1929-4

Advanced School on Quantum Monte Carlo Methods in Physics and Chemistry

21 January - 1 February, 2008

PIMC 3 Fermions.

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Fermion Path Integrals

1. Direct Fermion Path Integrals: *"the sign problem"*

2. Restricted Path Integrals
    A. Restricted Path Identity
    B. Para/ortho hydrogen example
    C. The reference point
    D. Free particle nodes
    E. Nodal Action
    F. Momentum distribution
    G. Superfluidity

3. Hot Dense Hydrogen
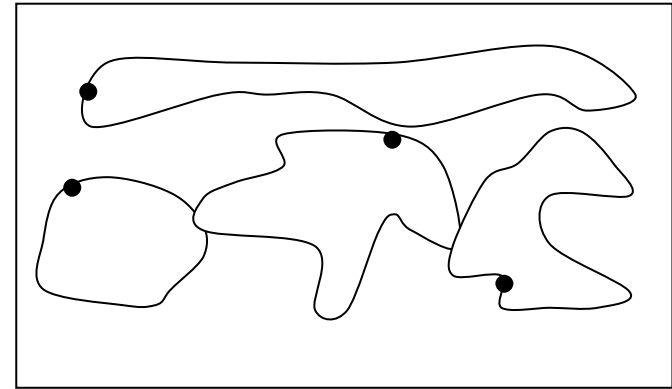
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"Direct" Fermion Path Integrals

- Path integrals map quantum mechanics into a system of cross-linking closed "polymers."

4 quantum paths

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

$R_0 = PR_M$, **P** permutation,

$S(R_i, R_{i+1})$ is "boltzmannon action"

- Bosons are easy: simply sample **P**.
- Fermions: sample the "action" and carry **$(-1)^P$** as a weight.
- Observable is **even P - odd P**. scales exponentially in N and T^{-1}!

$$\text{CPUtime} \quad \propto \varepsilon^{-2} e^{2N[F_F - F_B]/k_B T}$$

Importance Sampling

Given the integral
$$I = \int dx f(x)$$

How should we sample x to maximize the efficiency?

Estimator

Transform the integral to:
$$I = \int dx\, p(x) \left[\frac{f(x)}{p(x)} \right] = \left\langle \left[\frac{f(x)}{p(x)} \right] \right\rangle_p$$

The variance is:
$$\upsilon = \left\langle \left[\frac{f(x)}{p(x)} - I \right]^2 \right\rangle_p = \int dx \frac{f(x)^2}{p(x)} - I^2$$

Optimal sampling: $\dfrac{\delta \upsilon}{\delta p(x)} = 0$ with constraints

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Parameterize as:

$$p(x) = \frac{q^2(x)}{\int dx \, q^2(x)}$$

Solution:

$$p^*(x) = \frac{\left| f(x) \right|}{\int dx \left| f(x) \right|}$$

Estimator:

$$f(x) / p^*(x) = \frac{sign(f(x))}{\int dx \left| f(x) \right|}$$

If f(x) is entirely positive or negative, estimator is constant. "zero variance principle."

We can't sample $p^*(x)$, but its form can guide us.

Importance sampling is a general technique: it works in many dimensions.

Fermion variance

- Compute a fermion observable by sampling the boson probability and taking the sign as a weight

$$\langle O \rangle_F = \frac{\langle \sigma(P)O(R) \rangle_B}{\langle \sigma(P) \rangle_B} \quad \sigma(P) = (-1)^P$$

- The variance of O for this choice can be separated into a bosonic and fermionic contribution.

$$\upsilon_F(O) = \upsilon_B(O) \left[\frac{Z_B}{Z_F} \right]^2$$

- The fermion efficiency is

$$\xi = \left[\frac{Z_F}{Z_B} \right]^2 = \left[\frac{M_+ - M_-}{M} \right]^2 = e^{-2\beta N(\mu_F - \mu_B)}$$

- Big problem once N becomes large OR temperature becomes low-precisely when fermi statistics matter.

The Sign Problem

The expression for Fermi particles, such as He^3, is also easily written down. However, in the case of liquid He^3, the effect of the potential is very hard to evaluate quantitatively in an accurate manner. The reason for this is that the contribution of a cycle to the sum over permutations is either positive or negative depending on whether the cycle has an odd or even number of atoms in its length L. At very low temperature, the contributions of cycles such as L=51 and L=52 are very nearly equal but opposite in sign, and therefore they very nearly cancel. It is necessary to compute the difference between such terms, and this requires very careful calculation of each term separately. It is very difficult to sum an alternating series of large terms which are decreasing slowly in magnitude when a precise analytic formula for each term is not available. Progress could be made in this problem if it were possible to arrange the mathematics describing a Fermi system in a way that corresponds to a sum of positive terms. Some such schemes have been tried, but the resulting terms appear to be much too hard to evaluate even qualitatively.

The (explanation) of the superconducting state was first answered in a convincing way by Bardeen, Cooper, and Schrieffer. The path integral approach played no part in their analysis, and in fact has never proved useful for degenerate Fermi systems.

Feynman and Hibbs,1965.

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"Solved" Quantum Problems

- 1-D problems. (simply forbid exchanges)
- Bosons and Boltzmanons at any temperature
- Some lattice models: Heisenberg model, 1/2 filled Hubbard model on bipartite lattice (Hirsch) with high symmetry.
- Spin symmetric systems with purely attractive interactions: u<0 Hubbard model, some nuclear models.
- Harmonic oscillators or systems with many symmetries.
- <i|H|j> non-positive in some representation.
- Fermions in special boxes (Kalos)

UNSOLVED:

- *Quantum dynamics*
- *Fermions*
- *Bosons in special ensembles or with magnetic fields.*

To get around the sign problem, why not just use the fixed-node method?

What nodes? The ground state nodes are not necessarily the correct ones at T>>0.

The nodes of the density matrix have an imaginary time dependence.

$$\rho_F\left(R, R_0; t\right) = 0 \quad \text{with} \quad R_0, t \quad \text{fixed.}$$

High temperature

Low temperature
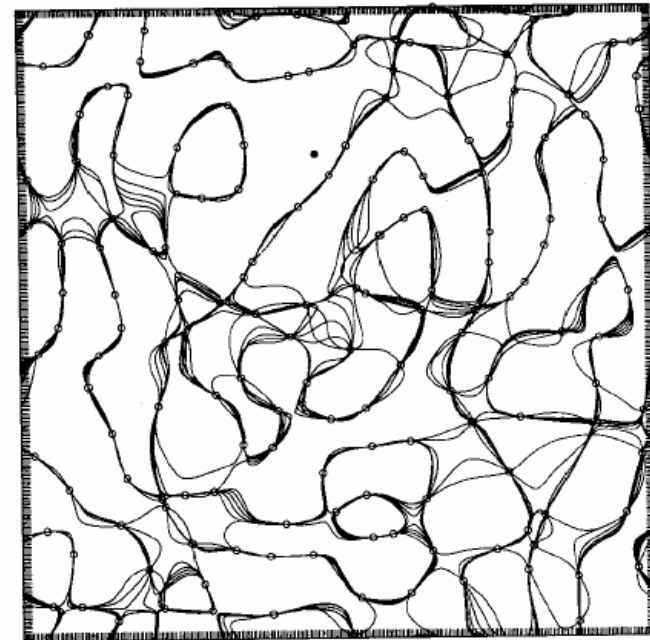
Fixed-Node method with PIMC

- 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.

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

- Classical correspondence 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 classical world we don't know V(R).)

Proof of the fixed node method

1. The density matrix satisfies the Bloch equation with initial conditions.

$$\frac{\partial \rho(R,t)}{\partial t} = \lambda \nabla^2 \rho(R,t) - V(R)\rho(R,t) \quad \rho(R,0) = \frac{1}{N!}\sum_P (-1)^P \delta(R - PR_0)$$

2. One can use more general boundary conditions, not only initial conditions, because solution at the interior is uniquely determined by the exterior-just like the equivalent electrostatic problem.

3. Suppose someone told us the surfaces where the density matrix vanishes (the nodes). Use them as boundary conditions.

4. Putting an infinite repulsive potential at the barrier will enforce the boundary condition.

5. Returning to PI's, any walk trying to cross the nodes will be killed.

6. This means that we just restrict path integrals to stay in one region.

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β

neg   pos   neg

R_0 PR_0

R

10
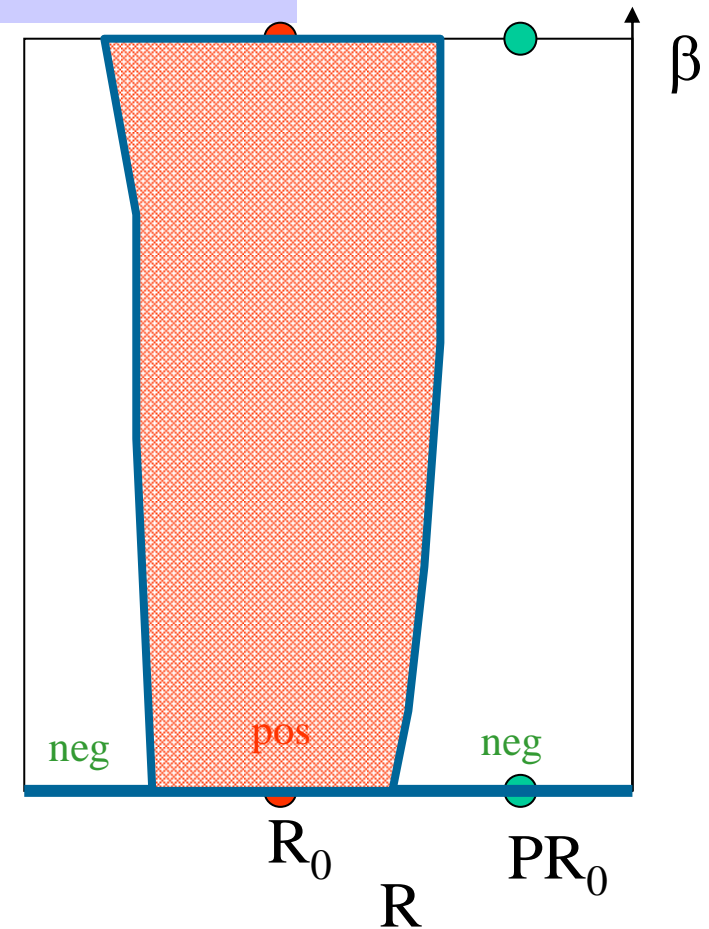
Ortho-para H_2 example

In many-body systems it is hard to visualize statistics.

- The simplest example of the effect of statistics is the H_2 molecule in electronic ground state.

- Protons are fermions-must be antisymmetric.

1. Spins symmetric ($\uparrow\uparrow$). spatial wf antisymmetric (ortho)   "fermions"
2. Spins antisymmetric ($\downarrow\uparrow$- $\uparrow\downarrow$). spatial wf symmetic (para) "bosons"
3. Non symmetrical case (HD)   "boltzmannons"

All 3 cases appear in nature!

- Go to relative coordinates: $r= r_1$-r_2

- Assume the bond length is fixed $|r|=a$. Paths are on surface of sphere of radius a.

PIMC task is to integrate over such paths with given symmetries.

For a single molecule there is no potential term, a "ring polymer" trapped on the surface of a sphere.

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Paths on a sphere

1. "boltzmannons" Ring polymers on sphere
   $O(r \to r)$
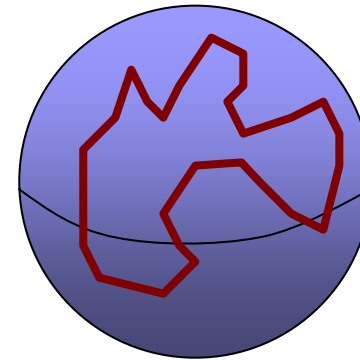
2. "bosons" 2 types of paths allowed.
   $O(r \to r) + O(r \to -r)$
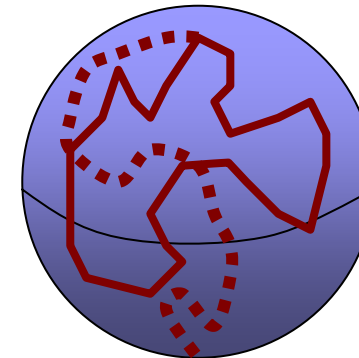
3. "fermions" 2 types of paths allowed
 $O(r \to r) - O(r \to -r)$
   Low efficiency as $\beta \to \infty$

$$\zeta = e^{-\beta(E_1 - E_0)}$$

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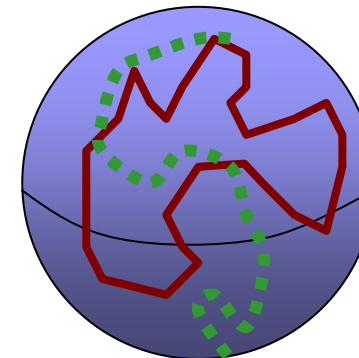
Restricted paths for ortho H_2

- Fix origin of path: the <u>reference point</u>.
- Only allow points on path with a positive density matrix. paths staying in the northern hemisphere: $r(t) \cdot r(0) > 0$
- Clearly negative paths are thrown out.
- They have cancelled against positive paths which went south and then came back north to close.
- The symmetrical rule in "t": $r(t) \cdot r(t') > 0$ is incorrect.
- Spherical symmetry is restored by averaging over the reference point: the north pole can be anywhere.
- Can do many H_2 the same way.
- Ortho H_2 is much more orientable than either HD or para H_2.
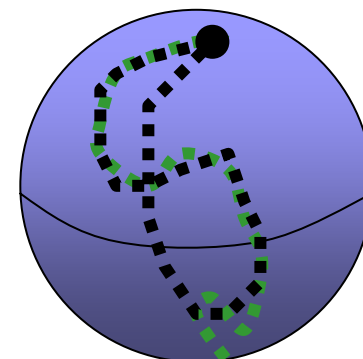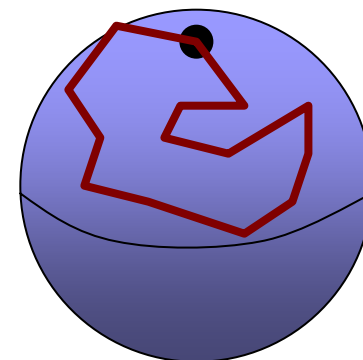
Nodal Properties

If we know the sign of the exact density matrix(the nodes), we can solve the fermion problem with the fixed-node method.

- If $\phi(R)$ is real, nodes are $\phi(R)=0$ where **R** is the **3N** dimensional vector.

- Nodes are a **3N-1** dimensional surface. (Do not confuse with single particle orbital nodes!)

- Coincidence points $\mathbf{r}_i = \mathbf{r}_j$ are **3N-3** dimensional hyper-planes

- In **1** spatial dimension these "points" exhaust the nodes. *fermion problem is easy to solve in 1D* with the "no crossing rule."

- Coincidence points (and other symmetries) only constrain nodes in higher dimensions, they do not determine them.

- The nodal surfaces define nodal volumes. How many nodal volumes are there? **Conjecture**: there are typically *only* 2 different volumes (+ and -) except in 1D. (but only demonstrated for free particles.)

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Reference Point

- Scalar averages can only be taken at the reference point. New feature compared with boson path integrals.

- Except partition function and all derivatives (energy) use information from the whole path.

- We lose time slice symmetry if nodes are time dependent. But this is probably necessary to fix phase of density matrix.

- Reference point moves are expensive and ultimately cause RPIMC to get "stuck" for $T<E_F/10$.

- One can use a 2 reference points. This restores time-reversal symmetry and means we only need nodes for $t<\beta/2$.

- More than 2 reference points brings back the "sign" problem.
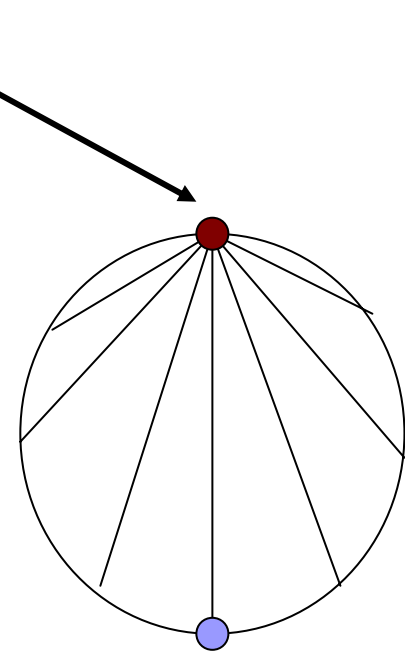
RPIMC with approximate nodes

- In almost all cases, we do not know the "nodal" surfaces.
- We must make an an ansatz.
- This means we get a fermion density matrix (function with the right symmetry) which satisfies the Bloch equation at all points except at the node.
- That is, it has all the exact "bosonic" correlation
- There will be a derivative mismatch across the nodal surface unless nodes are correct.
- In many cases, there is a free energy bound. (proved at high temperature and at zero temperature and when energy is always lower.)
- Maybe one can find the best nodes using the variational principle. (variational density matrix approach)

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.

$$g\left(r',r;t\right) = \left(4\pi\lambda\tau\right)^{-3/2} e^{-\frac{(r-r')^2}{4\lambda\tau}} + \text{periodic images}$$

At high T, nodes are hyperplanes.

At low T, nodes minimize the kinetic energy.

$\Rightarrow$Nodes have "time dependence".

- Problems: no spin-coupling in nodes, no formation of electronic bound states.
- Militzer-Pollock chose g(r,r′; t) with Hartree eqs. (VDM or variational density matrix)

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Nodal action

- "Primitive Rule:" simply reject paths if they cross a node.
- Will lead to an error proportional to $\sqrt{\lambda\tau}/r_{nn}$
- Improved nodal action: solve for a particle next to a planar node. Use method familiar from electrostatics, the method of images:

$$\rho(r',r;t)=e^{-\frac{(r-r')^2}{4\lambda\tau}} - e^{-\frac{(r-r^*)^2}{4\lambda\tau}} \qquad r^* = -r'$$
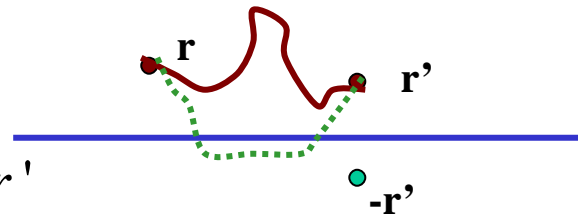
$$\delta S(r',r;t) = -\ln\left(1 - e^{-\frac{dd'}{\lambda\tau}}\right) \qquad \text{d=distance to node} \approx \left|\nabla\ln\left(\rho(R,R';\tau)\right)\right|^{-1}$$

- Determine nodal distance using "Newton estimate."
- As paths approach within a thermal wavelength of the node, we get a repulsion, to account for the probability that a path could have crossed and recrossed within τ.

Practical fermion issues

- Bosonic methods are applicable! Fermion code is built on top of bosonic code.
- Add a "gate" in multilevel Metropolis where:
  - Sign of density matrix is checked
  - Nodal action is computed and used
- Reference point moves are expensive: all slices must be checked for nodal violations.
- Permutations are still needed! However, 2 particle exchanges will always be rejected. Only odd particle cyclic exchanges (3,5,...) allowed as updates.
- Determinantal updates
  - Full determinant evaluation takes N^3 operations
  - However row/column updates take only N^2.
- Use inverse of Slater matrix to compute derivative needed for the gradient in the nodal action.

Momentum distribution

- For bosons the momentum distribution shows evidence of BEC.
  - Long exchange cycles$\Rightarrow$n(r) long range $\Rightarrow$ n_0 >0
- What is effect for fermions? Run logic in reverse.
  - For NI fermions, n(k) has discontinuity at k_F.
  - Hence $\quad n(r) \propto \cos(k_F r)/\left(k_F r\right)^2$
  - We must have cancellation of long-range positive and negative exchanges!
  - Negative permutations allowed/required off-diagonal.
- Algorithm recently tested by Militzer: *cond-mat/0310401*
- Exchanges are needed to get a Fermi-liquid.
- Long exchanges do not lead to a phase transition or superfluidity.

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Electron Gas n(k)
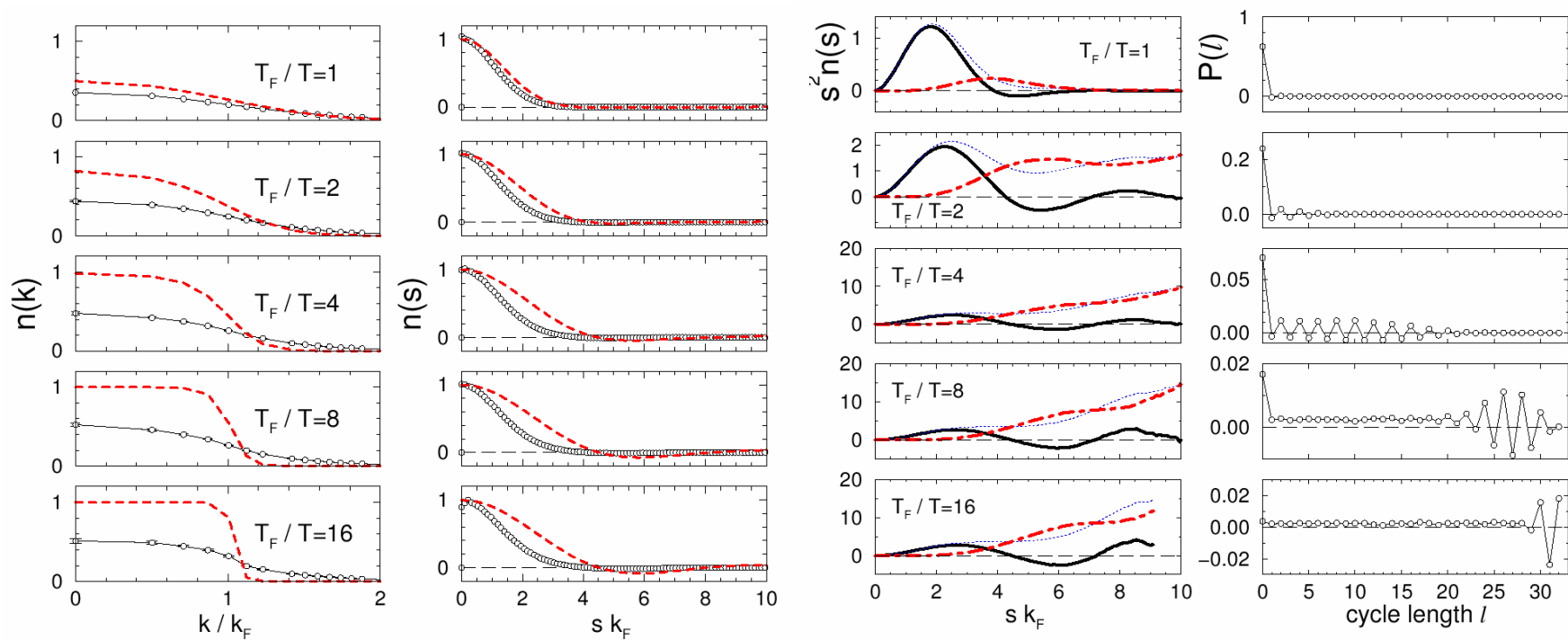
Fermion superfluidity

- Liquid ^{3}He becomes superfluid at very low temperatures ($T_c \sim 1mK$).
- With the exact nodal restriction this must also happen within RPIMC, because we can calculate the free energy.
- What happens to the paths at this phase transition?
- SPECULATION: there is a "Cooper" pairing of up and down spin exchanges, similar to a polymer blend
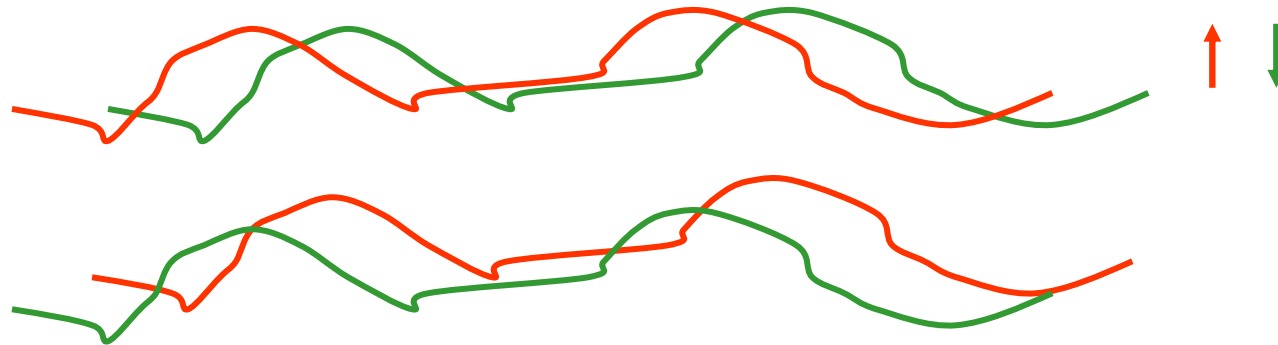
- Not tried in ^{3}He because of formidable practical difficulties (length, temperature scale) and lack of knowledge of nodal topology required.

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Exciton superfluidity

- What system is the most appropriate to observe superfluidity of fermions? (strongest pairing)
- Consider the simplest 1-band model of particles and holes in a semiconductor.
- Assume masses are isotropic and the same; only the charge is different.
- At low temperature a particle and hole can bind together to form an *exciton* (like a hydrogen atom) which is a boson.
- If the exciton density is high enough, they can bose condense.: $T\rho^{3/2} < 2.7$
- Shumway-Ceperley (1999) observed this transition for excitons.
- What do the paths look like?
- Observed in Oct 2003 in atom traps!

BCS region
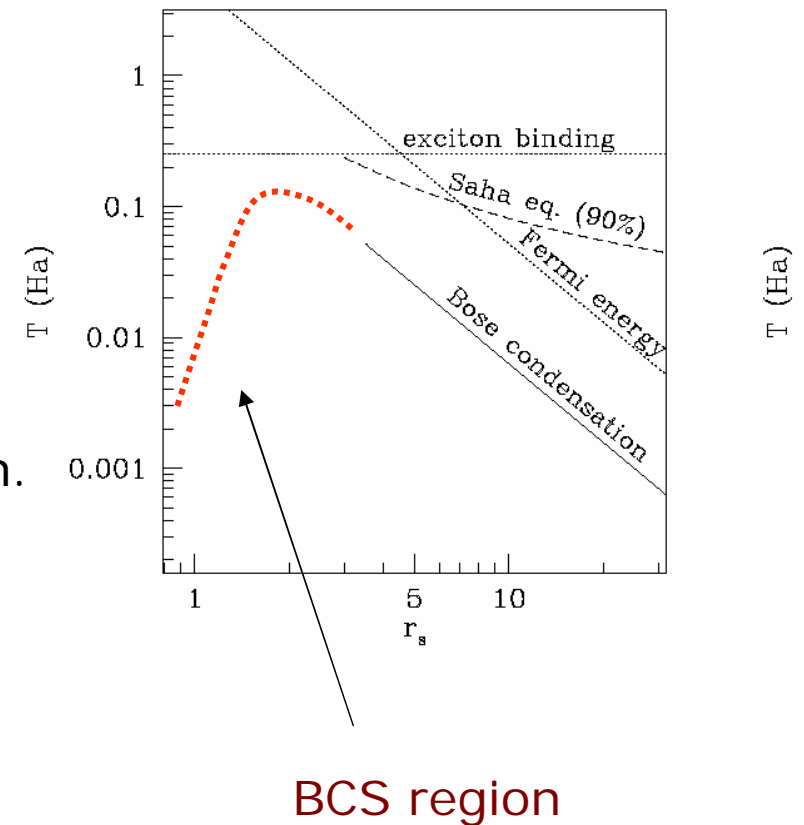
Pairing Nodes

- Free fermion nodes does not allow pairing because nodes of two species are independent.
    - Consider two pairs of fermions.
    - Possible exchanges are {I, $P_a P_b$} and {P_a, P_b}.
    - The permutation $P_a P_b$ represents an exciton exchange but it is forbidden if nodes are independent since the path will cross
      "a" nodes or "b" nodes first.
- Instead we used paired nodes: A{ $g(a_1-b_1)g(a_2-b_2)$.....} where g(r) is a pairing function (we used a Gaussian).
- Nodes are time-independent $\Rightarrow$ winding number formula for superfluid response.
- We can define 2 different responses. Let W_x be winding number of species x.
    - movement of walls: $<(W_a+W_b)^2>$
    - magnetic field: $<(W_a-W_b)^2>$

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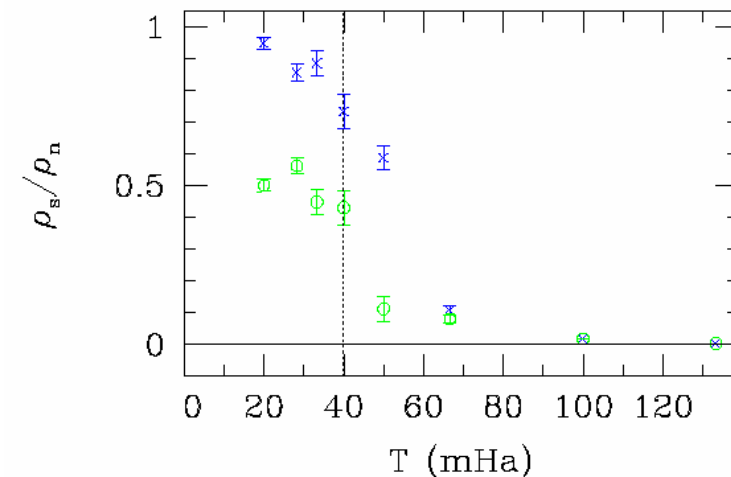
BEC of excitons   [$r_s=6$ $T<T_c$]
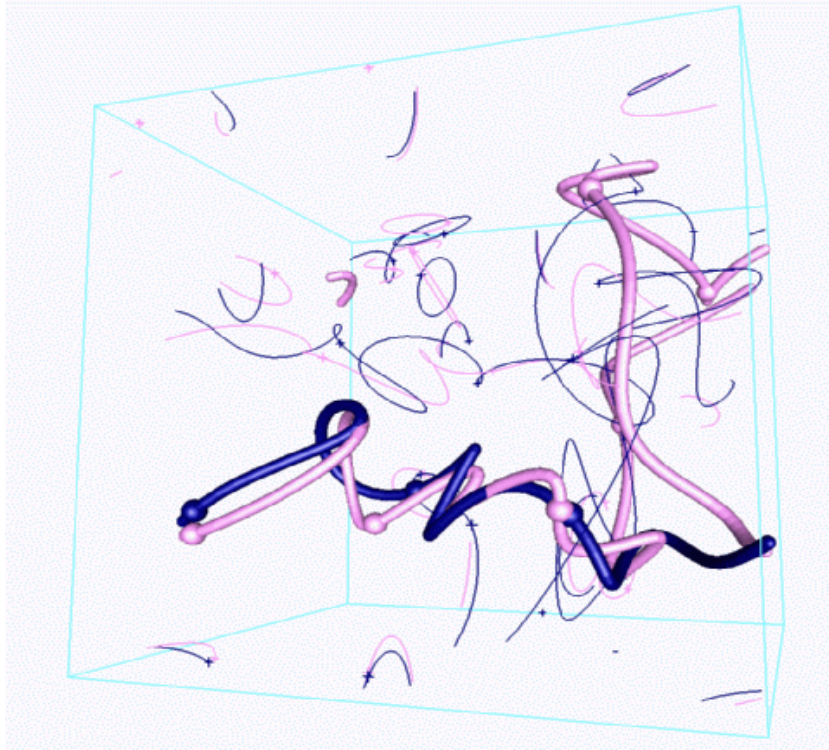
Winding exchange (3,6)
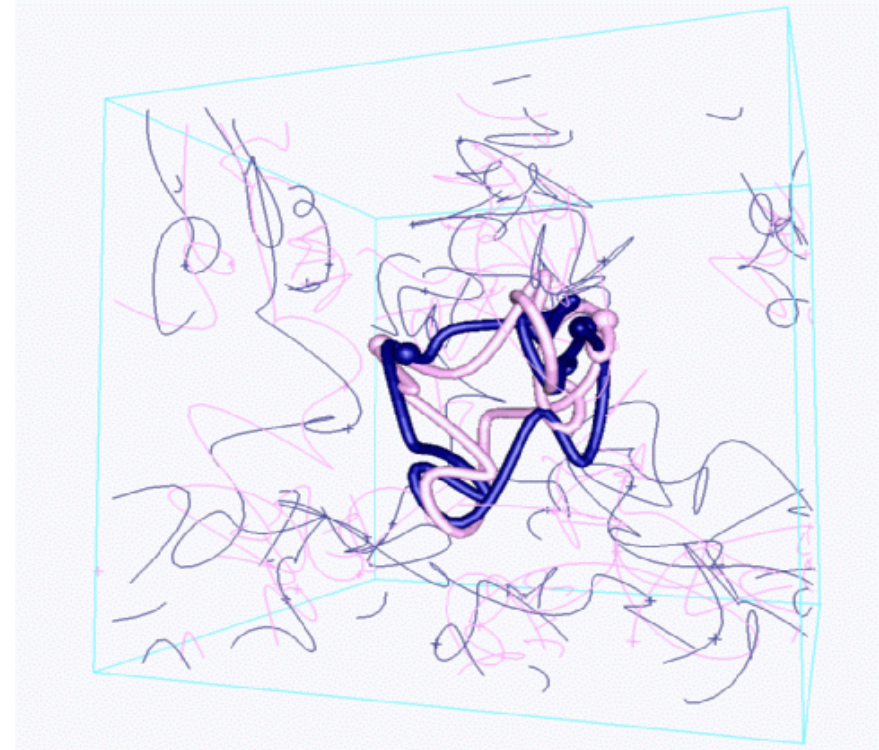
Pair exchange (2,2)

Blue=electron   lavendar=hole

Superconductivity is (cooper pairing) of paths.

Path Integral Applications

Bosons

- Superfluid ^{4}He
- Solid ^{4}He
- BEC in traps
- Superfluidity on surfaces (H$_2$ on silver)
- Helium droplets

- ....

Fermions

- Homogenous electrons/plasma
- High Temperature hydrogen/helium (interior of planets)
- Liquid/solid ^{3}He
- Electron-hole liquid
- BEC of fermions

- ....

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Hydrogen at high pressure:
a quantum soup made with path integrals

B. Militzer (LLNL)

D. Ceperley (UIUC)

W. Magro (Intel)

C. Pierleoni (Roma)

B. Bernu (Paris)
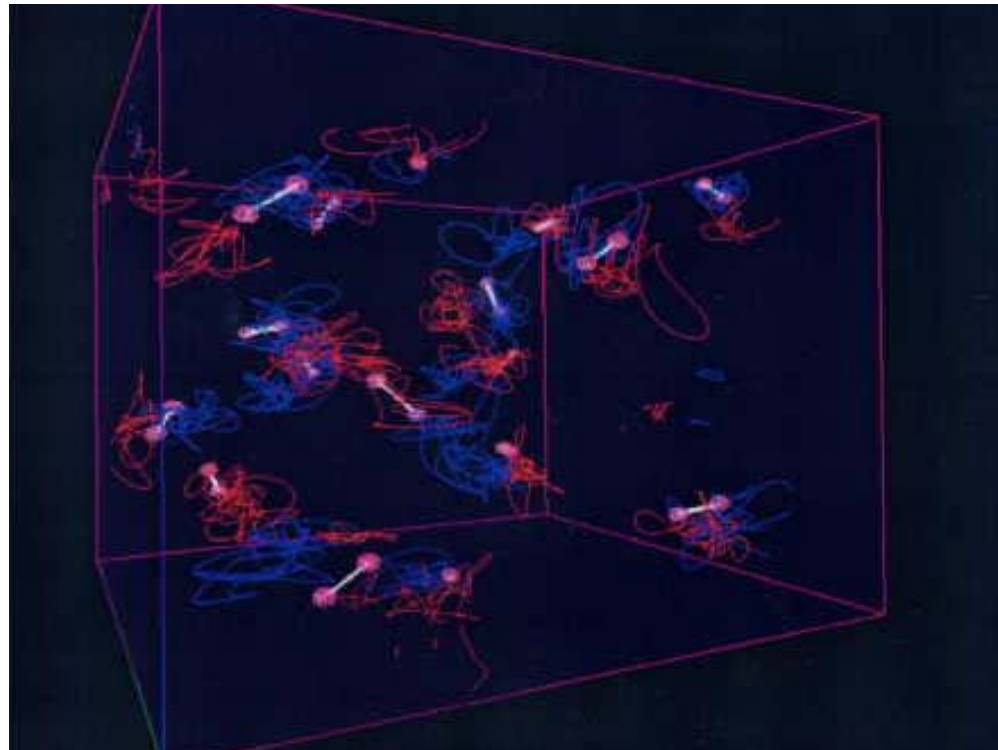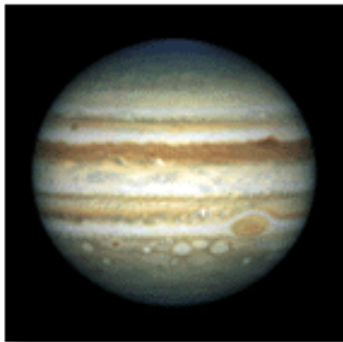
Hydrogen

- Hydrogen is the most abundant (important) element.
- What are properties of N e^- and N p^+?

$$H = -\sum_i \frac{\hbar^2}{2m_i}\nabla_i^2 + \sum_{i<j} \frac{e_i e_j}{r_{ij}}$$

- This should be the simplest problem for many body theory. Right?
- Many different physical regimes.
  - Molecular phase at low density
  - Metallic phase at high density or temperature
- At intermediate temperatures and densities everything comes in:
  - Protonic zero point effects
  - Bonding and bond breaking, ionization,
  - Various species (the soup)
  - Electron correlation

How can we treat this?

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Hot Dense Hydrogen

- How does hydrogen evolve from molecular to plasma state? Important for planetary interiors.

- Static experiments are limited to low P and T.

- Traditional EOS methods maybe unreliable in the intermediate regime.

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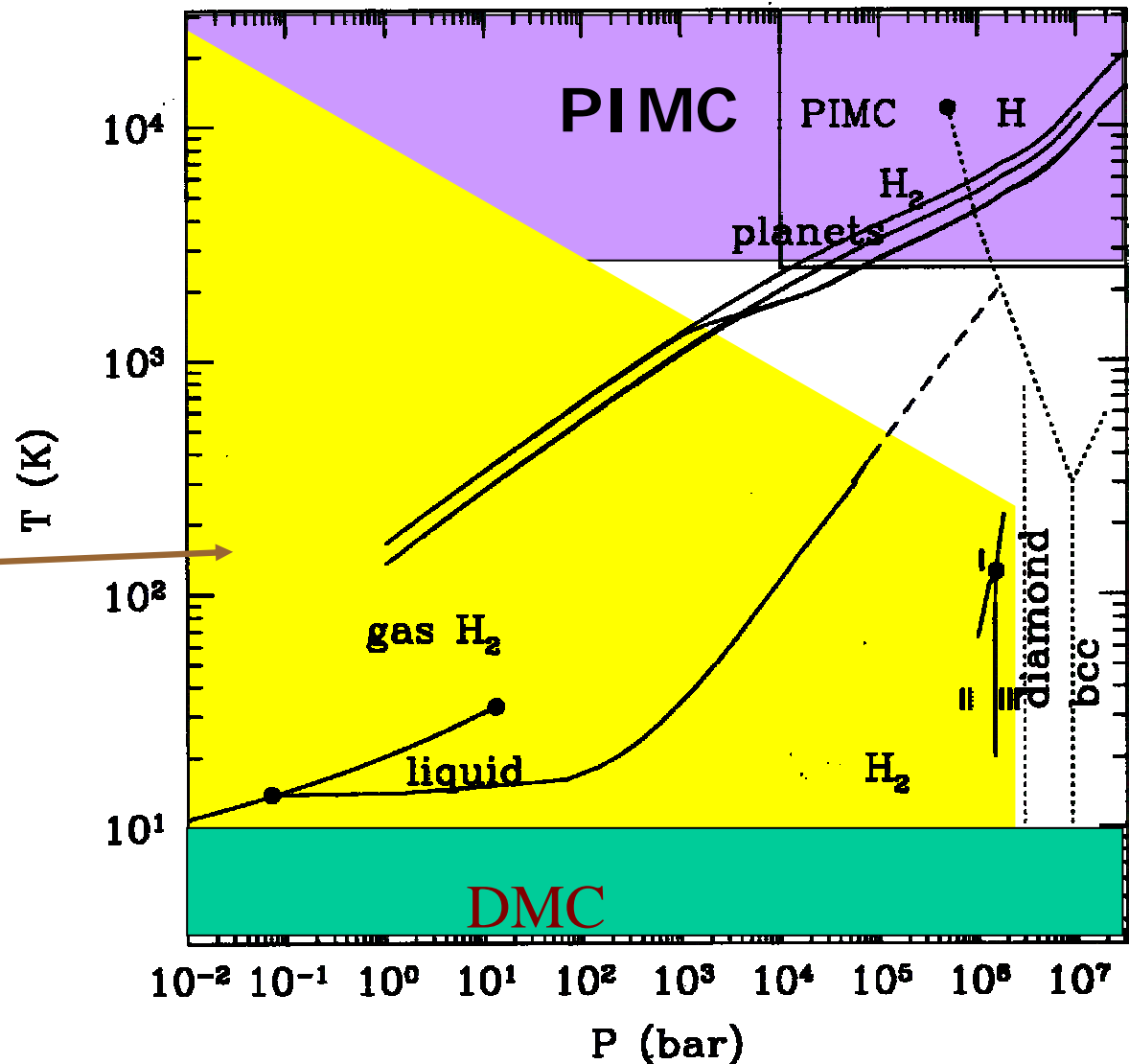
Variational Density Matrix

- Approximate density matrix by a determinant of single particle Gaussians.
- Follow evolution of center and width in imaginary time using a variational ansatz.
- Introduces electron-proton coupling in density matrix.
- Exact at high temperature.
- Goes to SCF at zero temperature.
- *Only used for restriction not for the action.*

H atom example

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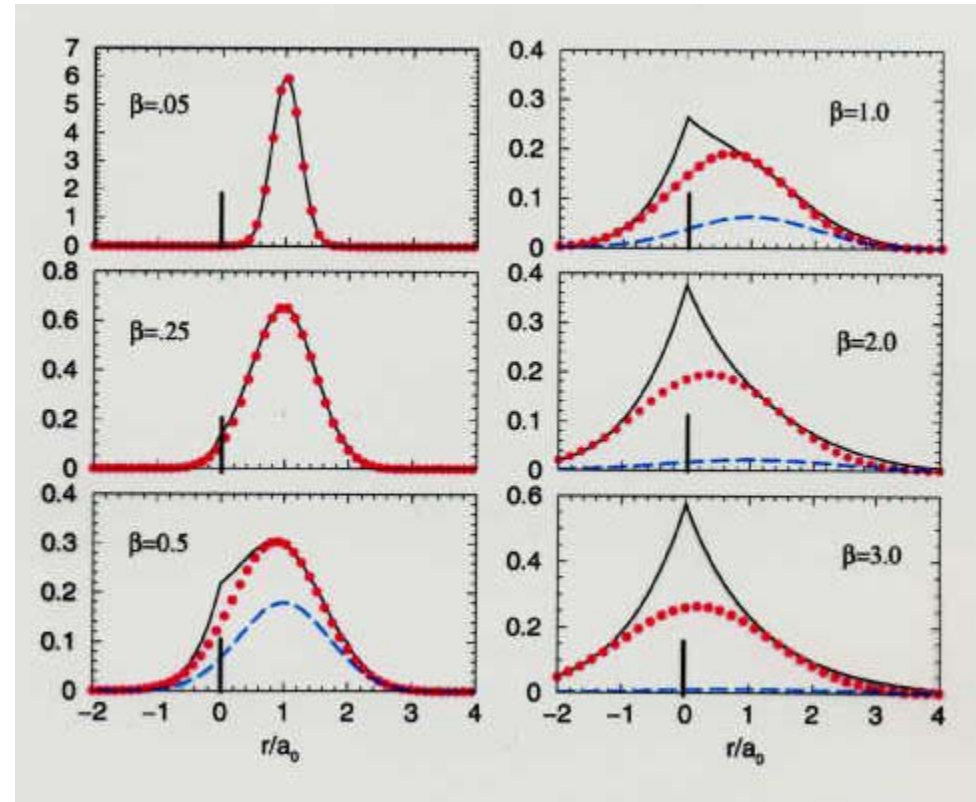
Properties of hot dense hydrogen

- How does hydrogen evolve from molecular to plasma state?
- Traditional EOS methods are unreliable in the intermediate transition regime.
- Large effort experimentally (shock experiments) and theoretically (EOS tables).

With PIMC

- No assumption of atoms or molecules, just Coulomb potential, and correct masses (no Born Oppenheimer approximation).
- Periodic boundary conditions, Ewald images for charges.
- Path integral calculations possible for systems of 100 atoms- but at edge of current feasibility for temperatures lower than 1 eV (10,000K).

$$r_s = a \,/\, a_0 \qquad 4\pi a^3 \rho_e \,/\, 3 = 1$$

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Visualization of hydrogenic PIMC
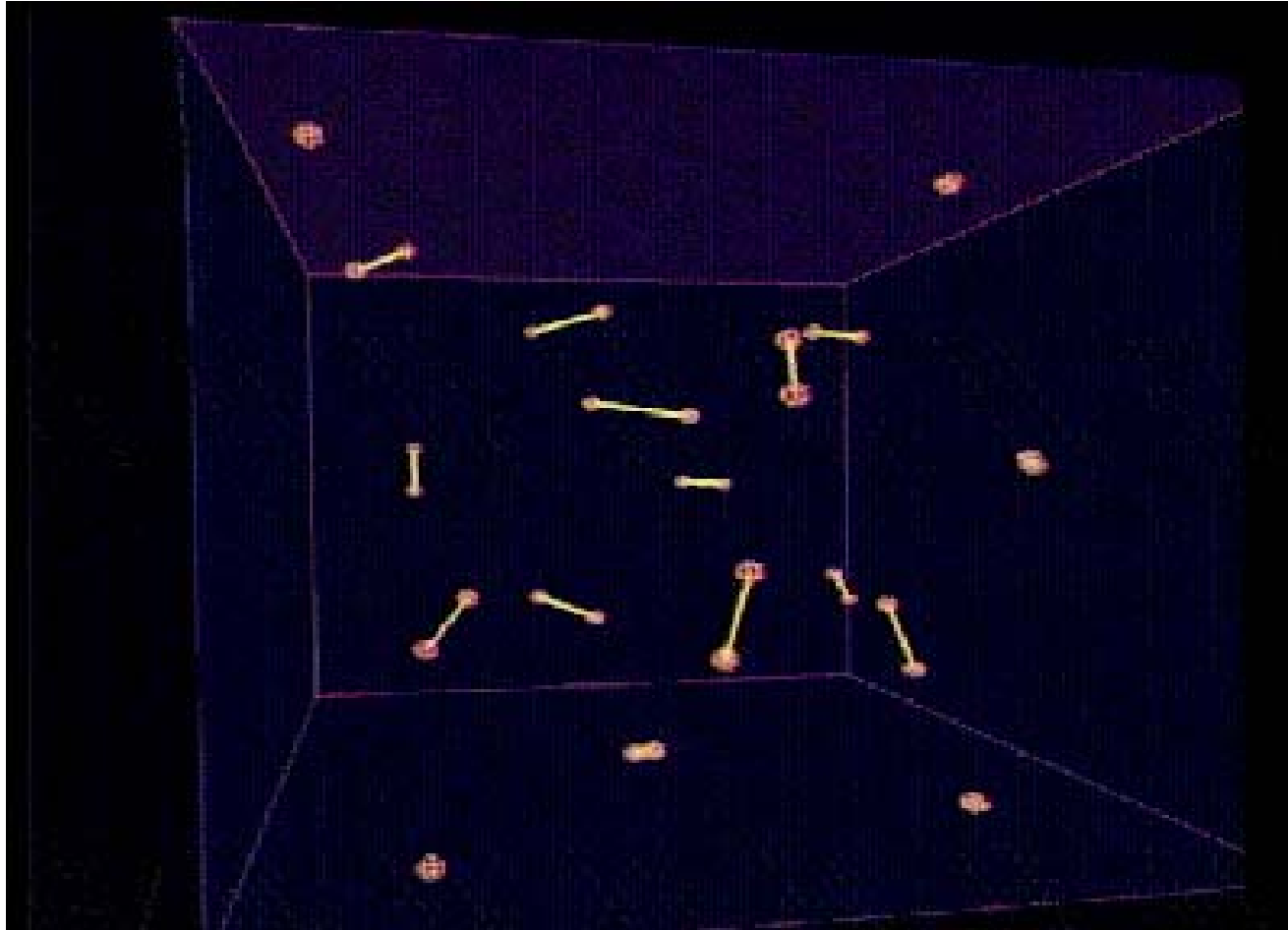
Programmed in the CAVE (a (4m)^3 projection screen)
by Burkhard Militzer and Rachel Brady.

Low Density Molecular Fluid

Hydrogen

T=5000K

$r_s=4.0$
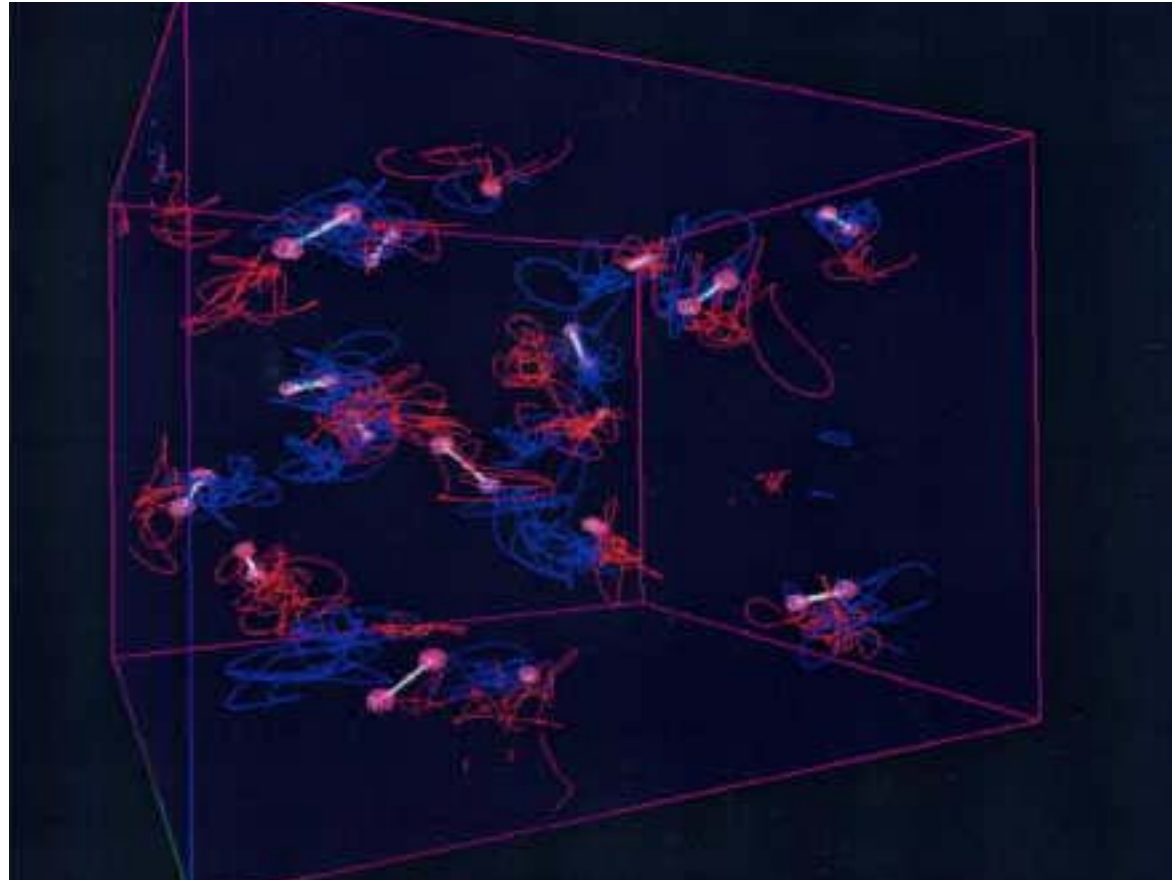
Molecular Metallic liquid

Deuterium

T=5000K

r_s=1.86
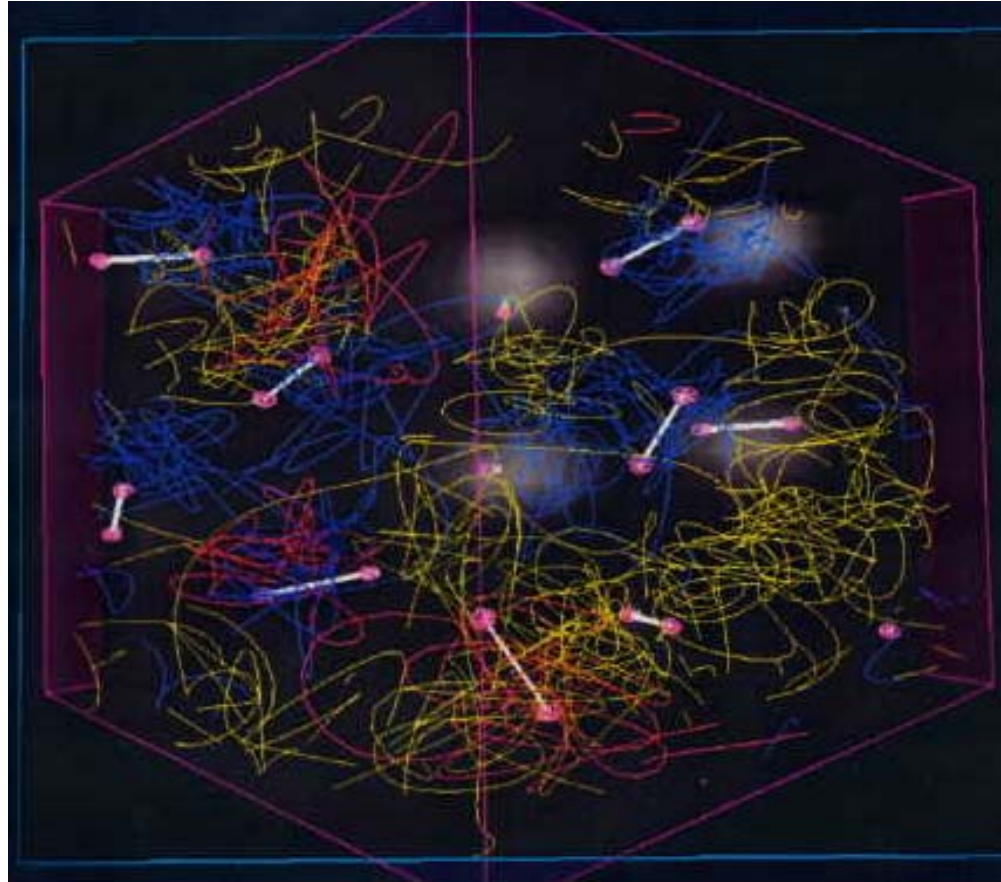
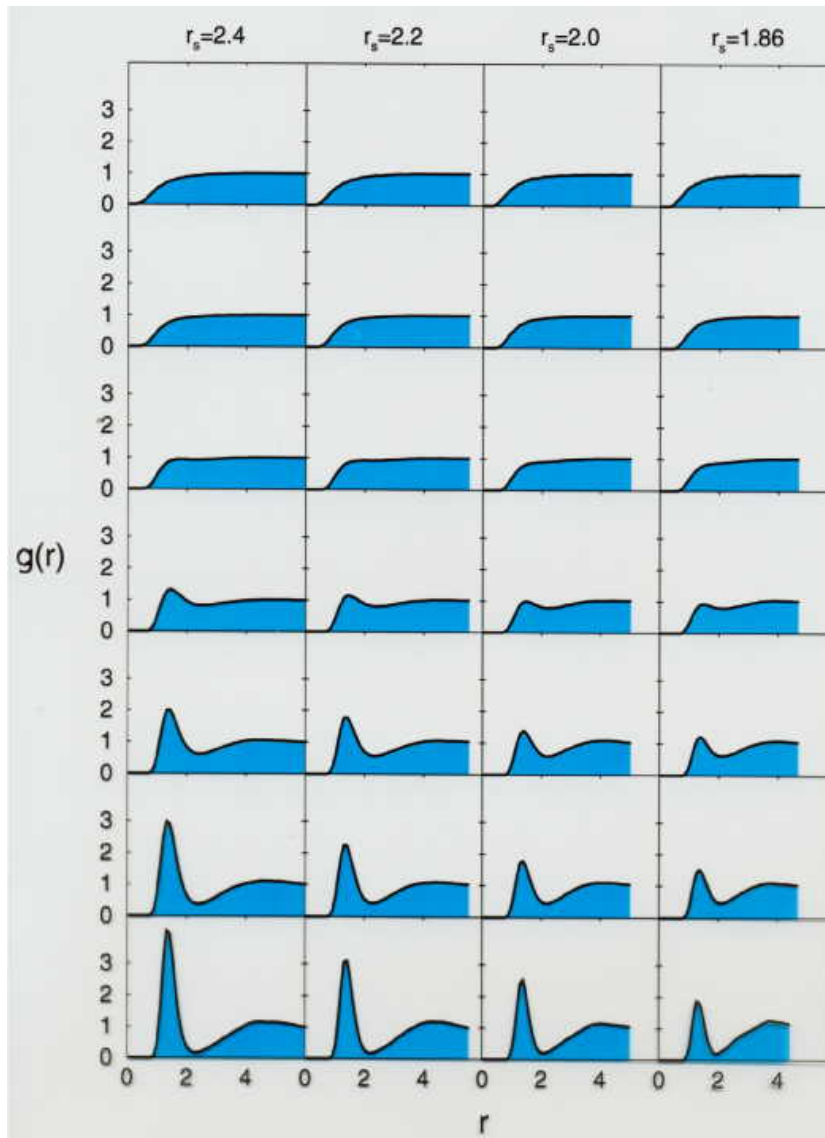# Ionized Fermi Liquid

Deuterium

T=6250K

r_s=1.60
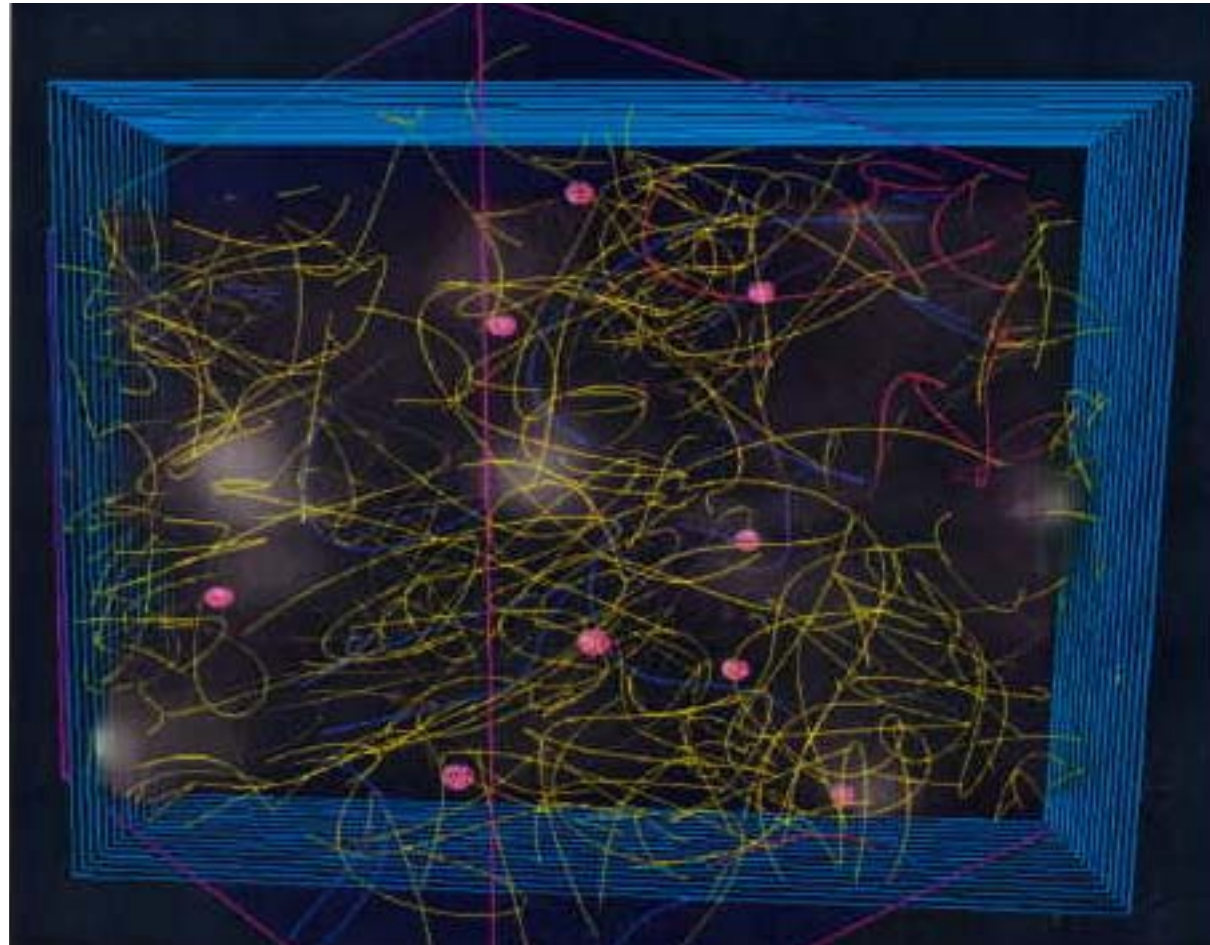
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Characterization of state
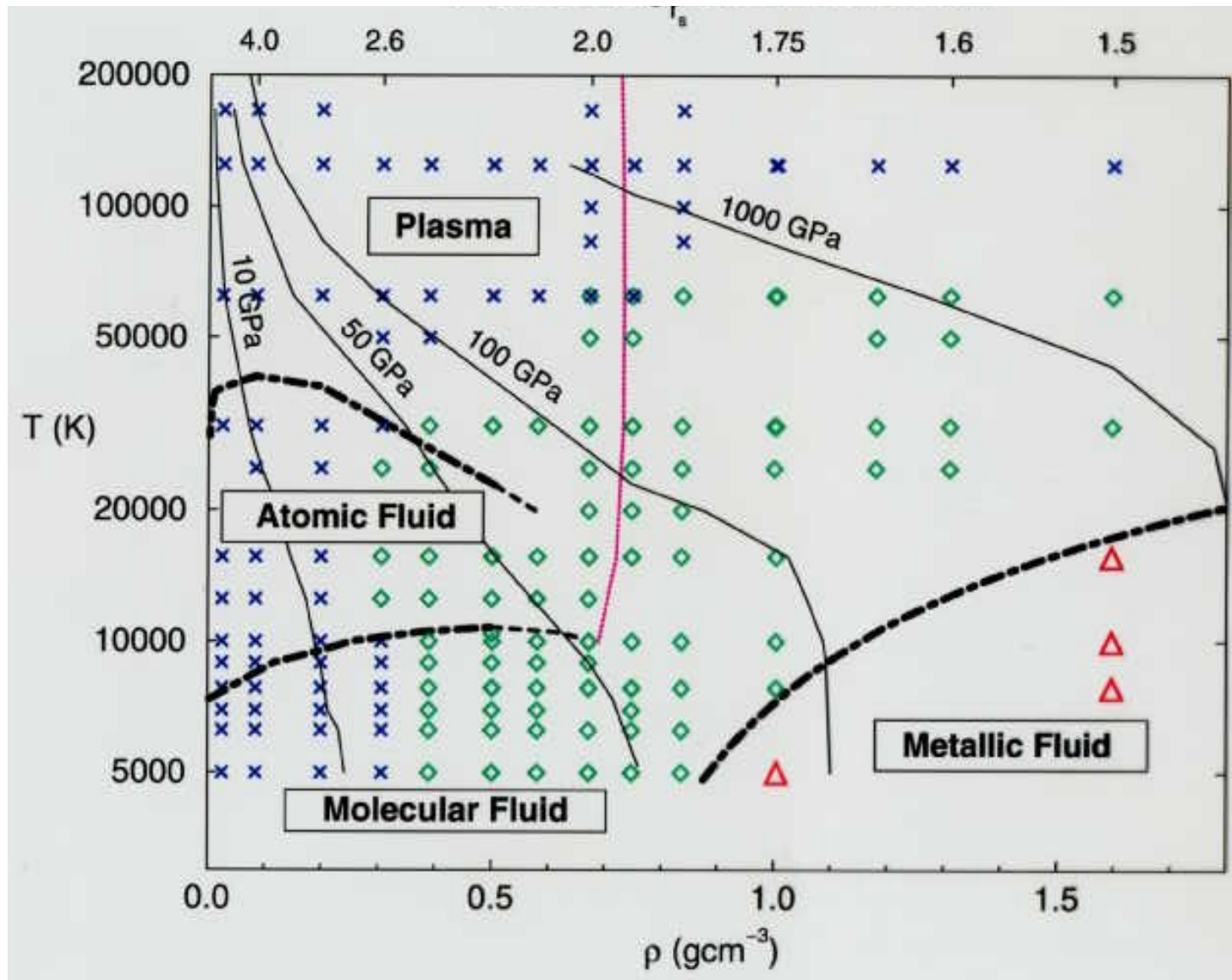
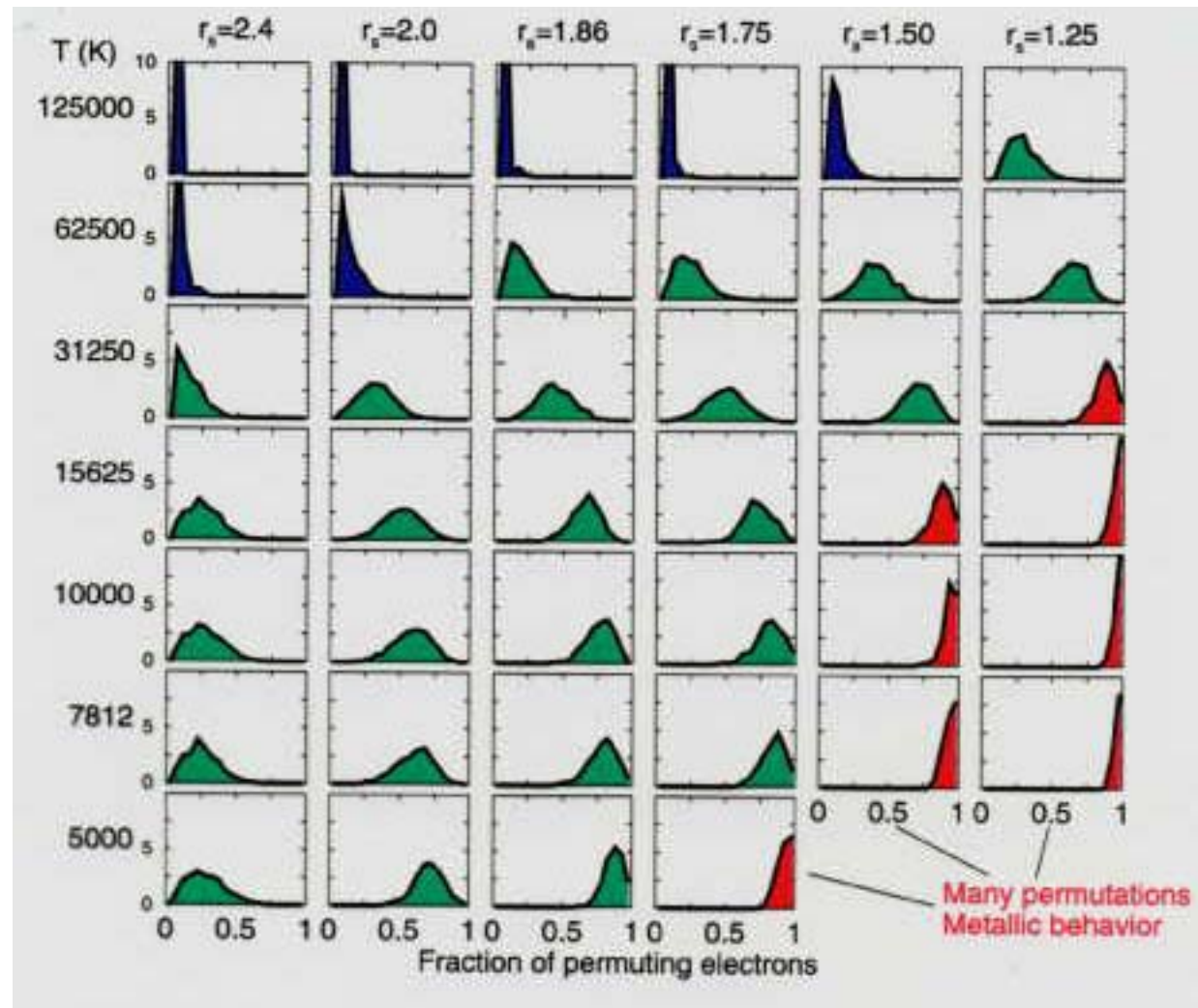# Proton-proton correlation

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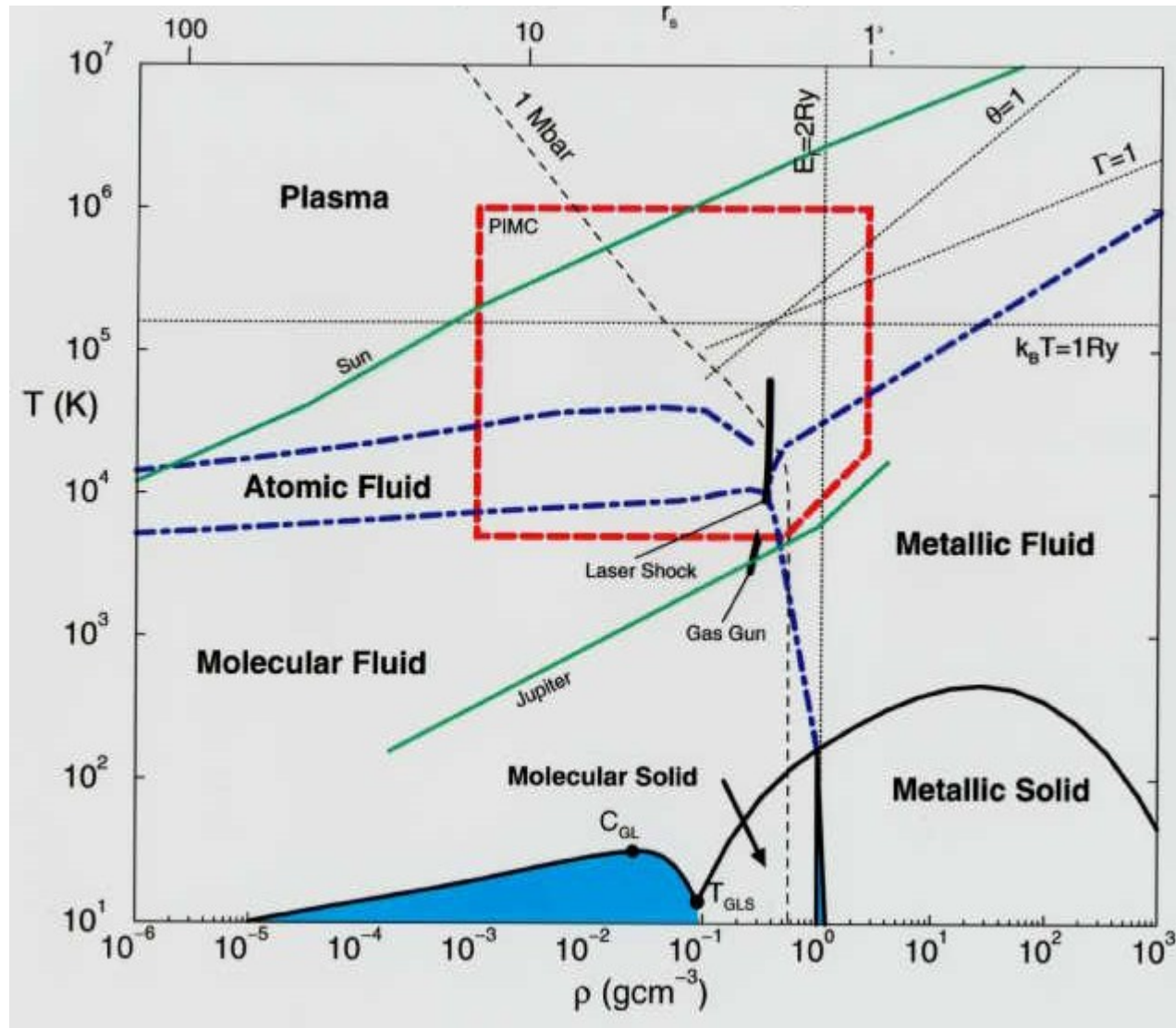
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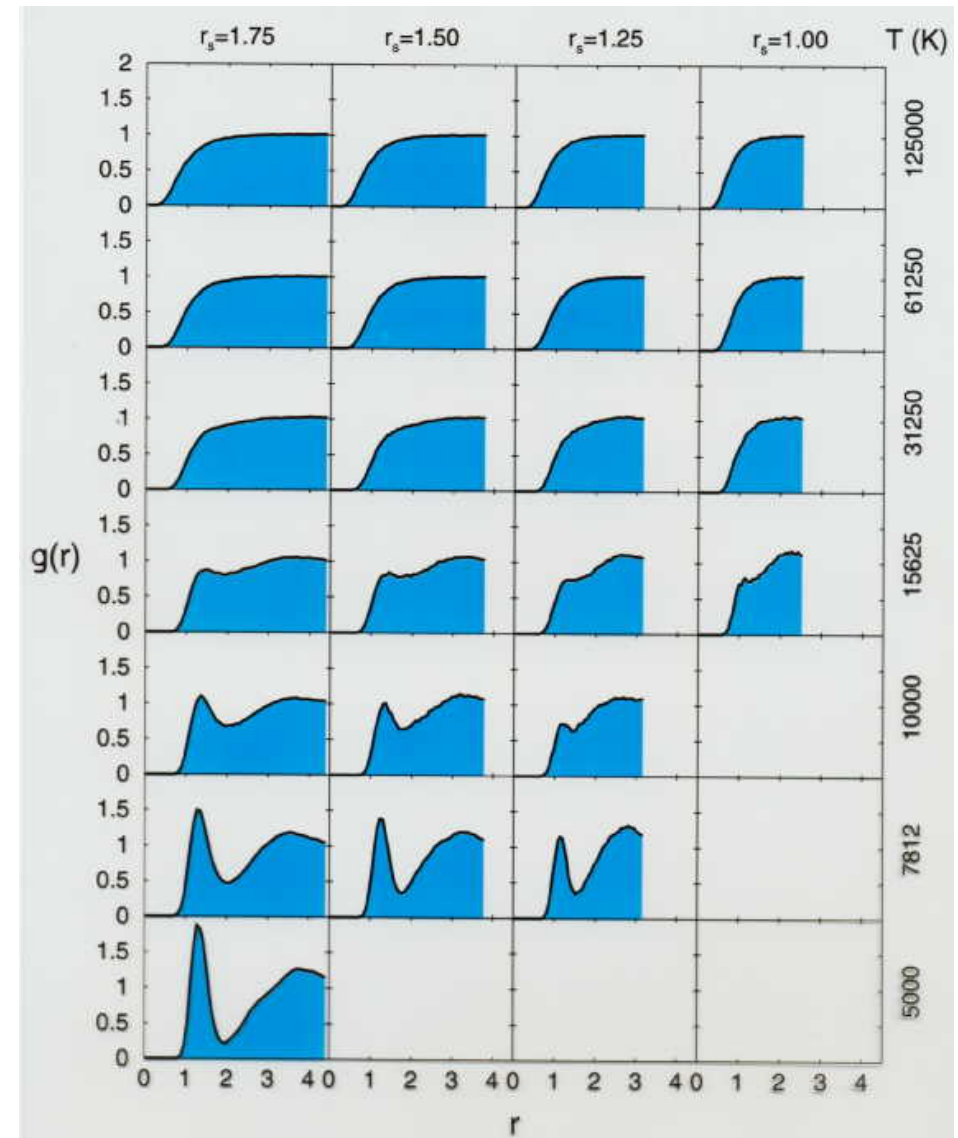
Electron exchange probability

- Nodes from optimized gaussians

- Blue represent classical electrons

- Red are metallic electrons (large exchanges imply fermi surface)
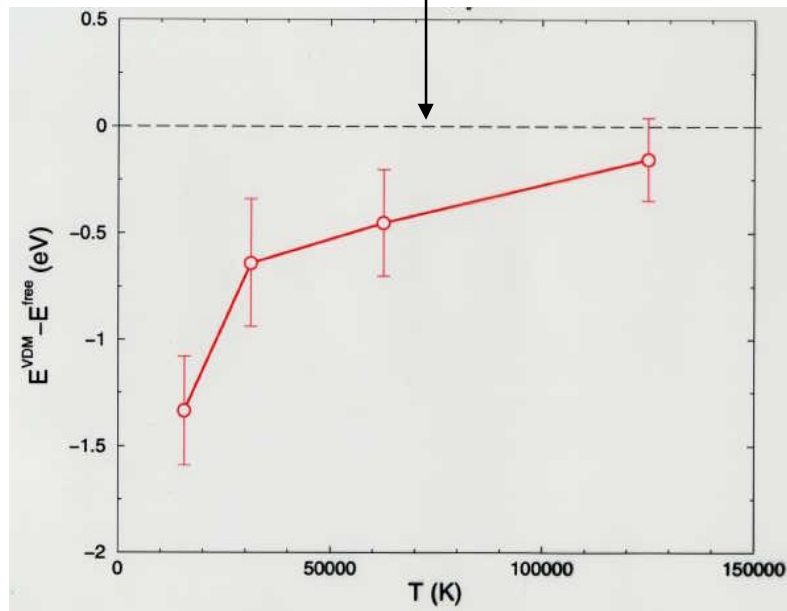
Regimes of Hydrogen
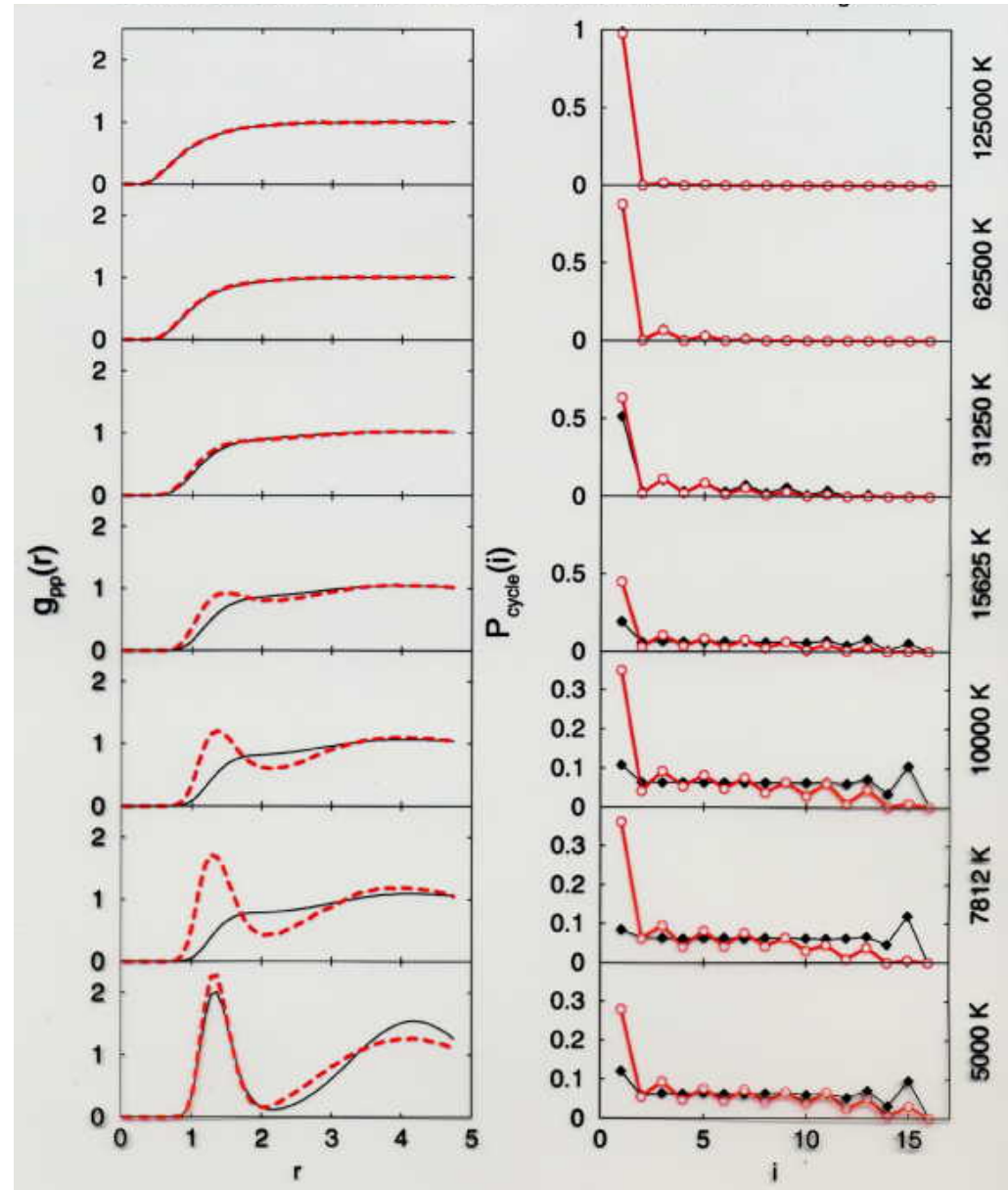
Comparison of free particle and gaussian nodes.

Nodes affect the transition to the molecular phase.
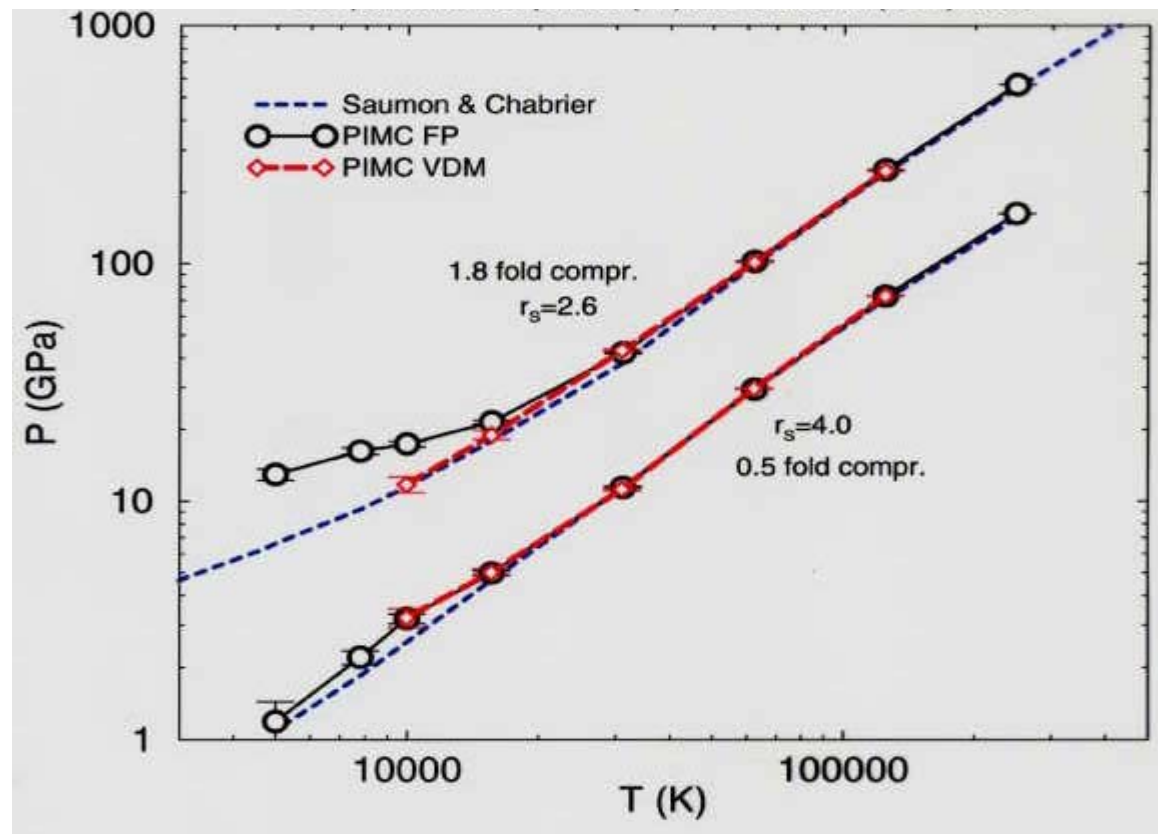
Lower energy means better.

$r_s = 2$

Equation of State:
Pressure vs. Temperature

- PIMC with VDM-nodes is in agreement with chemical models in the low density molecular phase.
- The semi-empirical Saumon and Chabrier model assumes H, H_2, e^- and p^+ with free energy functional.

Energy at low density

•Molecules form spontaneously

•Includes vibrational, rotational, translational degrees of freedom.

•Absolute accuracy in energy is 0.1eV.
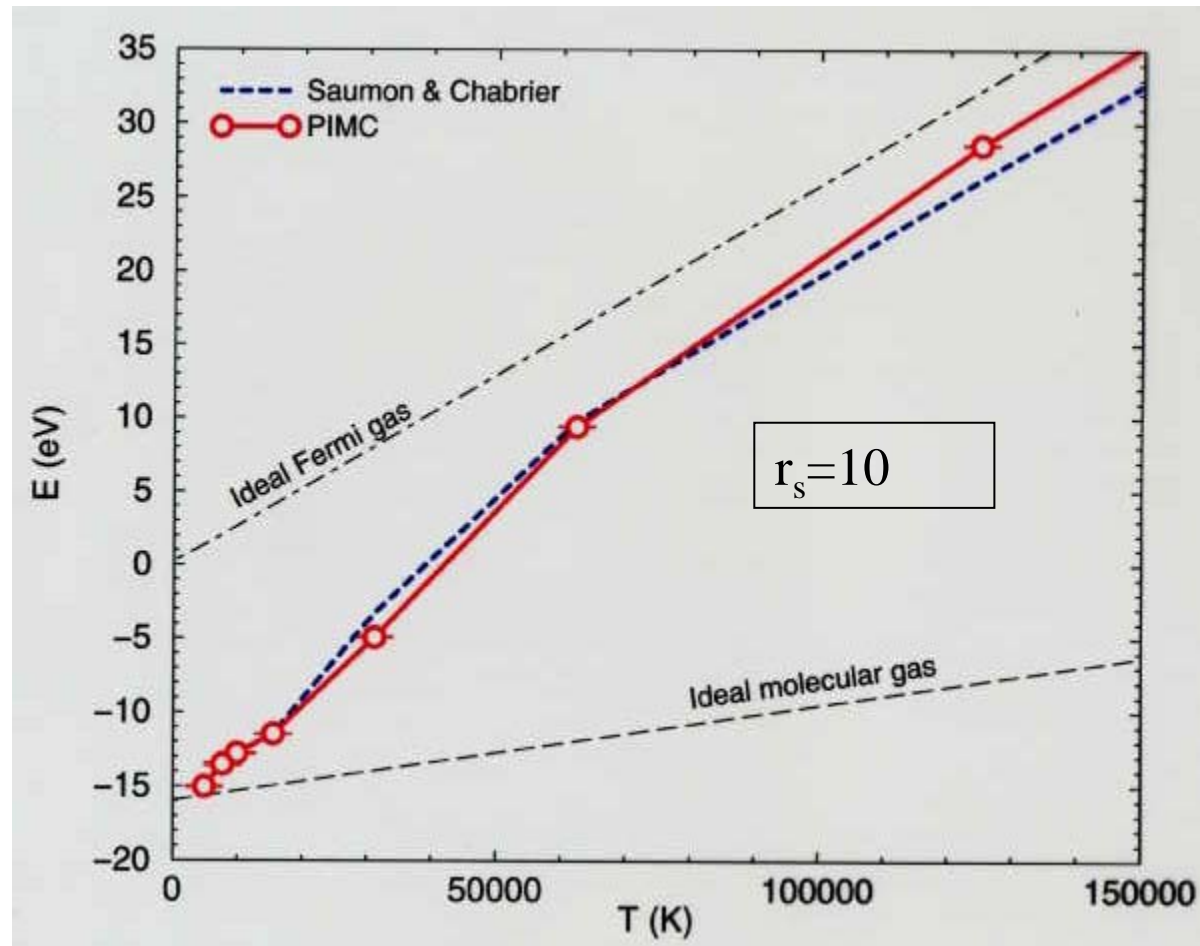
Militzer, Ceperley, Phys Rev. E63, 66404 (2001).

DMC

Analysis of number of bound protons

- By looking at $g_{ep}(r)$ we can estimate its state.

- Chemical model at intermediate temperatures (5-10eV) underestimate degree of ionization.
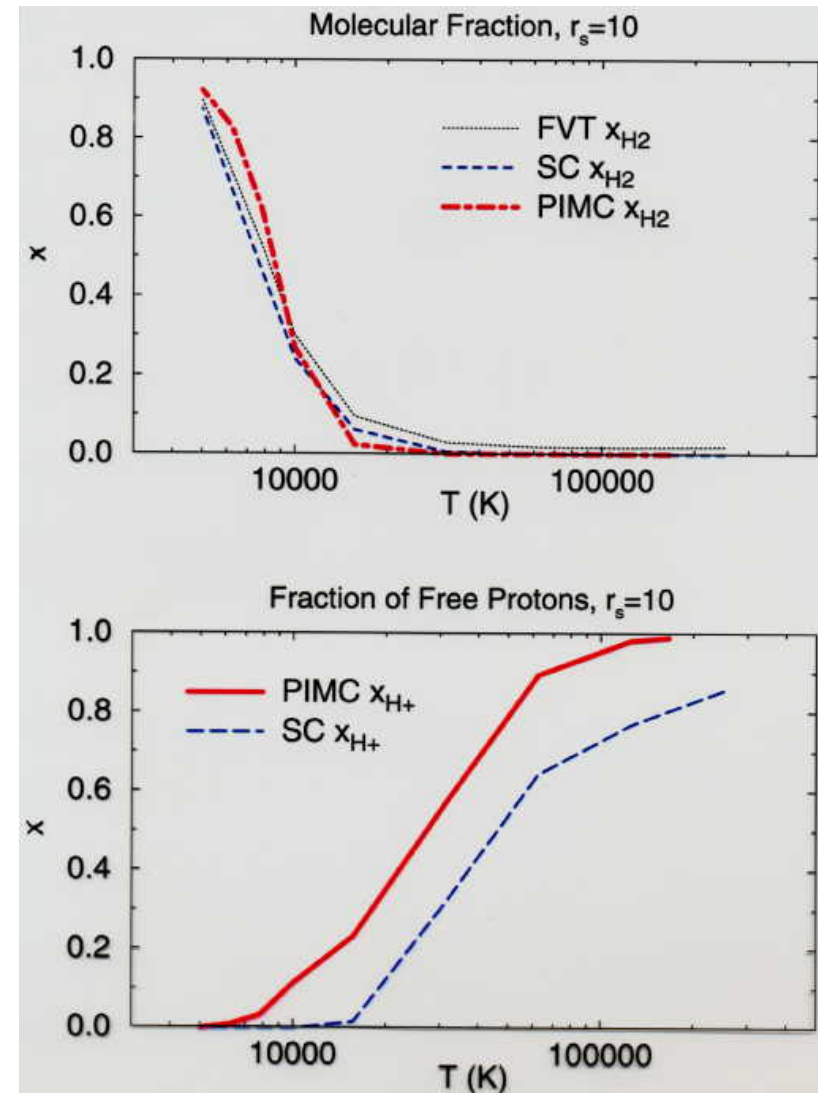
Shock wave experiments.

- Hit a sample of cold, solid D_2 with a bullet.
- Assume equilibrium after shock.
- Measurement of velocities, gives density pressure and energy.
- Varying initial energy, explores the "Hugoniot."
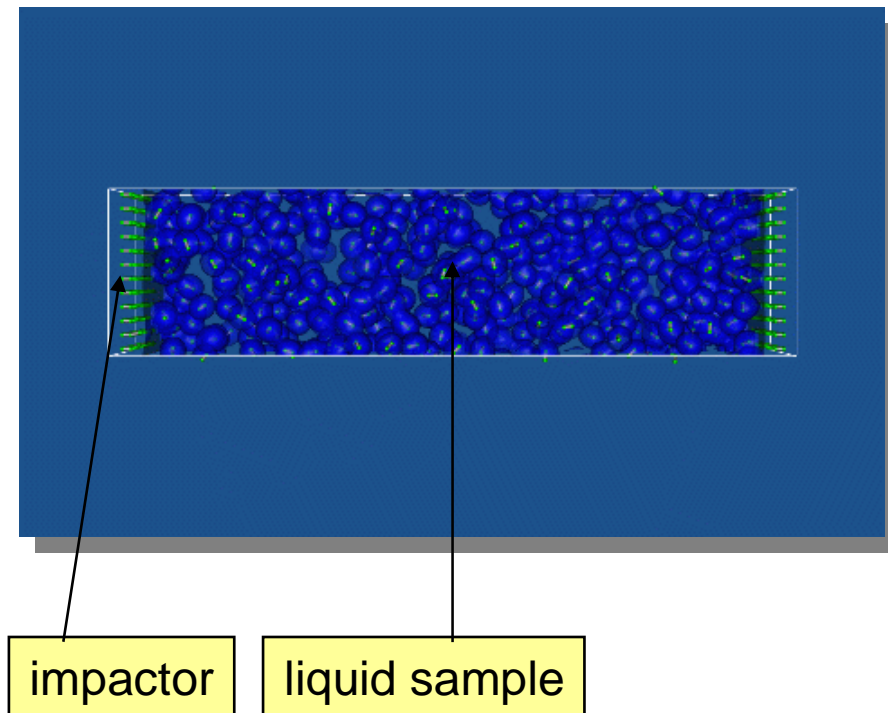- Laser shock allow us a way to check the PIMC in the metallic regime.

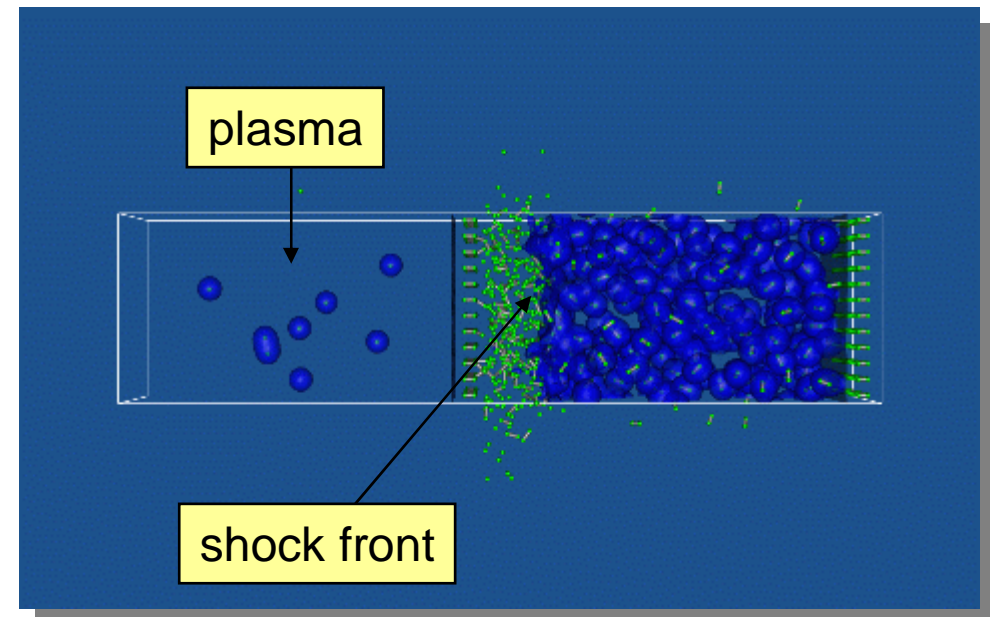| Conservation of Energy and Momentum |
| --- |
| $E = E_o + \frac{1}{2}(P + P_o)(V_o - V)$ |
| $P = \rho_o\, U_s\, U_p$
 $\frac{U_p}{U_s} = 1 - \frac{\rho_o}{\rho}$ |
| U_s = Shock velocity
 U_p = Particle velocity |

impactor liquid sample

plasma

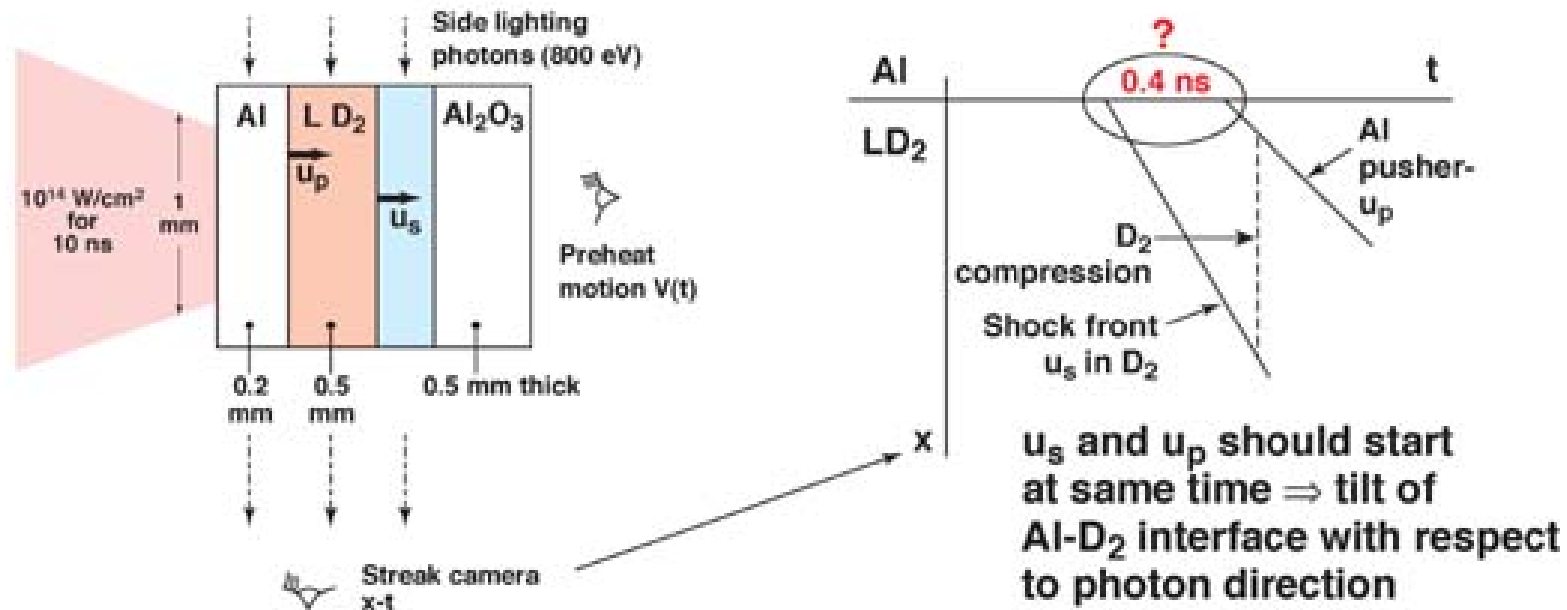shock front

DMC

Internal accuracy of PIMC
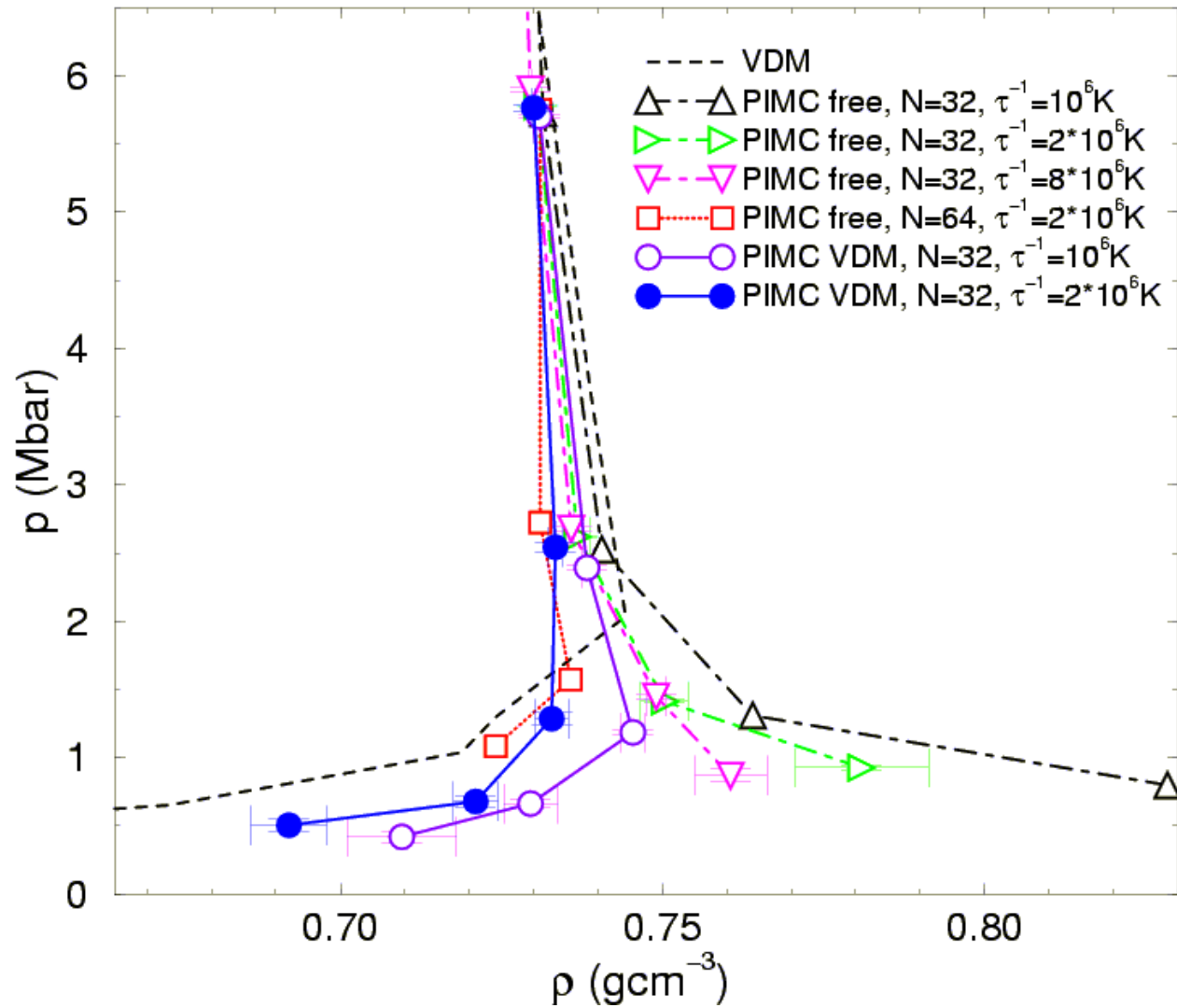
DMC   Results independent of nodes above 2MBars

Experimental methods for D_2 P-V curve by single shock (Hugoniot)
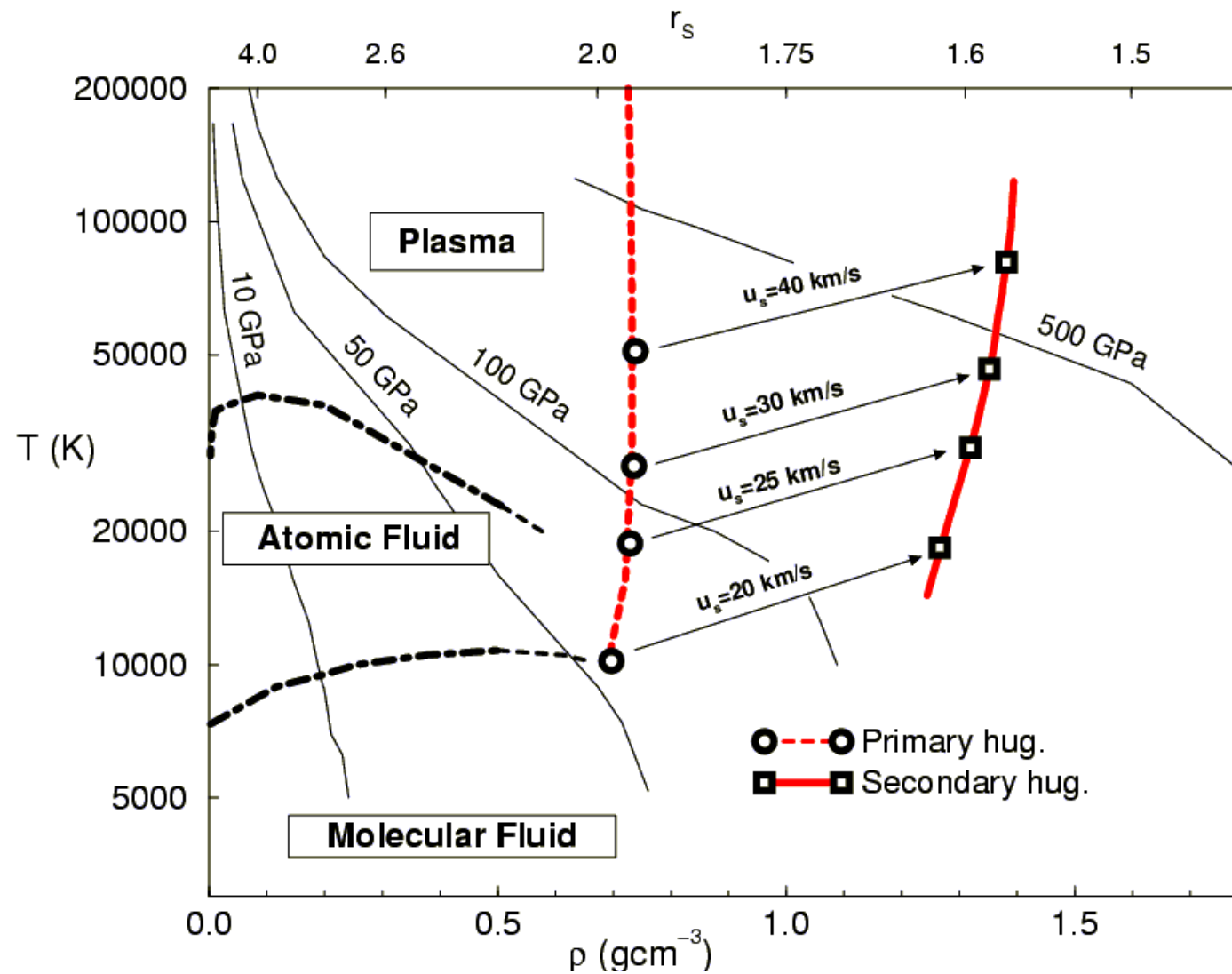
a) Nova laser — transverse measurement

First time used — requires steady shock front for a long distance behind shock front

This method is sensitive to parallel alignment: a tilt of 2°, which translates to 35 μm over 1 mm, explains the ? above
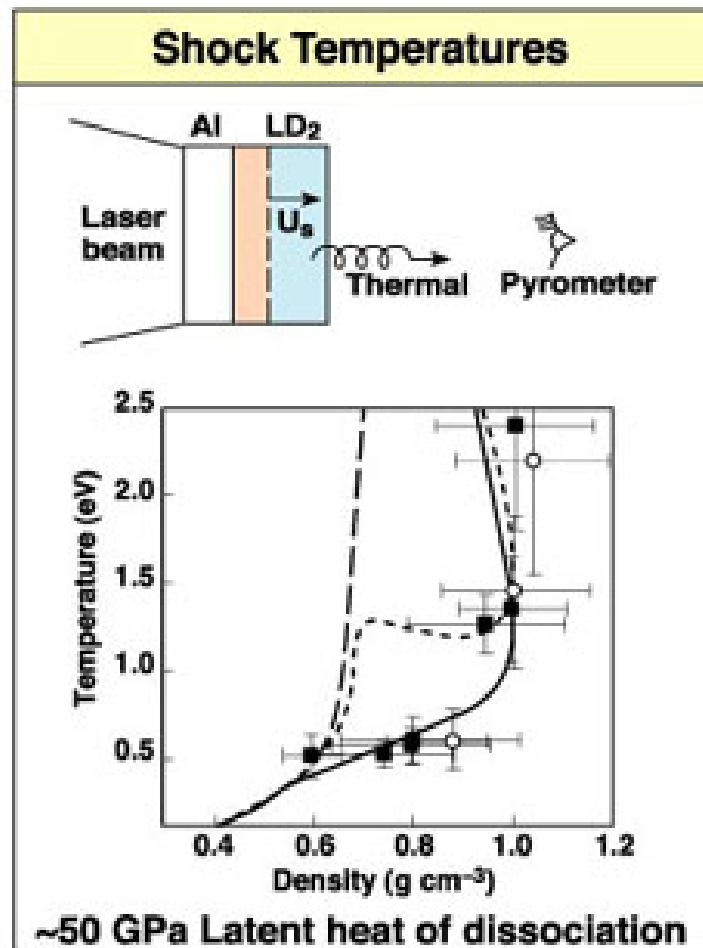
Da Silva et al., Phys Rev. Lett. 75, 483 (1997)

P02198-wjn-u-034

Shock Hugoniot in deuterium

Evidence for dissociation of D$_2$ at ~50 GPa shock pressure

Shock Temperatures

~50 GPa Latent heat of dissociation

G.W. Collins et al., Phys. Rev. Lett. 87, 165504-1 (2001)

Optical Reflectivities

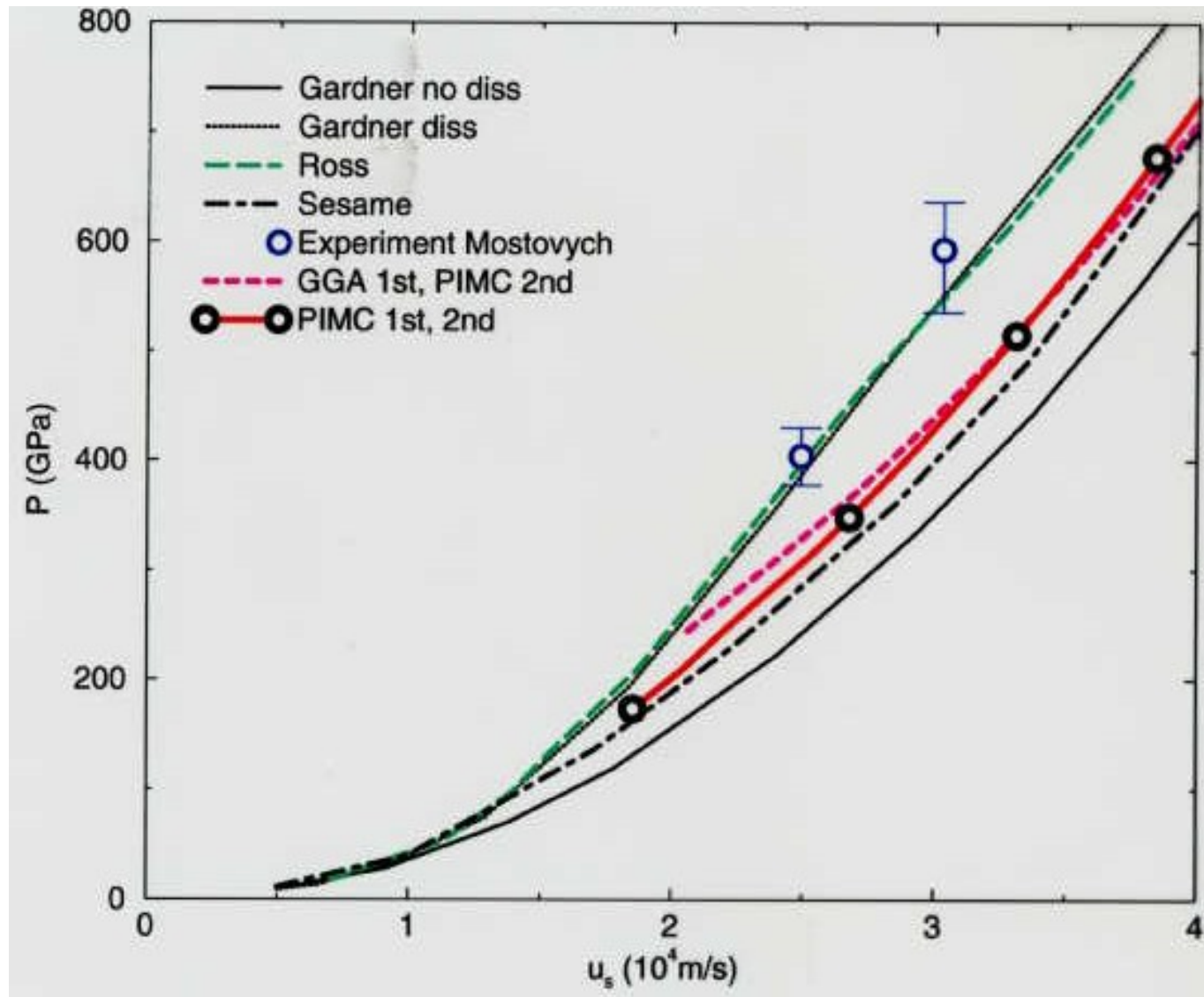Non-metal-metal transition completes at 50 GPa (temperature driven)
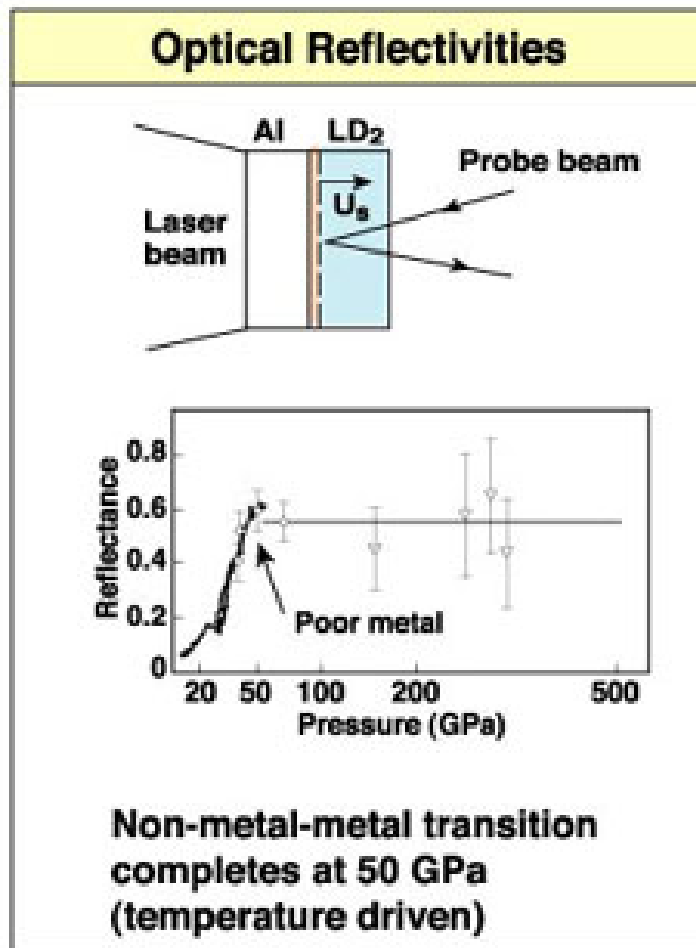
P.M. Celier et al., Phys. Rev. Lett. 84, 5564 (2000)

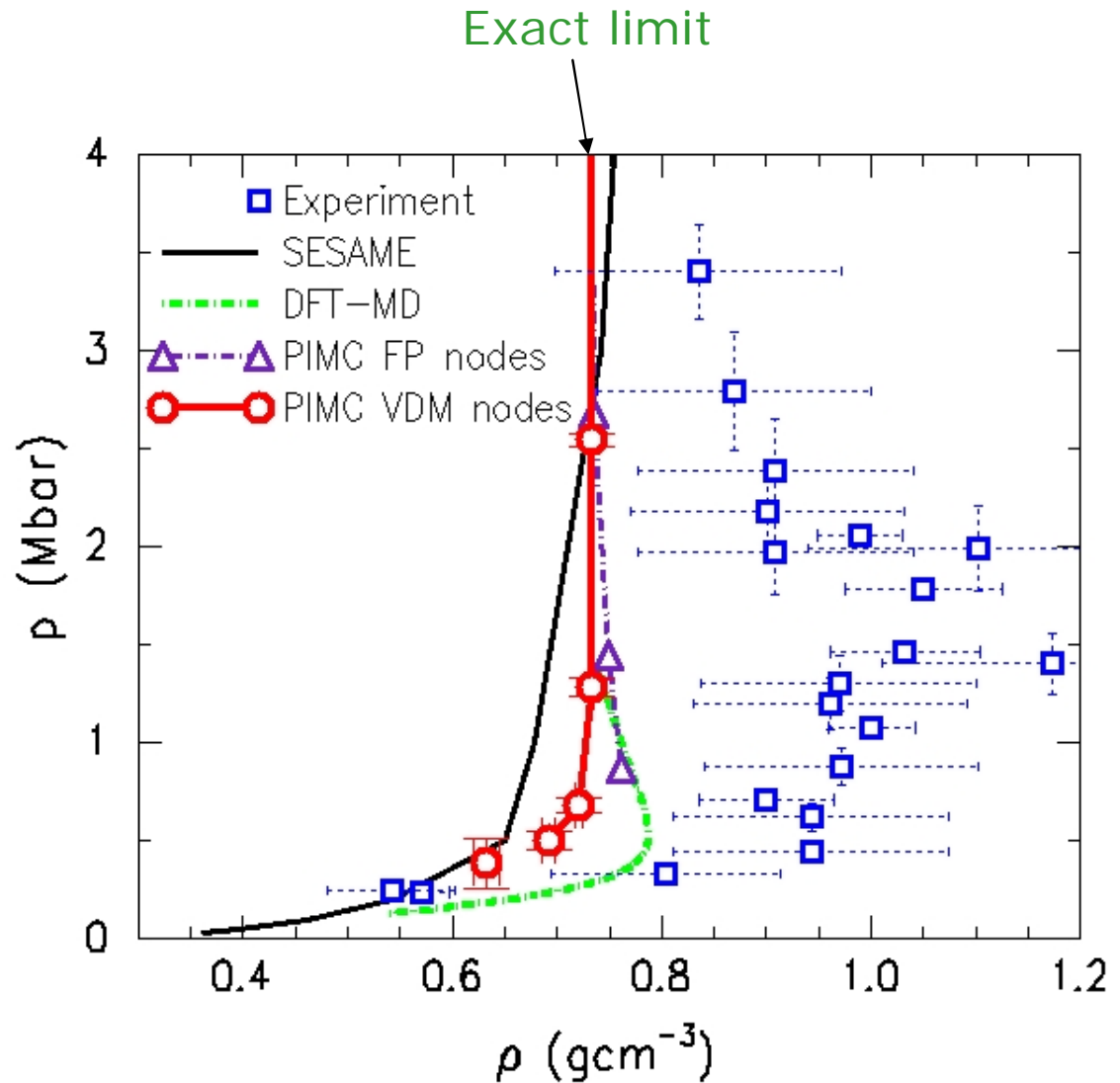# Reflected versus primary shock

Theory vs. experiment

NOVA (Livermore CA) laser shock experiments
Science **281**, 1178, 1998.

•Liquid is 50% more compressible than thought.

•Important implications for fusion (makes fusion much easier.)

•PIMC is not very accurate. About the same EOS as DFT.

DMC

Experimental methods for D$_2$ Hugoniot

b) Z pulsed-current machine-longitudinal measurement

~20 MA in 300 ns

Al   LD$_2$ Al$_2$O$_3$

20 km/s

u_l

5 mm

3 mm

0.3 mm

0.25 mm   0.5 mm   0.6 mm

$\Delta t \Rightarrow u_s$

$v(t) \Rightarrow u_l(t)$ and $u_s(t)$

$I \Rightarrow B \Rightarrow P \sim B^2 \Rightarrow u_l$
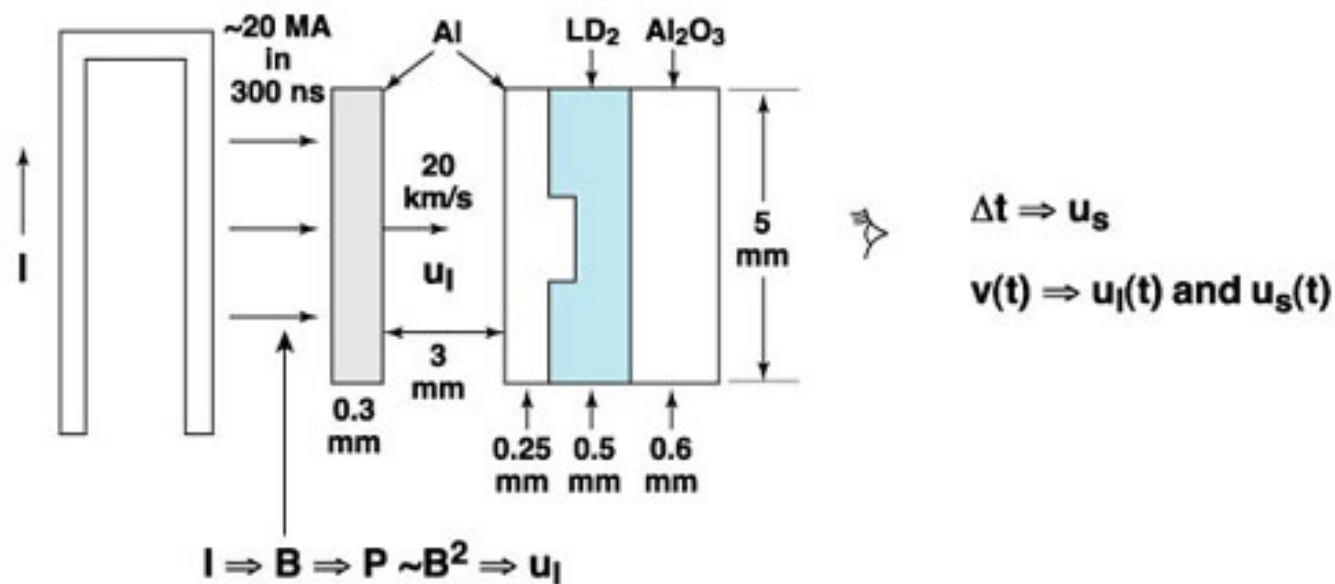
Classic method – requires steady shock a short distance behind shock front; insensitive to tilt

Knudson *et al.*, Phys Rev. Lett. **87**, 225501-1 (2001)

P02198-wjn-u-035

DMC

51

New experiment agrees!

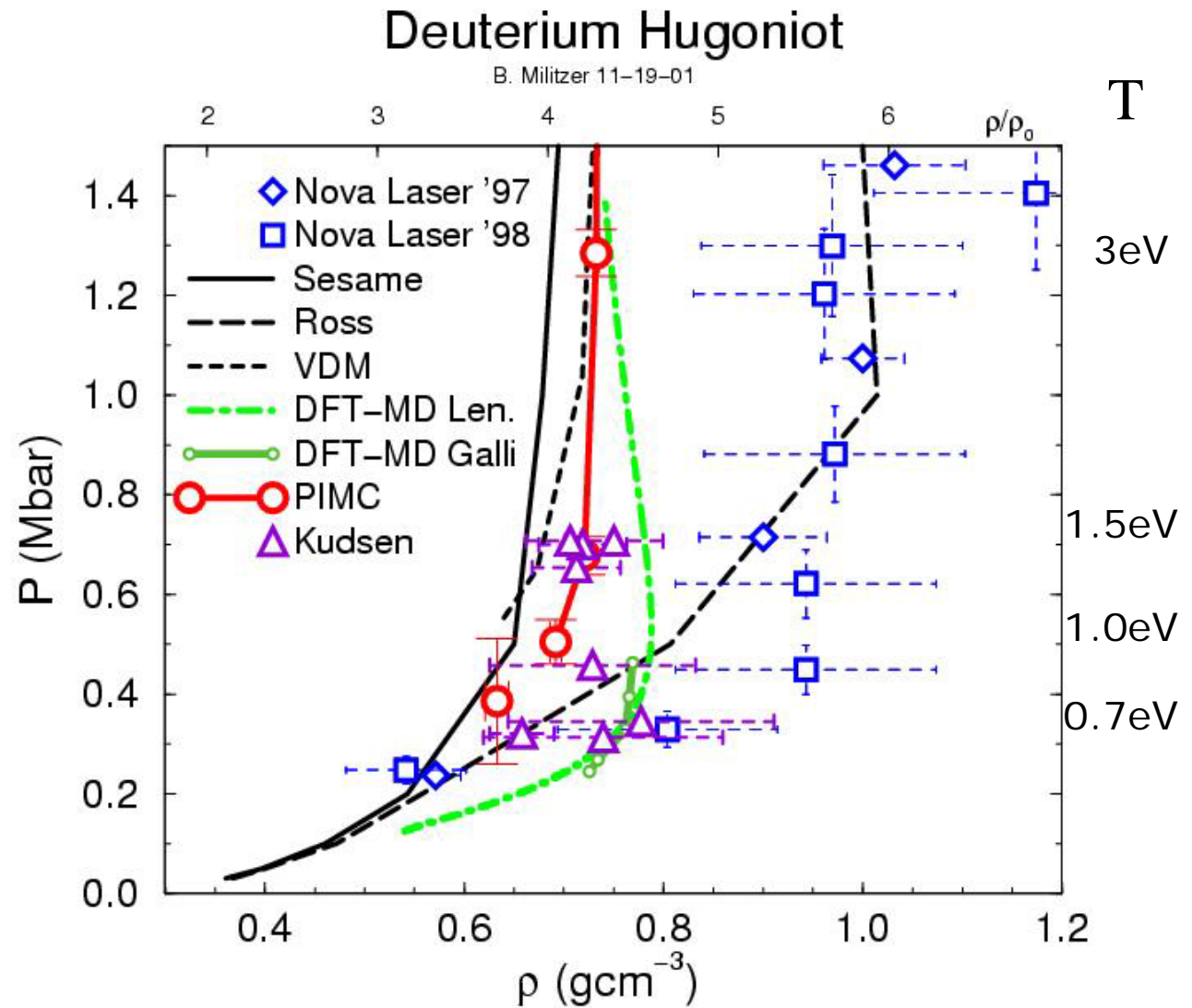- Recent Z-pinch experiments of *Knudsen et al., PRL 87, 225501 (2001)*

- Much larger samples using electromagnetic compression.

- Older laser shocks are incompatible with microscopic theory.

- Chemical models are not predictive in this regime.

Deuterium Hugoniot
B. Militzer 11–19–01

Dictionary of the Quantum-Classical Isomorphism

Attention: *some words have opposite meanings.*

Quantum	Classical
Bose condensation	Delocalization of ends
Boson statistics	Joining of polymers
Exchange frequency	Free energy to link polymers
Free energy	Free energy
Imaginary velocity	Bond vector
Kinetic energy	Negative spring energy
Momentum distribution	FT of end-end distribution
Particle	Ring polymer
Potential energy	Iso-time potential
Superfluid state	Macroscopic polymer
Temperature	Polymer length
Pauli Principle	Restricted Paths
Cooper Pairing	Paired Fermion Paths
Fermi Liquid	Winding restricted paths
Insulator	Nonexchanging paths

"fermion dictionary"?

DMC

Theoretical   # Practical

- Restricted paths allow realistic calculations of many fermion systems. No sign problem.
- Generalization of bosonic PIMC.
- Unifies theory of bose and fermi systems: ring exchanges important for both.
- Makes a nodal assumption which is only controlled for $T>T_F$

•No Born-Oppenheimer approximation

•Fully quantum protons

•No density functional needed

•No pseudopotential/k-space cutoff

•No empirical potentials/chemical model

•Paths get stuck at low temperature $T<0.1\ T_F$ unless you make other assumptions (e.g. ground state nodes.)

•CEIMC allows lower temperature PI simulations.

DMC