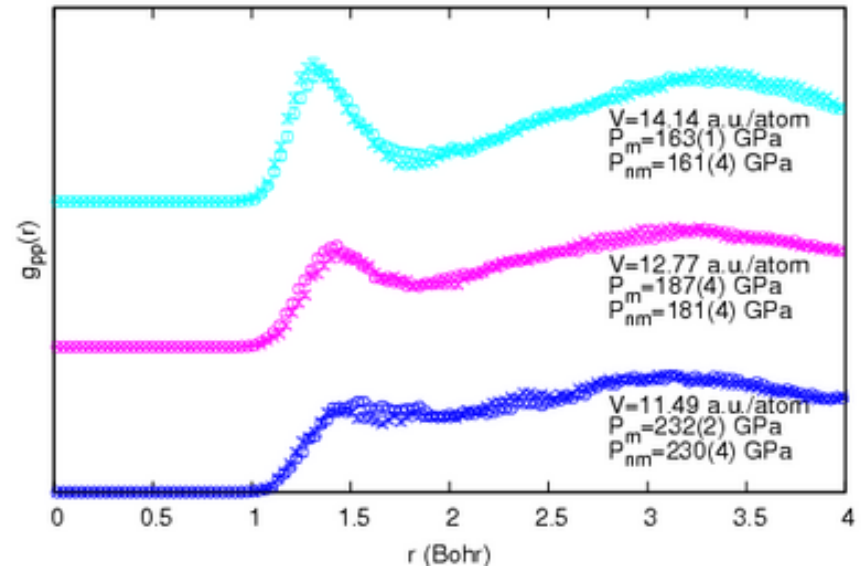
CEIMC (DMC energy) Simulations

- VMC: Hysteresis; probably 1st order transition.

- RQMC: No hysteresis; continuous transition.

- VMC trial function has difficulty with the mixed H_2-H state.
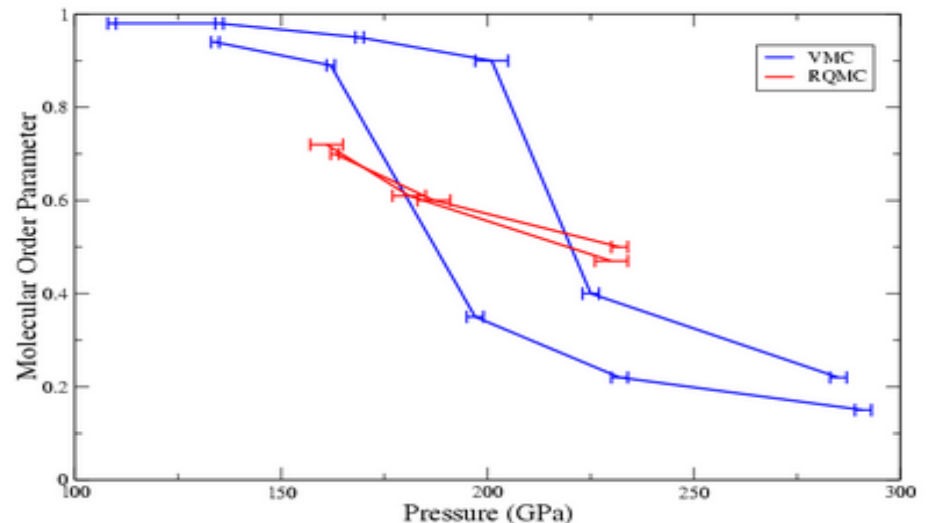
Collection of $g_{pp}(r)$s for T=2000K using RQMC

H$_2$ order parameter

$$g(r) = \lambda g_{mol}(r) + (1 - \lambda) g_{nonmol}(r)$$

Molecular to Non-molecular Fluid Phase Transition
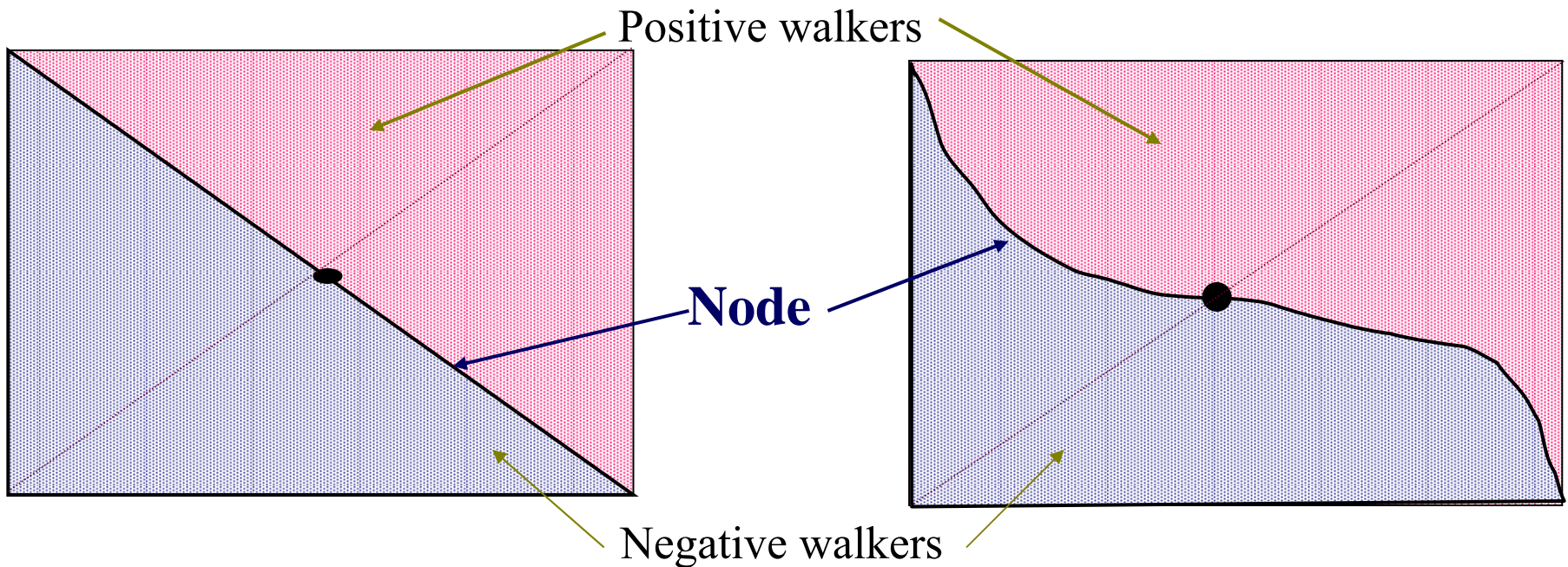
SIGN PROBLEM
Model: Particle in a box

Symmetric potential: $V(\mathbf{r}) = V(-\mathbf{r})$

Antisymmetric state: $\phi(\mathbf{r}) = -\phi(-\mathbf{r})$

Initial (trial) state

Final (exact) state

Positive walkers

Node

Negative walkers
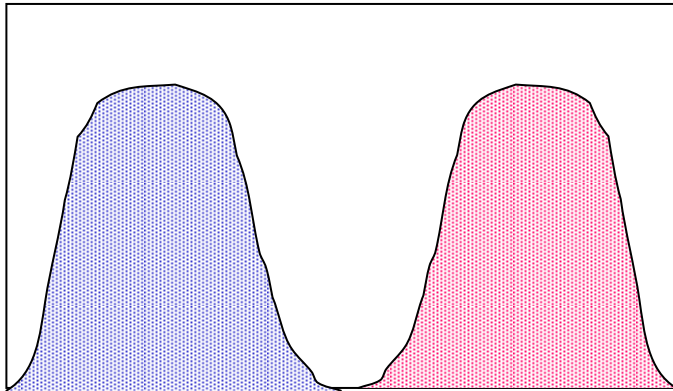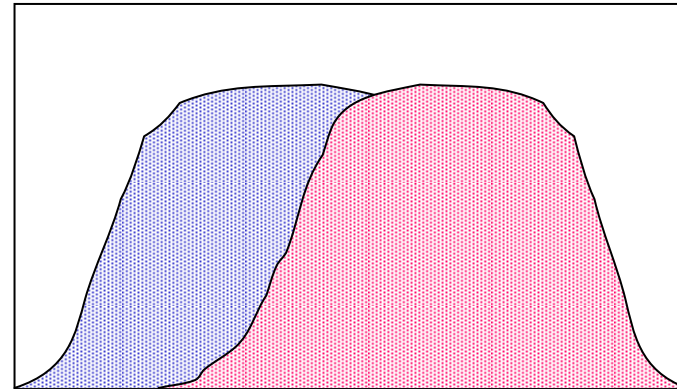
Sign of walkers fixed by initial position. They are allowed to diffuse freely. $\phi(r)$= number of positive-negative walkers. Node is dynamically established by diffusion process. (cancellation of positive and negative walkers.)

Scaling in Released-Node

Initial distribution

Later distribution

- At any point, positive and negative walkers will tend to cancel so the signal is overwhelmed by the fluctuations.

- Signal/noise ratio is : $e^{-t[E_F - E_B]}$ **t**=projection time

  E_F and E_B are Fermion, Bose energy (proportional to **N**)

- Converges but at a slower rate. Higher accuracy, larger **t**.

- For general excited states:

  Exponential complexity! $\text{CPUtime} \propto \varepsilon^{-2(1+\frac{E_F}{E_g})} \approx \varepsilon^{-2N\frac{e_F}{E_g}}$

- Not a fermion problem but an *excited state problem.*

General statement of the "fermion problem"

- Given a system with **N** fermions and a known Hamiltonian and a property **O** (usually the energy):
  - How much time **T** will it take to estimate **O** to an accuracy ε?
  - How does **T** scale with **N** and ε?
- If you can map the quantum system onto an equivalent problem in classical statistical mechanics then:

$$T \propto N^{\alpha} \varepsilon^{-2} \qquad \text{With } 0 < \alpha < 3$$

This would be a "solved" quantum problem!

•All approximations must be controlled!

•Algebraic scaling in N!

e.g. properties of Boltzmann or Bose systems in equilibrium.

Can we solve the problem of continuum electrons in the presence of ions?

SUMMARY

- No existing fermion methods are perfect but QMC today is competitive with other methods and usually much more accurate.
- Progress in "ab initio" simulations in last 40 years, coming from both
  - Computer power
  - Algorithmic power
- We are now in position to do much more accurate simulation of hydrogen, helium,…
- This is a great problem to solve. Intellectually **and** technologically very important. More work needed in algorithms to get higher accuracy, treat larger systems, heavier elements allowing:
  - benchmarking to validate cheaper approaches
  - replace more approximate approaches.