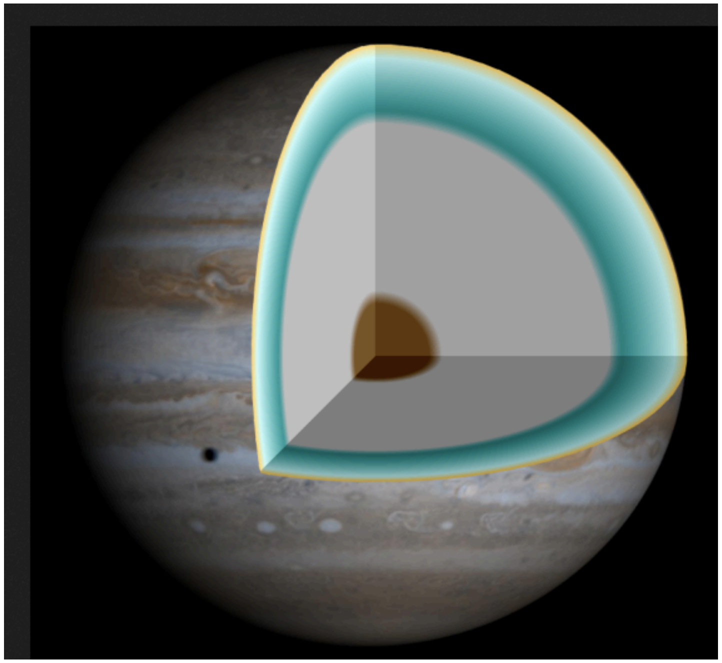
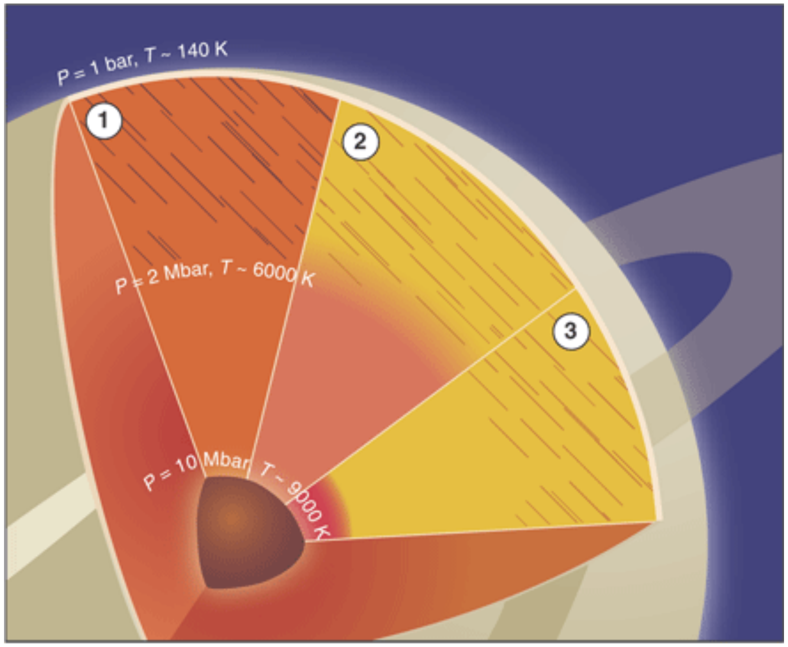
Simulations of dense hydrogen with Quantum Monte Carlo

David Ceperley
University of Illinois Urbana-Champaign





Simulations of dense hydrogen with Quantum Monte Carlo

David Ceperley *University of Illinois Urbana-Champaign*

Recent Collaborators

Miguel Morales *Livermore*

Carlo Pierleoni *L'Aquila, Italy*

AND many other collaborators over the years!

DOE-NNSA 0002911

INCITE & Blue Waters award of computer time

Why study dense Hydrogen?

- Applications:
  - Astrophysics: giant planets, exoplanets
  - Inertially confined fusion: NIF
- Fundamental physics:
  - What phases are stable?
  - Superfluid/ superconducting phases?
- Benchmark for simulation:
  - "Simple" electronic structure; no core states
  - But strong quantum effects from its nuclei

What do we know about Jupiter and Saturn from

- **measurement?**
  - Mass, radius, oblateness (shape),…
  - Surface properties: temperature, composition, ….
  - Rotation, radiation,magnetic field,….
- **theory?**
  - Composition of planets is “solar”: mostly H and He.
    - 71% hydrogen,
    - 24% helium and
    - 5% other elements by mass
  - 4.5 billion years old
  - Temperature in the core ~30,000C
  - Pressure in the core ~30 million atmospheres.
- Cassini (Saturn 2017) and Juno (Jupiter 2016) missions are giving much new data about their surfaces and interiors.

How big is Jupiter’s core?

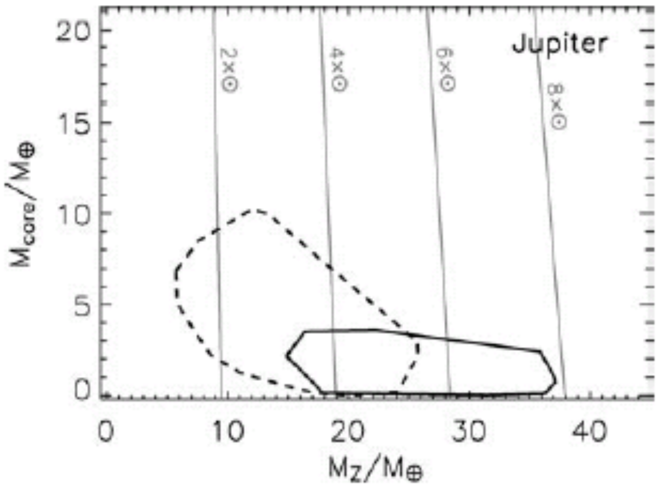
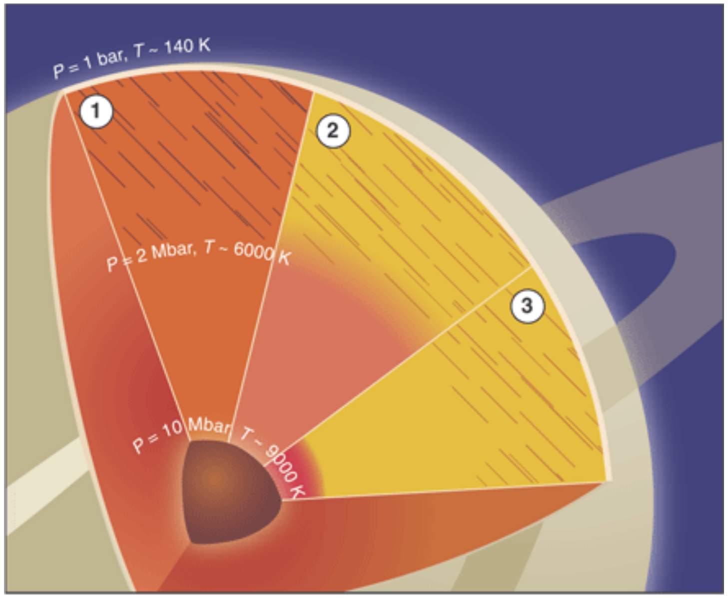


Figure 7 Constraints on Jupiter’s interior structure based on Saumon & Guillot (2004). The value of the core mass (M_{core}) is shown in function of the mass of heavy elements in the envelope (M_Z) for models matching all available observational constraints. The dashed region corresponds to models matching 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.

Planetary models need to know how materials behave in extreme conditions of pressure and temperature!

Big Puzzle: why are Jupiter and Saturn different?

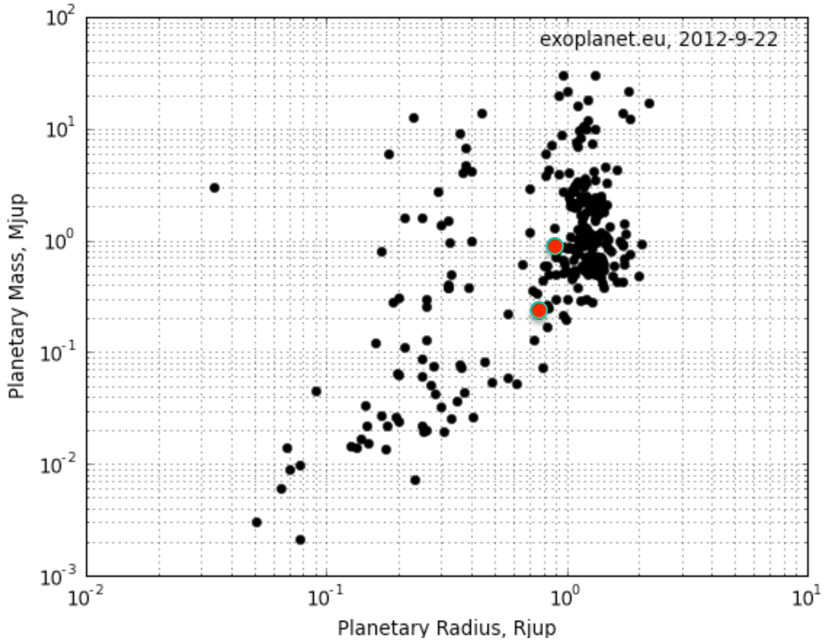


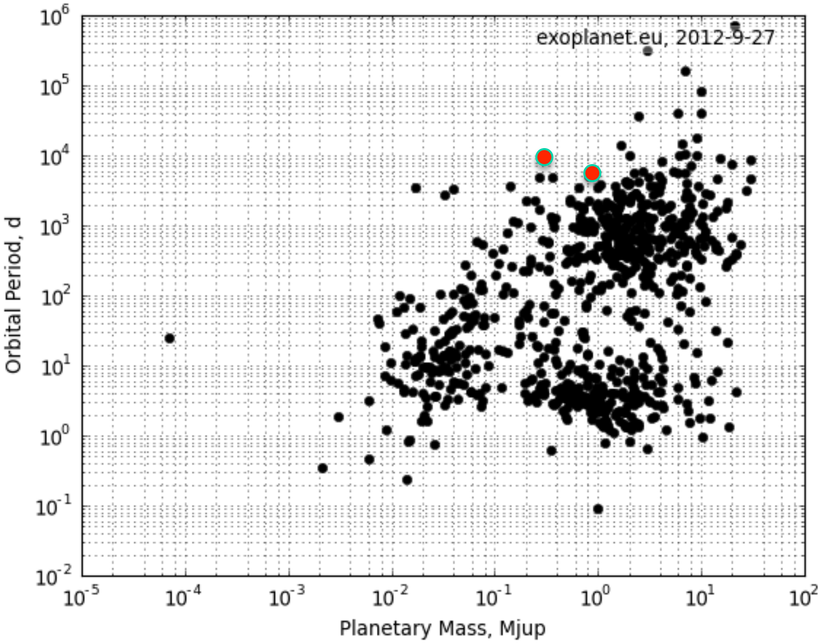
- Some helium is missing from Saturn's surface.
- Saturn is brighter than it should be for its age.
- Additional energy source in Saturn's interior is needed.
- Does it come from helium segregation (rain) as suggested by Smoluchowski in 1965?
- Materials question:

  When does Helium mix with Hydrogen?

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

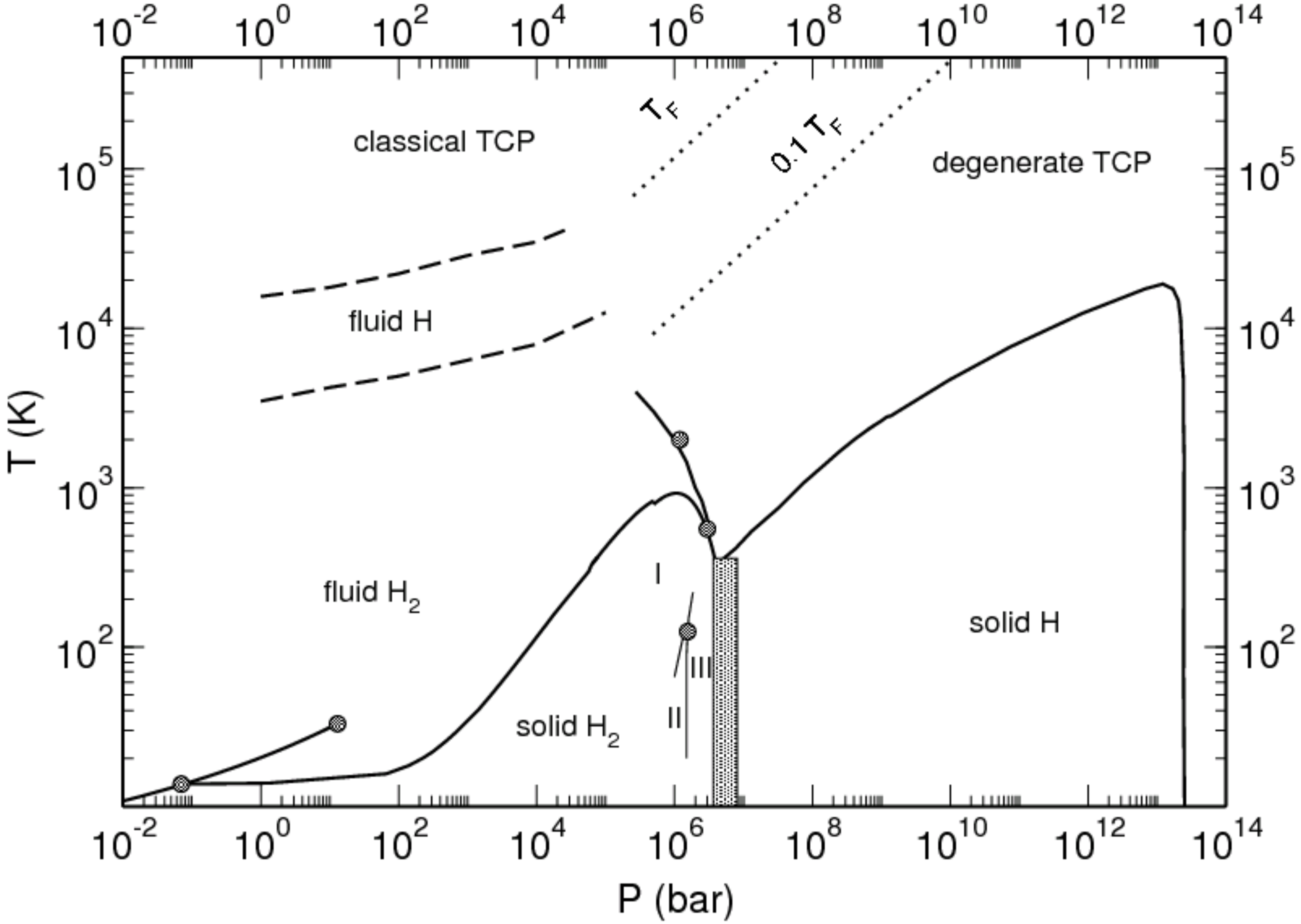
Observed exoplanets in last 10 years





- Jupiter and Saturn are our benchmarks to understanding all of these objects
- The H and He properties under extreme conditions are at heart of models.
- Can experiment measure those properties?

Simplified H Phase Diagram

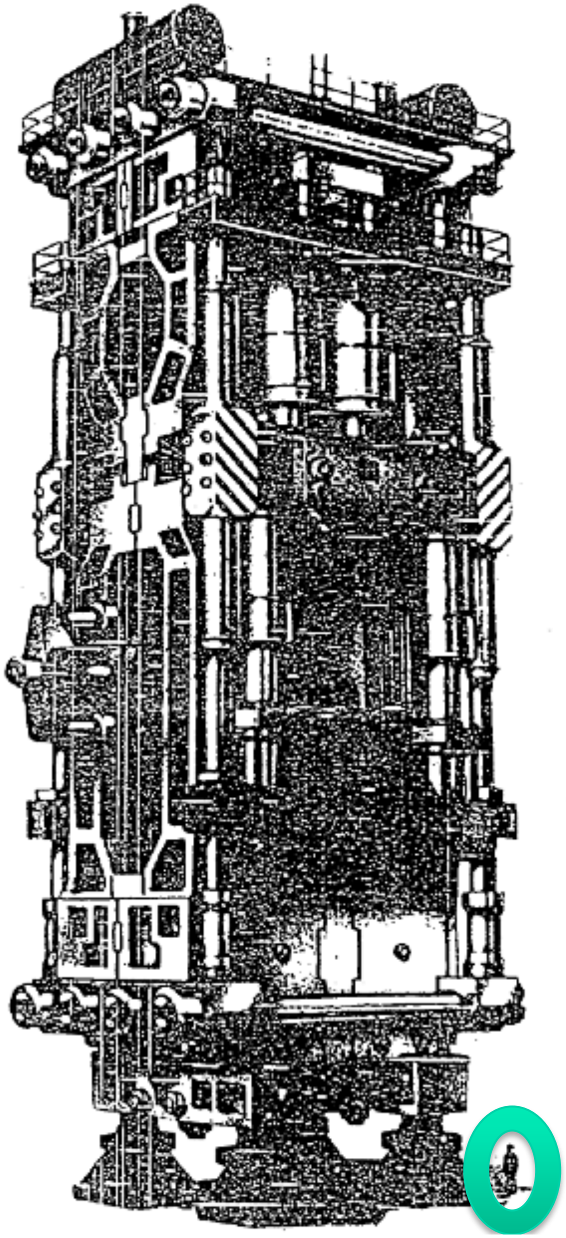


Questions about the phase diagram of hydrogen

1. Is there a liquid-liquid transition in dense hydrogen?
2. How does the atomic/molecular or insulator/metal transition take place?
3. What are the crystal structures of solid H?
4. Could dense hydrogen be a quantum fluid? What is its melting temperature?
5. Are there superfluid/superconducting phases?
6. Is helium soluble in hydrogen?
7. What are its detailed properties under extreme conditions?

The "Soviet" experimental approach

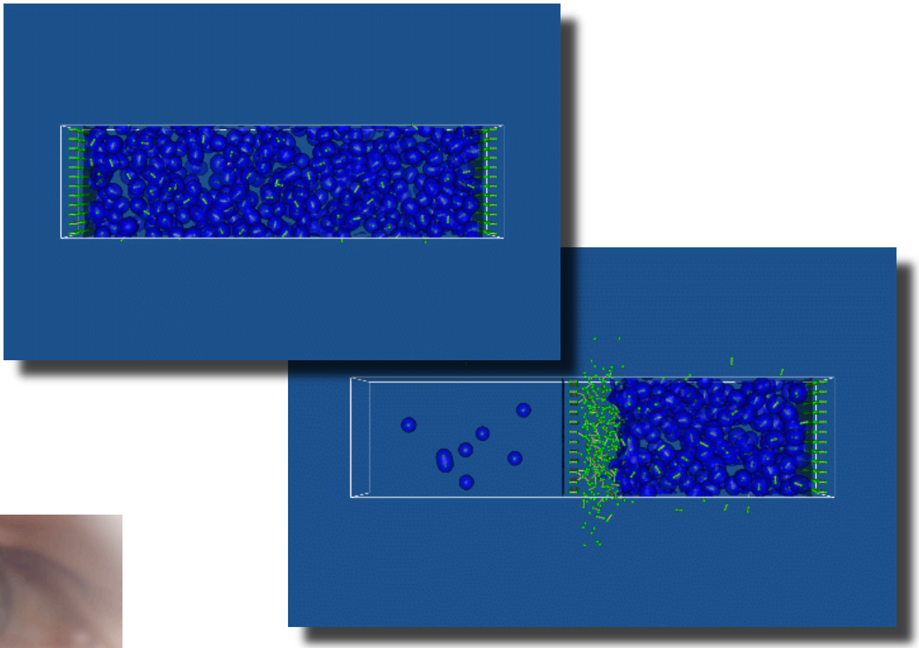
Figure 1. Soviet artist's drawing of a 65,000-ton press built for export to France. The 50,000-ton research press at the Institute of High-Pressure Physics (IFVD) apparently is almost identical to the press shown here (note figure for scale). The IFVD press took a decade to build. Its original purpose was to produce metallic hydrogen; that project has failed. The press has turned out to be a white elephant, and all plans to procure a still-larger successor press have been quietly dropped



POOR QUALITY PAGE

Shock Wave Experiments

- Bullets/cannon balls
- Chemical/nuclear explosions
- Magnetic implosion
- Focused lasers



National Ignition Facility (fusion testbed)
Lawrence Livermore National Laboratory

Another Experimental Approach

Diamond Anvil Cell

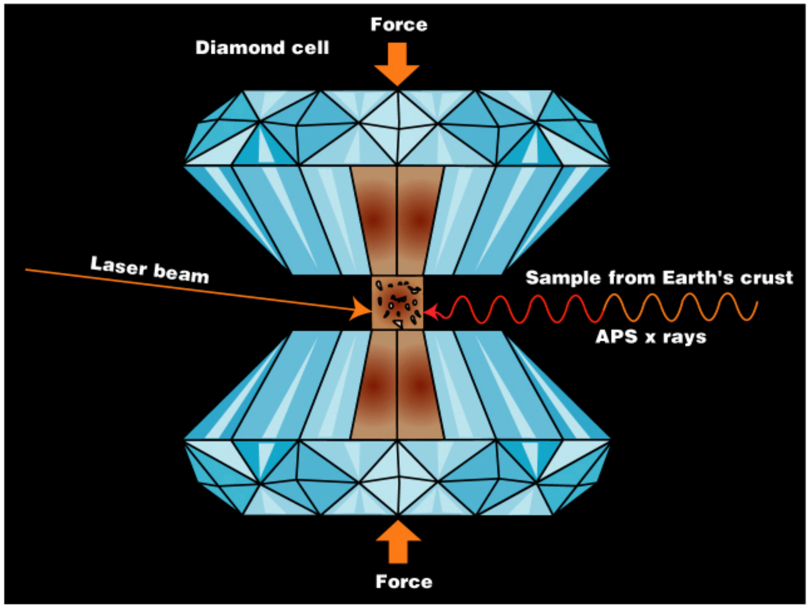
Table-top experiment

- By making Area small we can make P large
- Diamonds are strong!
- Also they are transparent

Static reproducible experiments

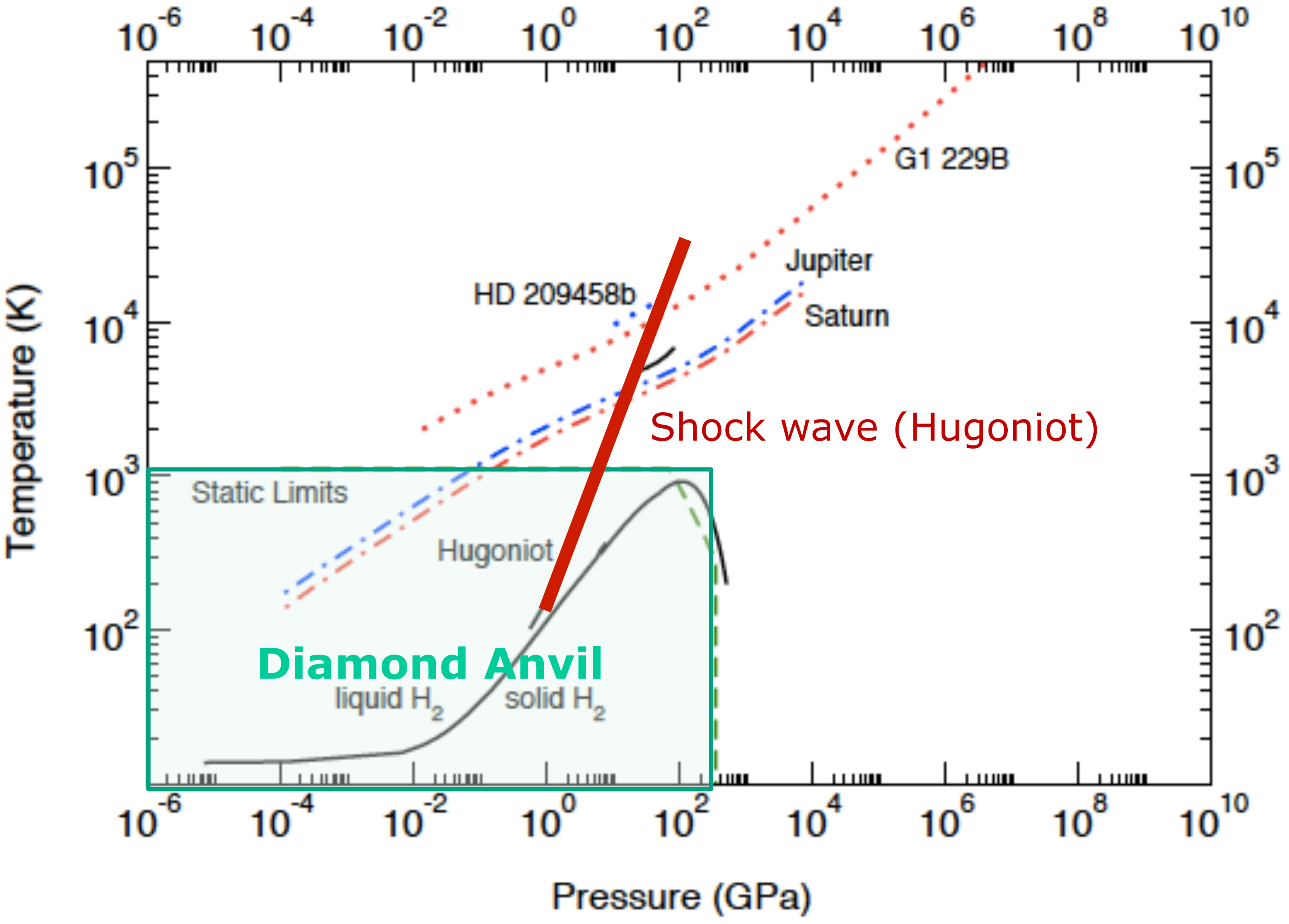
- Can get to 3 MBars before diamond breaks
- 0<T<1000K

Extend range of P,T by shocking compressed hydrogen



$$P = Force \,/\, Area$$

Experiments on hydrogen



> *"The general theory of quantum mechanics is now almost complete. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."*
>
> *Dirac, 1929*

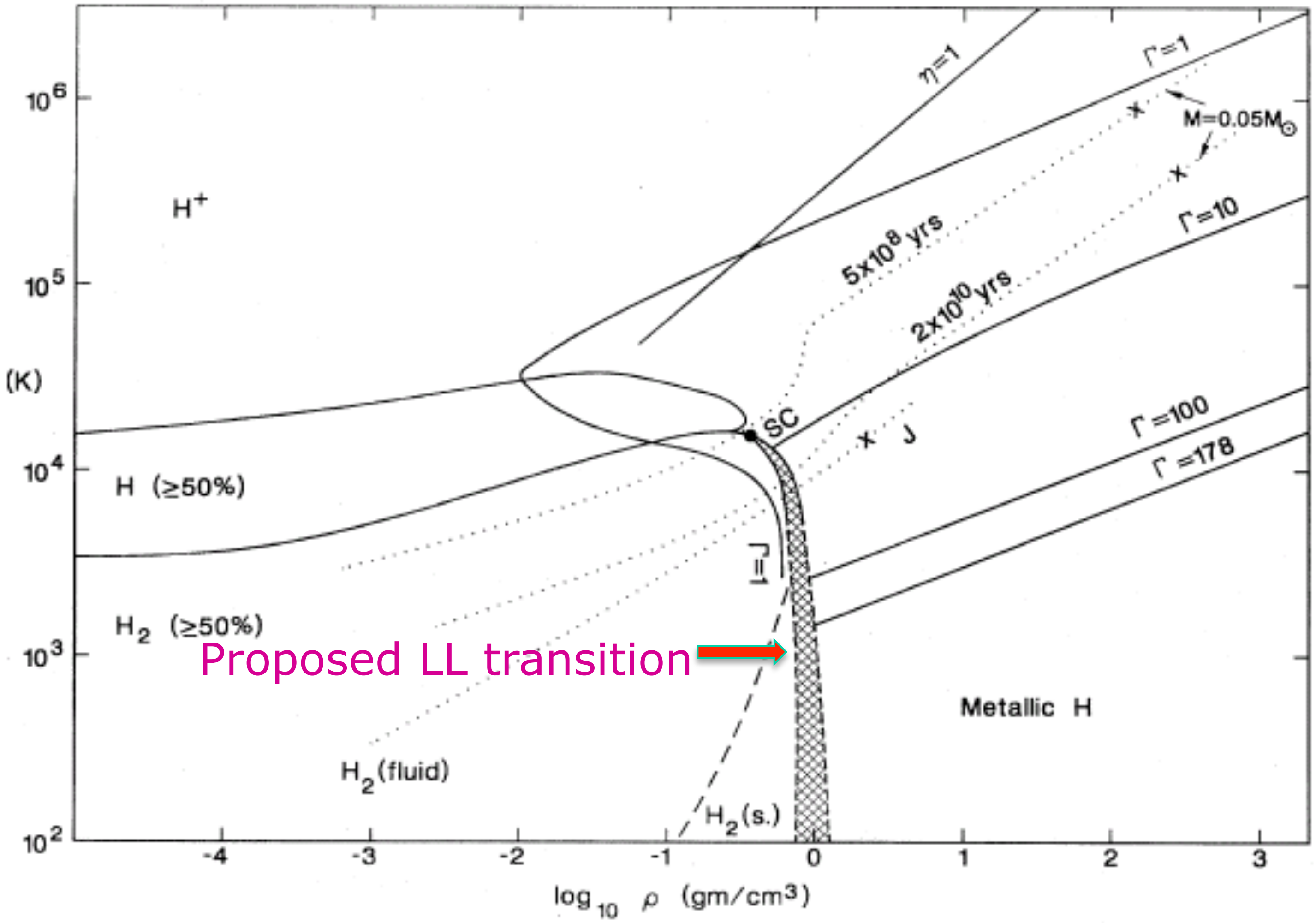
$$\hat{H} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i<j} \frac{e_i e_j}{r_{ij}} \qquad \hat{H}\Psi(r_1, r_2, \ldots) = E\Psi(r_1, r_2, \ldots)$$

Maxwell, Boltzmann and Schrödinger gave us the model (at least for condensed matter physics.) Hopefully, all we must do is numerically solve the mathematical problem and determine the properties. Without numerical calculations, the predictive power of quantum mechanics is limited.

Why is it so difficult?

- Many particles, all interacting!
- They are waves not particles!
- Need high precision!

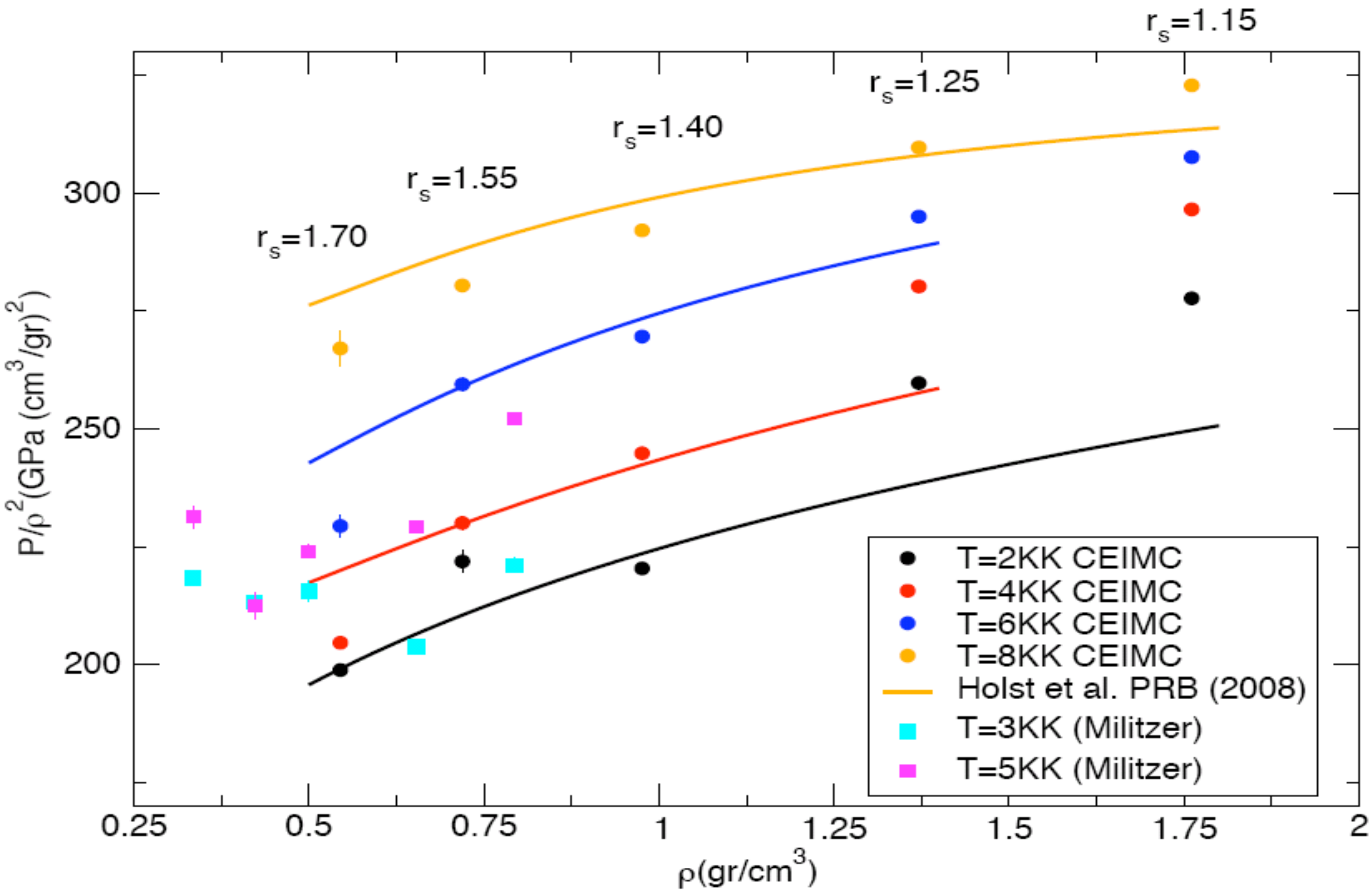
A. Burrows and J. Liebert: The science of brown dwarfs



Proposed LL transition

Based on a the usual model EOS for H (Saumon-Chabrier)

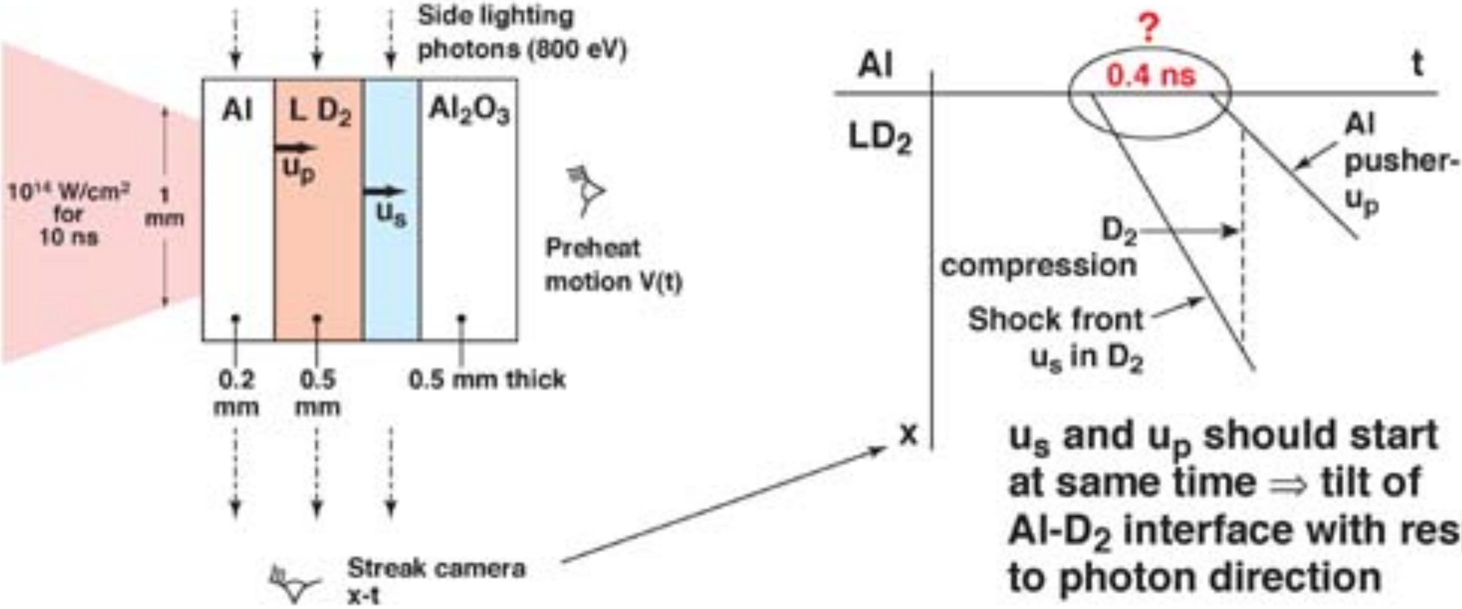
EOS: CEIMC vs BOMD



Planetary calculations will require P to 1% !

Experimental methods for D_2 P-V curve by single shock (Hugoniot)

a) Nova laser — transverse measurement



u_s and u_p should start at same time ⇒ tilt of Al-D_2 interface with respect to photon direction

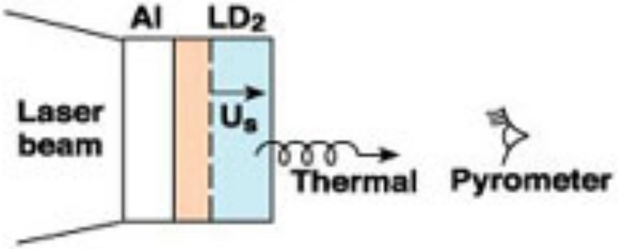
First time used — requires steady shock front for a long distance behind shock front

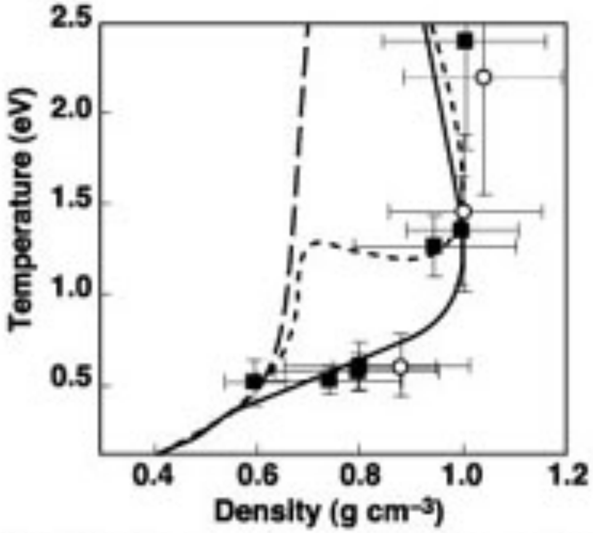
This method is sensitive to parallel alignment: a tilt of 2°, which translates to 35 μm over 1 mm, explains the ? above

Da Silva *et al.*, Phys Rev. Lett. 75, 483 (1997)

Evidence for dissociation of D_2 at ~50 GPa shock pressure

Shock Temperatures

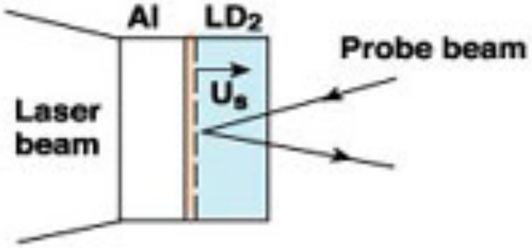


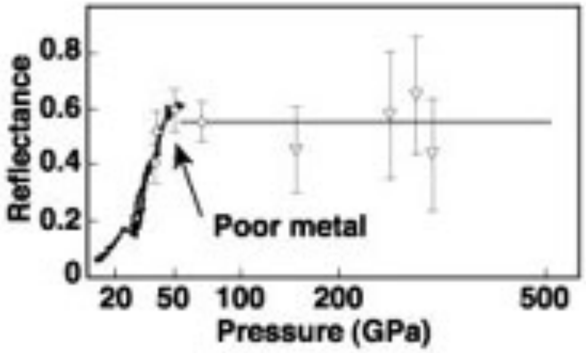


~50 GPa Latent heat of dissociation

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

Optical Reflectivities



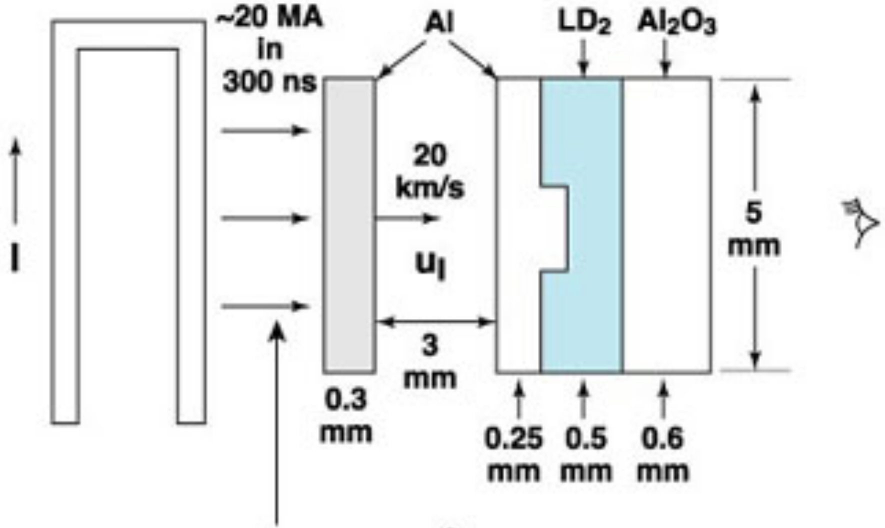


Non-metal-metal transition completes at 50 GPa (temperature driven)

P.M. Cellier et al., Phys. Rev. Lett. 84, 5564 (2000)

Experimental methods for D_2 Hugoniot

b) Z pulsed-current machine-longitudinal measurement



$\Delta t \Rightarrow u_s$

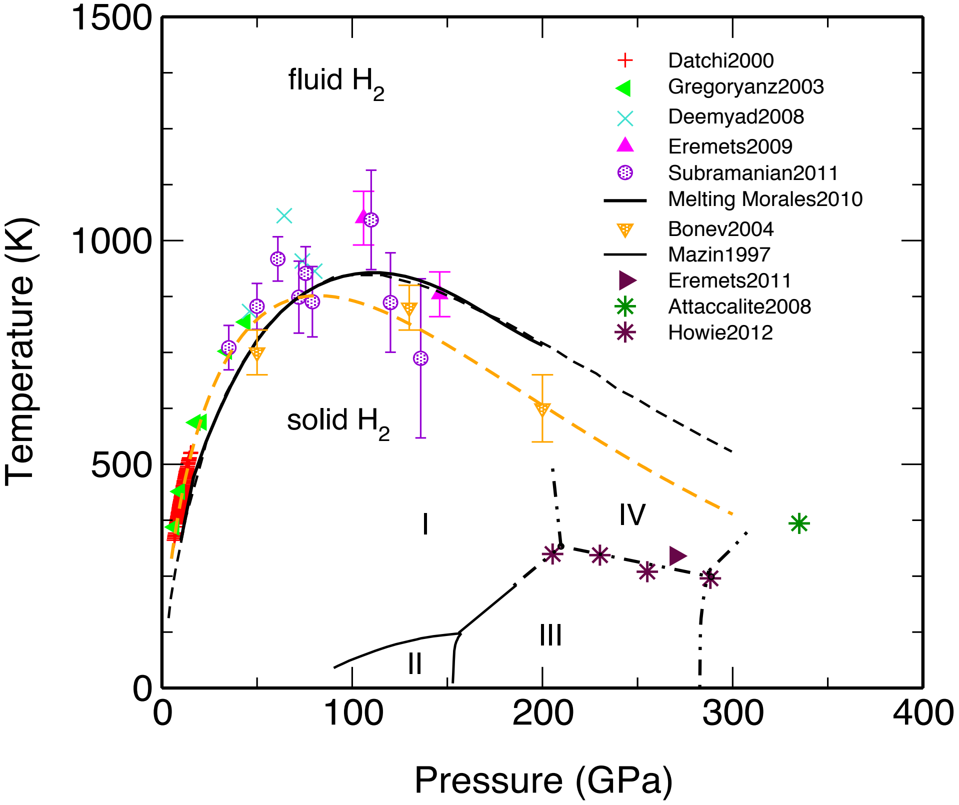
$v(t) \Rightarrow u_l(t)$ and $u_s(t)$

$I \Rightarrow B \Rightarrow P \sim B^2 \Rightarrow u_l$

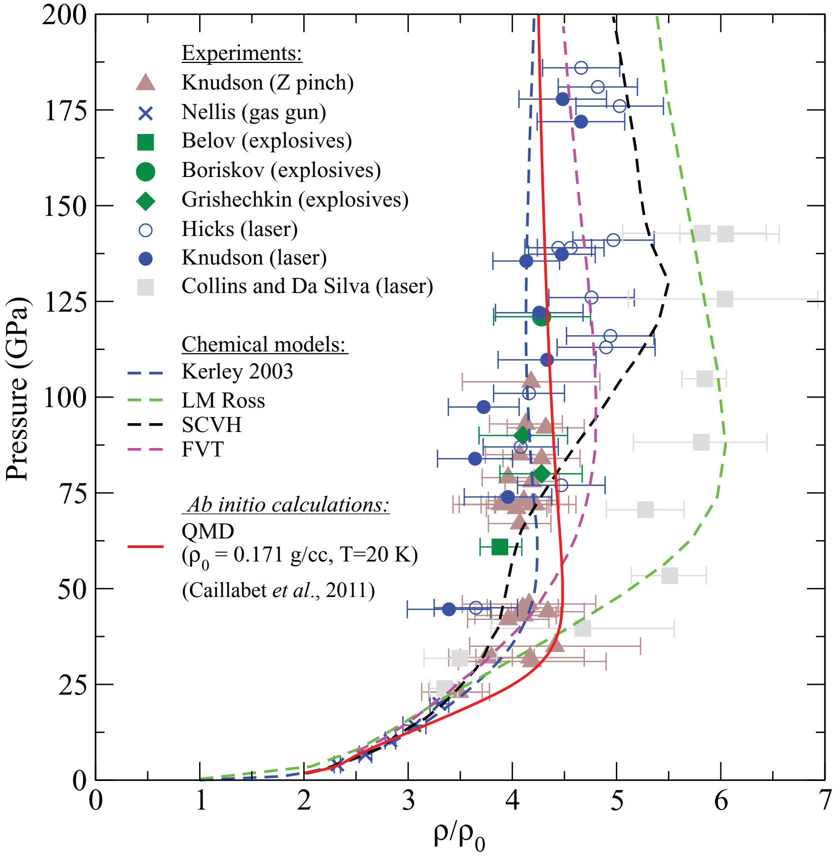
Classic method – requires steady shock a short distance behind shock front; insensitive to tilt

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

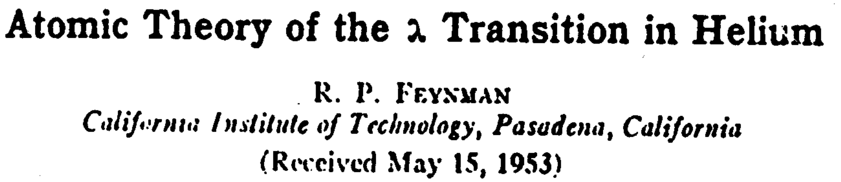
Diamond anvil cell phase diagram



Hugoniot from shocks

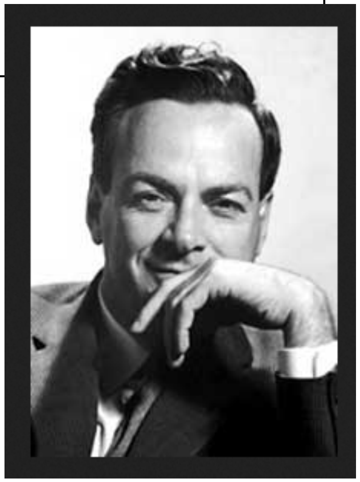


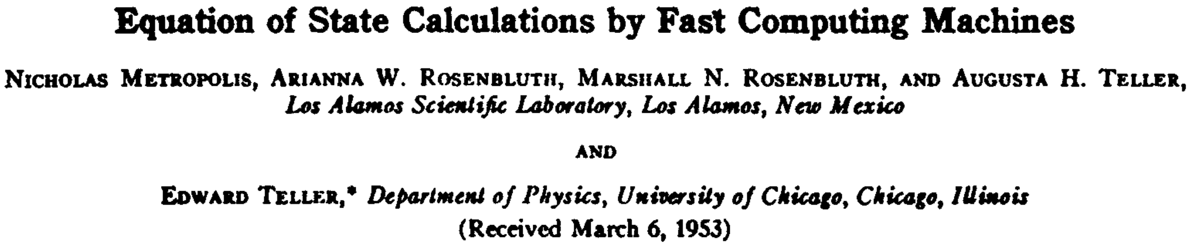
The algorithms for solving these problems came in 1953



Atomic Theory of the λ Transition in Helium

R. P. FEYNMAN
California Institute of Technology, Pasadena, California
(Received May 15, 1953)





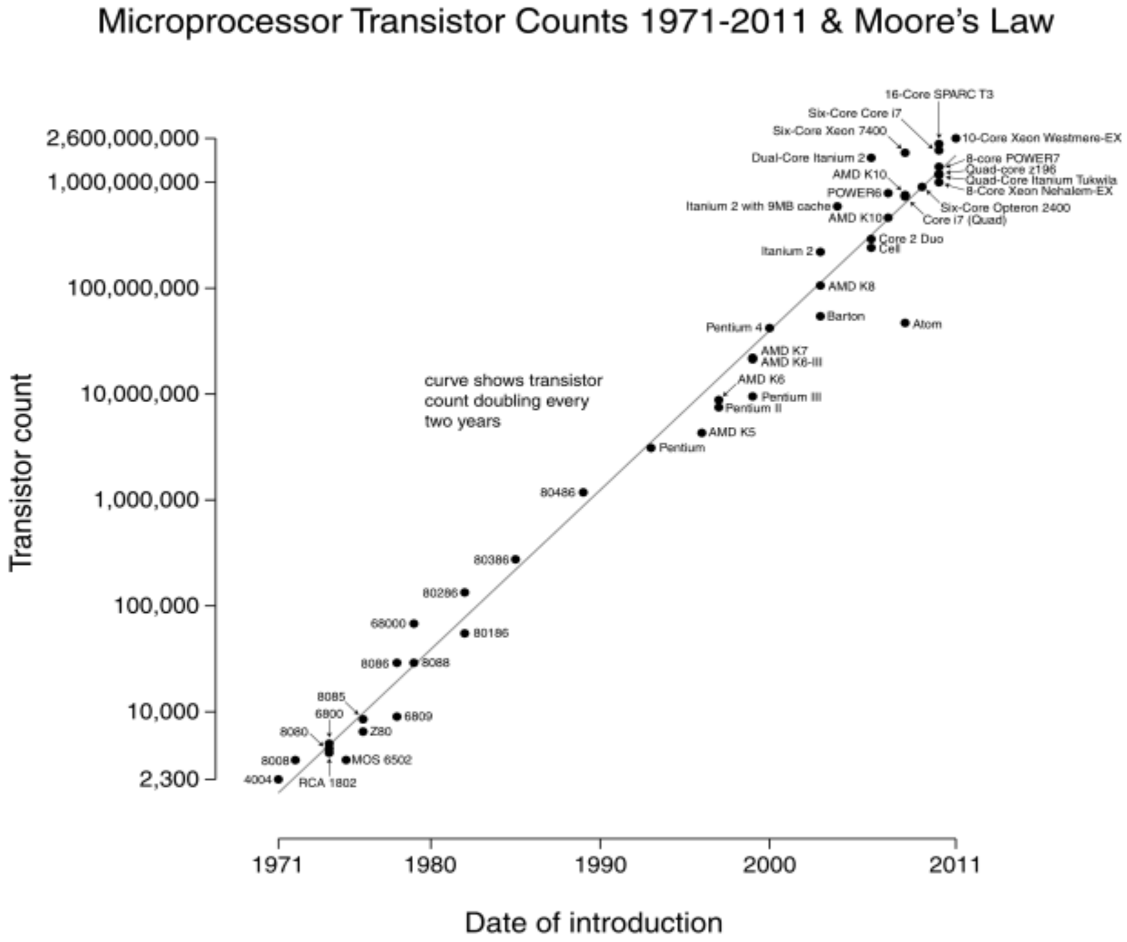
Equation of State Calculations by Fast Computing Machines

NICHOLAS METROPOLIS, ARIANNA W. ROSENBLUTH, MARSHALL N. ROSENBLUTH, AND AUGUSTA H. TELLER,
Los Alamos Scientific Laboratory, Los Alamos, New Mexico

AND

EDWARD TELLER,* *Department of Physics, University of Chicago, Chicago, Illinois*
(Received March 6, 1953)

Computer technology


Microprocessor Transistor Counts 1971-2011 & Moore’s Law

Blue Waters, National Petascale Facility at Illinois

Petascale is about one million laptops working together

Petaflop = 10^{15} operations/second.

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: VMC/DMC 1980, PIMC 1990
CEIMC 2000

- Initial simulations used interatomic potentials based on experiment. But are they accurate enough.
- Much progress with "ab initio" molecular dynamics simulations where the effects of electrons are solved for each step.
- Progress is limited by the accuracy of the DFT exchange and correlation functionals for hydrogen
- The most accurate approach is to simulate both the electrons and ions

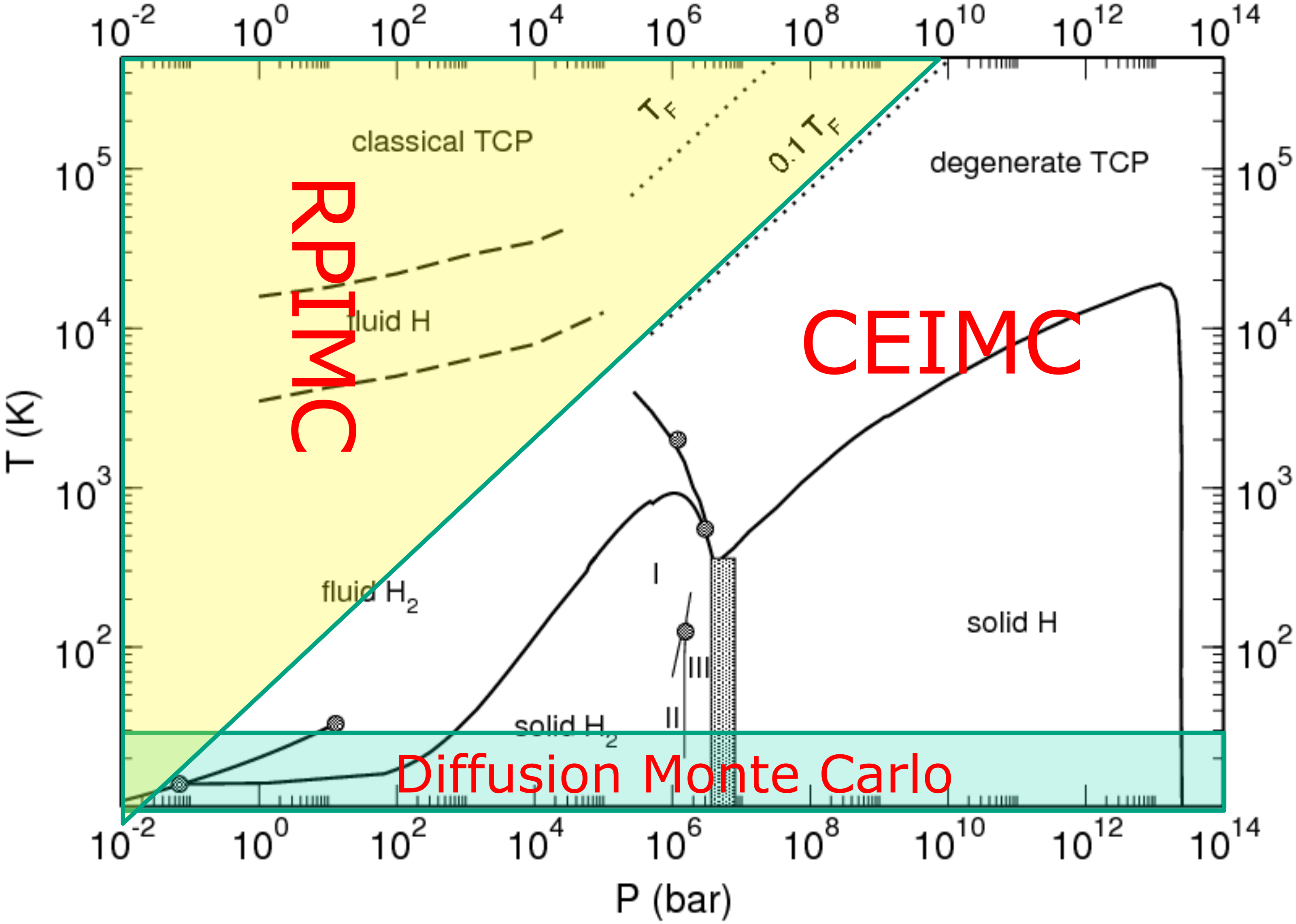
Hydrogen simulations

- Young: MD 1960’s
- Band structure calculations of lattices
- Ceperley & Alder 1985: VMC & DMC
- Natoli et al. 1990: VMC & DMC
- Kohanof 1990: AIMD
- Bonev, Galli, Gygi, Militzer 2005: AIMD
- Magro, Pierleoni, Militizer 1995-2000: PIMC
- Dewing, Pierleoni, Morales, 2004-now : CEIMC

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.
- Primarily based on Feynman’s imaginary time path integrals.
- 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)**

Regimes for Quantum Monte Carlo



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.
- We use"backflow" the 3-body terms.
- No sign problem, and with classical complexity.

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

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

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

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

Projector Monte Carlo

e.g. Diffusion Monte Carlo (DMC)

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

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

- 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 excited states 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

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

Fixed-node method

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

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

- 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 like the VMC method, as N^3 or better.
- Generalizes to the “Fixed Phase” method for complex wavefunctions.

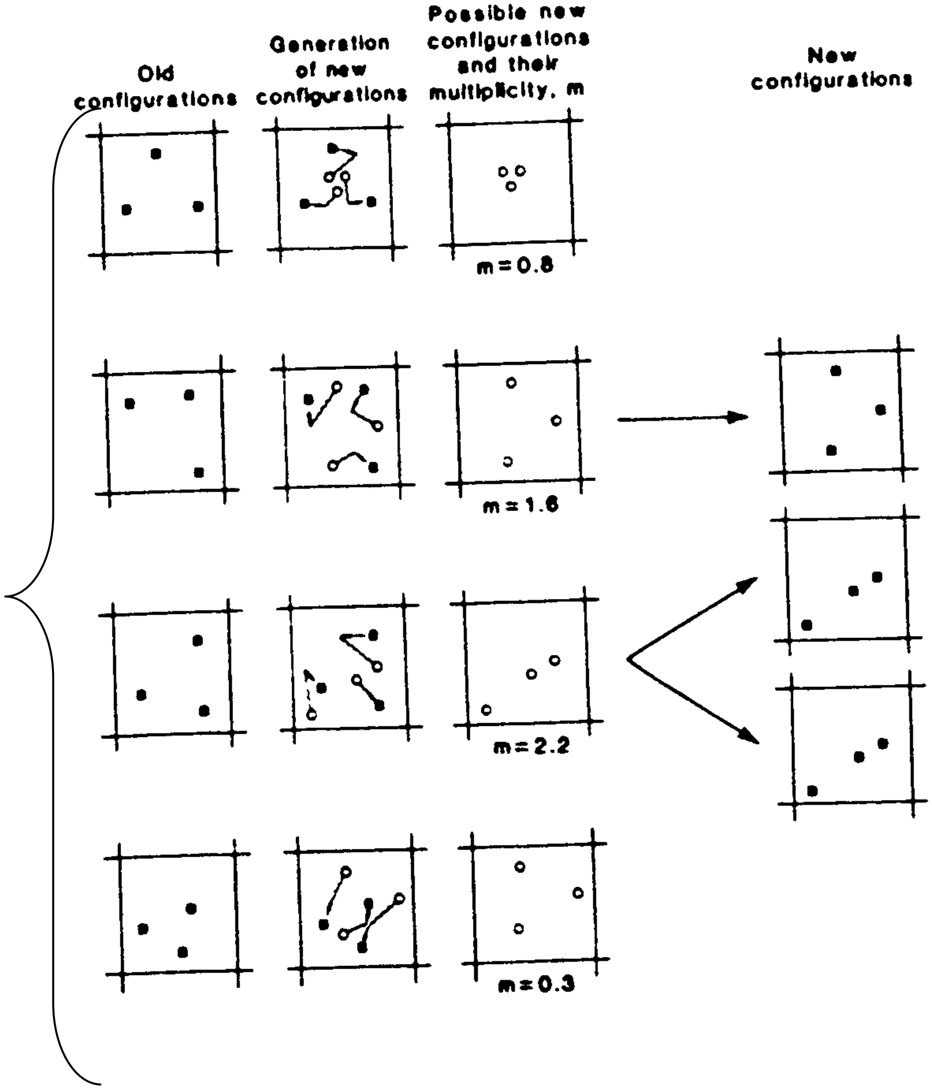
Schematic of DMC

Ensemble evolves according to

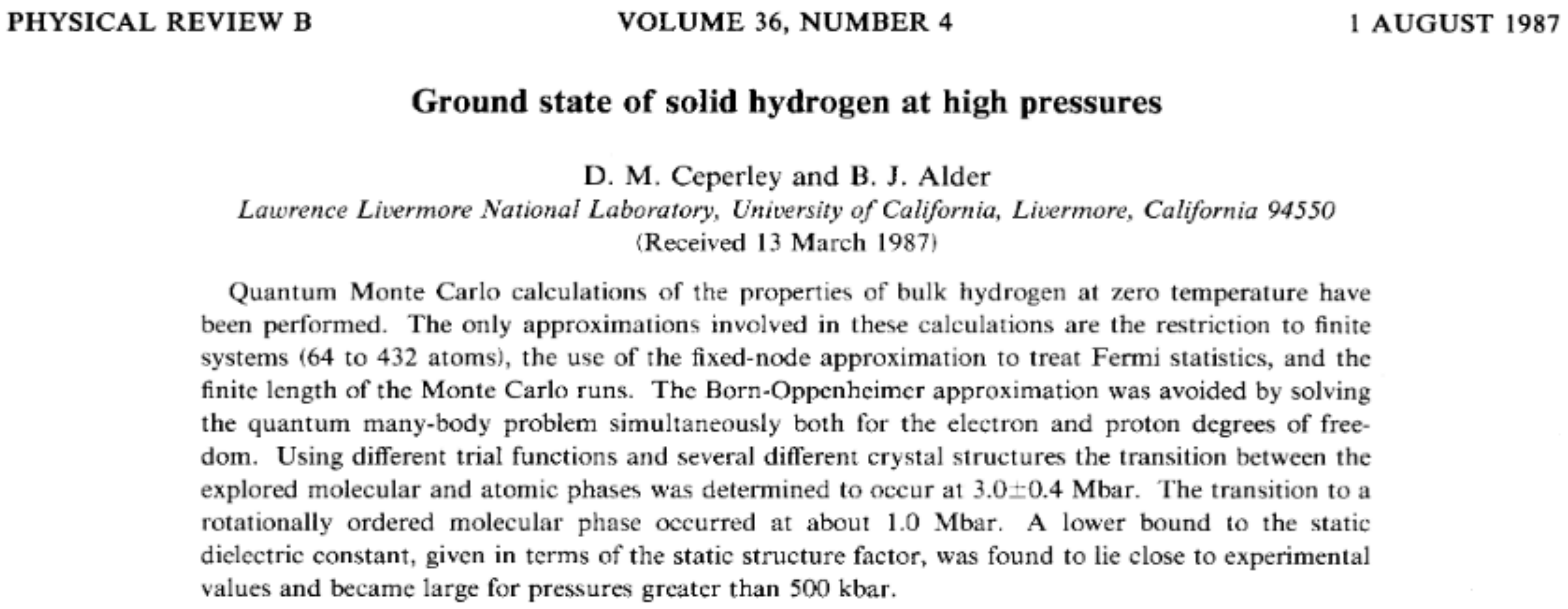
- Diffusion
- Drift
- branching

ensemble

Easy to parallelize over walkers



DMC calculation of Dense Hydrogen



PHYSICAL REVIEW B **VOLUME 36, NUMBER 4** **1 AUGUST 1987**

Ground state of solid hydrogen at high pressures

D. M. Ceperley and B. J. Alder
Lawrence Livermore National Laboratory, University of California, Livermore, California 94550

(Received 13 March 1987)

Quantum Monte Carlo calculations of the properties of bulk hydrogen at zero temperature have been performed. The only approximations involved in these calculations are the restriction to finite systems (64 to 432 atoms), the use of the fixed-node approximation to treat Fermi statistics, and the finite length of the Monte Carlo runs. The Born-Oppenheimer approximation was avoided by solving the quantum many-body problem simultaneously both for the electron and proton degrees of freedom. Using different trial functions and several different crystal structures the transition between the explored molecular and atomic phases was determined to occur at 3.0±0.4 Mbar. The transition to a rotationally ordered molecular phase occurred at about 1.0 Mbar. A lower bound to the static dielectric constant, given in terms of the static structure factor, was found to lie close to experimental values and became large for pressures greater than 500 kbar.

- Predicted two $T=0$ transitions.
- But using wrong crystal structure for the atomic phase
- Differing time scales of protons and electrons caused very slow convergence.

Current 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 a dynamics 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 generalize them to many-body hydrogen: no free parameters, but they only work well for the atomic phase.

How good are QMC energies for many-body hydrogen?

- QMC energies are accurate to about 100K/ atom(estimate comes from energies and variances)

- Relative energies between similar bonding structures should be more accurate than this.

- Lower is better!

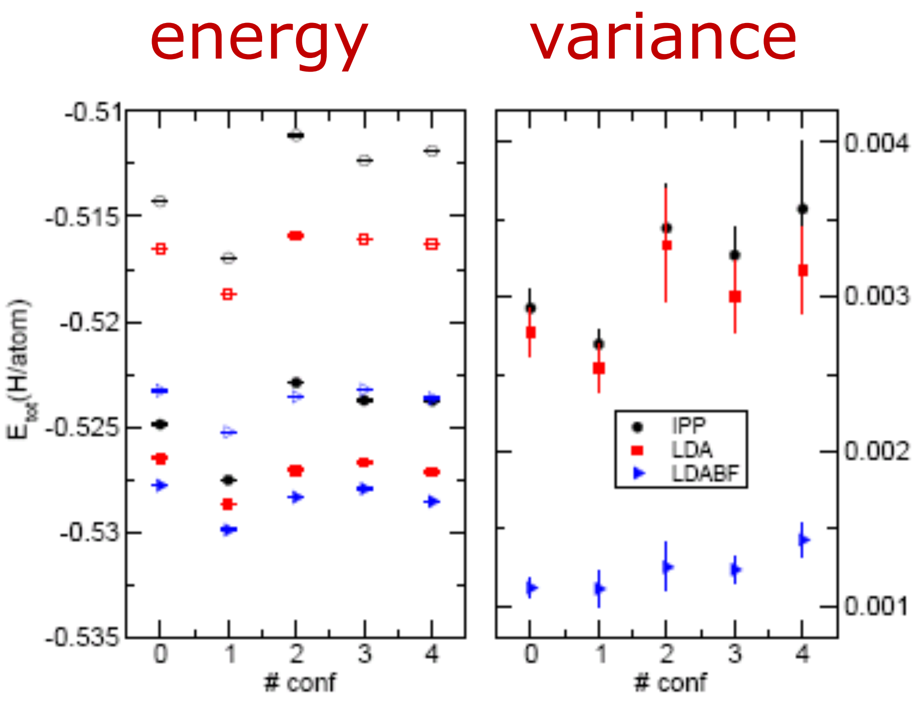
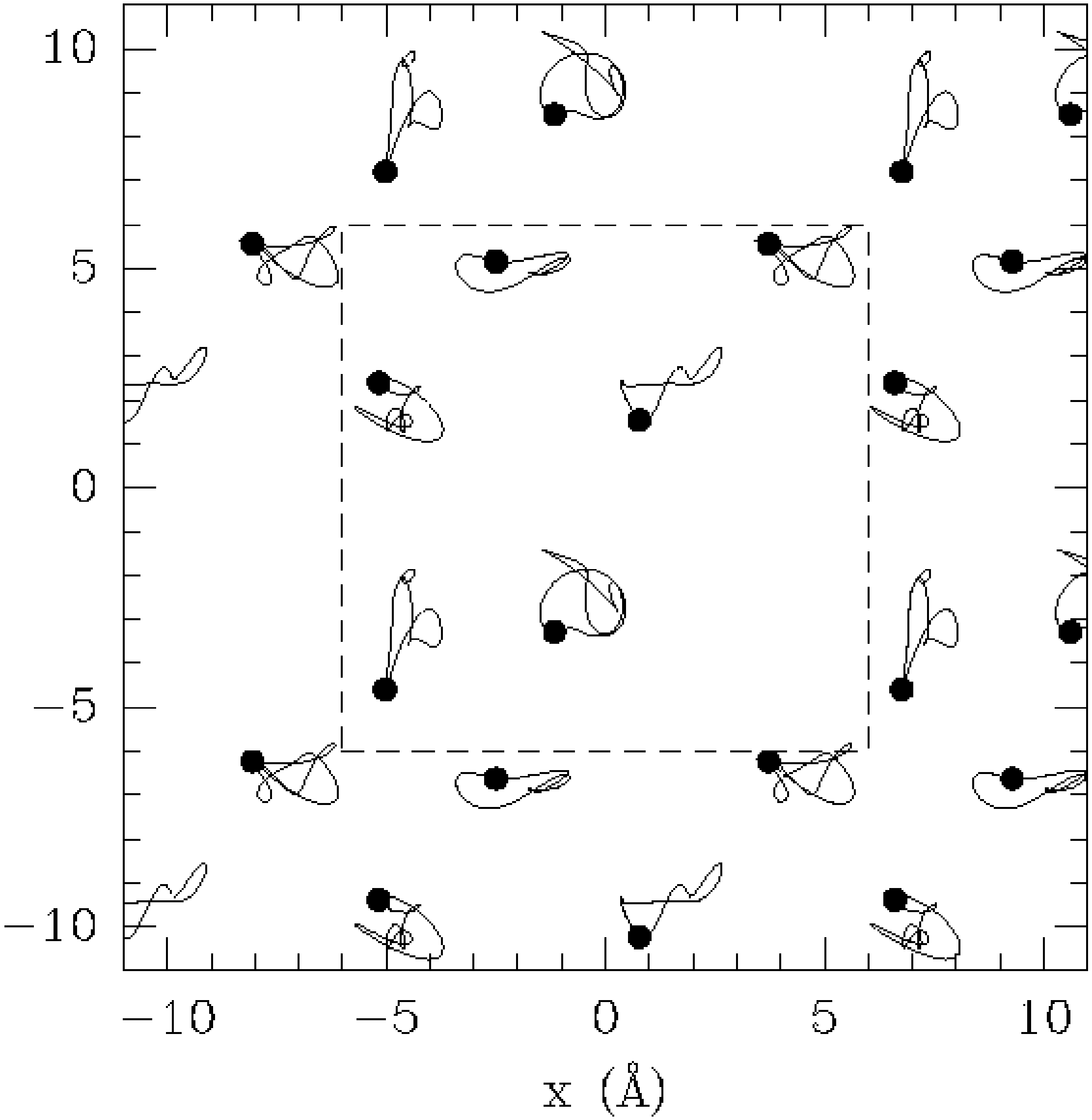


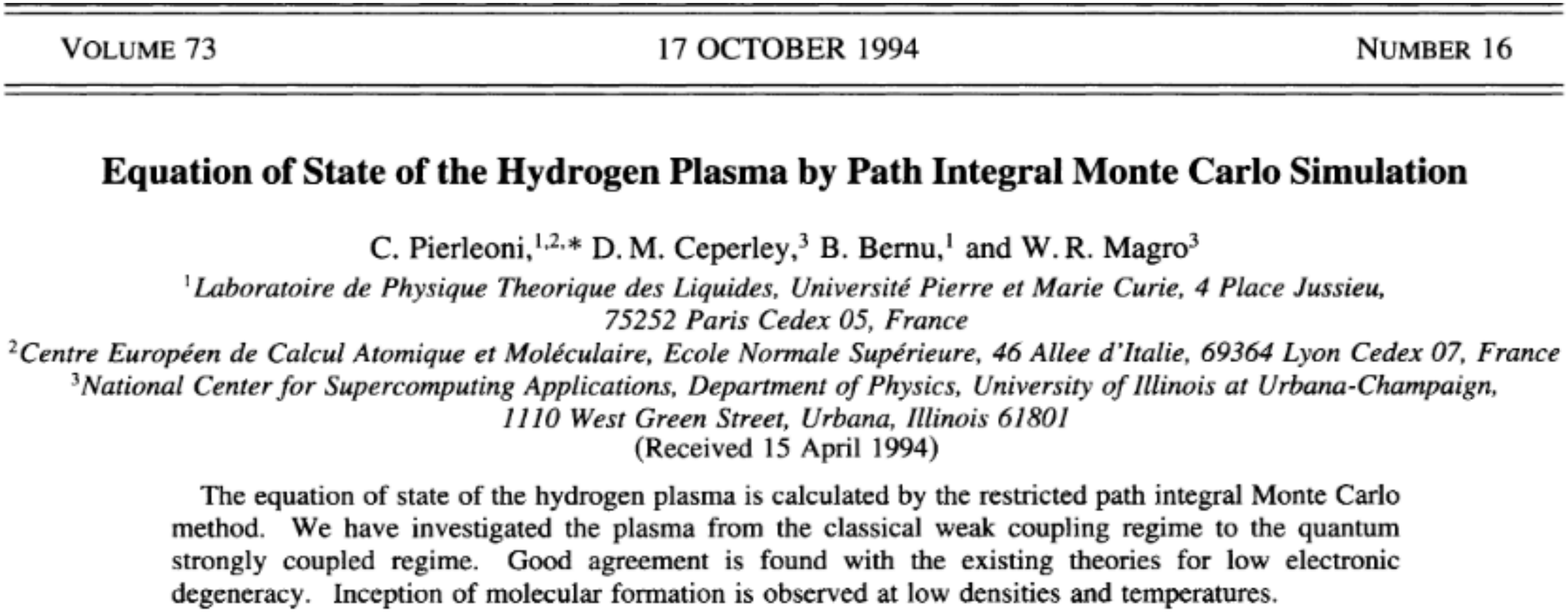
Fig. 4. Total energy (left panel) and quality parameter (right panel) for a number of static proton configurations as obtained with the metallic and the LDABF trial functions at $r_s = 1.40$. TABC with a 6x6x6 fixed grid in the twist space is performed. Energies are in h/atom. In the right panel open 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.

PIMC: Quantum particles are replaced by paths

- Each atom becomes a rubber band.
- **This is an exact representation of a quantum particle.**
- The probability of a path depends on the electrostatic interaction.
- Average over all paths. This is what takes so much time.
- The lower the temperature, the longer the band and the more spread out the wavepacket.



Restricted Path Integral MC



VOLUME 73 17 OCTOBER 1994 NUMBER 16

Equation of State of the Hydrogen Plasma by Path Integral Monte Carlo Simulation

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[2]*Centre Européen de Calcul Atomique et Moléculaire, Ecole Normale Supérieure, 46 Allee d'Italie, 69364 Lyon Cedex 07, France*
[3]*National Center for Supercomputing Applications, Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801*

(Received 15 April 1994)

The equation of state of the hydrogen plasma is calculated by the restricted path integral Monte Carlo method. We have investigated the plasma from the classical weak coupling regime to the quantum strongly coupled regime. Good agreement is found with the existing theories for low electronic degeneracy. Inception of molecular formation is observed at low densities and temperatures.

- Restricted Path Integrals use the fixed-node method at T>0
- Difficult to get down to low temperatures
- Trial density matrix is not as accurate as the wave function.

Path integral picture of molecular hydrogen at low density

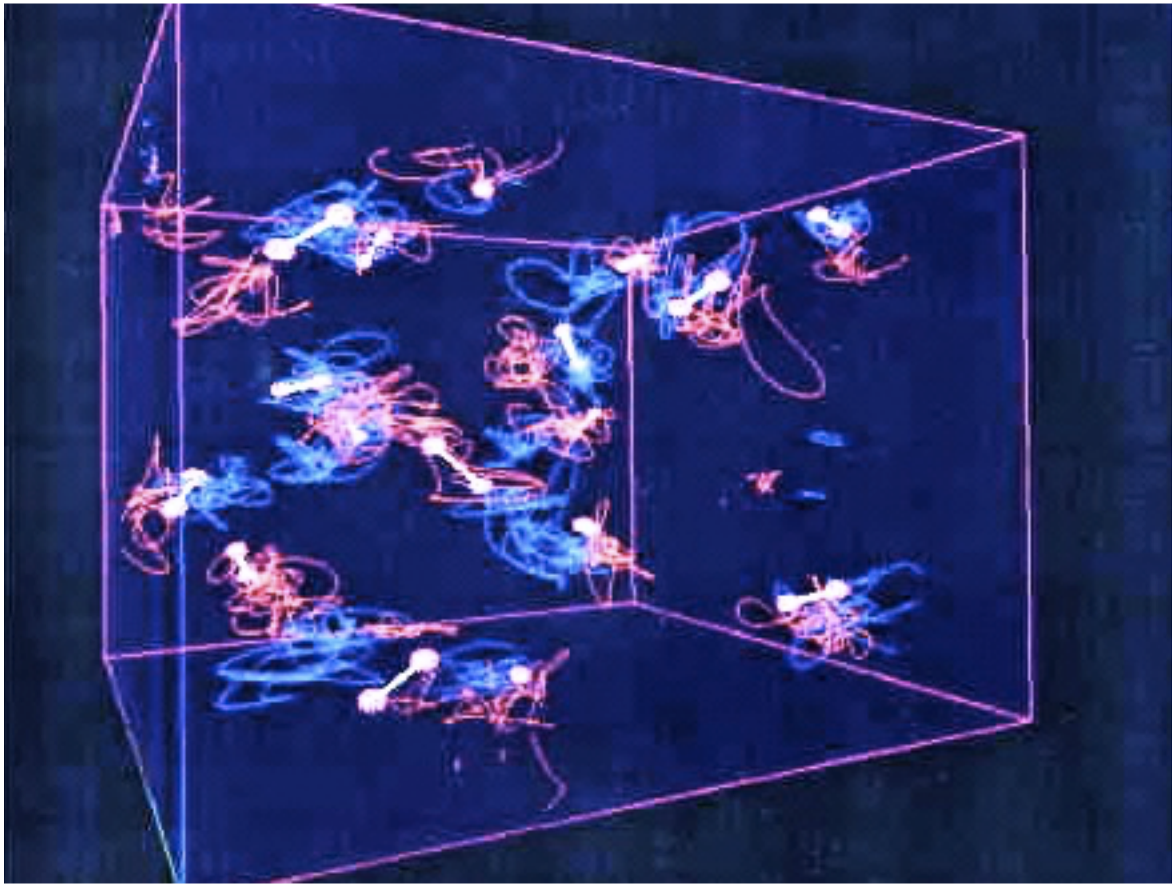
Pink and blue paths are up and down electrons.

Smaller pink dots are protons, 40 times smaller.

Why?

$M_p/M_e=1836$

T=5000K

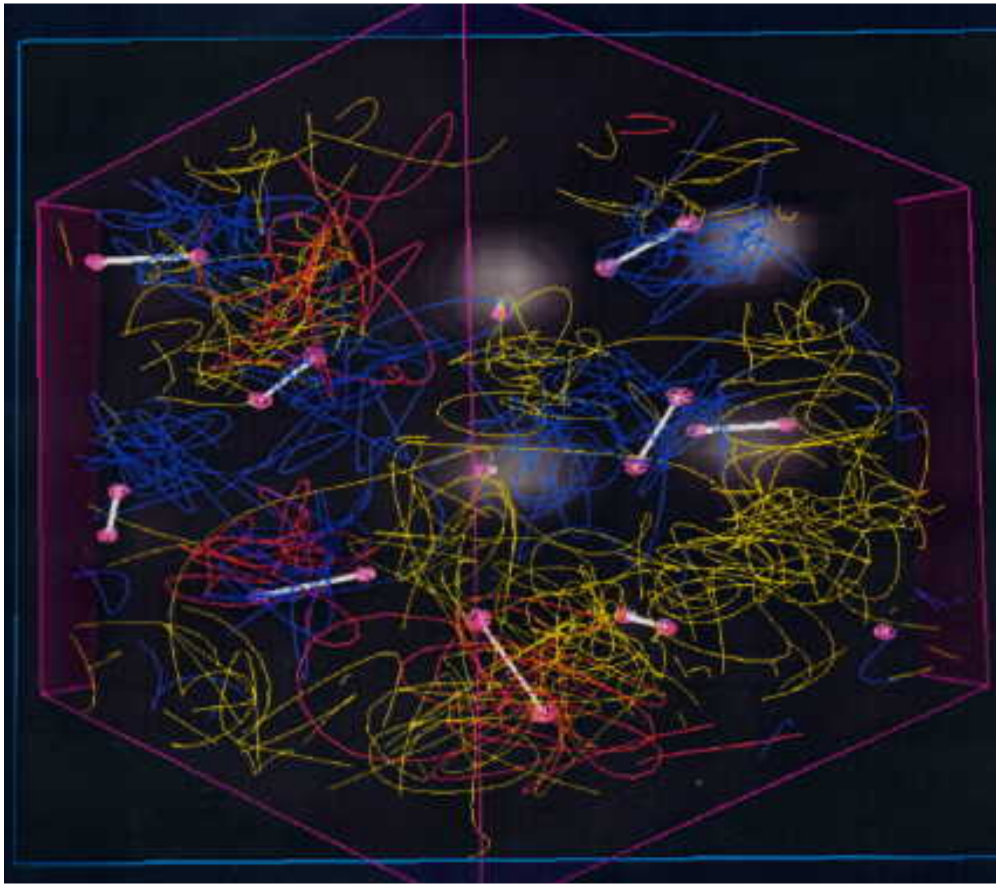


Molecular Metallic liquid

Deuterium

T=5000K

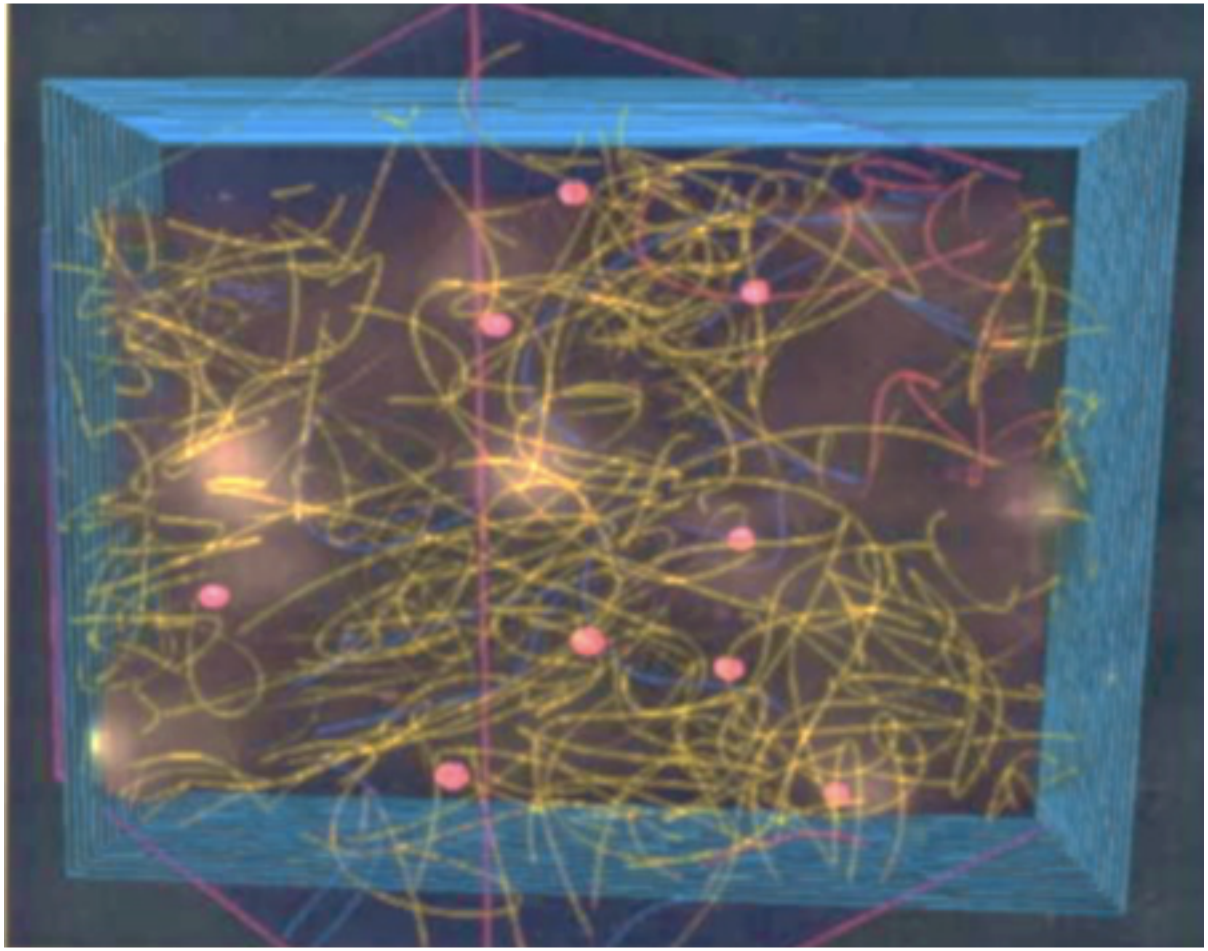
r_s=1.86



Ionized hydrogen

$T=6250K$

$r_s=1.60$



Path Integral Monte Carlo Calculation of the Deuterium Hugoniot

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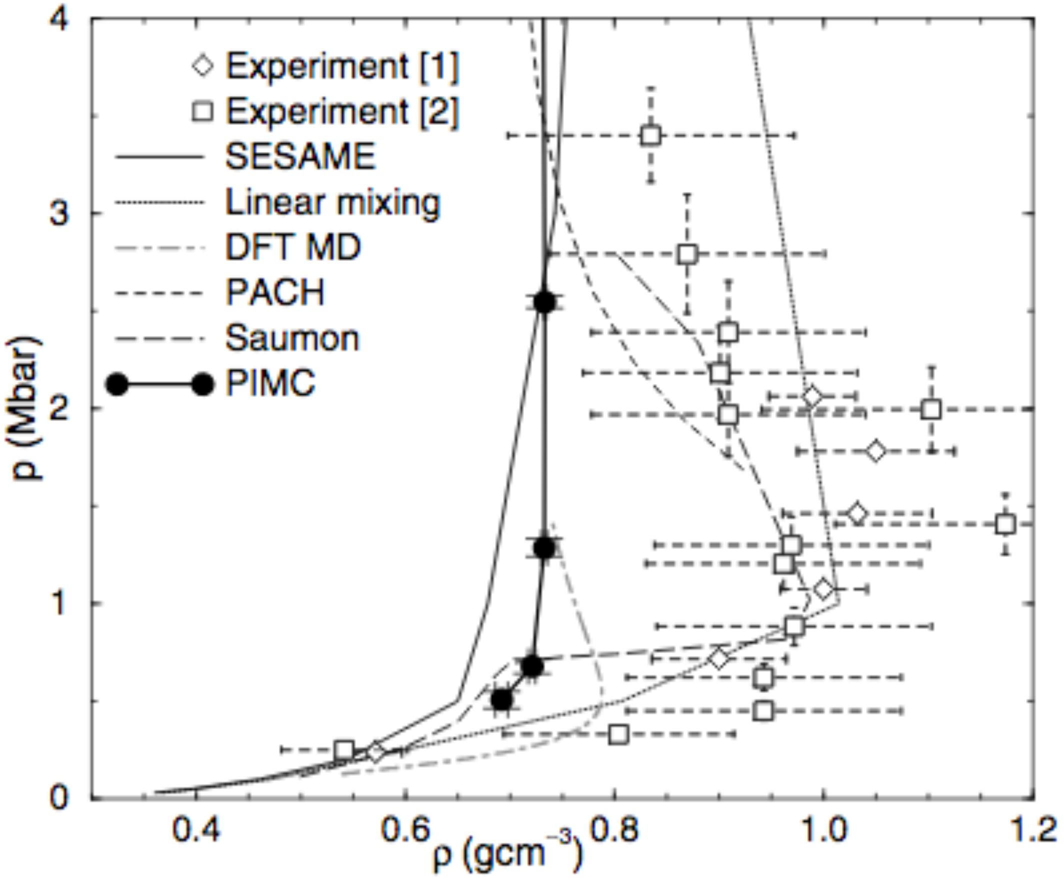
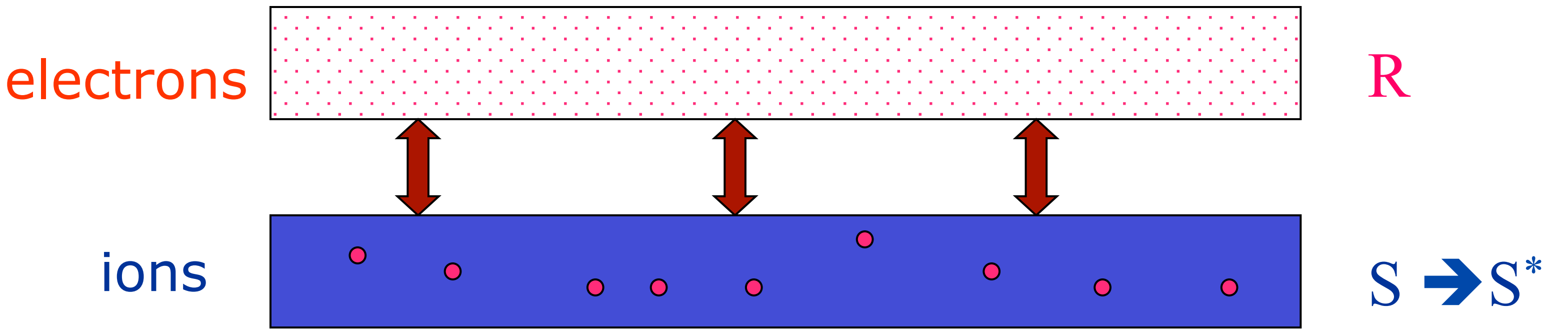
Urbana, Illinois 61801



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 $T<<E_F$.
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.

ab-initio with QMC

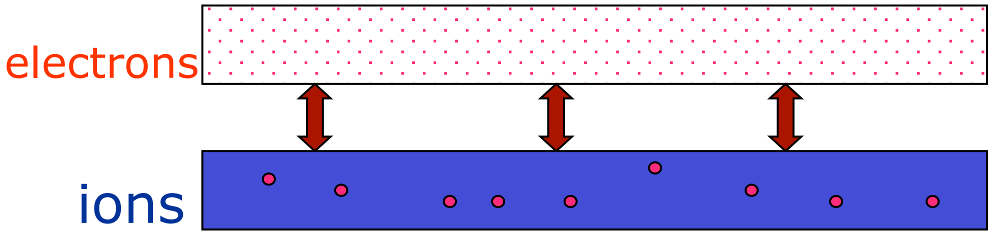
Coupled Electron-Ion MC (CEIMC)

CEIMC

- Perform MC for ions with “noisy” energies from T=0K QMC reptation method
- Penalty Method:
  - Enforce detailed balance on average-no bias from noise!
  - Causes extra rejections

$$A(R \rightarrow R') = \min\left[1, \exp\left(-\beta \Delta E_{BO} - \frac{\beta^2 \sigma^2}{2}\right)\right]$$

- Correlated sampling for efficient energy differences



Reptation QMC

$$Z(\beta) = \left\langle \Psi \middle| e^{-\beta H} \middle| \Psi \right\rangle$$

$$= \int dR' \;\; dR \quad \Psi^*(R') \left\langle R' \middle| e^{-\beta H} \middle| R \right\rangle \Psi(R)$$

$$E(\beta) = -\frac{d \ln Z(\beta)}{d\beta}$$

- Use path integrals to evaluate
- Project trial wavefunction into ground state consistent with chosen nodes to avoid fermion sign problem. But upper bound!
- Direct evaluation of ground state distribution
- Correlated Sampling for small ion displacements

The Penalty method

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

- **Assume** estimated 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 $k_B T$) is more efficient than low noise, because the QMC will then be faster.

Reptation Monte Carlo

good for energy differences and properties

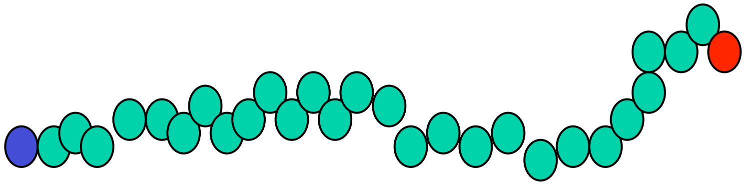
$$\Psi(\beta) = e^{-\frac{\beta}{2}H}\Psi$$

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

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

- Ψ(β) 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.

$$\boxed{\left(\operatorname{Im} \nabla \ln \Psi\right)^2}$$



New computational techniques

- Better algorithms, e.g. reptation, structure searching
- Better finite-size scaling methods (Holzmann et al)
  - Twist averaging for kinetic energy
  - Coulomb corrections for potential energy
- Better trial wavefunctions, e.g. analytic backflow → better treatment of fermion statistics
- Coupled electron-ion Monte Carlo allows lower temperatures T~300K
- Optimization of trial function parameters
- Explicit calculation of entropy, free energy
- Computers/parallelization: huge increase in resources

Approximations can now be controlled

Most older results were not converged

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.

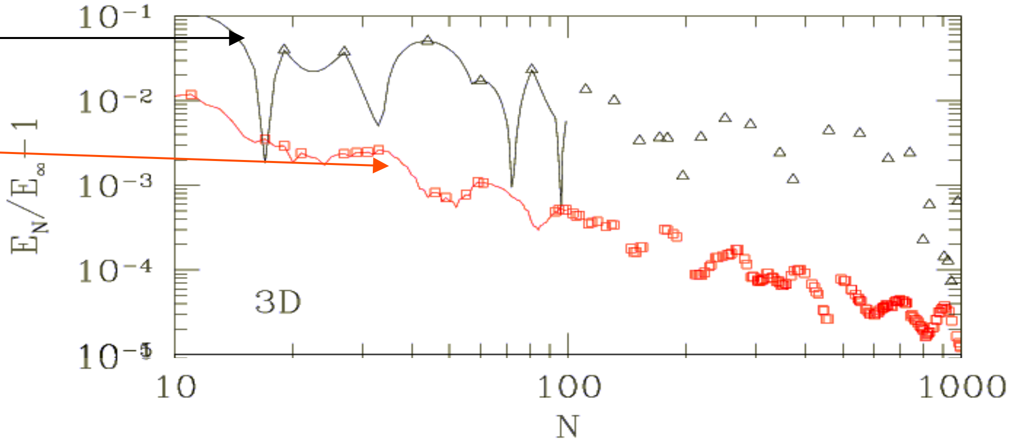
$$\Psi(x+L) = e^{i\theta}\Psi(x)$$

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

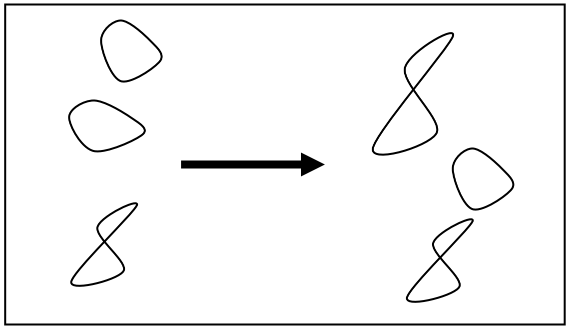
Error with PBC

Error with TABC

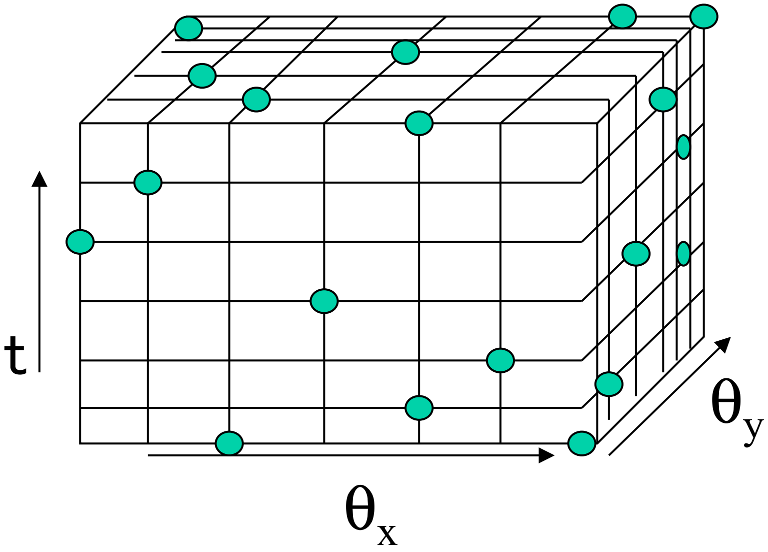
Error is zero in the grand canonical ensemble at the mean field level.



- Make a move of the protonic paths
- Partition the 4D lattice of boundary conditions $(\theta_x\ \theta_y\ \theta_z)$ and imaginary time (t) in such a way that each variable is uniformly sampled (stratified)
- Send them all out to M separate processes
- Do QMC to get energy differences and variances
- Combine to get global difference and variance.



$$R_\tau \rightarrow R_\tau^{'}$$



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

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

An advantage of Monte Carlo

Extra averaging is free! (almost)

Types of averaging we use:

- Average over liquid states
- Path Integrals for ions (for protons or light ions)
  - (M_1 time slices to average over.)
- 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_1M_2.
- With QMC there will be little increase in time since imaginary time and/or k are simply new variables to average over.
- Each give more parallelization.

The result is a code scaling well to tens of thousands of nodes and competitive with "ab initio" MD.

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.

Simulation Methods

Density Functional Theory

Molecular Dynamics

Path Integral MD

- Electron energy is an assumed functional of electron density
- Born-Oppenheimer approx.
- Norm-conserving pseudopotentials
- Number of atoms< 432

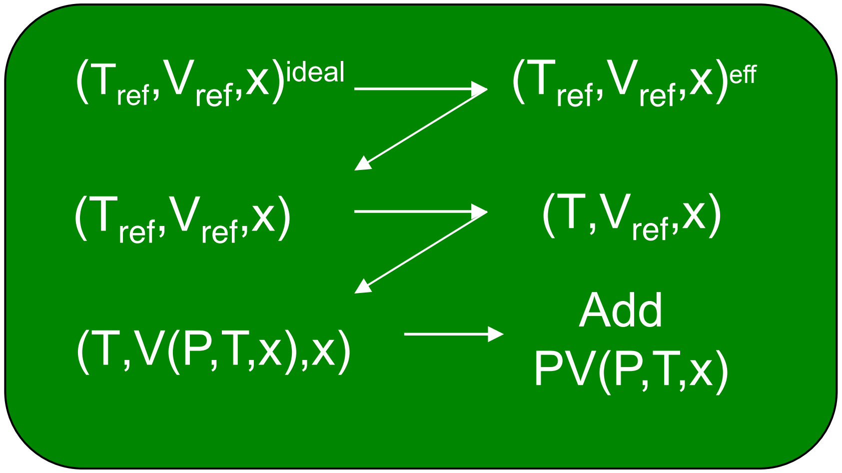
Quantum Monte Carlo

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

- No density functional
- No energy cutoff
- No pseudopotentials

The most accurate method for computing transition temperatures is with the free energy

Not easy to do with simulations: requires more work but *parallelizable* work



$(T_{ref},V_{ref},x)^{ideal} \rightarrow (T_{ref},V_{ref},x)^{eff}$

$(T_{ref},V_{ref},x) \rightarrow (T,V_{ref},x)$

$(T,V(P,T,x),x) \rightarrow$ Add $PV(P,T,x)$

Thermodynamic Integration

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

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

Coupling Constant Integration

$$V(\lambda)=\lambda V_1+(1-\lambda)V_2$$

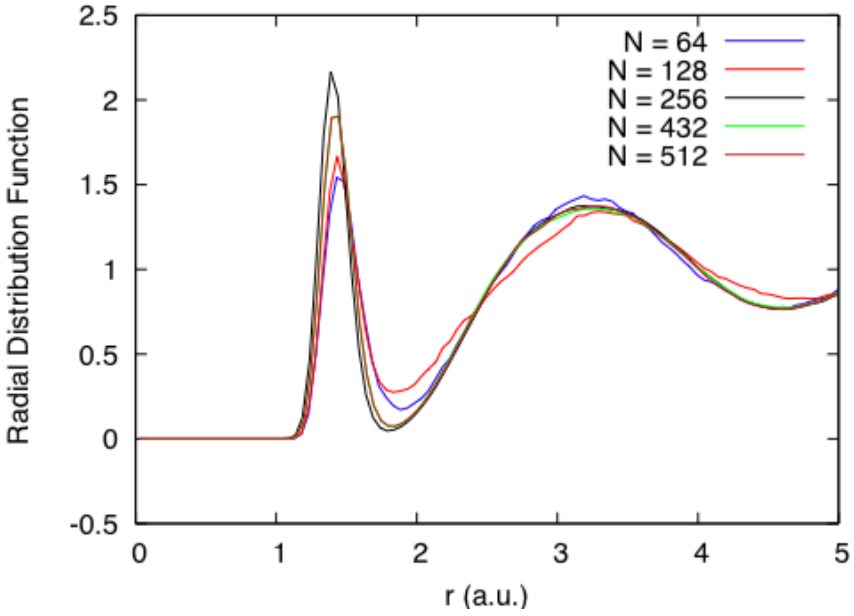
$$F_1(T,V,N)-F_0(T,V,N)=\int_0^1 d\lambda\left(\frac{dF(\lambda)}{d\lambda}\right)$$

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

Size Effects

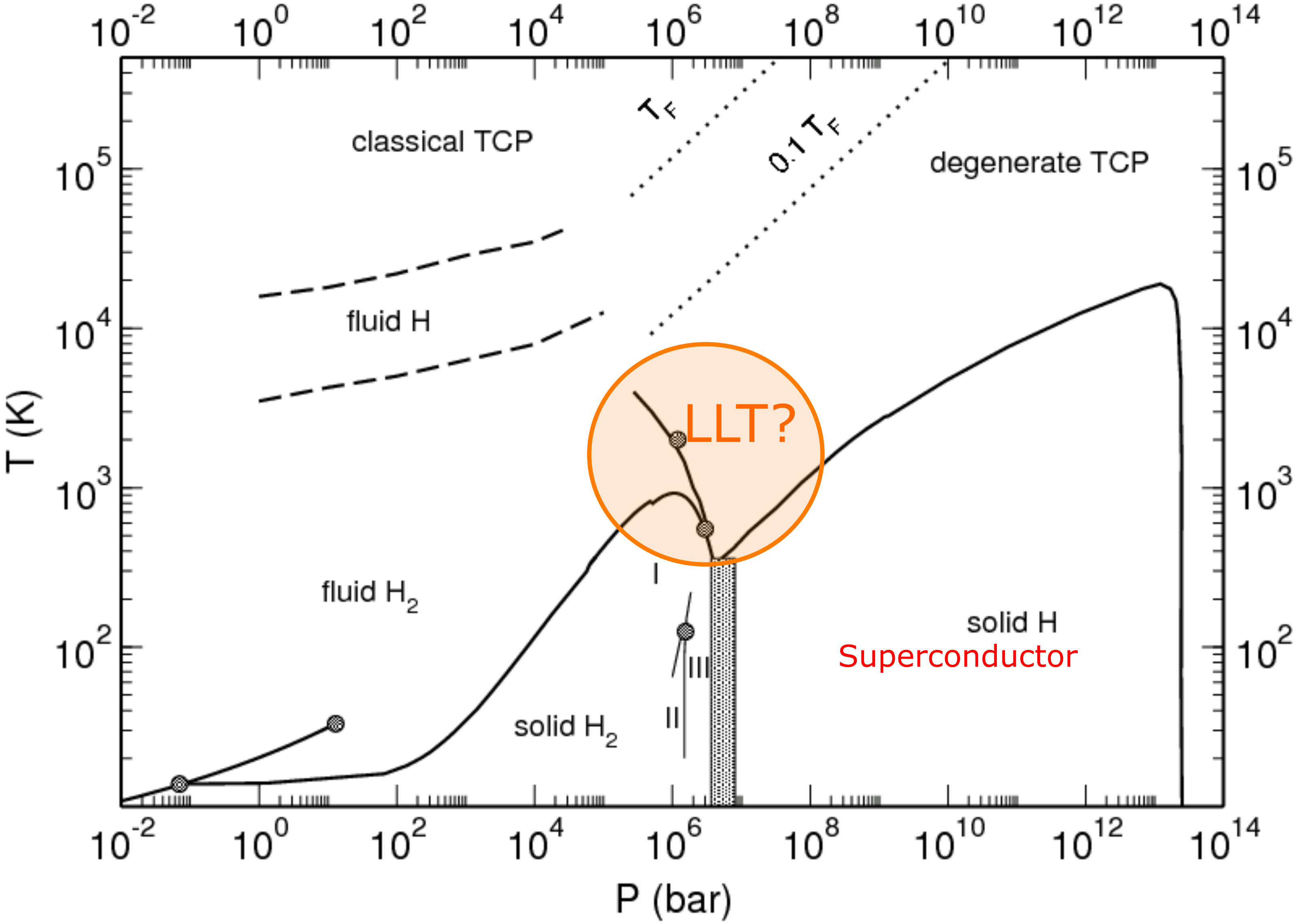
Strong electronic size effects in pair correlations:

-transition appears with grid of 3x3x3 K-points,
-Transition is absent at the G point (for N<400)



New effective theory of finite size scaling for coulomb interaction (Markus Holzmann)

Liquid-Liquid transition?



Я. Зельдович и Л. Ландау, О соотношении между жидким и газообразным состоянием у металлов, *Журнал Экспериментальной и Теоретической Физики* 14, 32 (1944).

L. Landau and G. Zeldovich, On the relation between the liquid and gaseous states of metals, *Acta Phys.-chim. USSR*, 18, 194 (1943).

A Metal sharply differs from a dielectric with respect to its spectrum of electron energy levels at absolute zero temperature. The fundamental state of the metal borders upon a continuous spectrum of states: this explains the fact that even the weakest electrical field gives rise in a metal to an electrical current, due to a transition of the system to adjacent levels. On the contrary, the electron energy spectrum of a dielectric is characterised by the existence of a finite "gap", i.e. of a definite energy difference between the fundamental state with the lowest energy (corresponding to the absence of a current) and the nearest excited states, in which one of the electrons of the dielectric becomes free and the electric conductivity appears.

- Predicted a first order liquid-liquid transition in Hg, with change in conductivity

(3) the rise of temperature within a certain pressure range must be expected to be accompanied by the transition of the liquid metal into a liquid non-conducting phase (on the line TMD), which thereafter on the line TLG is transformed into a gas. The loss of metallic properties takes place as a phase transition metal–gas also at value of T and p much larger than those which correspond to the critical point liquid-gas. In the two latter cases a triple point T appears corresponding to the co-existence of two metallic and one dielectric phase in case 2 and one metal and two dielectric phases (liquid and gaseous) in the third case.

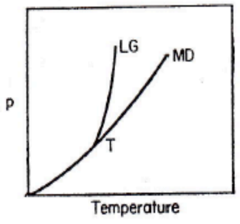


Fig 1.

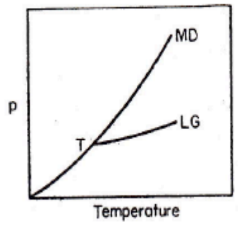


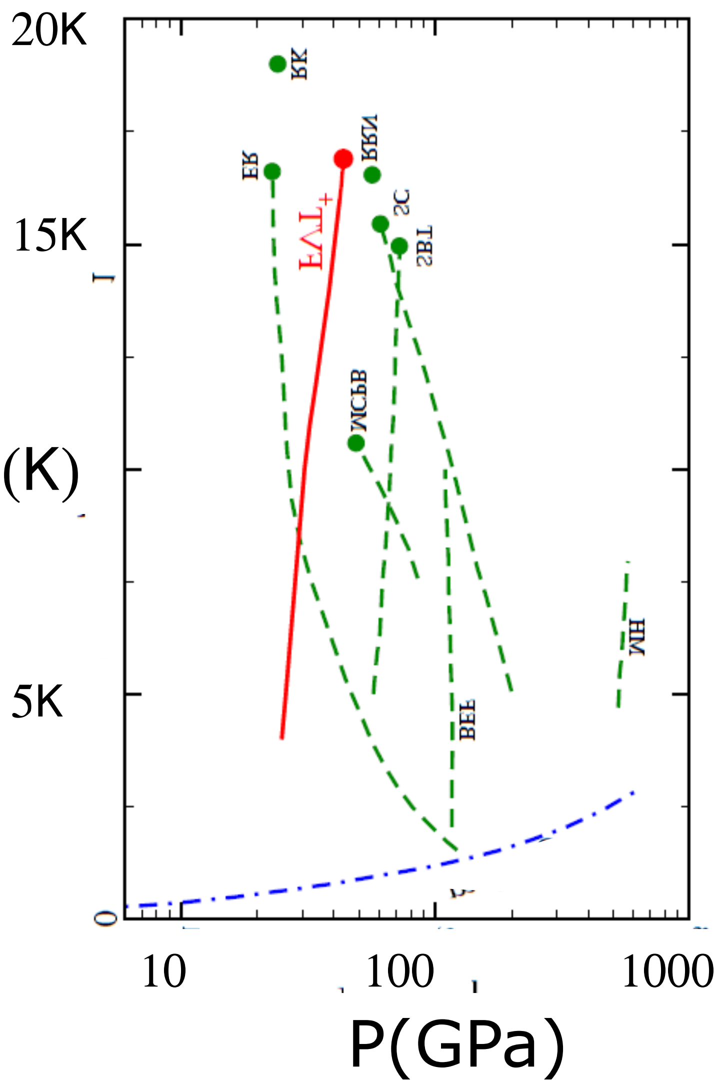
Fig. 2.

In the case of mercury the relatively small evaporation heat indicates that LG point is relatively low (1000–1500° K according to different estimates), whereas the MD point is probably inaccessible experimentally at the present time. There follows from our considerations that here our third case is to be expected. Our physical predictions thus are as follows (1) there exists a non-conducting liquid phase and (2) at a temperature and pressure lying above the critical values a phase transition with a discontinuous change of the electrical conductivity, volume and other properties must take place.

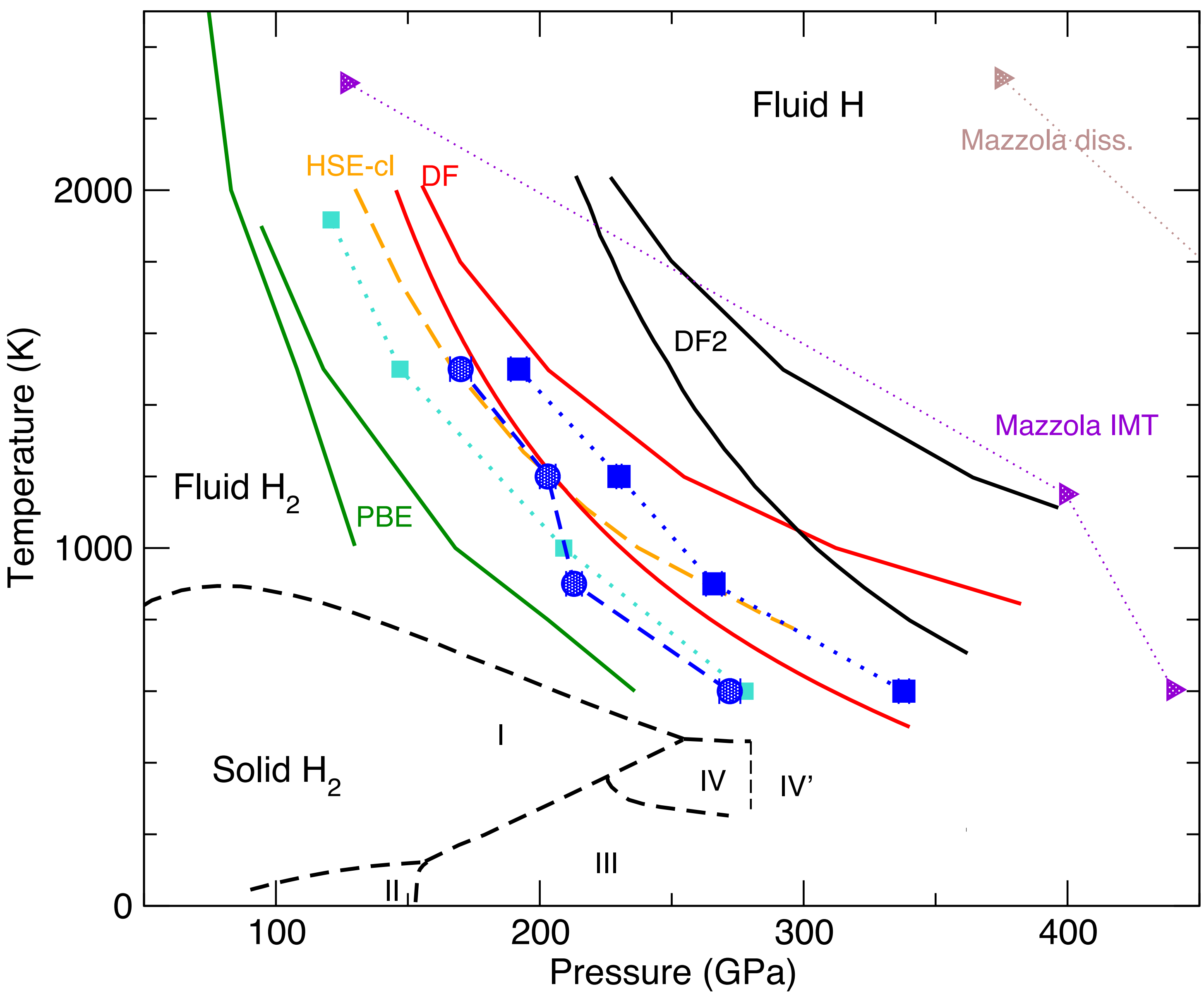
Liquid-Liquid transition

aka “Plasma Phase 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 have a transition since it is difficult to have an smooth crossover between 2 models (e.g. in the Saumon-Chabrier hydrogen EOS)



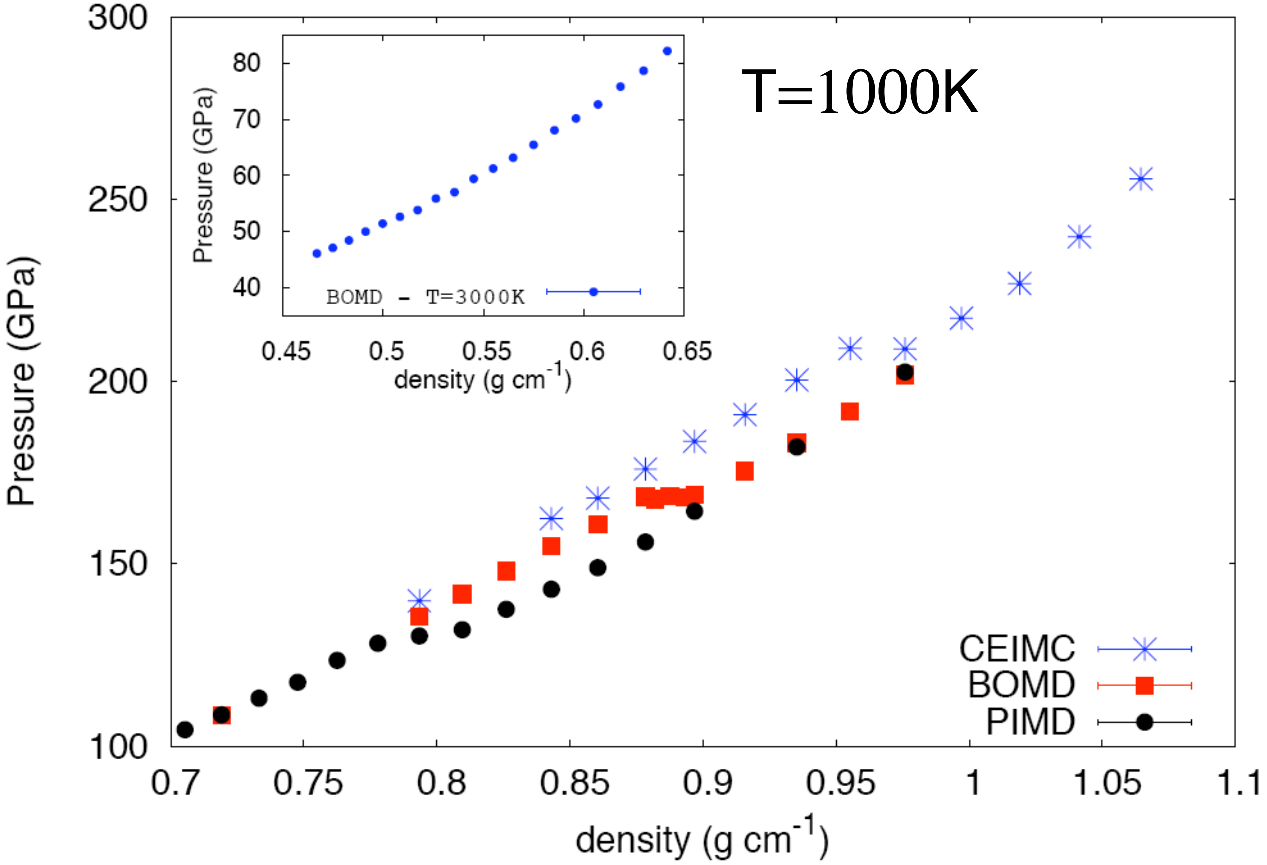
DFT calculations are not very predictive



Liquid-Liquid Transition

Morales,Pierleoni, Schwegler,DMC, PNAS 2010.

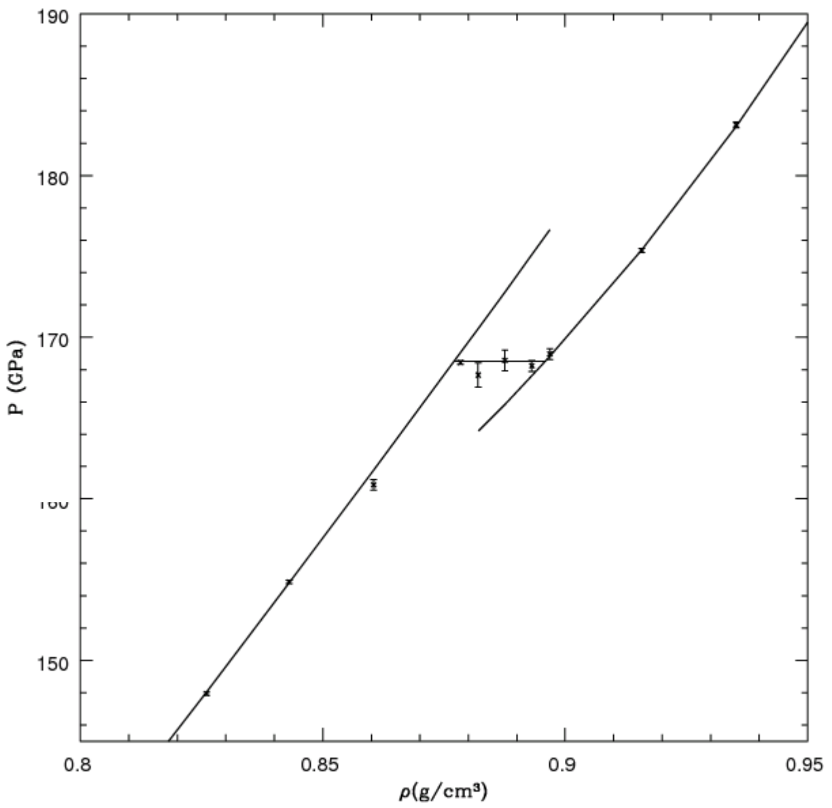
- Pressure plateau at low temperatures (T<2000K)- signature of a 1st order phase transition
- Seen in CEIMC and BOMD at different densities
- Finite size effects are very important
- Narrow transition (~2% width in V)
- Low critical temperature
- Small energy differences



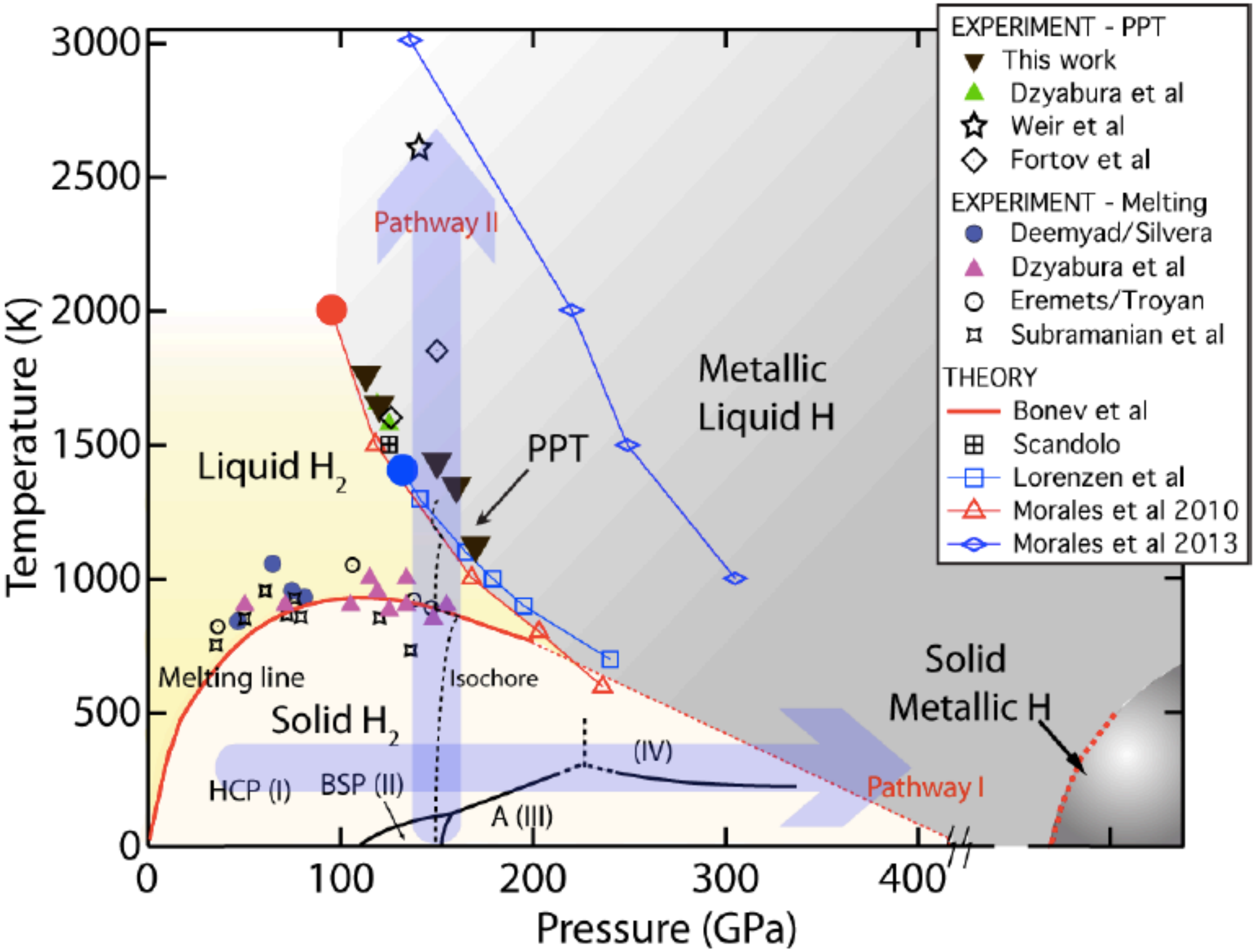
Three experimental confirmations since 2015!!

First order transition

- Pressure plateau at T=1000K
- Jump in compressibility

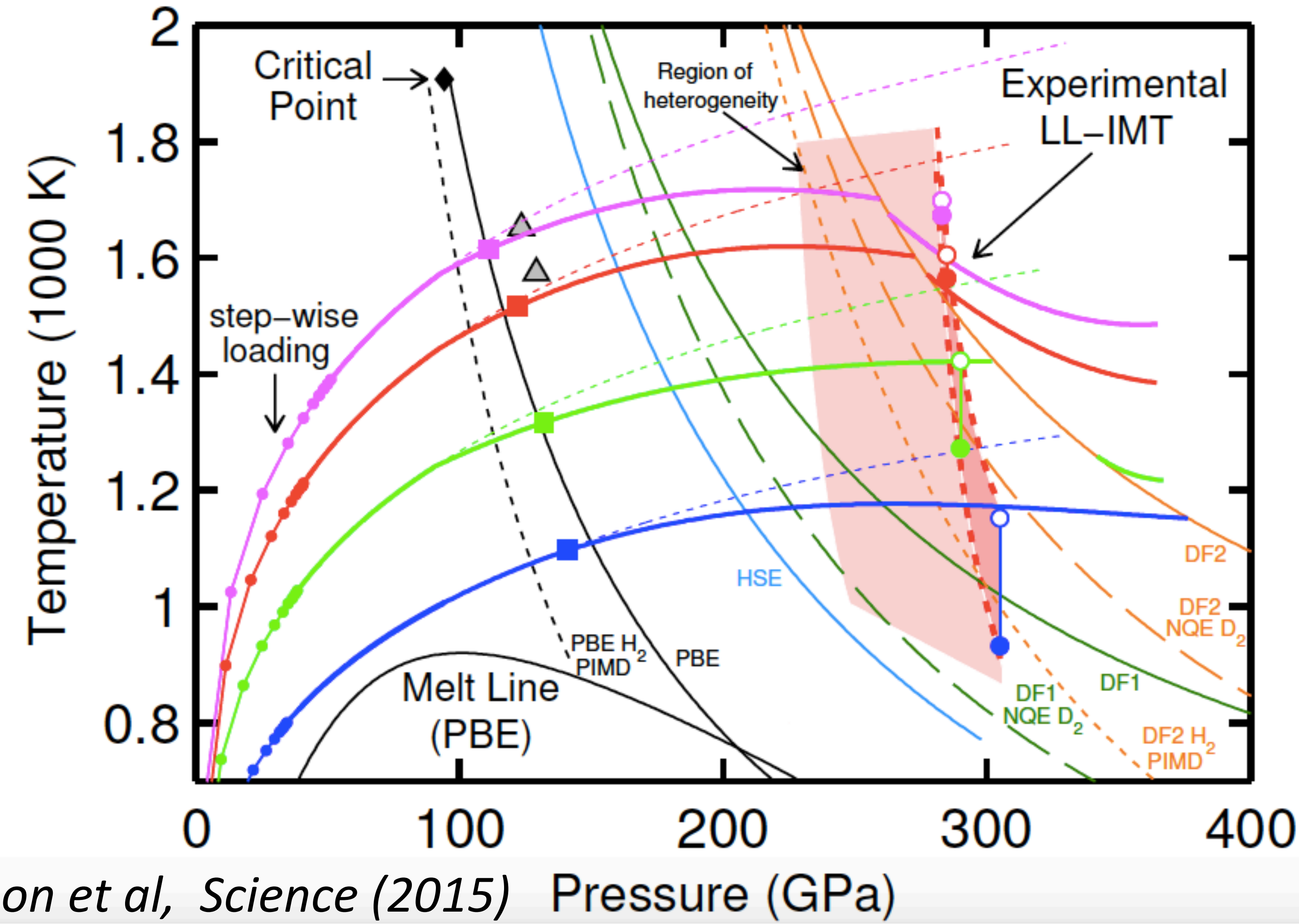


Dynamic heating within DAC (Harvard)



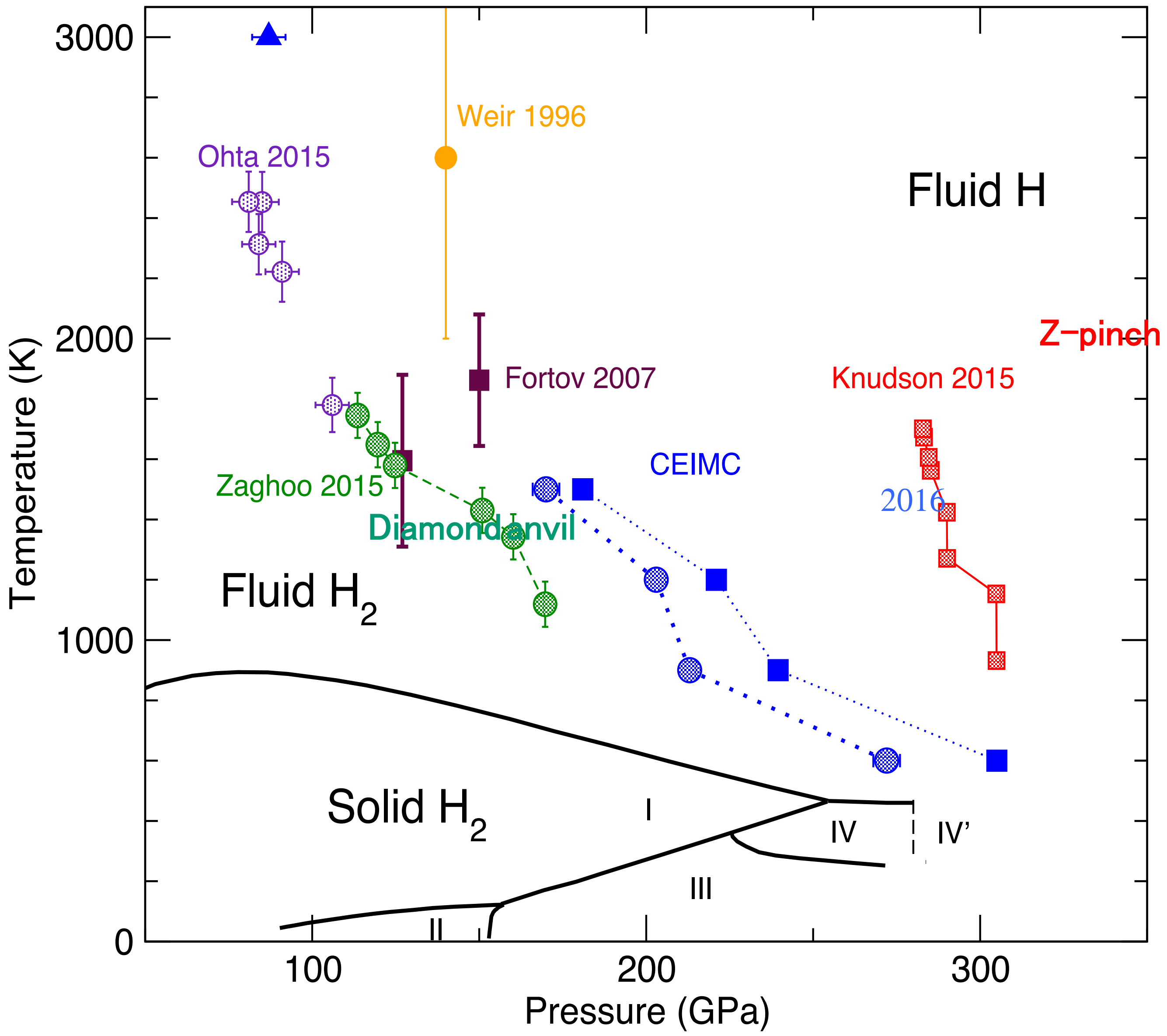
M. Zaghoo, A. Salamat, and I. Silvera (2015)

Ramp shock at Z-pinch (Sandia)



Knudson et al, Science (2015)

Experimental results differ by a factor 2!!
CEIMC is in the middle.



Settling Arguments About Hydrogen With 168 Giant Lasers

Scientists at Lawrence Livermore National Laboratory said they were “converging on the truth” in an experiment to understand hydrogen in its liquid metallic state.

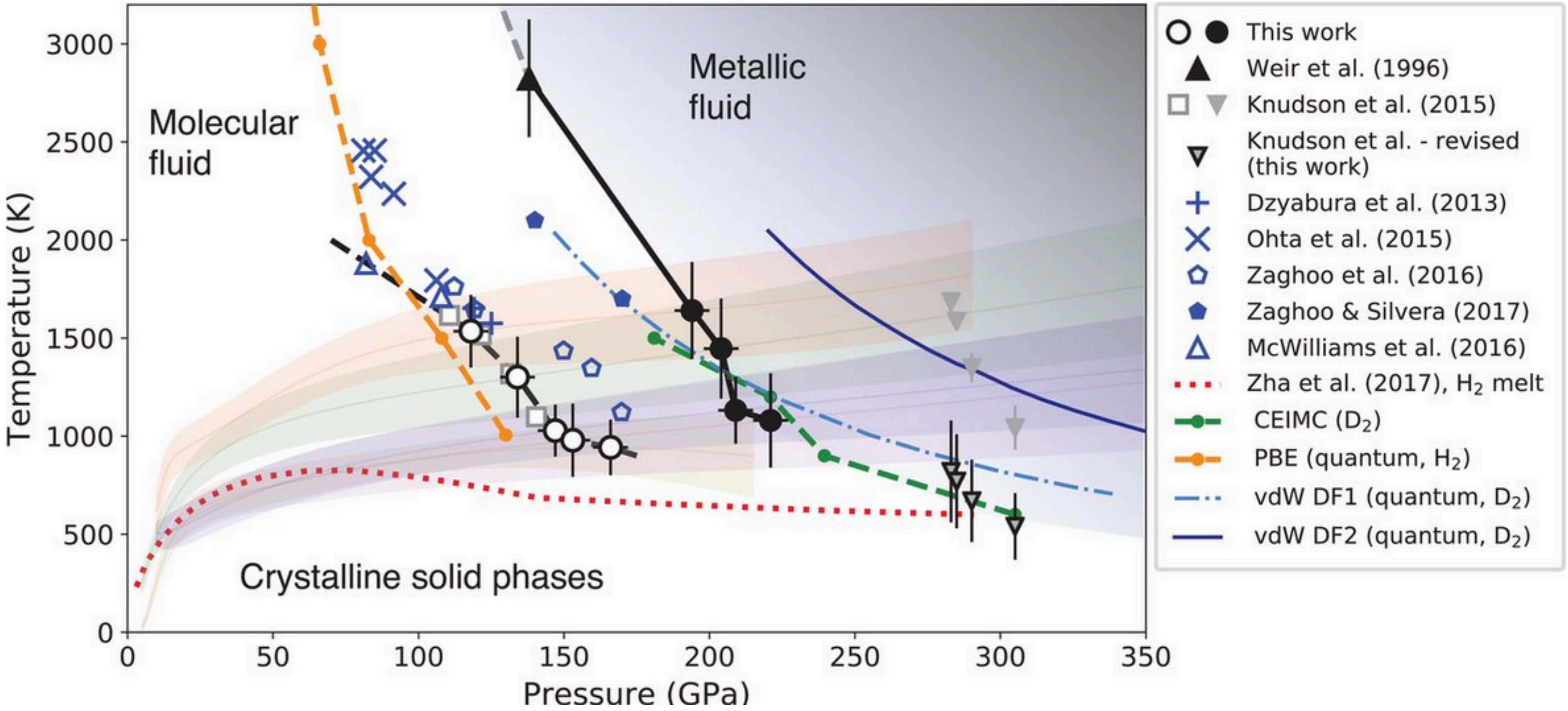
Liquid metallic hydrogen does not occur naturally on Earth, except possibly at the core, but scientists believe the interiors of Jupiter and Saturn are awash in hydrogen in that state.

NASA/Reuters

By Kenneth Chang

Aug. 16, 2018

Possible resolution (Livermore, 2018)



HIGH-PRESSURE PHYSICS

Insulator-metal transition in dense fluid deuterium

Peter M. Celliers[1]*, Marius Millot[1], Stephanie Brygoo[2], R. Stewart McWilliams[3], Dayne E. Fratanduono[1], J. Ryan Rygg[1,4], Alexander F. Goncharov[5], Paul Loubeyre[2], Jon H. Eggert[1], J. Luc Peterson[1], Nathan B. Meezan[1], Sebastien Le Pape[1], Gilbert W. Collins[1,4], Raymond Jeanloz[6], Russell J. Hemley[7]

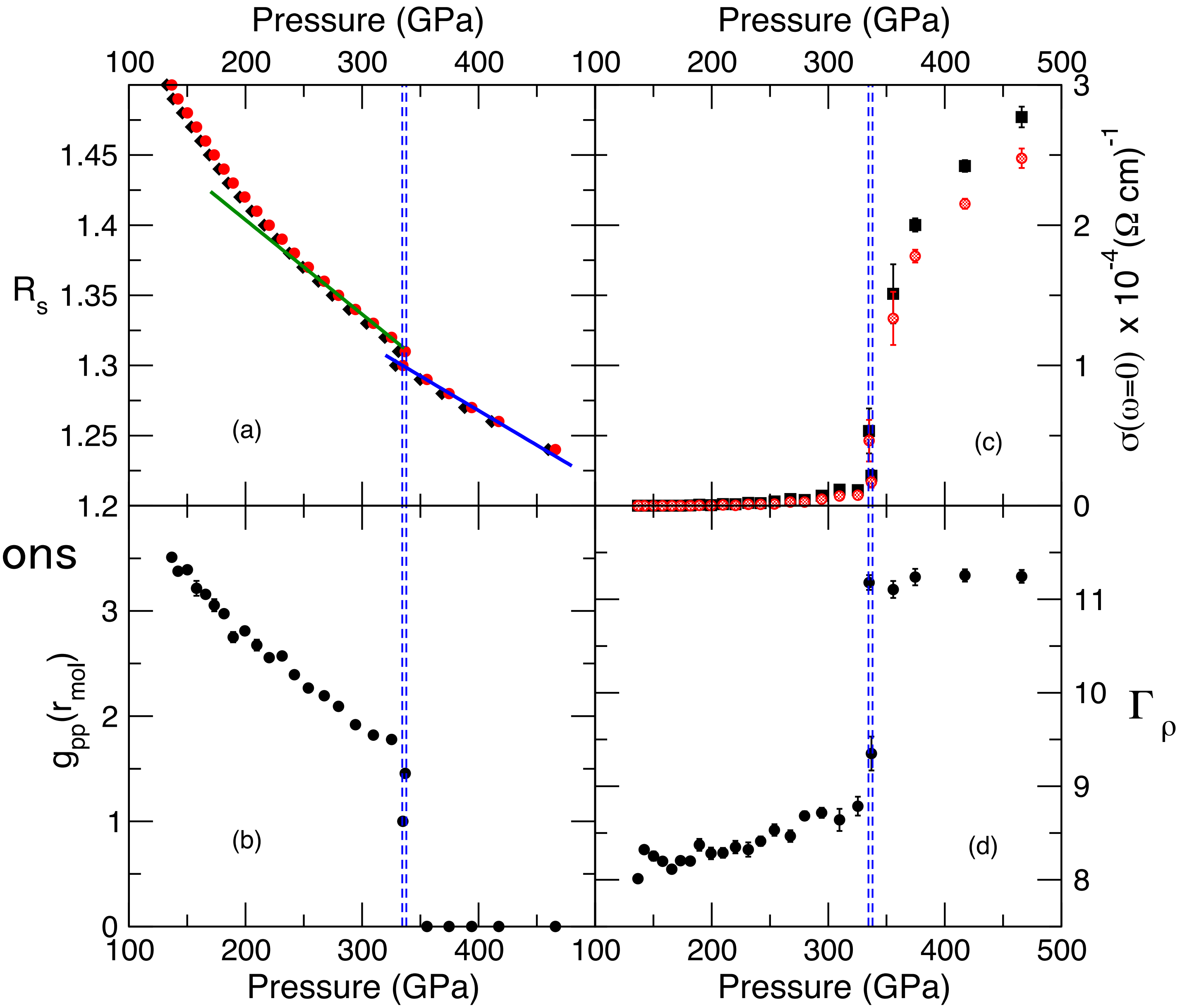
Science **361**, 677–682 (2018)

Signatures of the transition

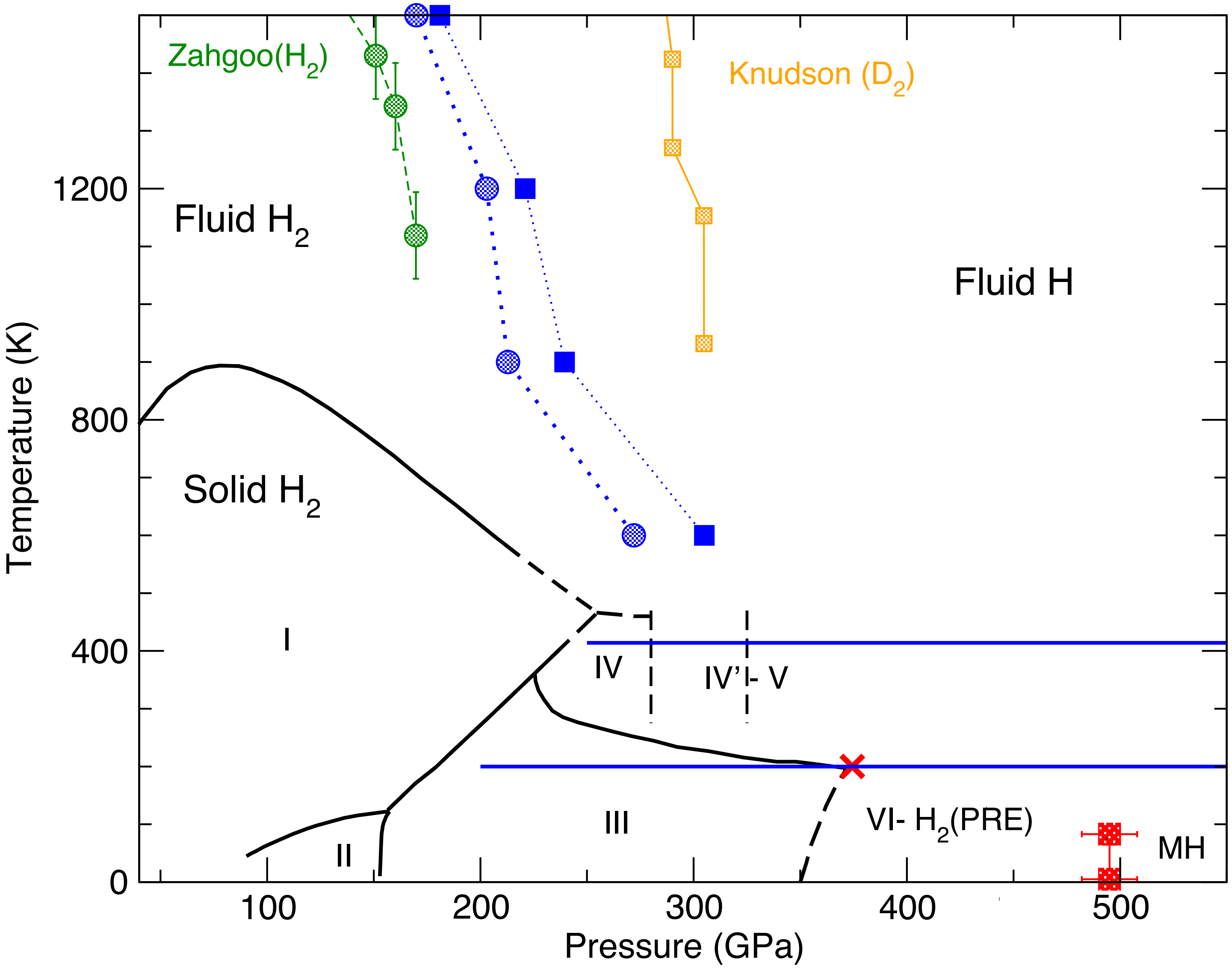
atomic-molecular & metal-insulator

T=600K

Classical protons

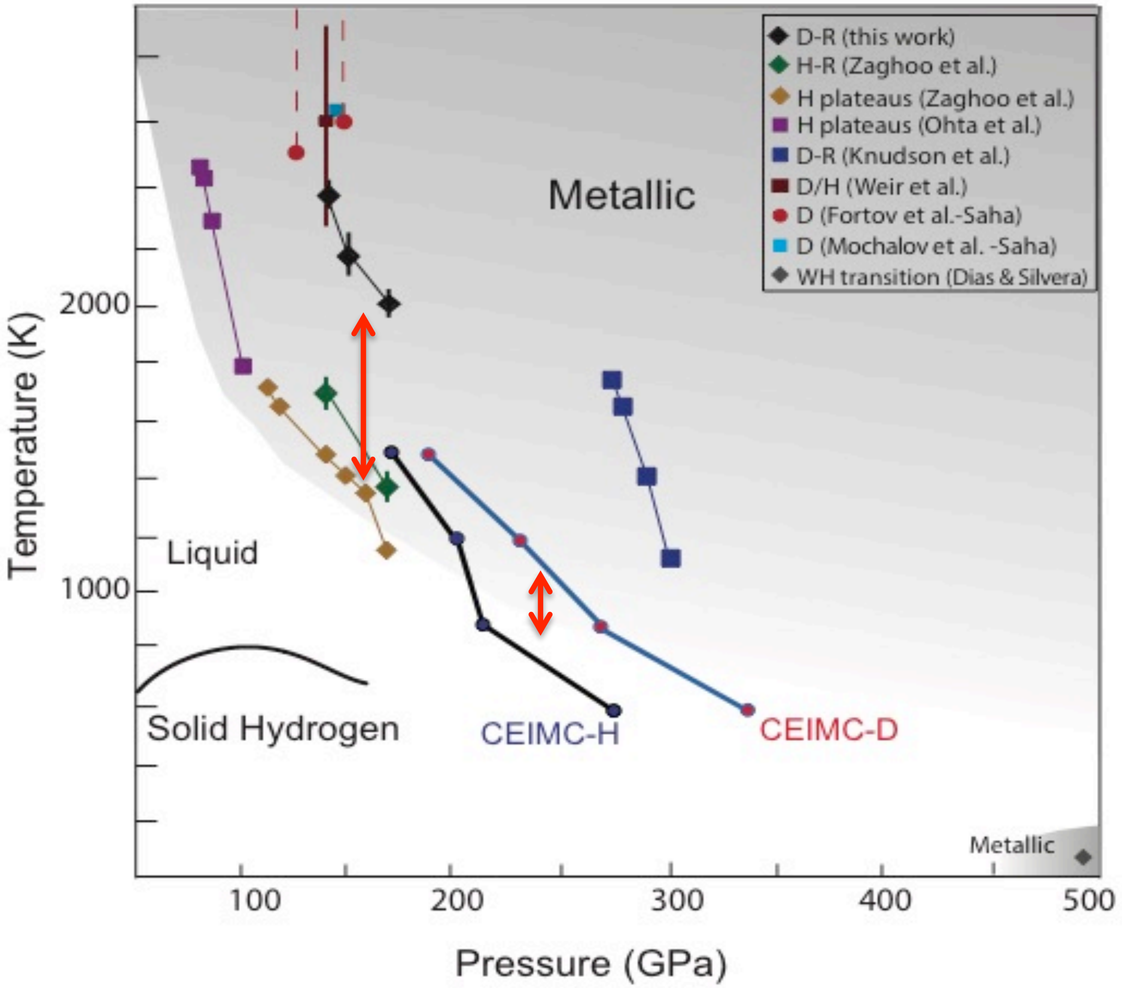


Experimental results differ by a factor 2!!
CEIMC is in the middle

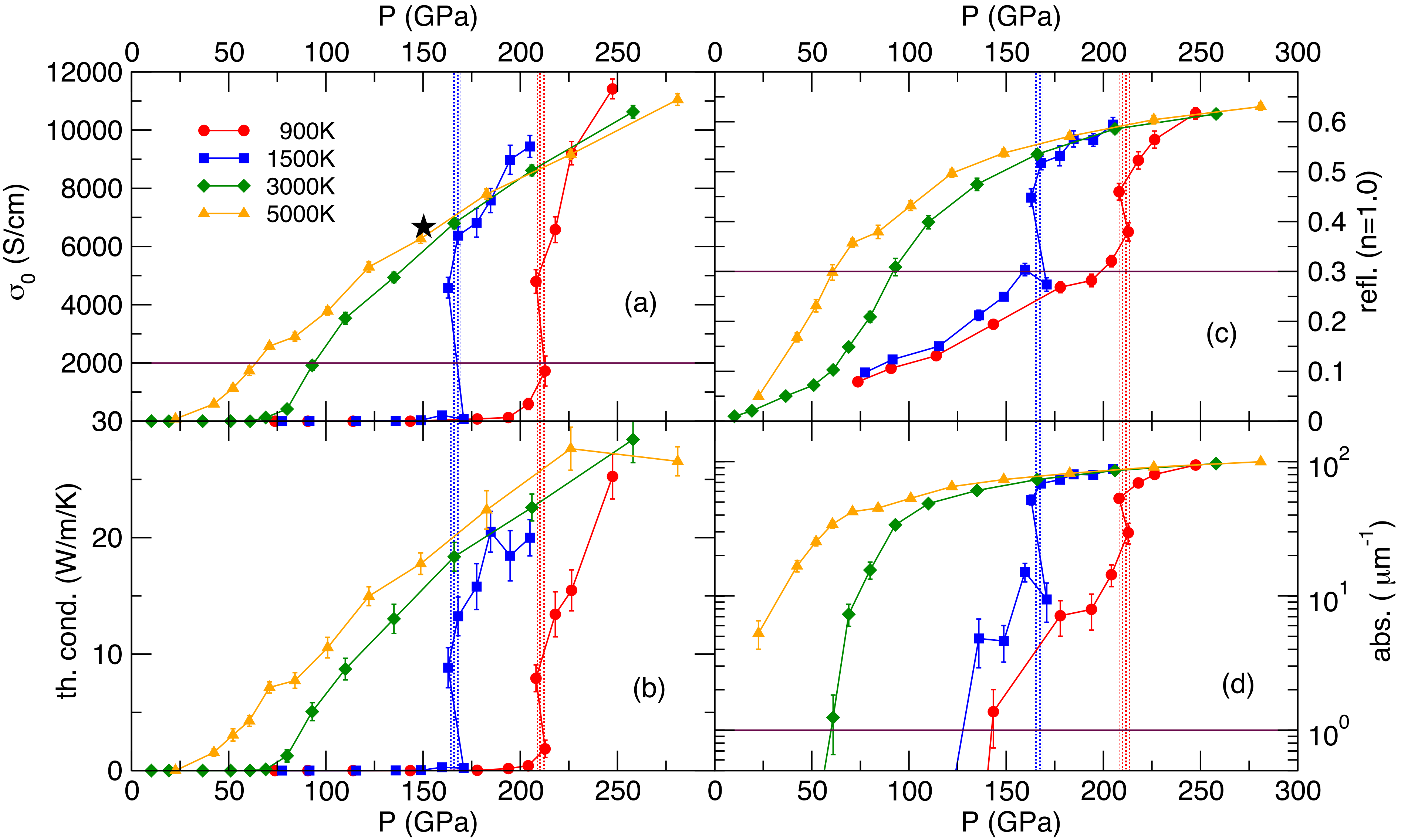


Experiments disagree with each other

CEIMC sits in the middle



Properties across the transition

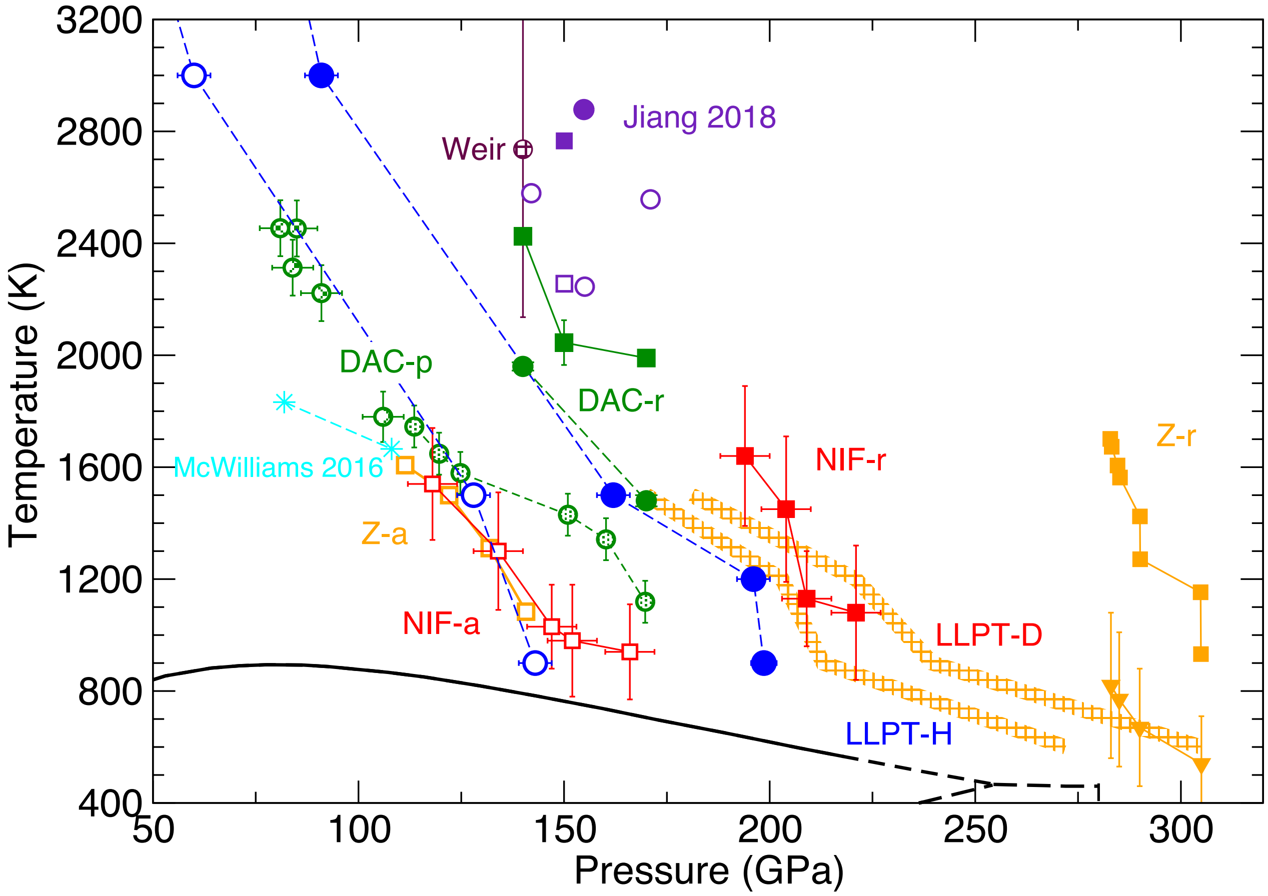


Rillo, Morales, DMC, Pierleoni, PNAS (2019)

Comparison of optical properties

“a” adsorption
“r” reflectance
“p” plateau

○ Hydrogen
■ Deuterium

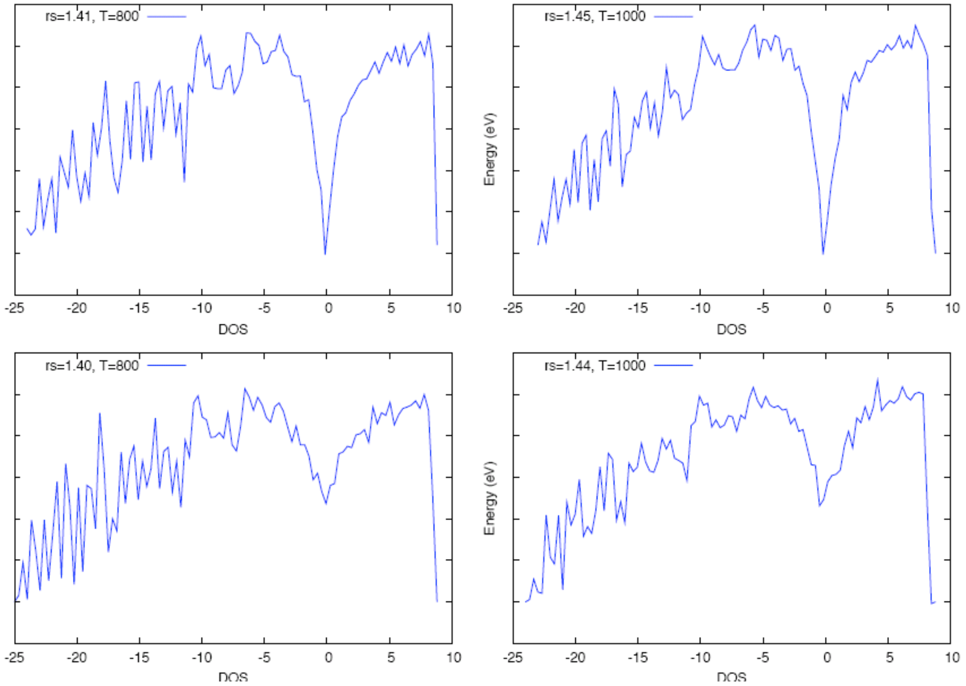


Rillo, Morales, DMC, Pierleoni, PNAS, in press, (2019).

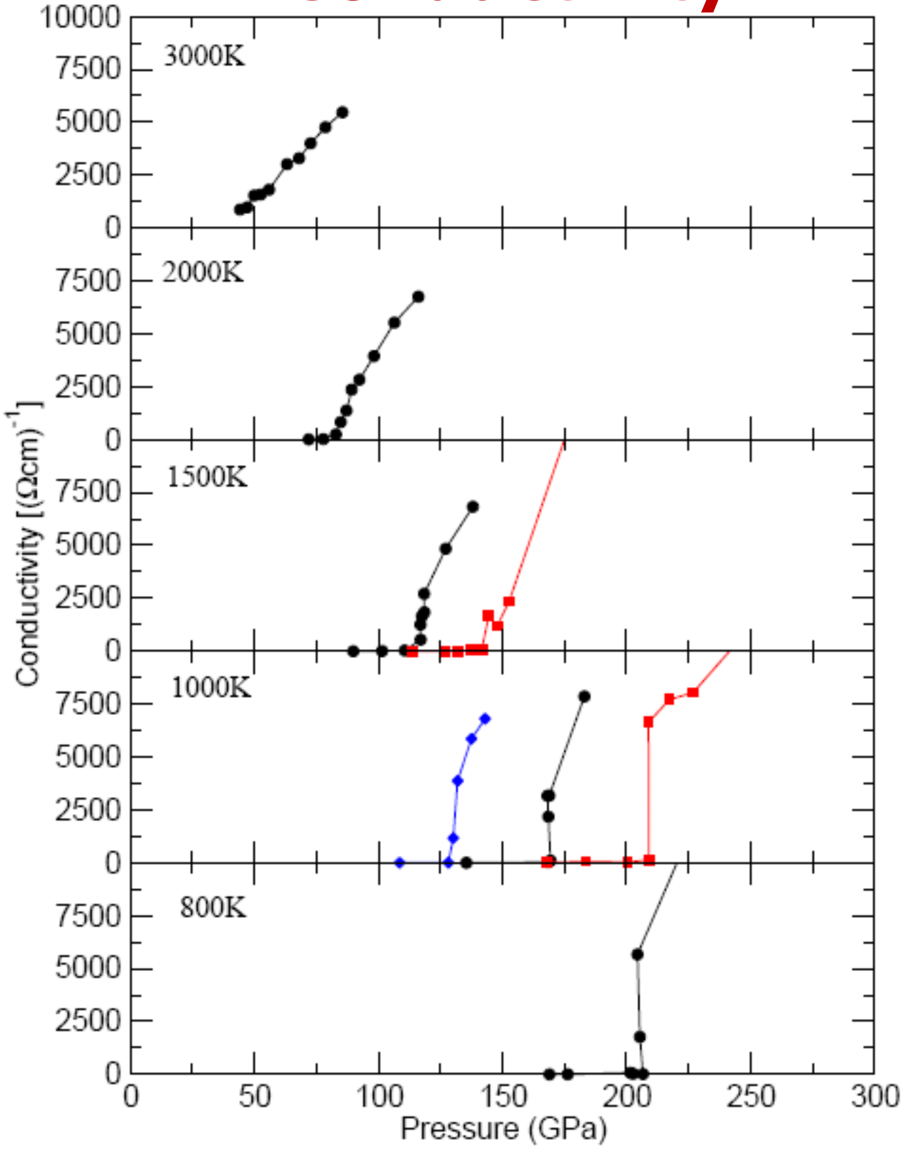
Conductivity across the transition

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

Density of states



Conductivity



Shock wave experiments.

- Hit a sample of cold, solid hydrogen
- Measurement of velocities, gives the density and pressure.
- Varying initial energy, gives the Hugoniot curve (1851-1887)
- Experiment is over in a fraction of a microsecond.
- Expensive and inaccurate

Conservation of Energy and Momentum

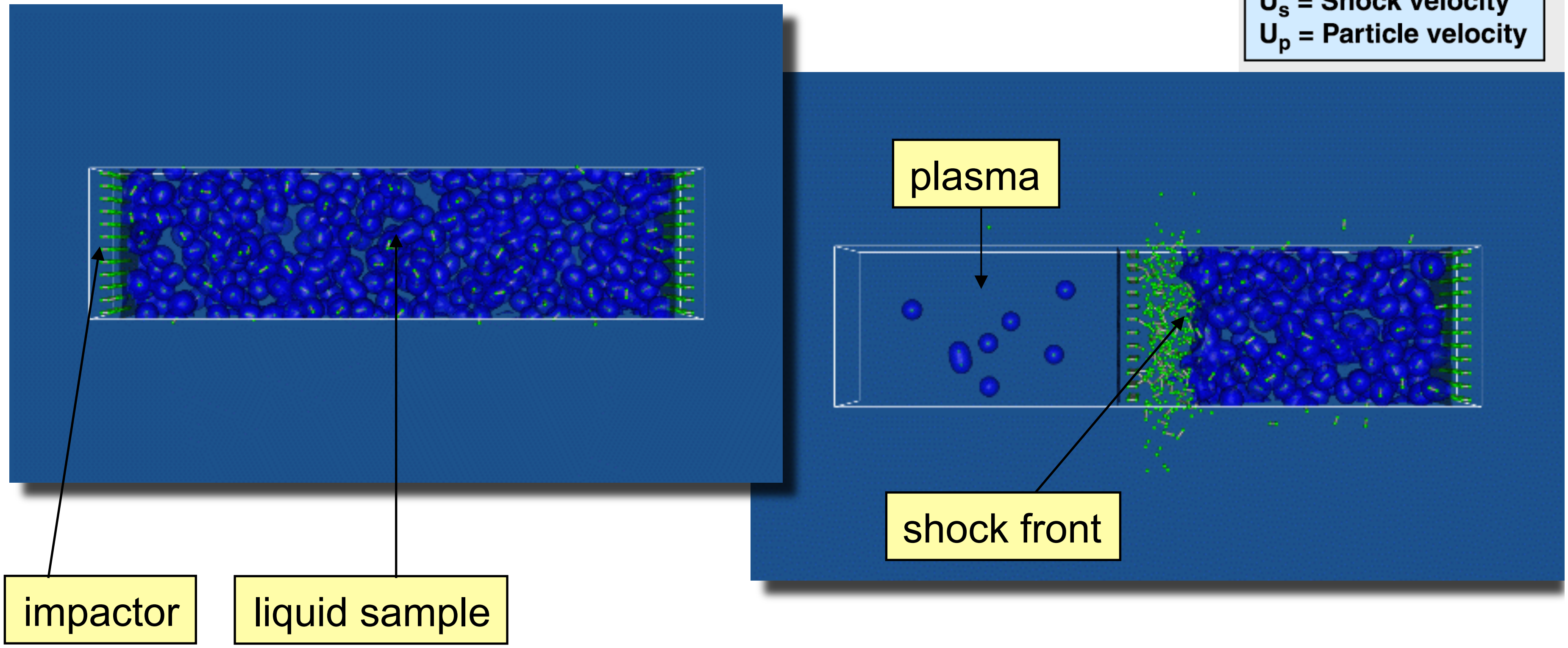
$$E = E_o + \frac{1}{2}(P + P_o)(V_o - V)$$

$$P = \rho_o U_s U_p$$

$$\frac{U_p}{U_s} = 1 - \frac{\rho_o}{\rho}$$

U_s = Shock velocity

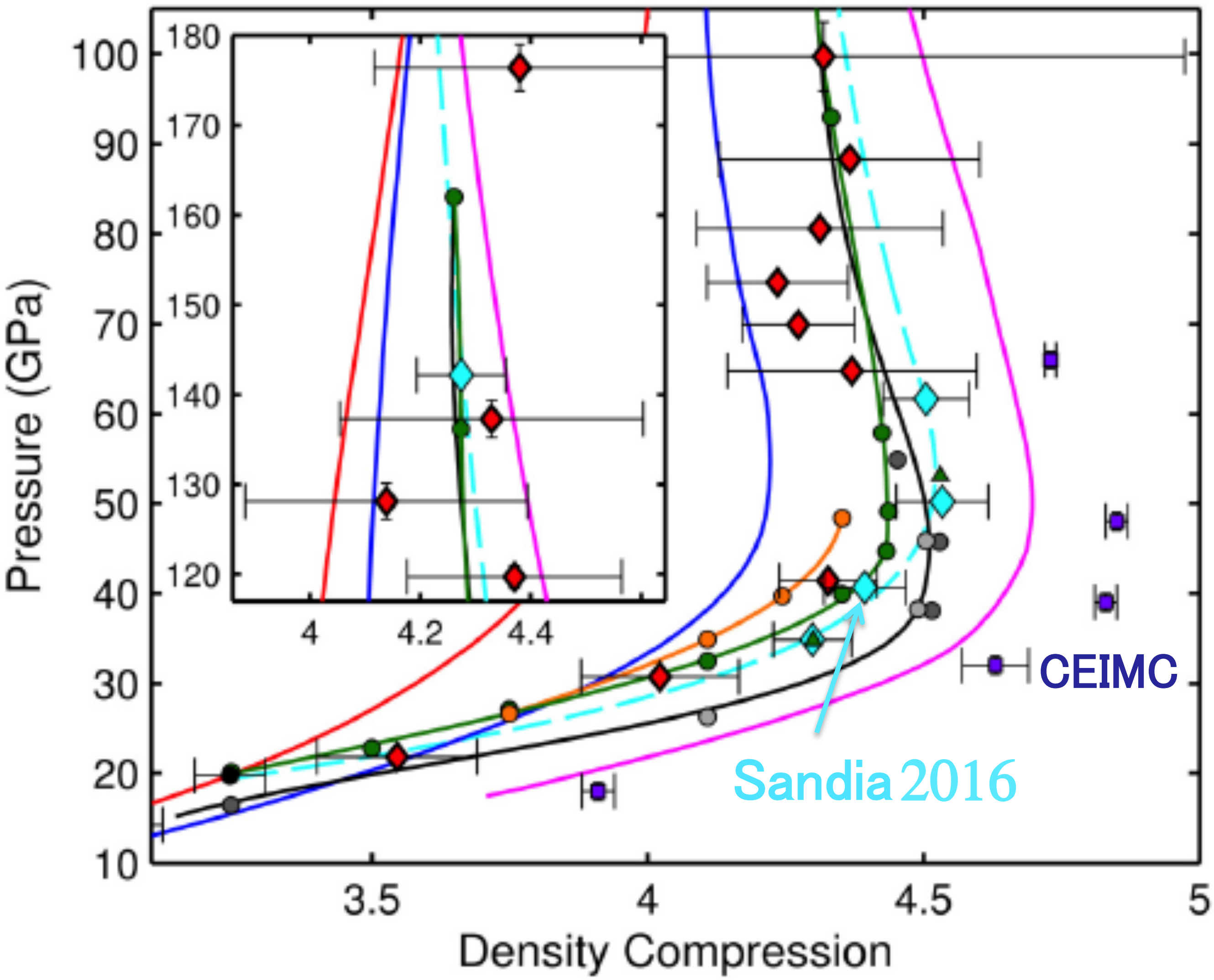
U_p = Particle velocity



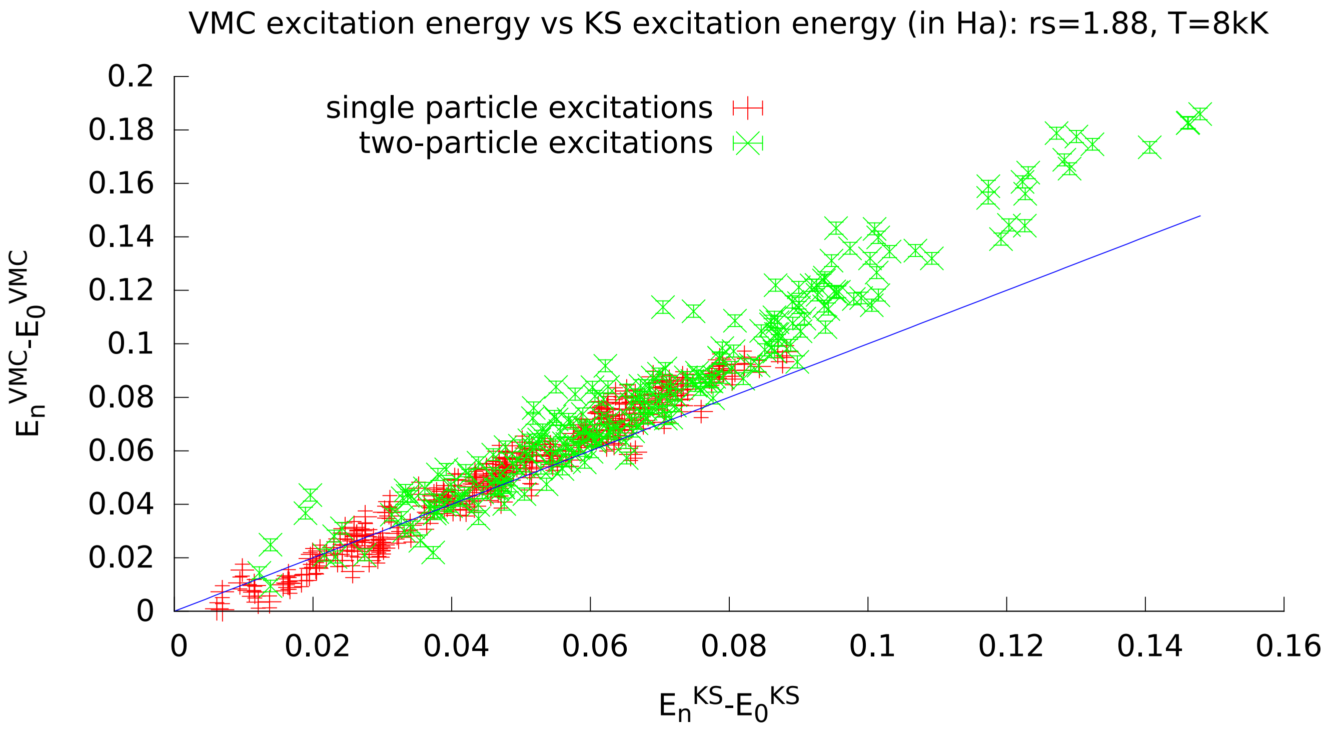
Many problems remain with hydrogen

- Hugoniot comparison with shock data
- What are the crystal structures at T=0?
- Is hydrogen a liquid at low temperatures? When does it melt?
- What are the properties of liquid hydrogen?
- How can we scale to larger, more complex systems?

Deuterium Hugoniot

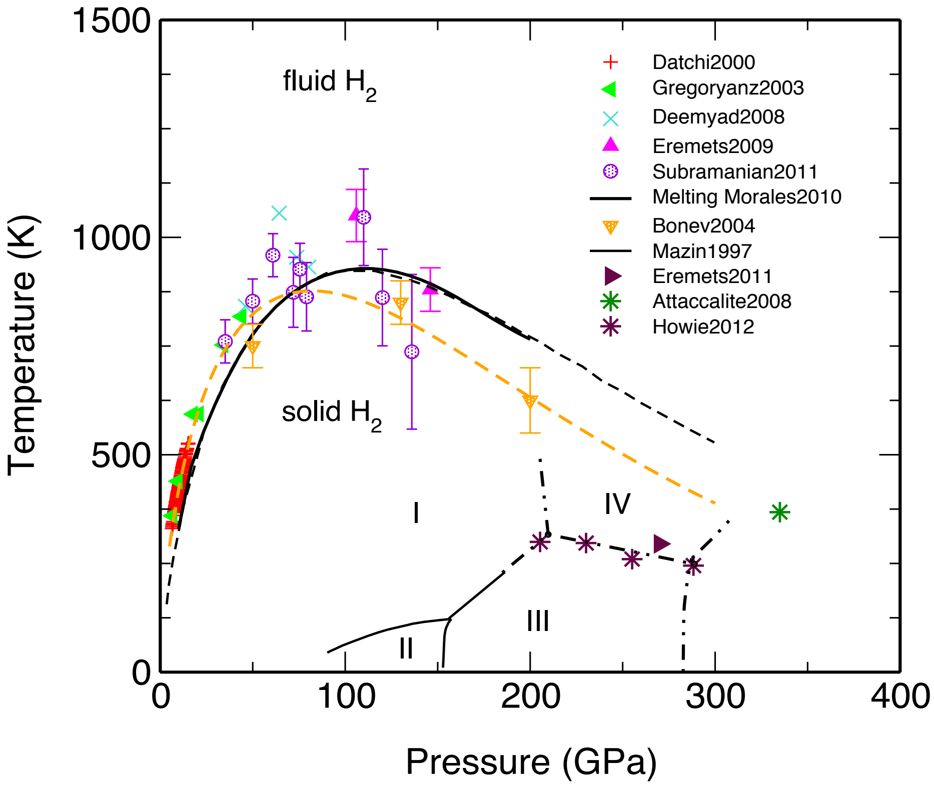


Thermal Excitations with QMC



- Excite 1 or 2 electrons
- Average over protonic configurations, vary twist angle
- Result is close to Kohn–Sham excitation energy
- Not a significant effect!

Solid hydrogen



What happens at higher pressure?

How does it become atomic & metallic?

RESEARCH ARTICLE | HIGH-PRESSURE PHYSICS

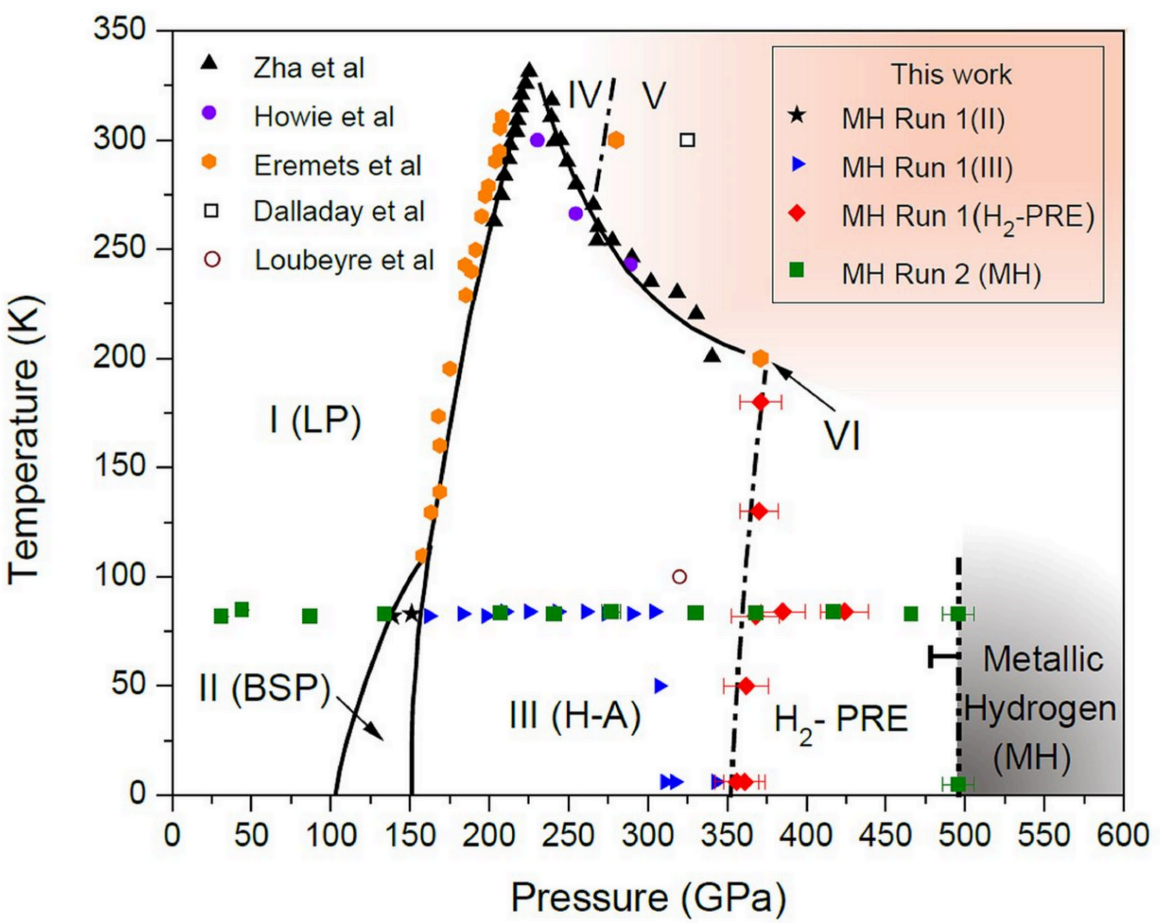
Observation of the Wigner-Huntington transition to metallic hydrogen

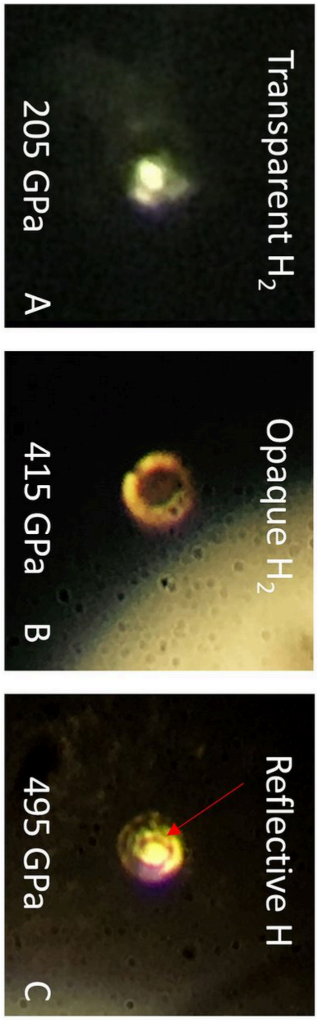
Ranga P. Dias, Isaac F. Silvera*

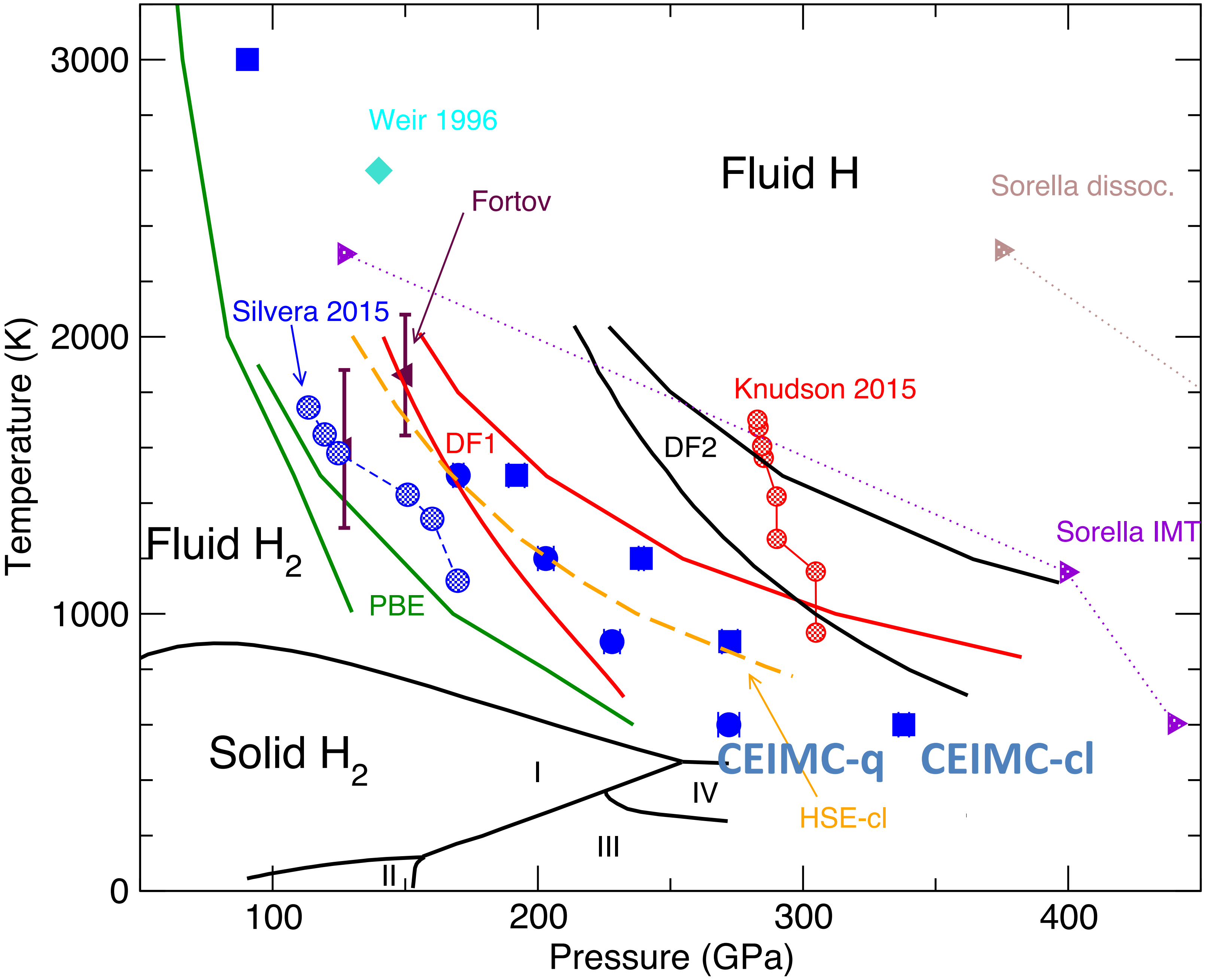
\+ Author Affiliations

*Corresponding author. Email: silvera@physics.harvard.edu

Science 26 Jan 2017:

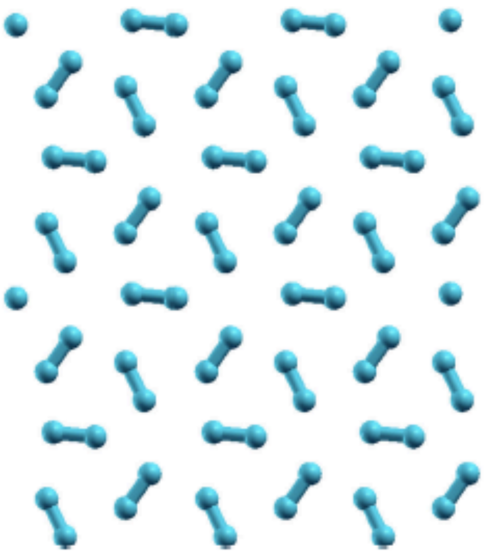




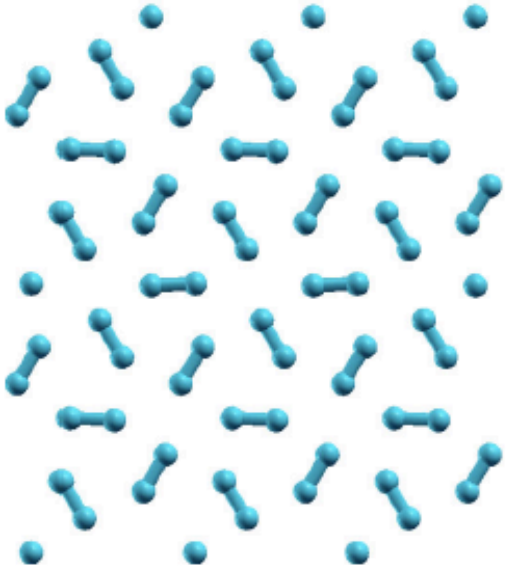

Weir 1996
Fluid H
Sorella dissoc.
Fortov
Silvera 2015
Knudson 2015
DF1
DF2
Sorella IMT
Fluid H_2
PBE
Solid H_2
I
IV
III
II
CEIMC-q
CEIMC-cl
HSE-cl
Temperature (K)
3000
2000
1000
0
100
200
300
400
Pressure (GPa)

T=200K: Phase III and VI(?)

C$_2$/c

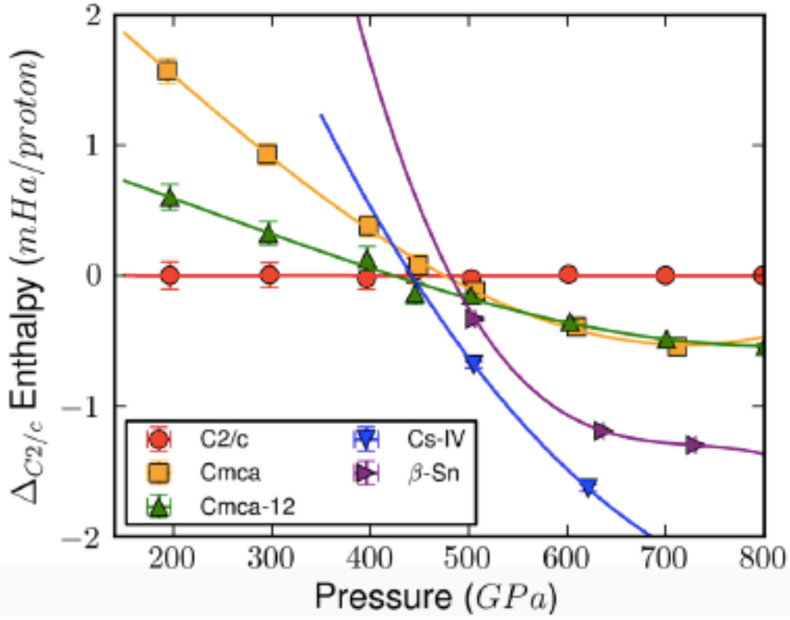


Cmca12



Most favorable structures according to AIRSS with GGA-PBE and zero point energy accounted by Self-consistent harmonic approximation

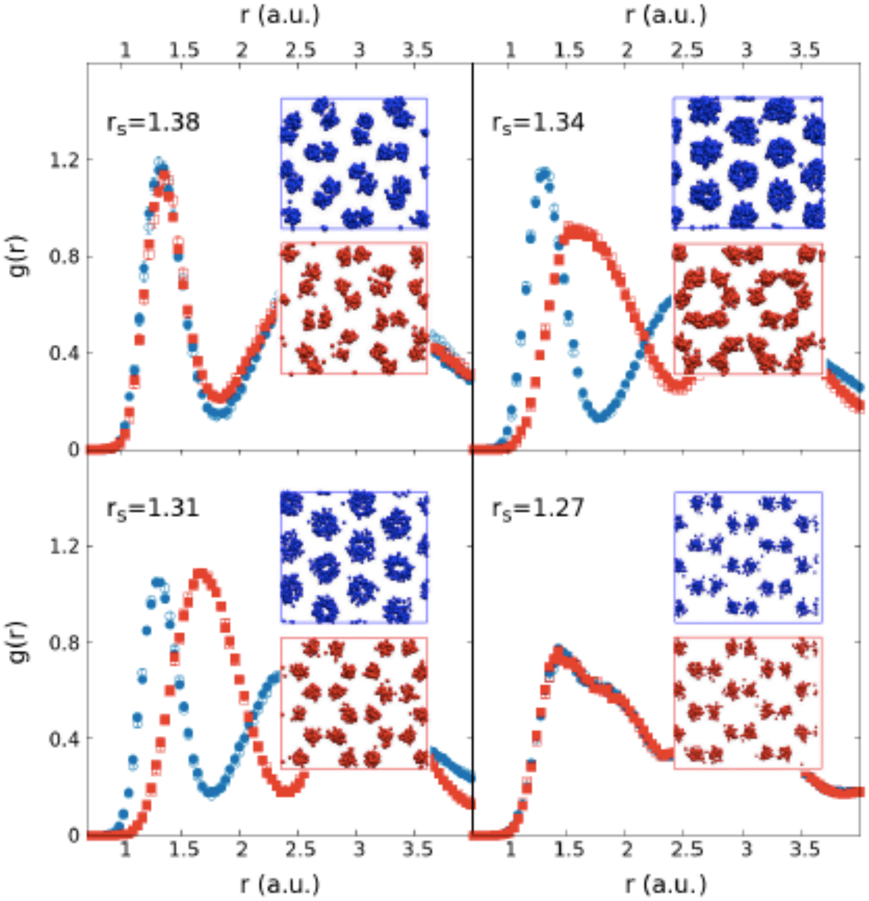
Pickard-Needs, Nature Physics 3, 473 (2007)



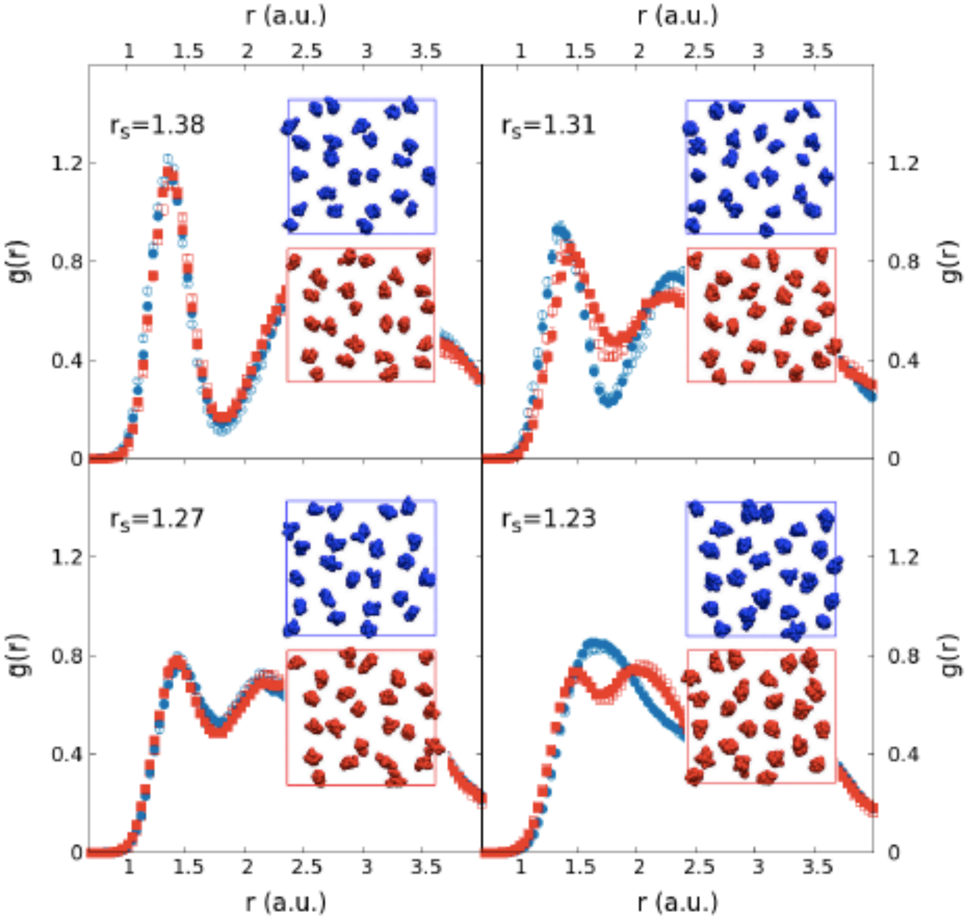
C2/c is favored in the QMC ground state with ZPE (SCHA) until the atomic phase with Cs-IV structure is reached.

McMinis et al. PRL 2015.

vdW-DF-PIMD



CEIMC-PIMC



Initial configurations relaxed at constant pressure with DFT

with DFT-vdW-DF, C2/c is dynamical unstable towards:

- layered structures at intermediate densities
- metallic Cmca-4 structure at rs=1.27

with CEIMC no instabilities are seen, molecules progressively disappear with pressure

Molecular Crystal: Rotation

G. Rillo et. al.,
J. Chem. Phys. **148**,
102314 (2018).

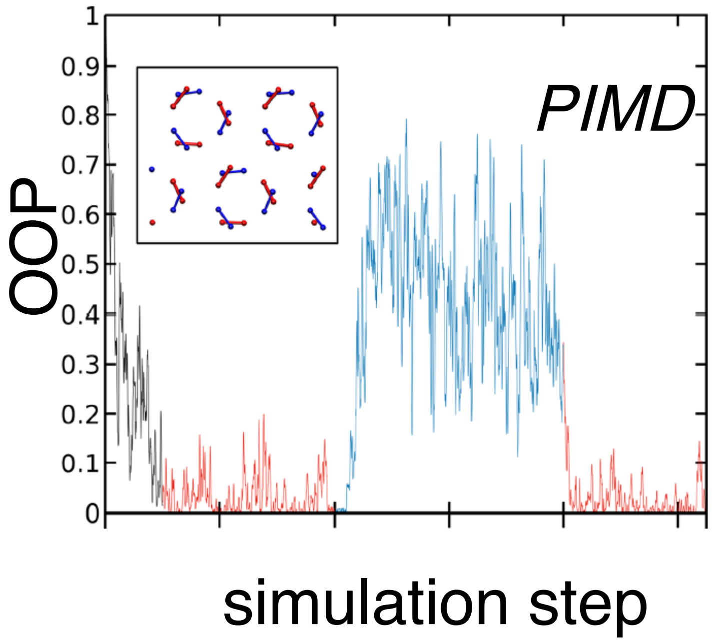
Hexagonal rings rotate within layer in *PIMD*

Hexagonal rings do NOT rotate within layer in **CEIMC**

CEIMC results consistent with C2/c or Cmca-12 as starting structure

$$OOP = \left\langle \left[\frac{1}{N_{mol}} \sum_{i=1}^{N_{mol}} P_2(\Omega_i \cdot e_i) \right]^2 \right\rangle$$

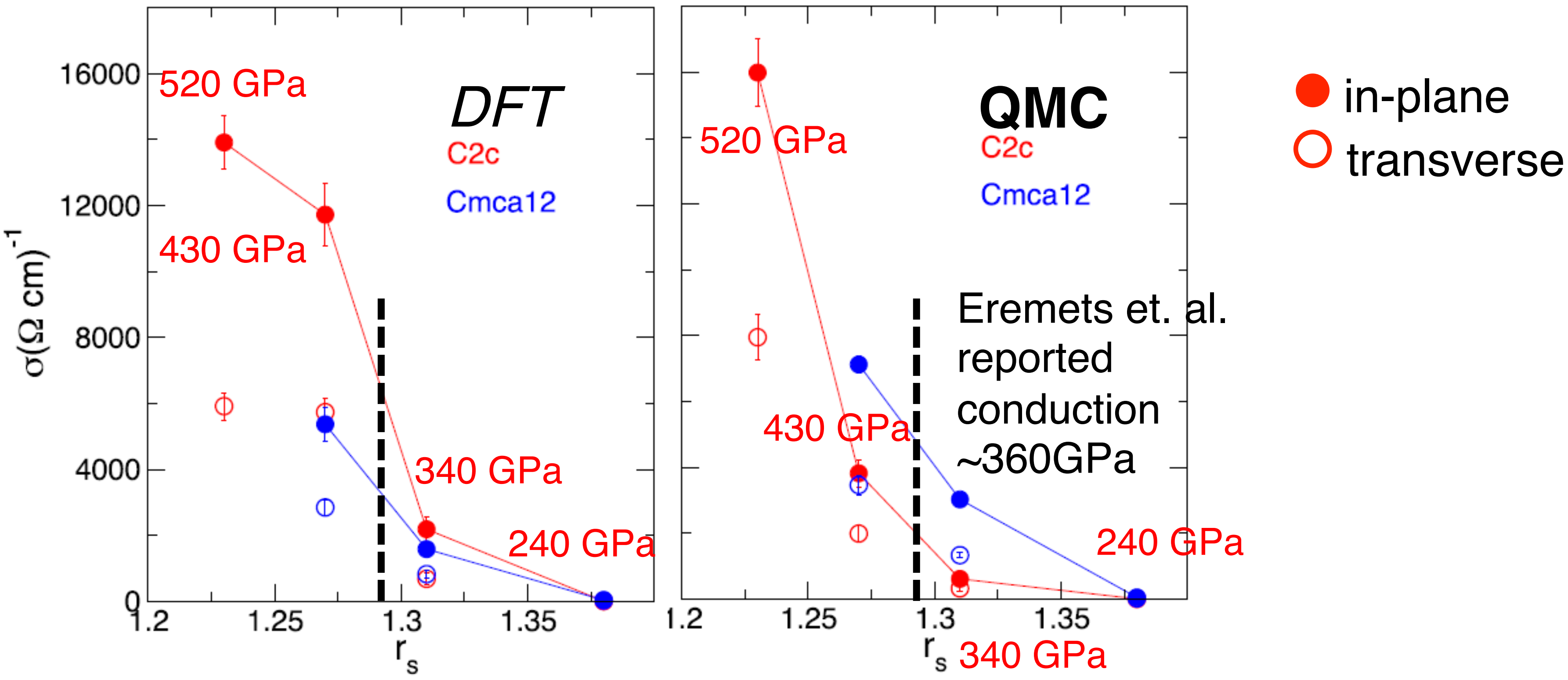
PIMD results differ significantly from **CEIMC** when starting with C2/c



Molecular Crystal: Conductivity

Phase III C2/c-24 conducts in-plane at P~250 GPa in *PIMD (DFT)*

Phase III C2/c-24 conducts in-plane at P~350 GPa in **CEIMC (QMC)**



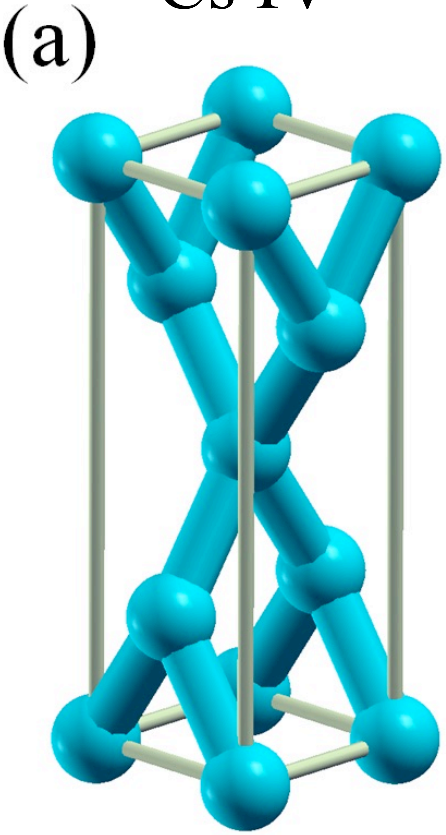
Eremets et. al. reported conduction ~360GPa

M. I. Eremets, A. P. Drozdov, P. P. Kong, H. Wang, “Molecular semimetallic hydrogen,” arXiv:1708.05217

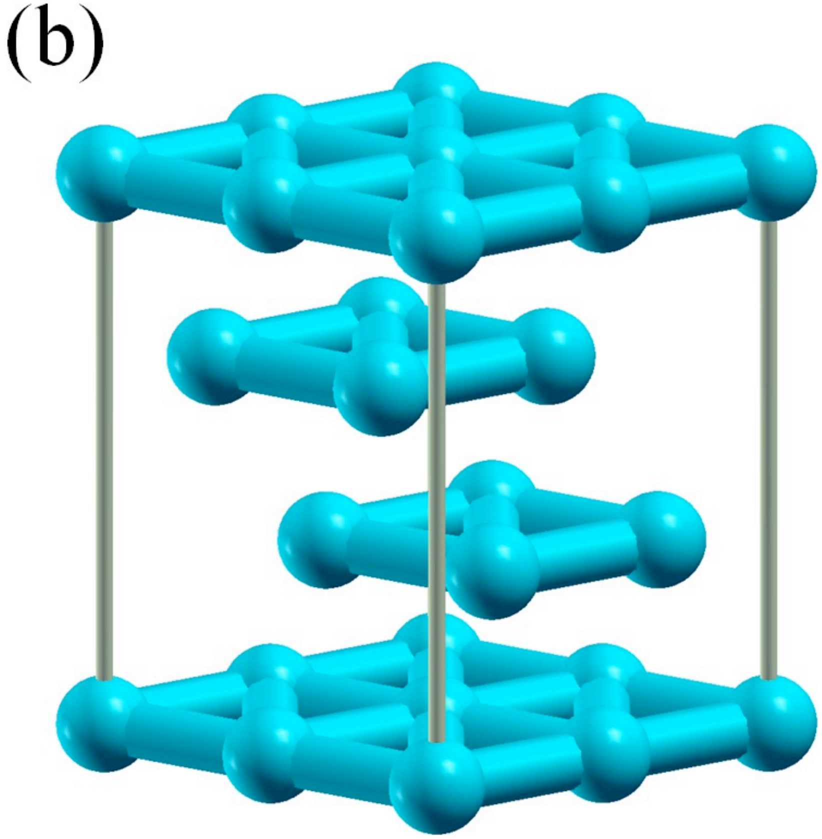
- Structures searching gives many new possible crystal structures.
- Not b.c.c as had been assumed in the atomic phase!

$I4_1/amd$

Cs IV



$R\text{-}3m$



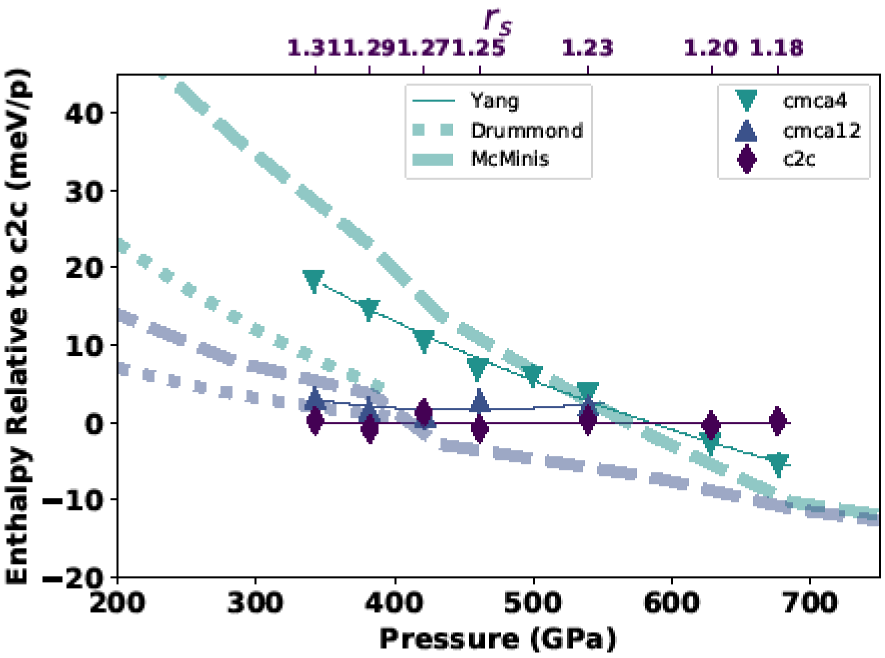
T=0K Structural Transitions

Classical-proton results agree well with previous QMC studies

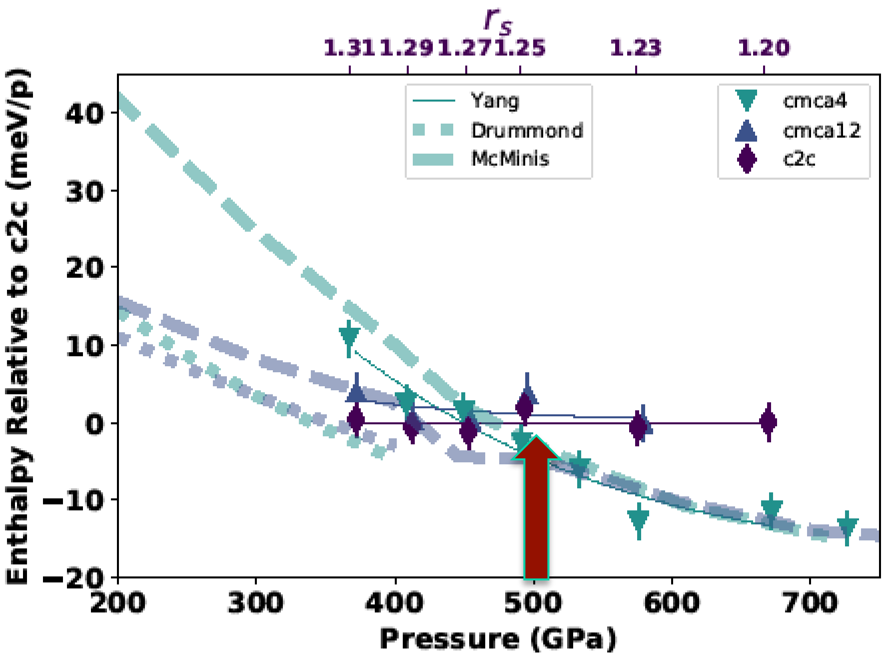
Proton zero-point motion stabilizes Cmca-4

Molecular crystal C2/c to Cmca symmetry ~450 GPa

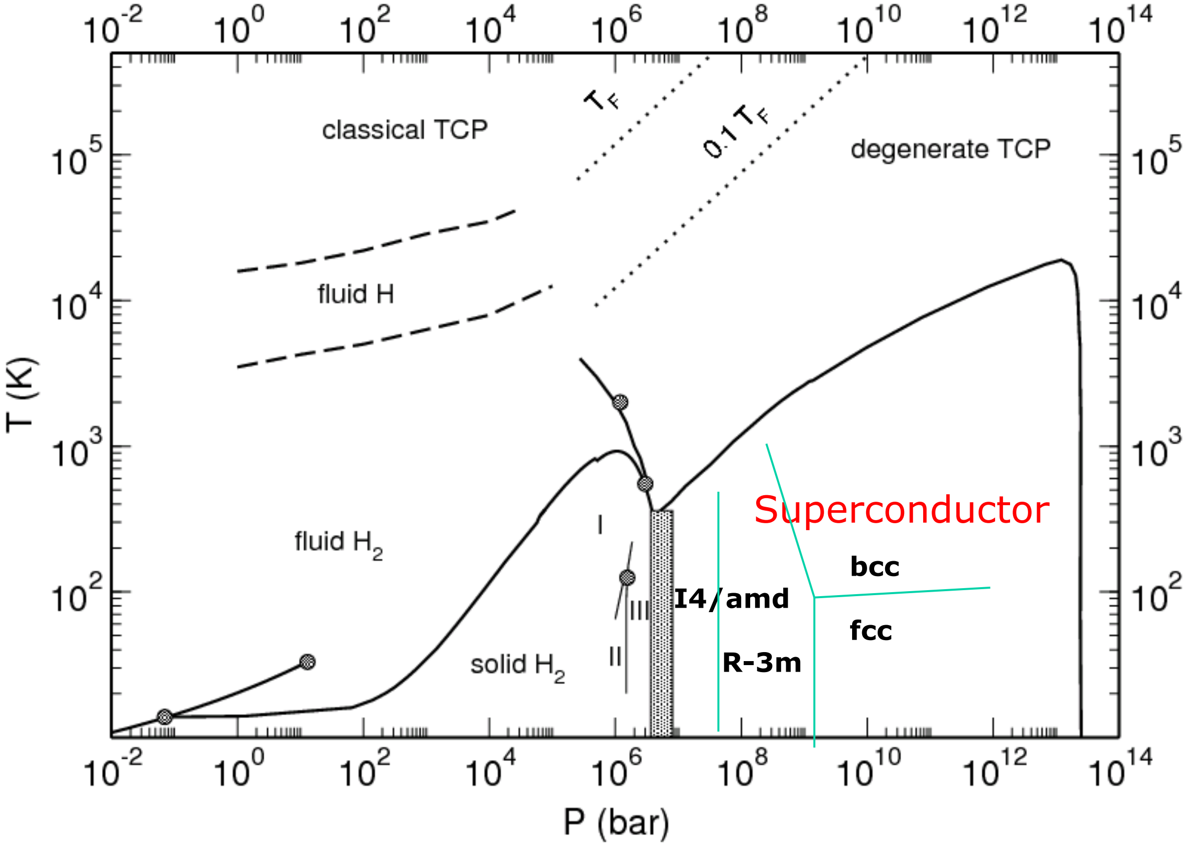
Classical Protons



Quantum Protons



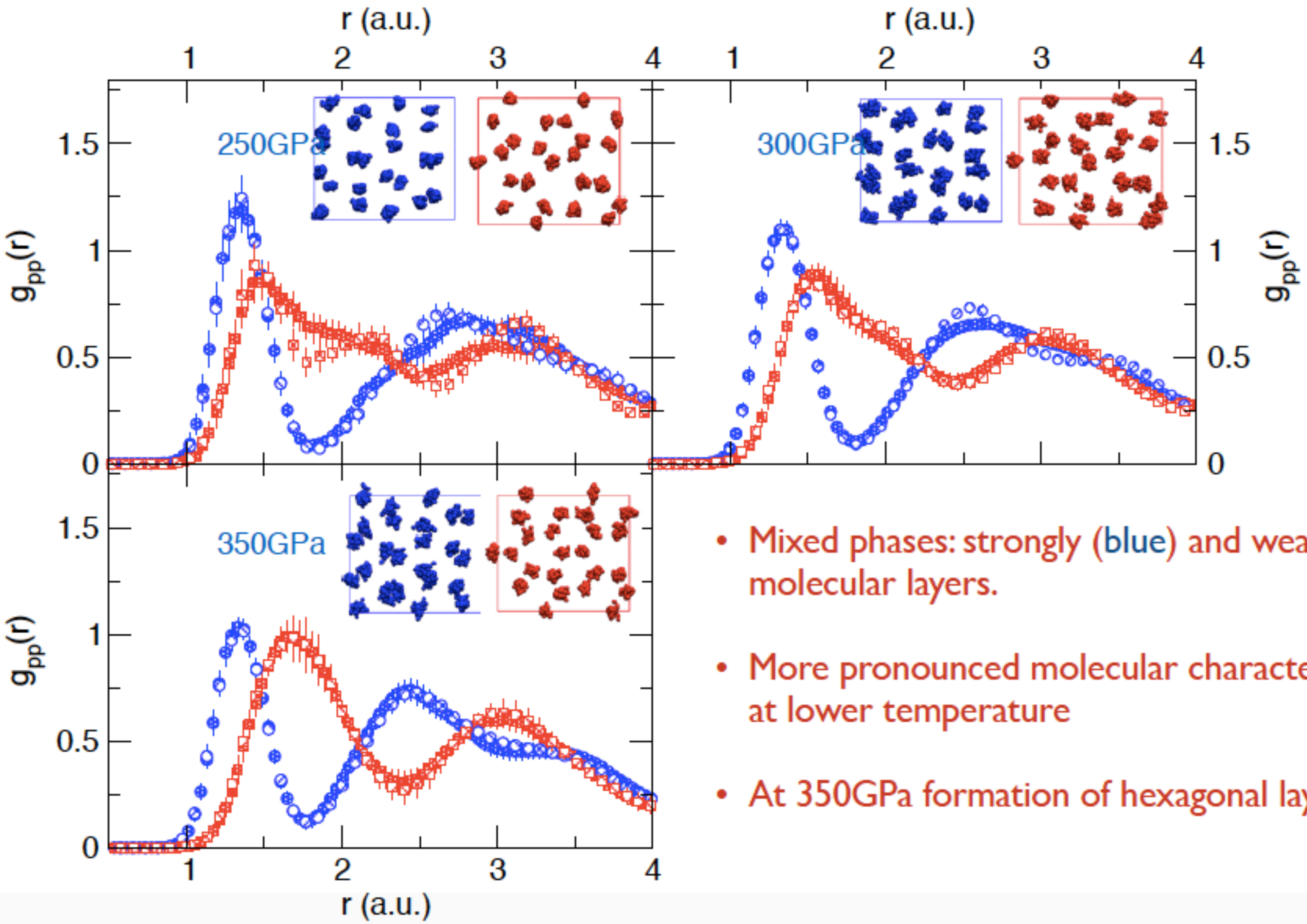
Hydrogen Phase Diagram



Based on the BCS theory estimates, we expect entire atomic solid to be superconducting at high T

But at high pressure!

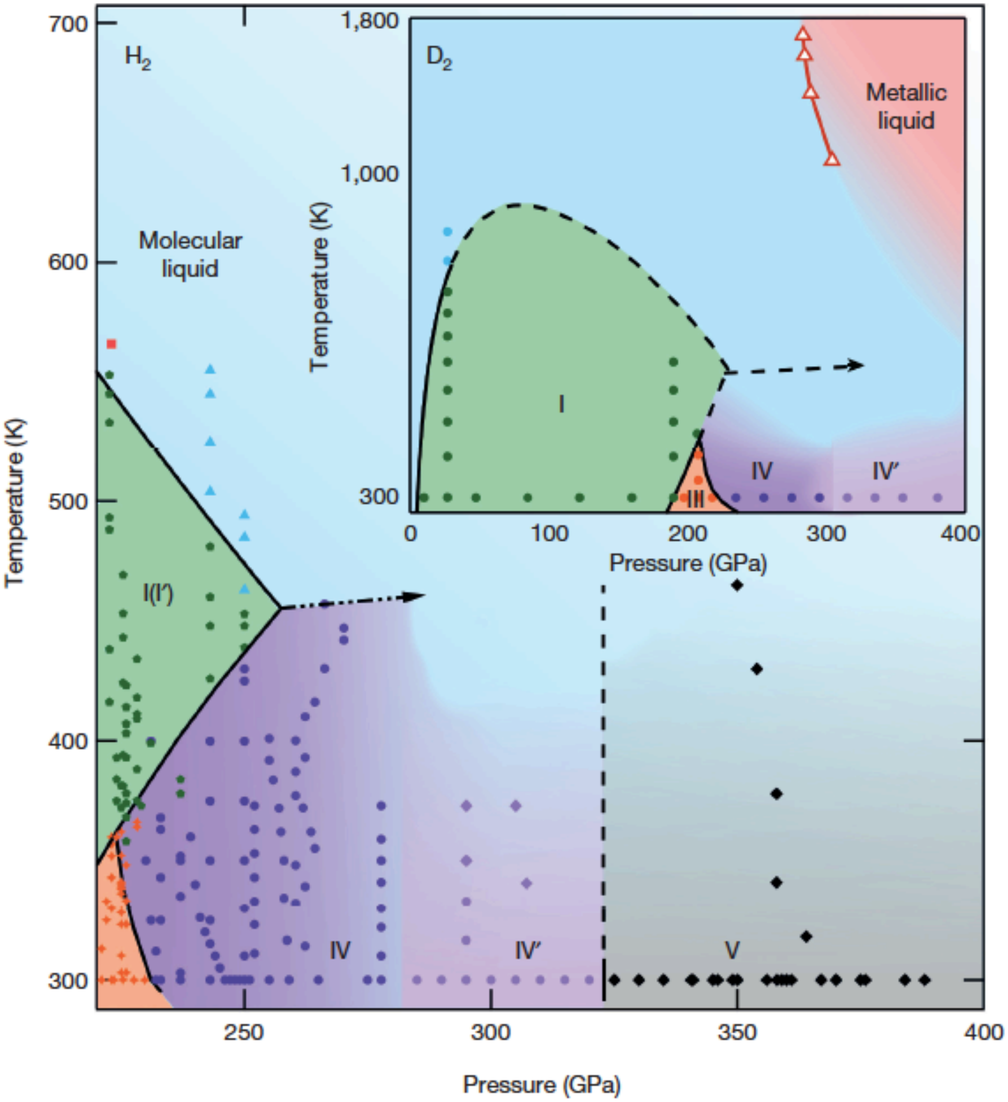
Pc48: structural properties CEIMC



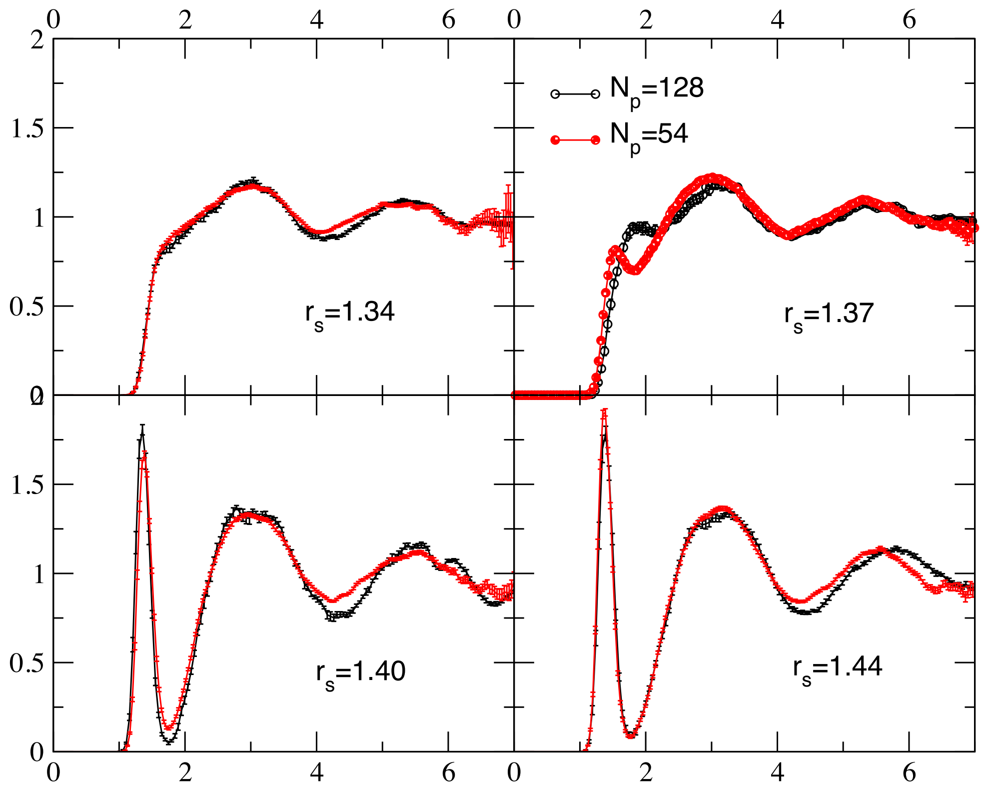
- Mixed phases: strongly (blue) and weakly (red) molecular layers.
- More pronounced molecular character than at lower temperature
- At 350GPa formation of hexagonal layers

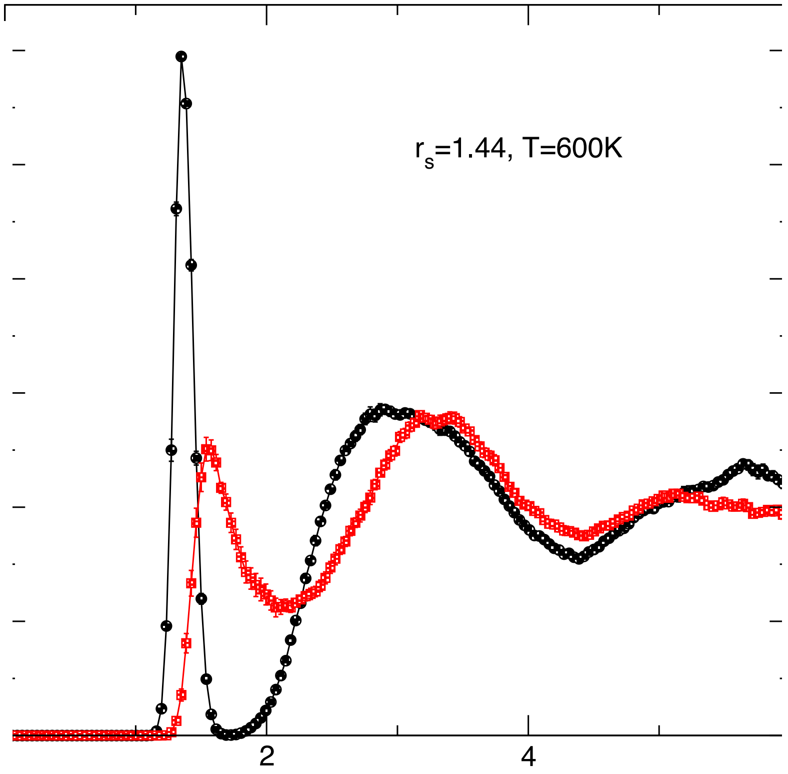
New DAC experiments, Phase V

Dalladay-Simpson, Howie, Gregoryanz (2016)

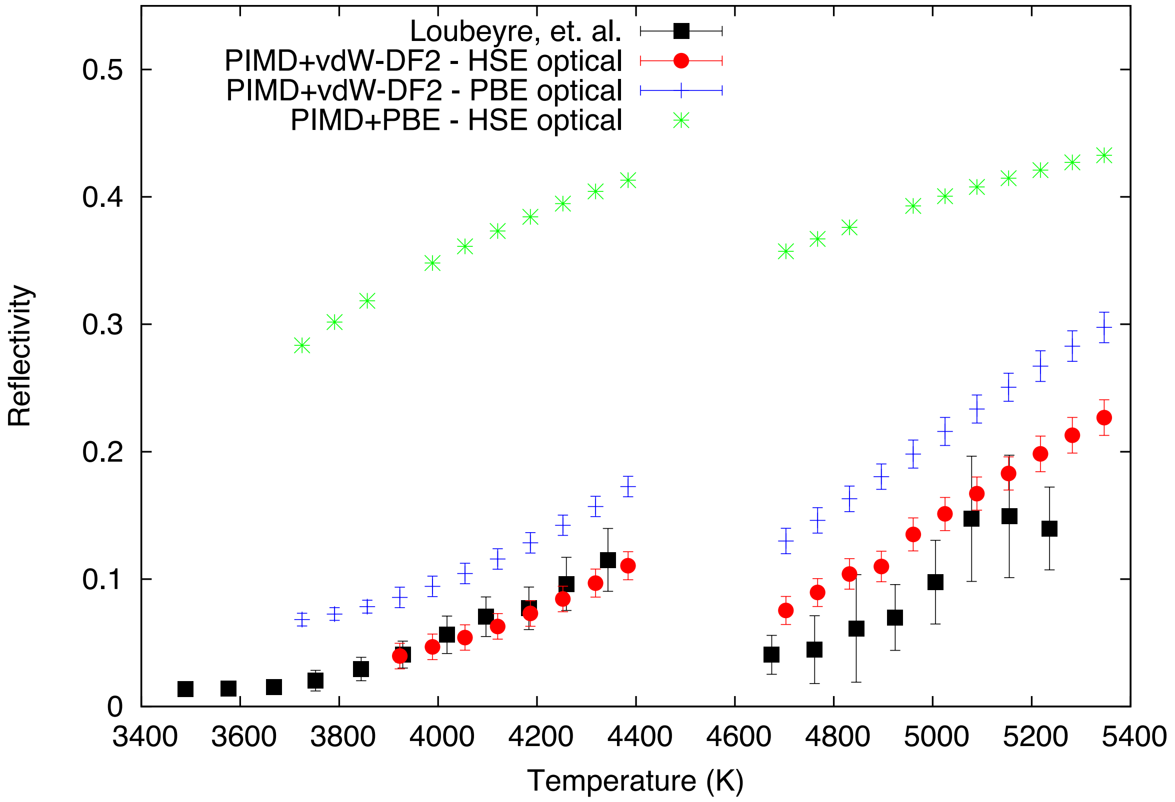


Calculations are delicate near the transitions. Sensitive to functional.



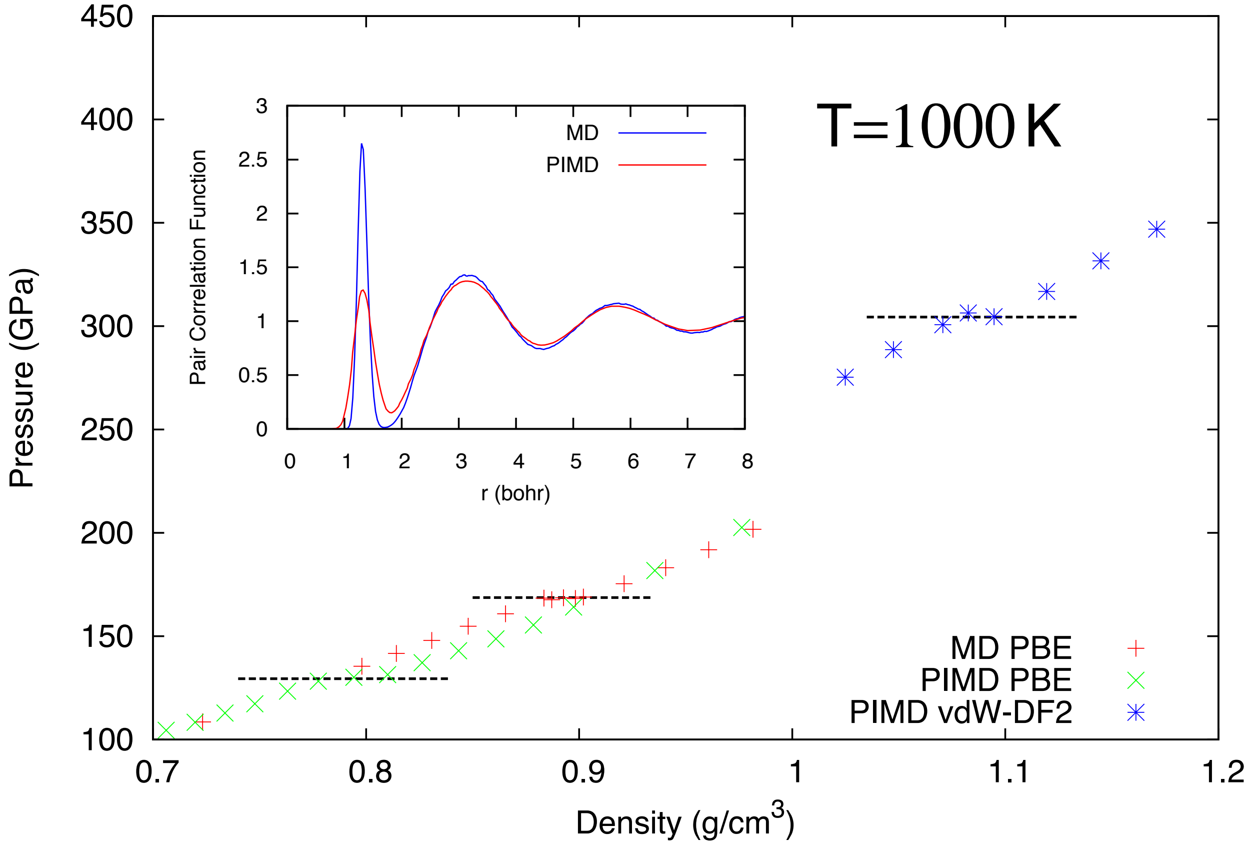


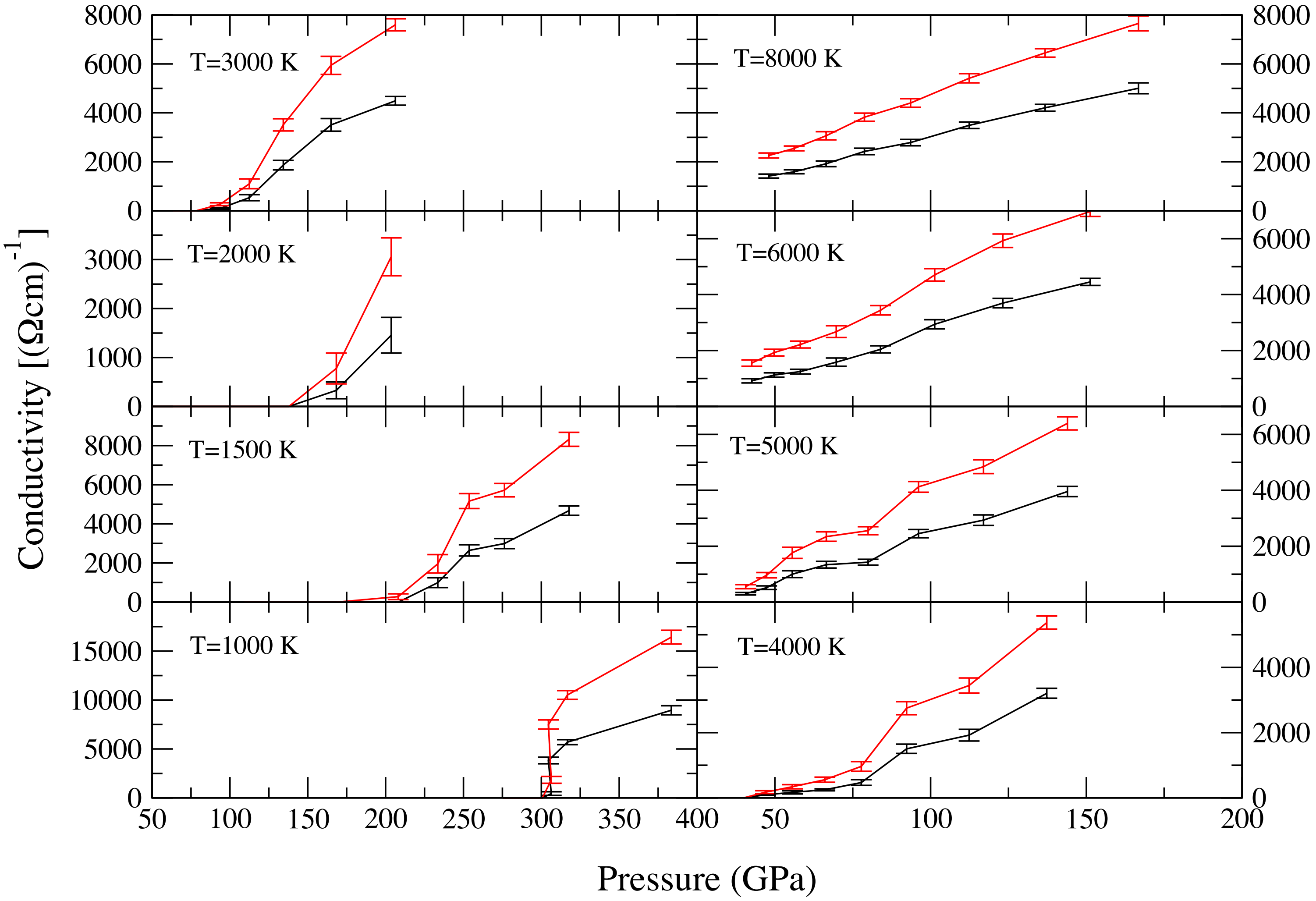
We find good agreement with experimental reflectivity along Hugoniot. (configurations come from vdW-DF2 functional)



Experiment: Loubeyre et al, High Press Res 24, 25 (2004).

Transition depends on functional and zero point effects



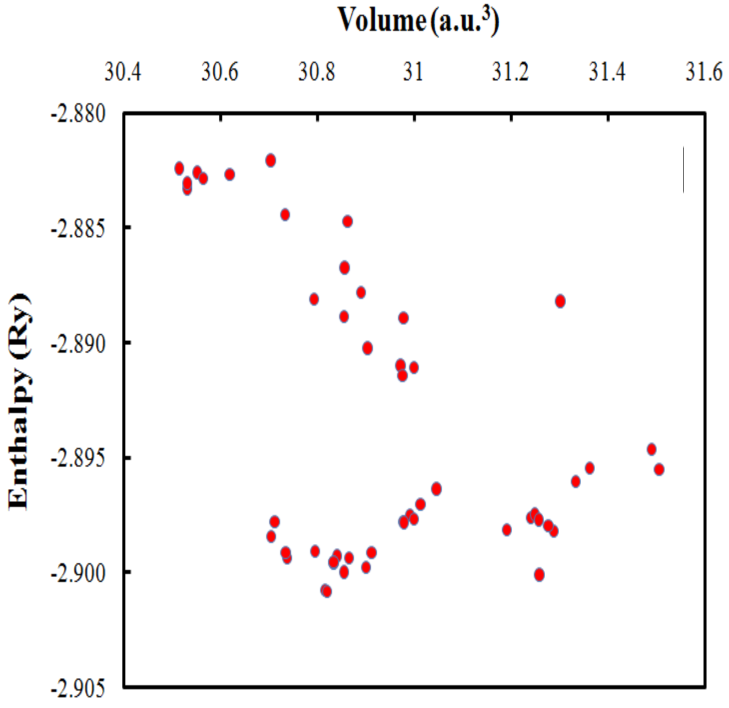


Conductivity differs with functional, but transition is robust

Structure Searching

- We need the crystal structure for estimating any property of the solid
- With available computer resources, brute force approach is now feasible

1) For a fixed pressure and number of atoms (or molecules) per unit cell, generate *n* random structures:
    a) Generate random primitive vectors
    b) Scale vectors so volume is close to desired value
    c) Generate random atomic positions
2) Relax structures to a minimum in Gibbs free energy
3) Determine lowest energy crystal structures



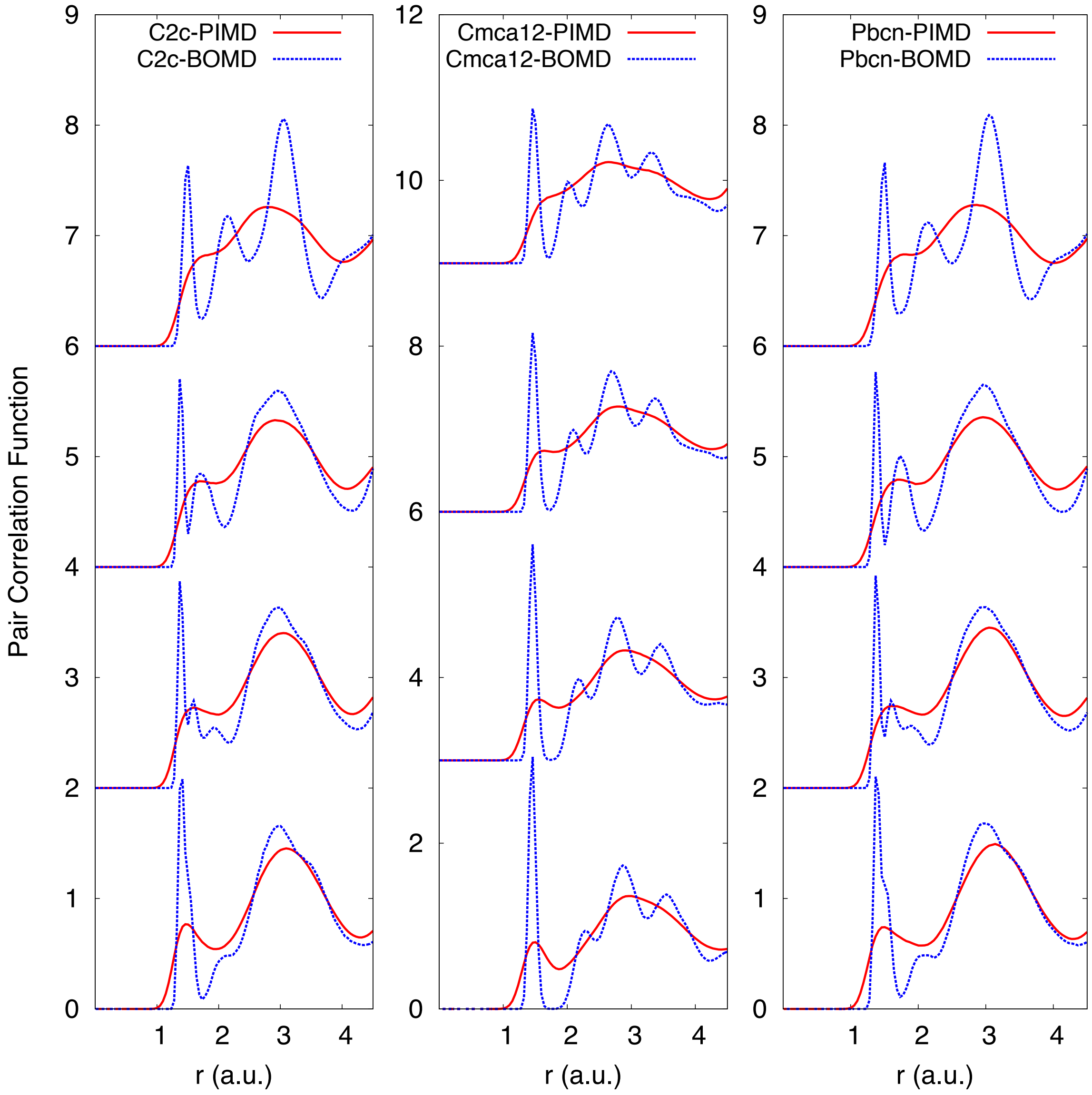
H_2 structure depends strongly on zero point effects T=200K (PBE energies)

200GPa

250GPa

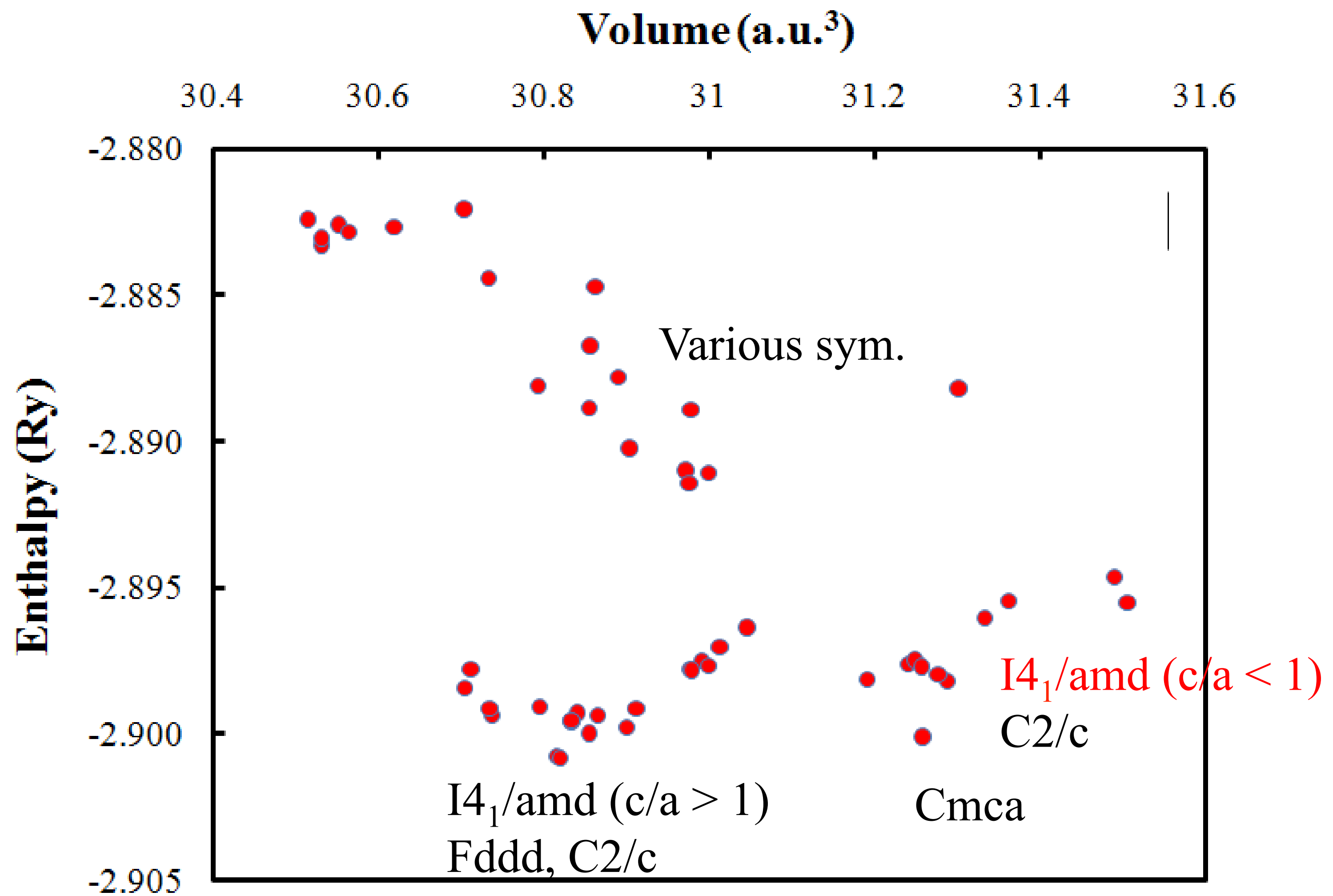
300GPa

350GPa



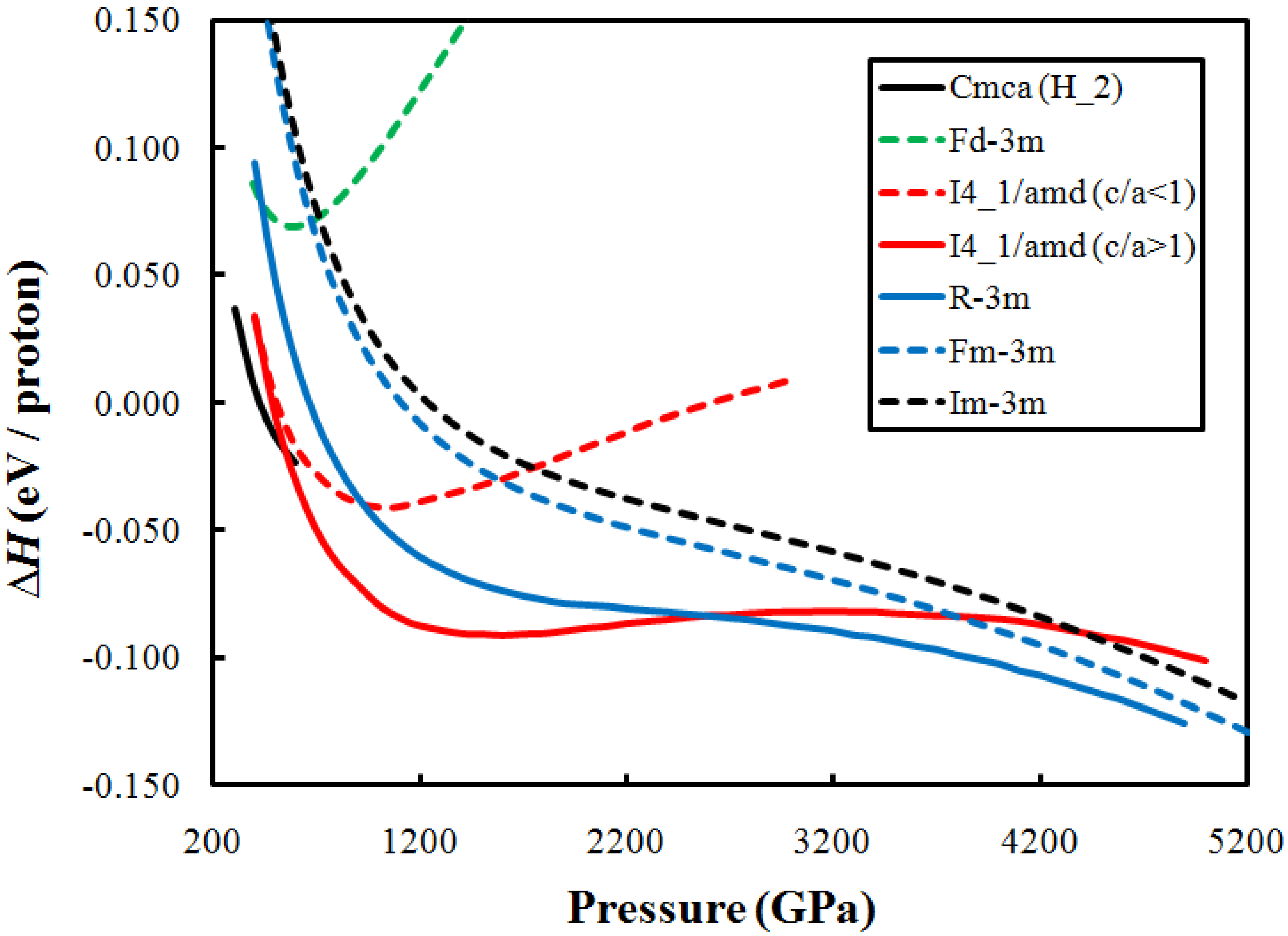
Random Structure Relaxation

500 GPa



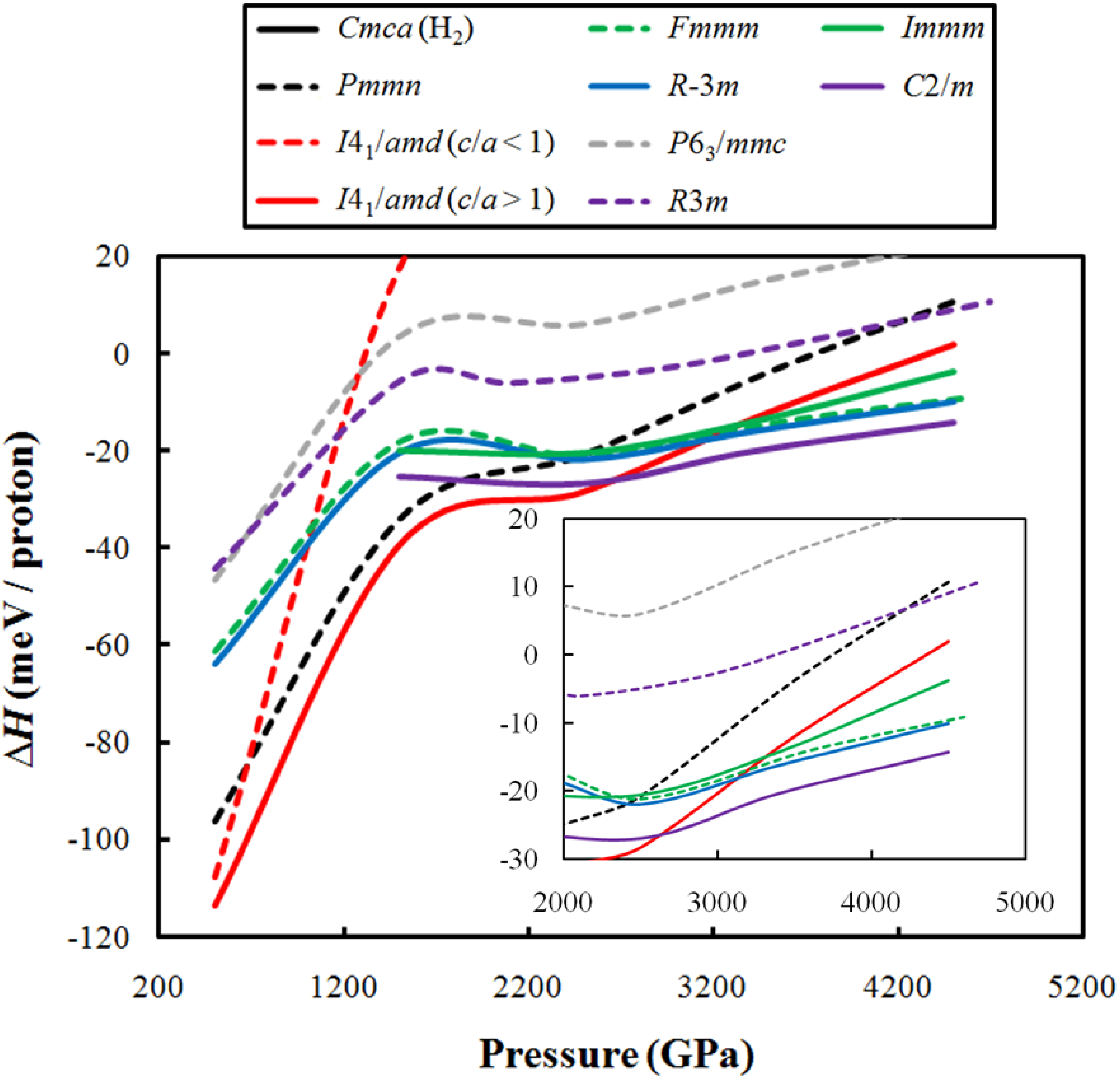
6 atom relaxations and 4 atom relaxations give similar results.

At higher pressure, hopefully things are better controlled (T=0K , classical protons, PBE functional)

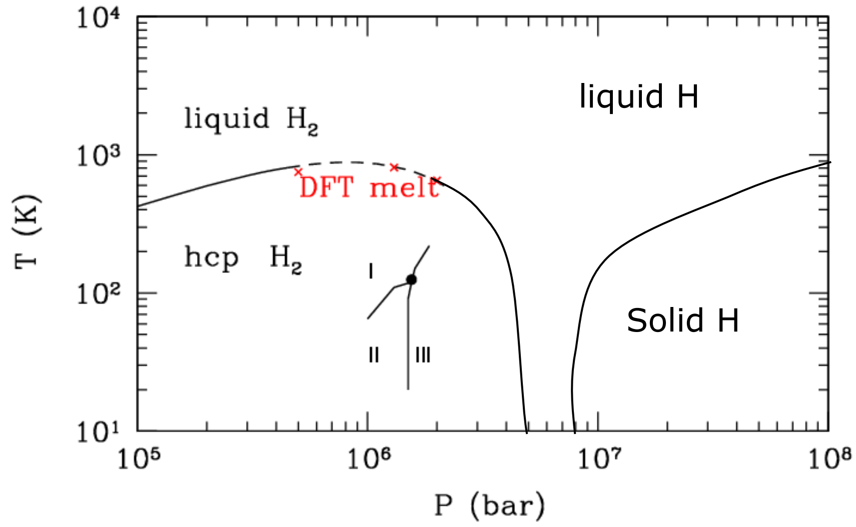


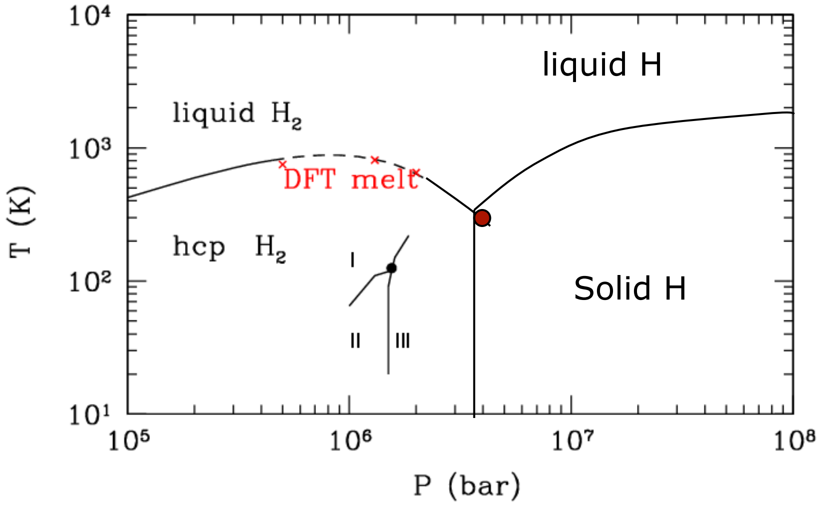
Estimate zero point energy of protons using phonon energies.

Using Eliashberg eq. ***We find the entire solid H phase is superconducting*** as Ashcroft has suggested.



Can Hydrogen be a quantum liquid?





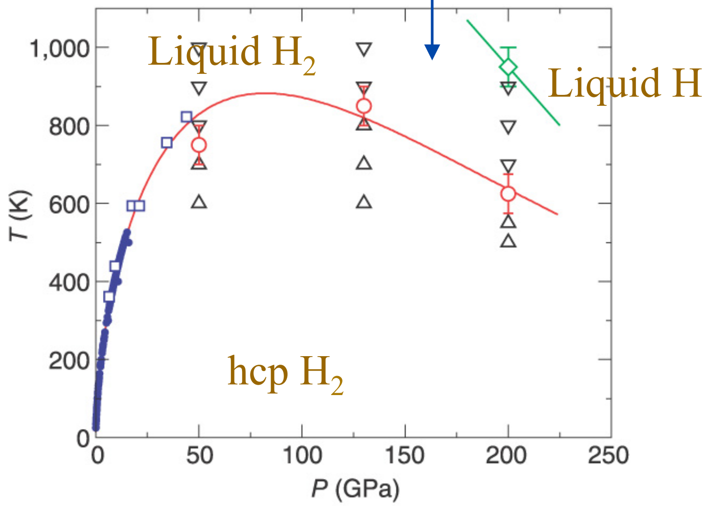
Ashcroft suggested a low temperature liquid metallic ground state.

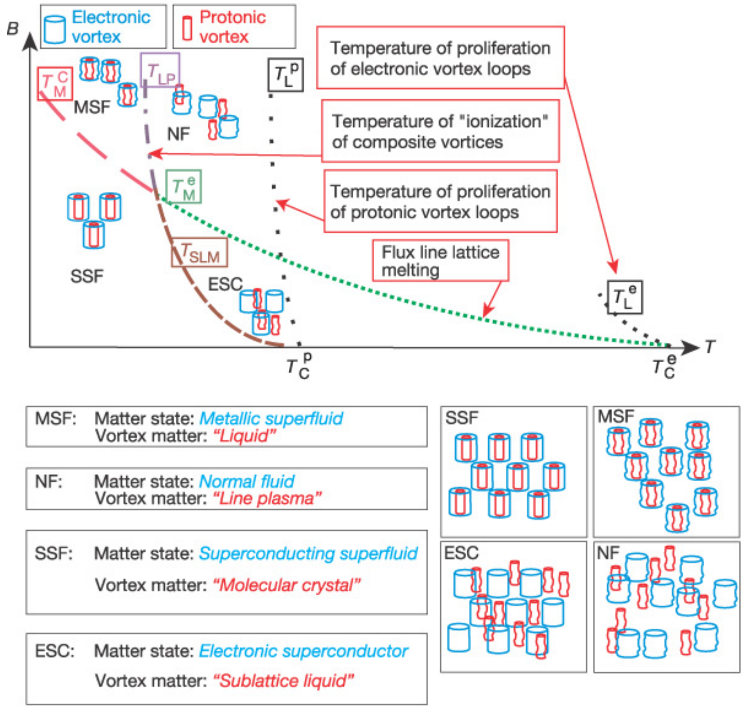
- Is there a T=0K liquid?
- What temperature is needed to see quantum protonic transitions?

07 October 2004

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 liquid metallic hydrogen E. BABAEV, A. SUDBØ & N. W. ASHCROFT





MSF: Matter state: *Metallic superfluid*
Vortex matter: *"Liquid"*

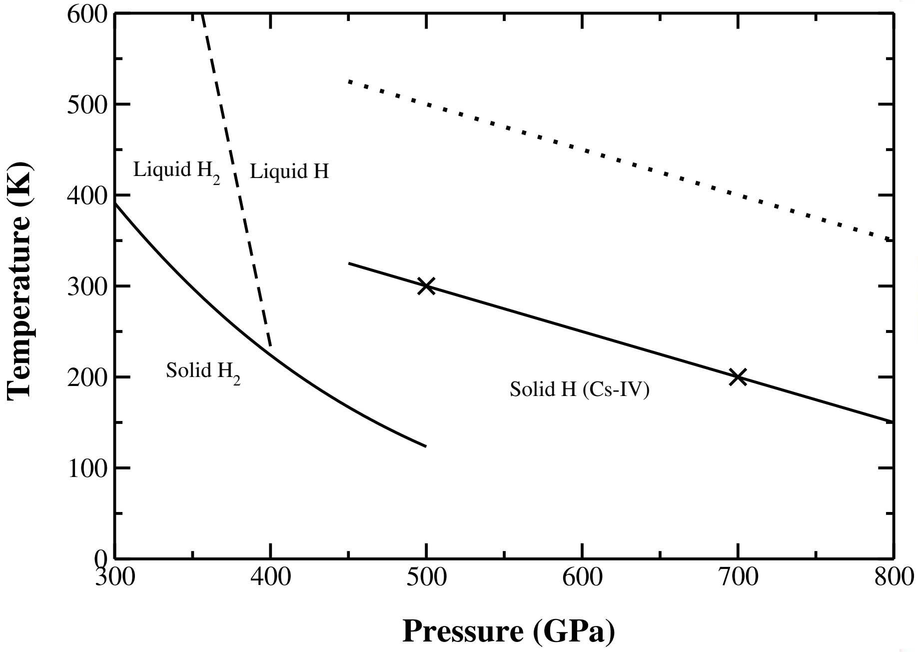
NF: Matter state: *Normal fluid*
Vortex matter: *"Line plasma"*

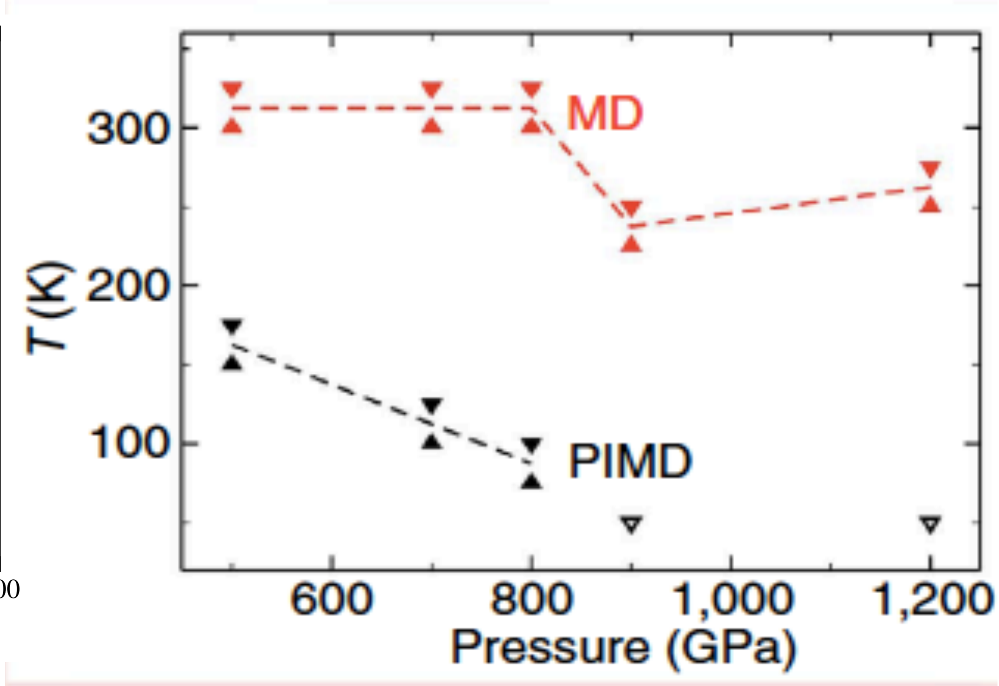
SSF: Matter state: *Superconducting superfluid*
Vortex matter: *"Molecular crystal"*

ESC: Matter state: *Electronic superconductor*
Vortex matter: *"Sublattice liquid"*

Could hydrogen be a quantum fluid like helium?

Melting temperature of solid H

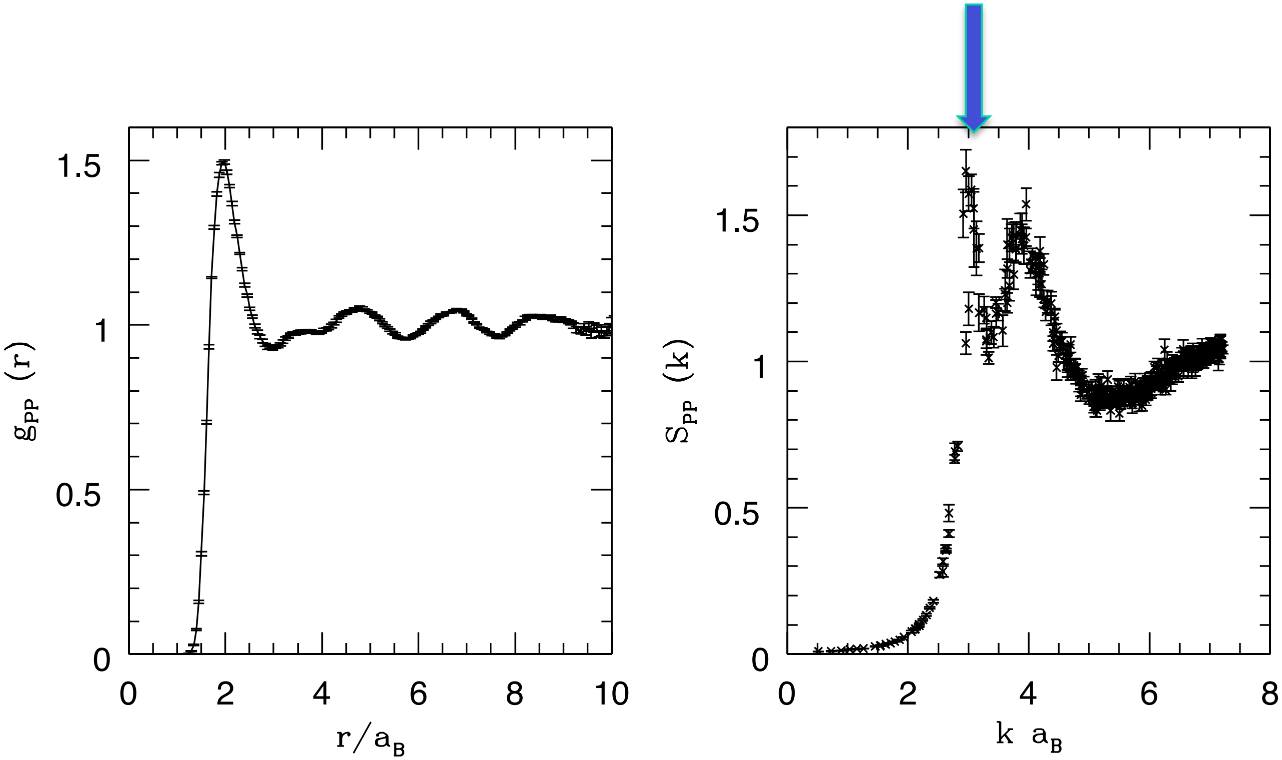




Chen et al Nature 2013

- Only Cs-IV structure for atomic H is dynamically stable, but only at low temperatures.
- Melting temperature decreases with pressure.

Structure of the atomic liquid



Unusual double peak structure factor for an atomic liquid

What type of liquid is this? Two types of order present:

- hard sphere packing
- ordering at $2k_F$ caused by Fermi surface.

The T=0 structures of H_2 & H: (assuming PBE + harmonic phonons)

- Cmca H_2 dissociates into $I4_1/amd$ H near 500 Gpa
- $I4_1/amd$ (Cs IV) remains the stable phase to 2.5 Tpa
- Near 2.5 TPa $I4_1/amd$ transforms into an ABAB… layered R-3m structure
- Transition to bcc likely occurs at hundreds of TPa

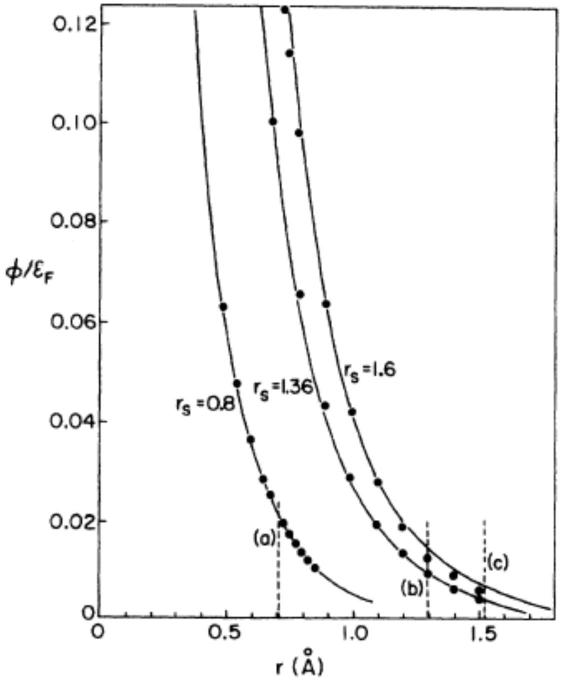
Future Work

- Determine the structure and free energy of the liquid just above the melting temperature including quantum effects.
- Using Coupled electron-Ion Monte Carlo, make a better estimate of the zero point energy of the low energy structures.
- Trace the actual thermodynamic melting line of H, particularly around r_s ~1.2, including quantum proton corrections
- Calculate the superconducting transition temperatures of atomic metallic H. Initial calculations suggest that for $I4_1/amd$ T_c ~300 K around 500 GPa

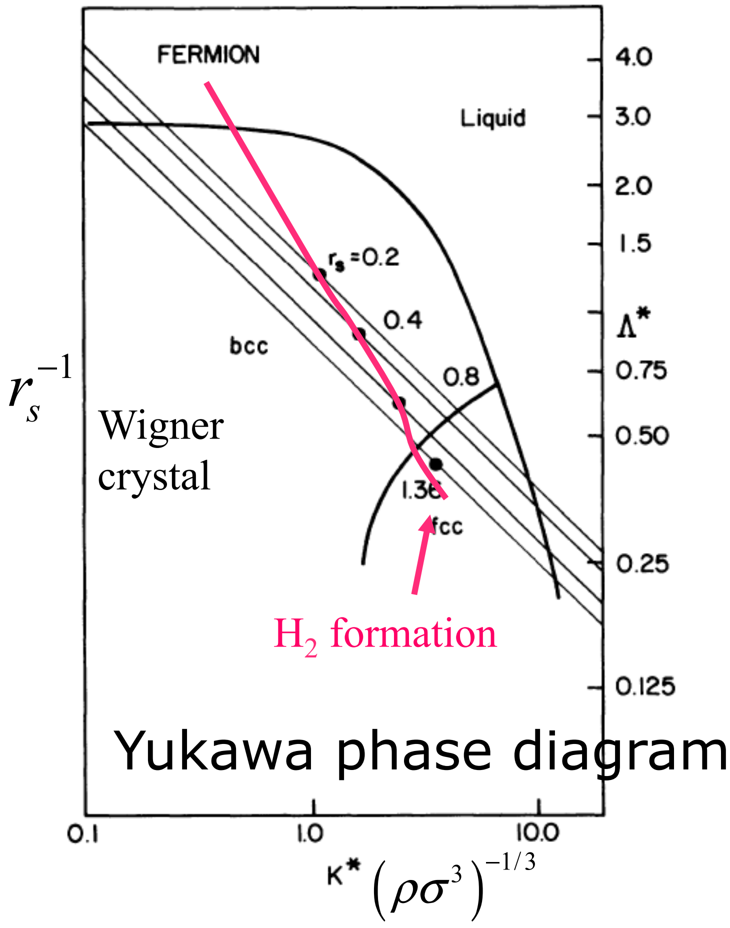
Why would H be liquid?
Screened Coulomb potential

Electrons screen p-p interaction

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



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



Yukawa phase diagram

Previous work has assumed simple atomic structures, simplified electron correlation, Lindemann criterion for melting with harmonic phonons.

McMahan et al.:

- Use QMC to determine accurate DFT functional
- Determine crystal structures with DFT+harmonic phonons and structure searching.
- Perform path integral molecular dynamics calculations of relevant crystal structures and liquid hydrogen
- PBE functional
- Fit energies and integrate to get free energies

Chen et al: (Nature 2013)

- PIMD with coexisting liquid-crystal sample

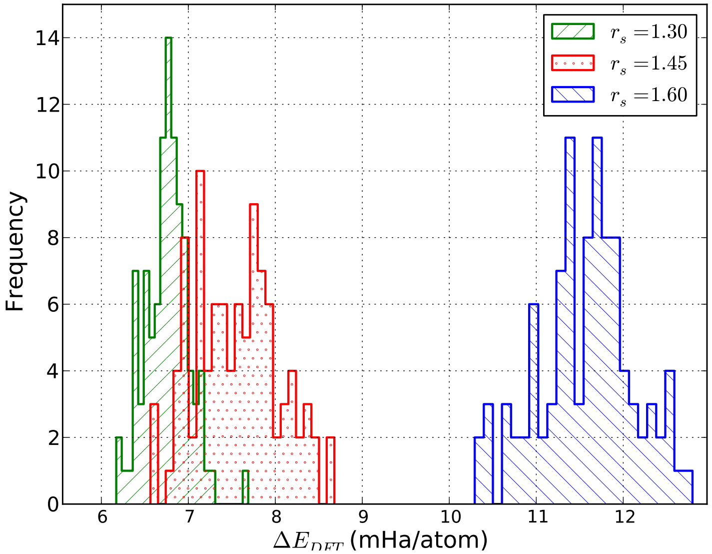
How can we use QMC to enable calculations for larger systems at longer times?

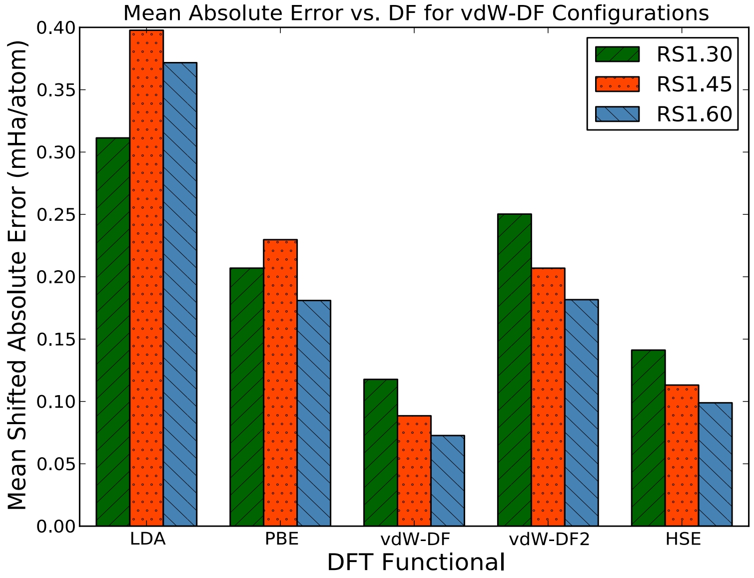
- Find better DFT functionals
- Find better “semi-empirical” potentials

Use QMC to find the most accurate DFT functional.

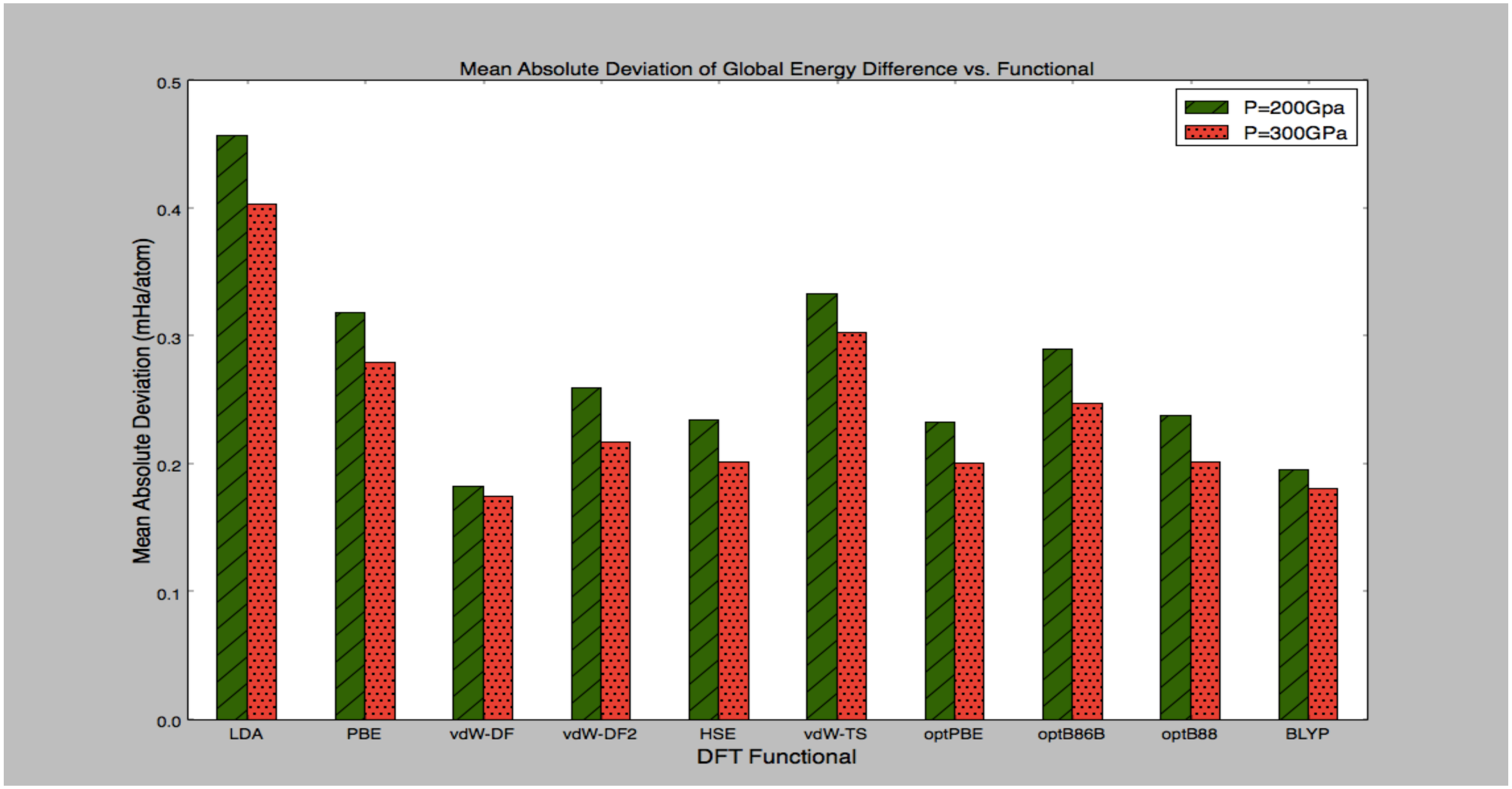
- Generate 100's of 54-96 atom configurations of both liquids and solids.
- Determine accurate energies (better than 0.1mH/atom) with DMC.
- LDA and PBE functionals do poorly in the molecular phase.

Histogram of errors in PBE at 3 densities



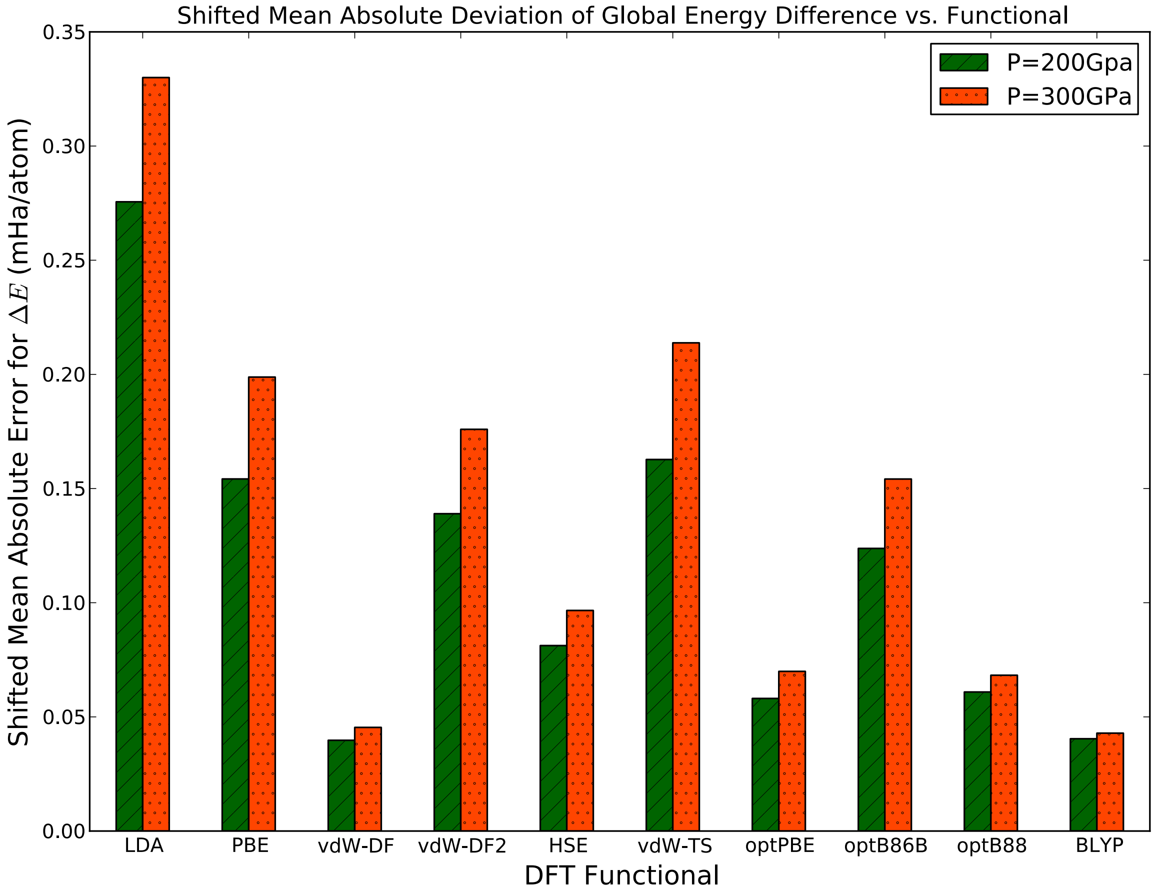


Average errors vs functional and density

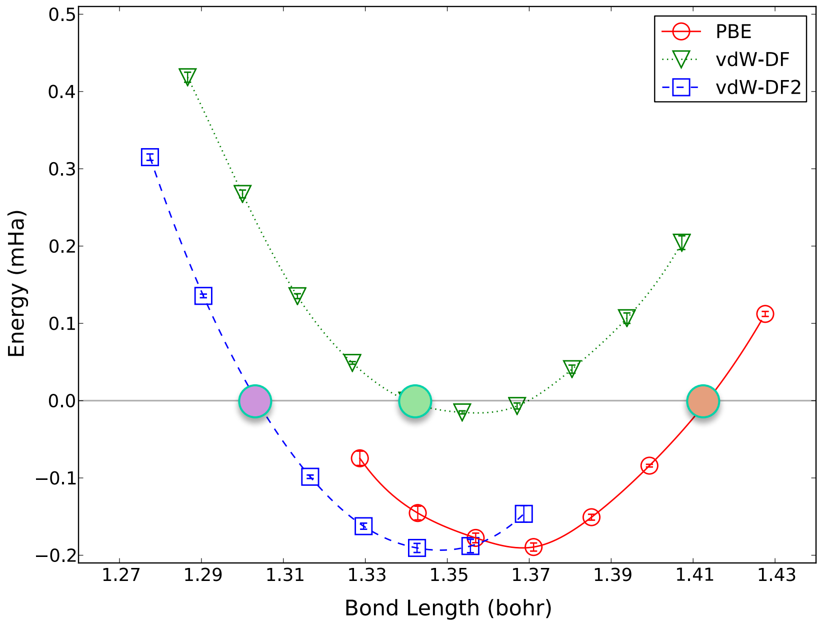


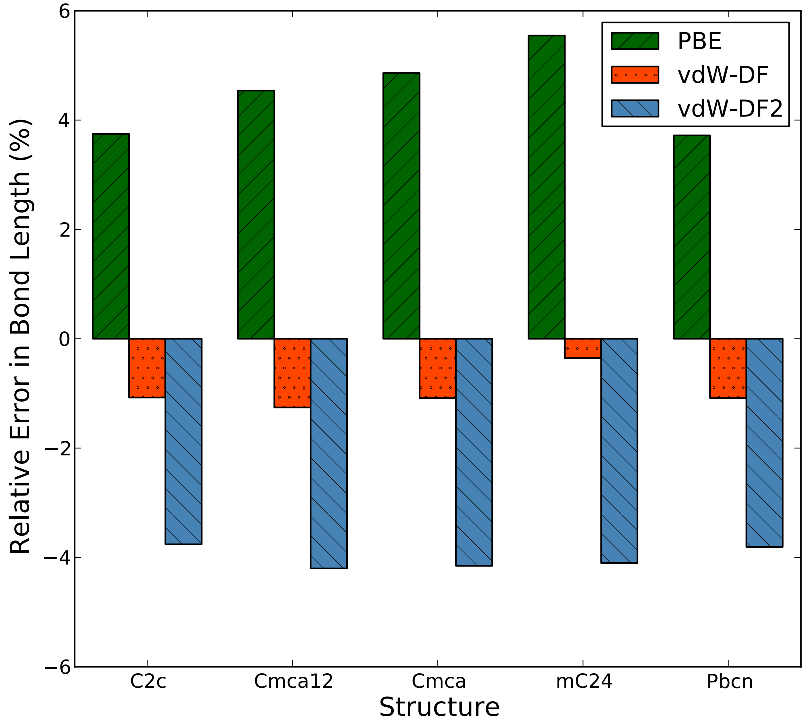
- Sample some configurations of solid H_2 using PIMD at 200K
- Shown is average error over 10 different crystal structures
- vdW-DF has lowest errors.

In one solid structure find dispersion of errors. Then average over solid structures vdW-DF is most accurate.



Which functional predicts the correct H_2 bond length in crystal?



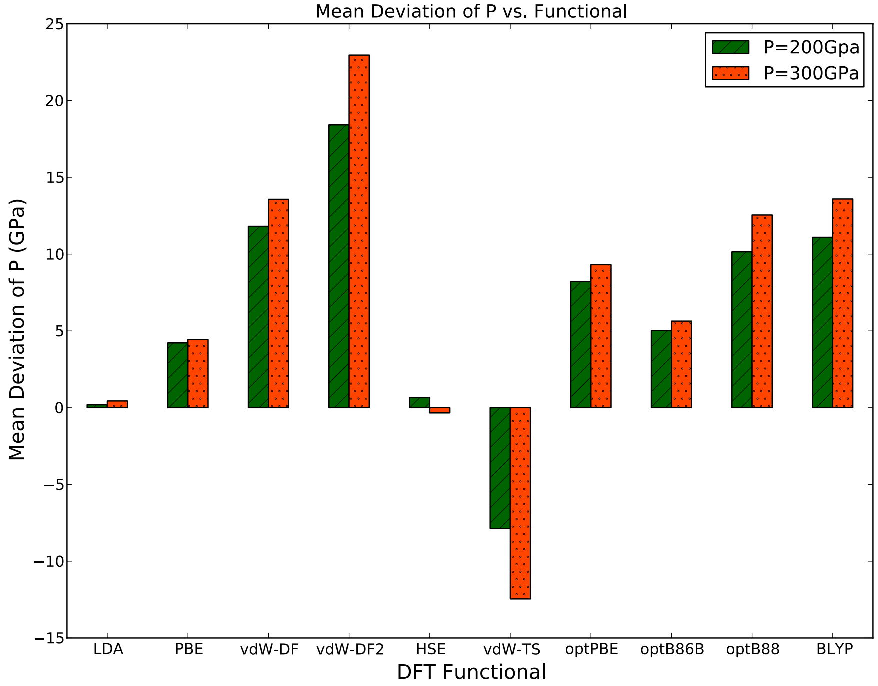


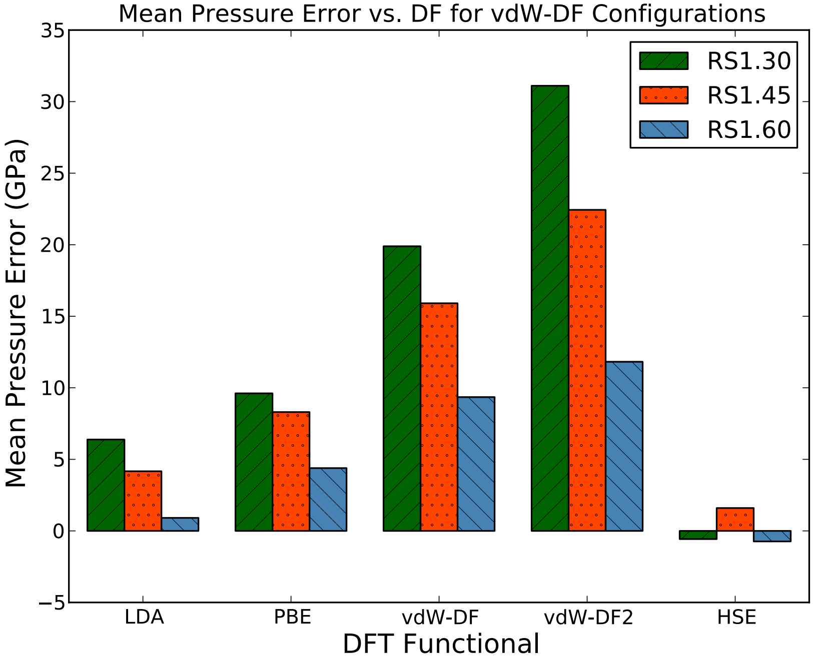
- Optimize H_2 structure within PBE,vdW-DF, vdW-DF2
- Then calculate total energy with QMC

Pressure errors

solids

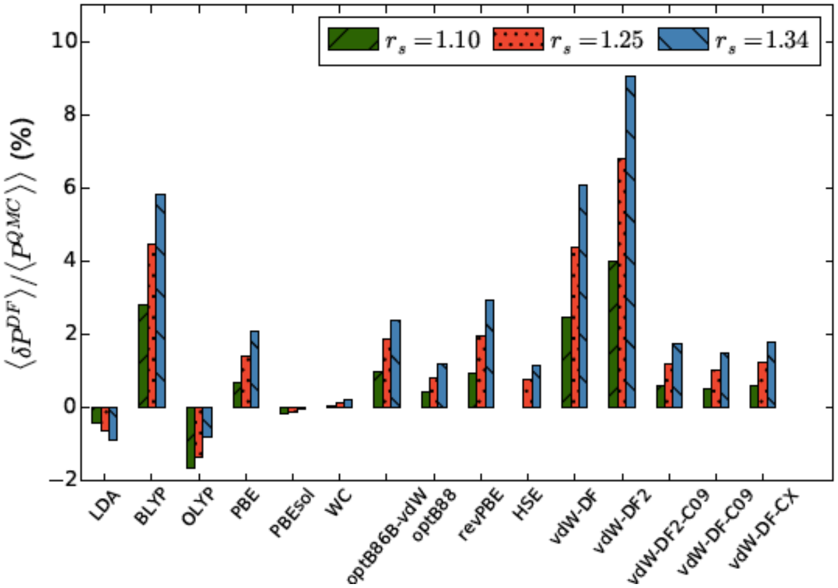
liquid

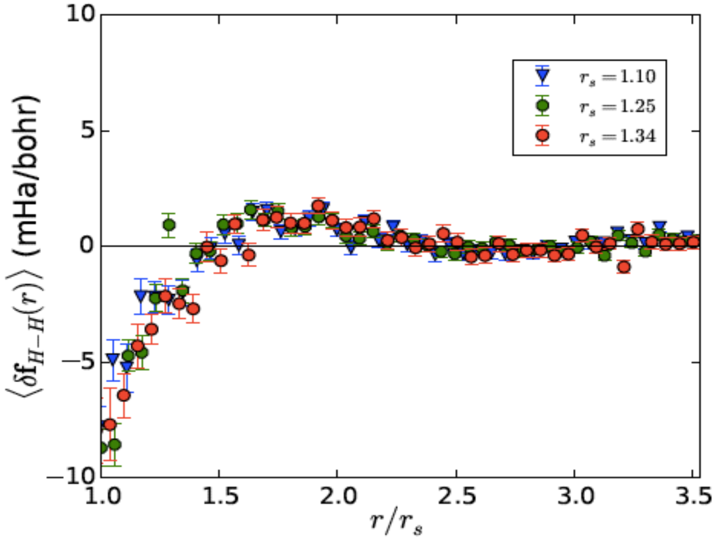

Mean Deviation of P vs. Functional


Mean Pressure Error vs. DF for vdW-DF Configurations

- LDA and HSE determine the pressure most accurately
- Use vdW-DF to simulate a structure, recalibrate pressure with QMC or LDA.

- Benchmark calculation of H-He mixtures. Comparison of DFT functionals
- Construction of potentials of dense hydrogen and helium. Use QMC forces





Complementary Aspects of Methods

Density Functional Theory

- What density functional to use?
- How to treat T>0 electronic excitations?
- How accurate are dynamical properties?

Use QMC to judge functionals

Quantum Monte Carlo

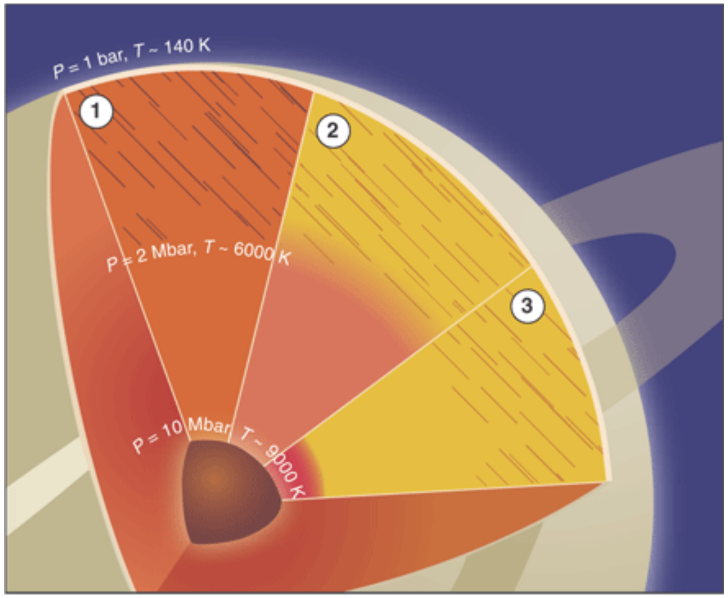
- Fermion sign problem

Upper bound property of energy is used to rank wavefunctions

- Conversion of Imaginary to real time dynamics is approximate

Use DFT to scale to larger systems

Big Puzzle: why are Jupiter and Saturn different?



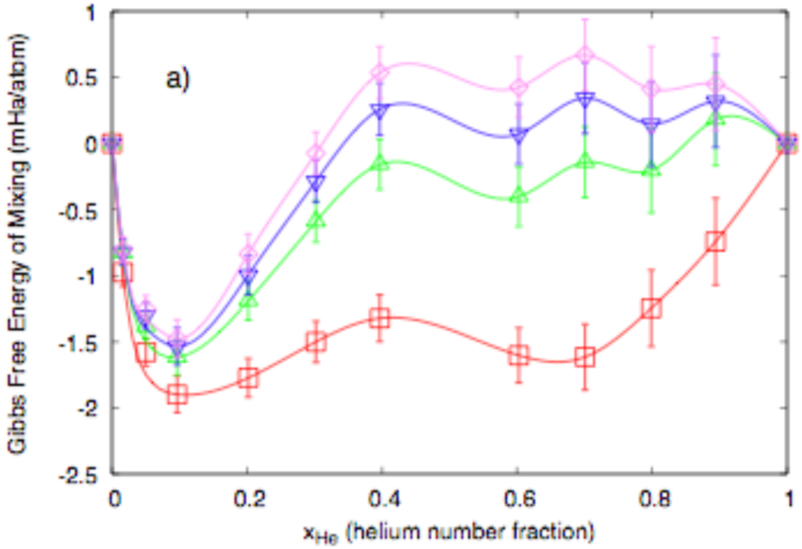
Taken from: Fortney J. J., *Science* **305**, 1414 (2004).

- Some helium is missing from Saturn’s surface.
- Saturn is brighter than it should be for its age.
- Additional energy source in planet’s interior is needed.
- Does it come from Helium segregation (rain) as suggested by Smoluchowski in 1965?
- Key question: when does Helium mix with Hydrogen?

Mixing Free Energy for He in H

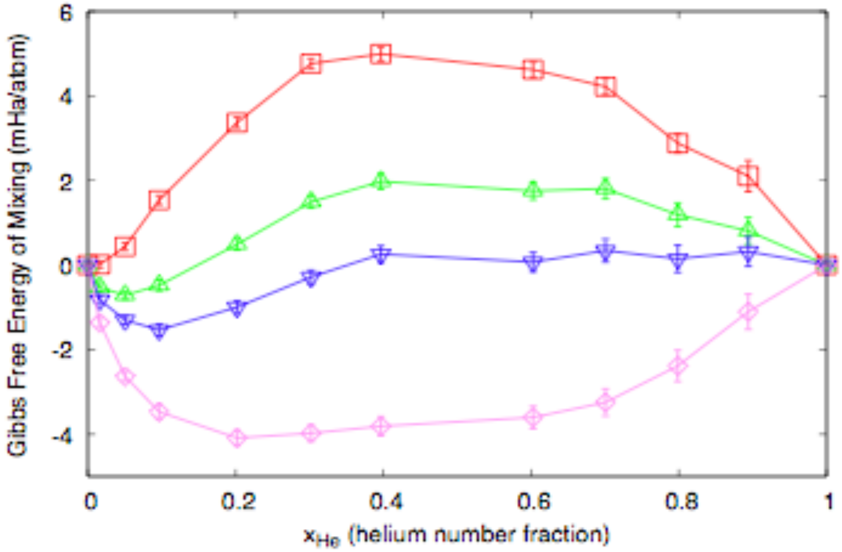
Morales, Schwegler, DMC, Pierleoni, Hamel, Caspersen, PNAS 2009.

T=8000 K



— 4 Mbar
— 10 Mbar
— 8 Mbar
— 12 Mbar

P=10 Mbar



— 4000 K
— 9000 K
— 7000 K
— 10000 K

- Clear minimum at low helium fraction.
- Very strong temperature dependence, fairly insensitive to pressure.

H-He mixtures

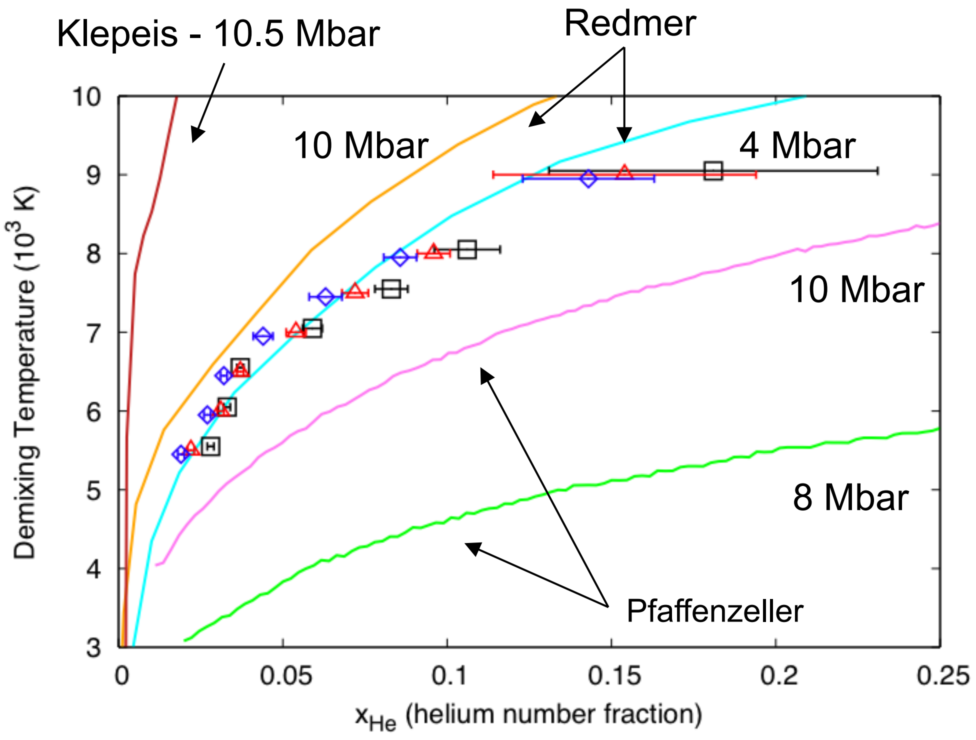
Fully ionized models

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

First Principles

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

H-He Demixing Temperature

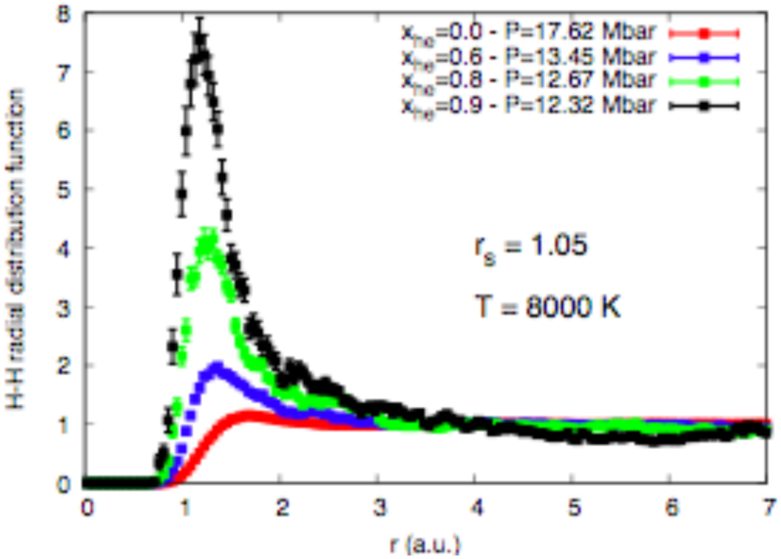


❑ 4 Mbar
△ 8 Mbar
◊ 12 Mbar

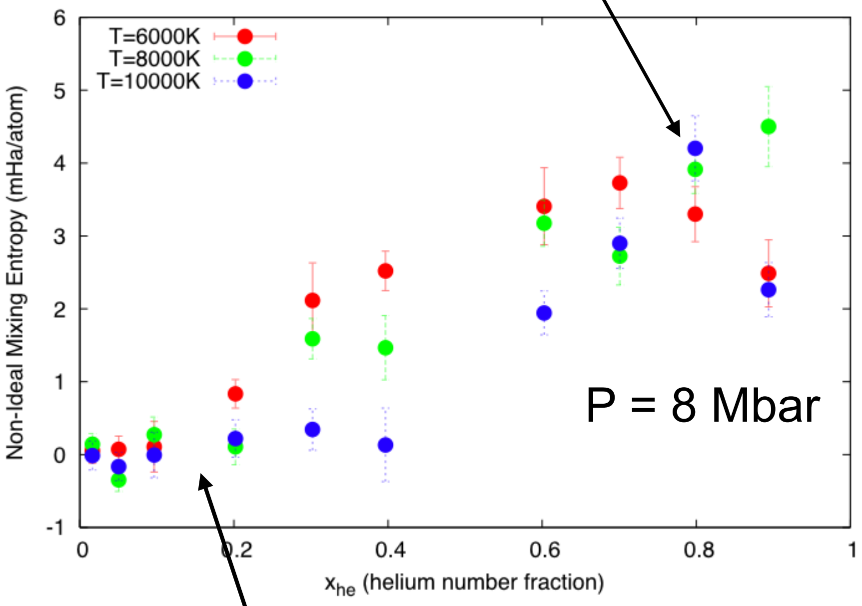
Demixing transition temperatures as a function of helium number fraction, for several pressures

- Previous CPMD simulations underestimate demixing temperature.
- Differences come from non-ideal effects

Molecular-like Correlations



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

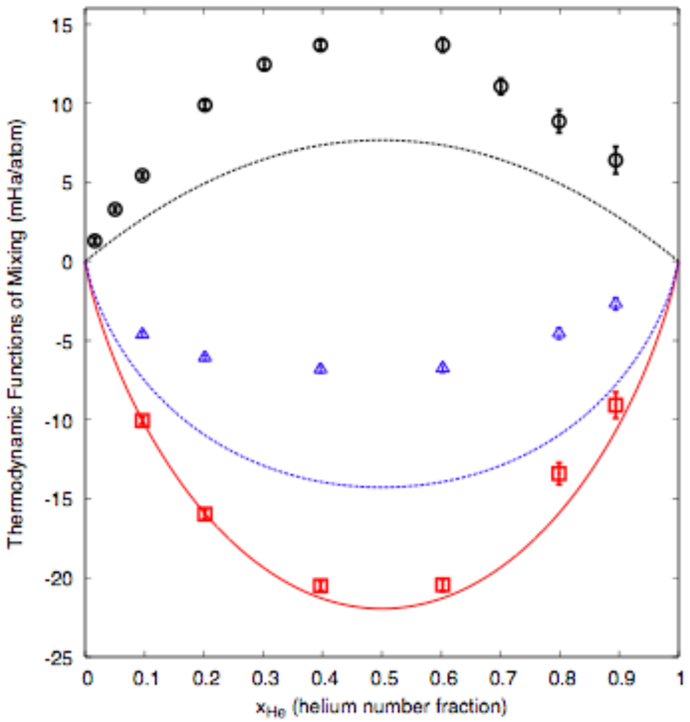


Non-ideal mixing fails

Ideal mixing works

Results at Reference Point

- Ideal mixing approx. is good at low helium concentration.
- Internal energy and Helmholtz free energy of mixing are larger than previous calculations.
  - Finite temperature effects are important



o Internal Energy of Mixing

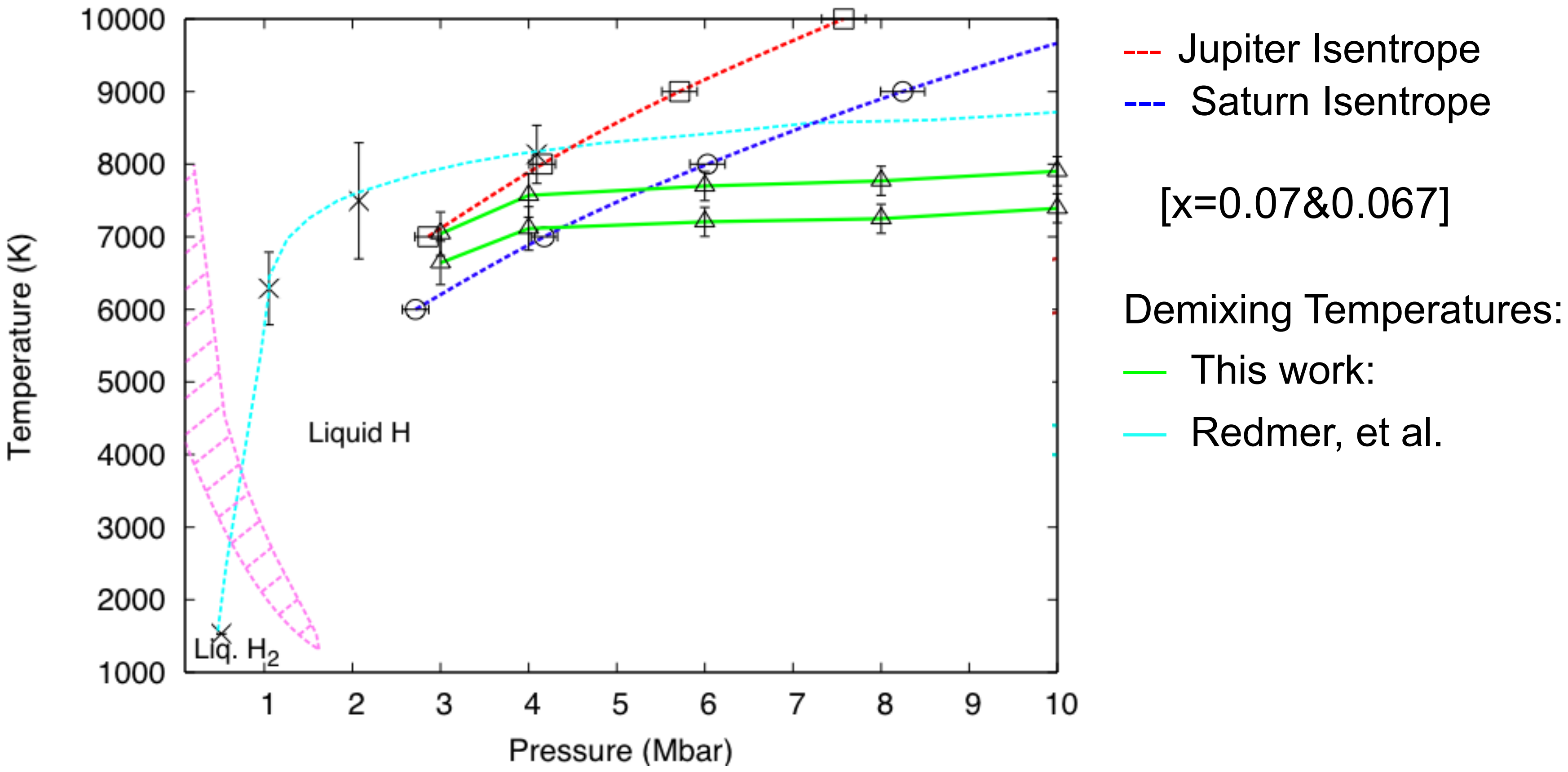
△ Helmholtz Free Energy of Mixing

❑ (Mixing) Entropic contribution to FE

– dashed lines - *Pfaffenzeller et al

— Ideal mixing approximation

Mixing Phase Diagram



Liquid hydrogen does not mix with helium at T<8000K.

Could explain the difference between Jupiter and Saturn!

Publications

- J. M. McMahon, M. A. Morales, C. Pierleoni, and D. M. Ceperley, The properties of hydrogen and helium under extreme conditions, Rev. Mod. Phys. **84**; 1607-1653 (2012).
- M. A. Morales, J. M. McMahon, C. Pierleoni and D. M. Ceperley, *Nuclear quantum effects and nonlocal exchange-correlation functionals in liquid hydrogen at high pressure*, **Phys. Rev. Lett. 110**, 065702 (2013); *Towards a predictive first-principles description of solid molecular hydrogen with DFT*, Phys. Rev. B 87, 184107 (2013); *Melting of Atomic Hydrogen*, Submitted.
- N. M. Tubman, E. Liberatore, M. Holzmann, C. Pierleoni, D. M. Ceperley, *CEIMC calculation of the Deuterium Hugoniot*, in press PRL (2015).
- J. McMinis, M. A. Morales, D. M. Ceperley, J. Kim*, The Transition to the Metallic State in Low Density Hydrogen* , submitted.
- R. C. Clay, J. B. McMinis, J. M. McMahon, C. Pierleoni, D. M. Ceperley, M. A. Morales, *Benchmark of Exchange-Correlation Functionals for High Pressure Hydrogen using QMC*, Phys. Rev. B 89, 184106 (2014). *QMC Benchmark of Exchange-Correlation Functionals for Bulk Water*. **J. Chem. Theory Comput.**, 10, 2355–2362 (2014).
- E. Brown, M. A. Morales, C. Pierleoni and D. Ceperley, *QMC Techniques and Applications for Warm Dense Matter*, in ***Frontiers and Challenges in Warm Dense Matter***, pgs. 123-149, ed. F. Graziani et. al., Springer, (2014)
- M. A. Morales, R. Clay, C. Pierleoni and D. M. Ceperley, *First Principles Methods: A perspective from QMC* . **Entropy** 16, 287-321 (2014).

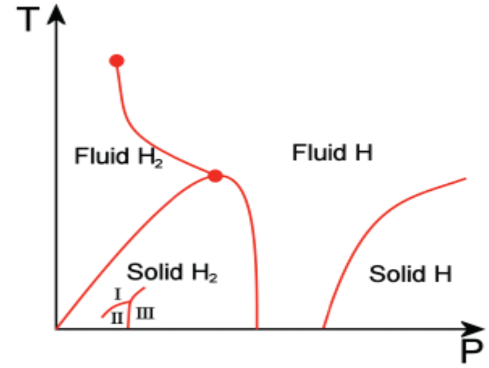
Published Work 2017-18

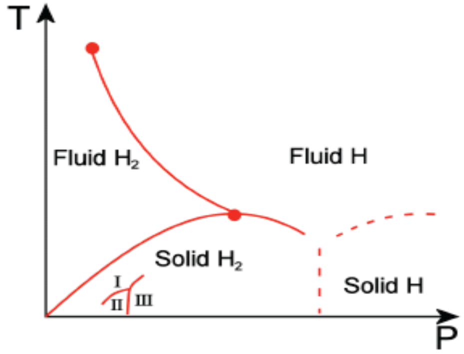
[1] G. Rillo, M. A. Morales, D. M. Ceperley, C. Pierleoni, “Coupled Electron-Ion Monte Carlo simulation of hydrogen molecular crystals,” *J. Chem. Phys.* **148**, 102314 (2018).

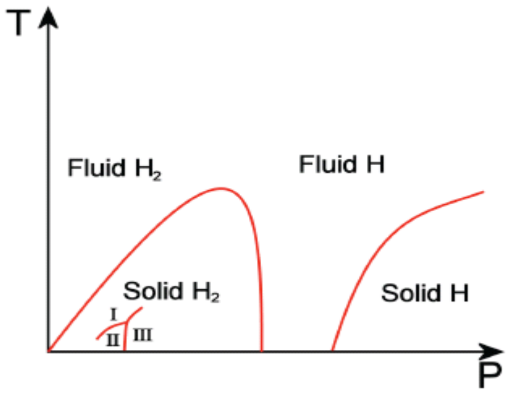
[2] C. Pierleoni, M. Holzmann, D. M. Ceperley, “Local structure in dense hydrogen at the liquid-liquid phase transition by Coupled Electron-Ion Monte Carlo,” Contributions to Plasma Physics, in press (2017).

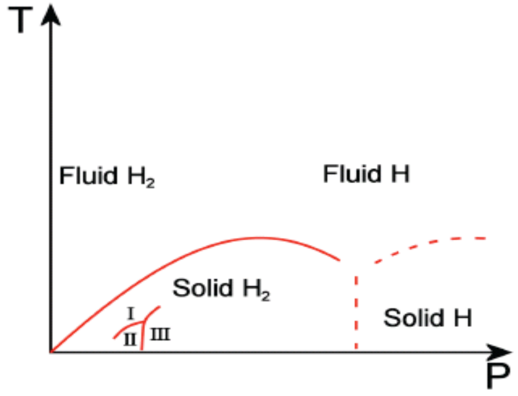
[3] C. Pierleoni, G. Rillo, D. M. Ceperley, M. Holzmann, “Electron localization properties in high pressure hydrogen at the liquid-liquid phase transition by Coupled Electron-Ion Monte Carlo,” Proceedings of Strongly Coupled Coulomb System (2018).

Some Possible Phase Diagrams for high pressure hydrogen









Efficient Energy differences

- We need a fast way of computing difference: [E(S)-E(S*)]
- Naïve (direct) method is to do separate (uncorrelated) samples of S and S*. Noise increases by ⍰2.
- Correlated methods map S walks into S* walks.
- “re-weighting” using an importance function
- lowest variance importance function for the energy difference? (ignoring autocorrelation effects)
- Generalizable to reptation MC
- 2 orders of magnitude faster (lower variance)

$$E(S^*) \approx \frac{\sum_{i=1}^{M} w_i(S^*) E_L(R_i;S^*)}{\sum_{i=1}^{M} w_i(S^*)}$$

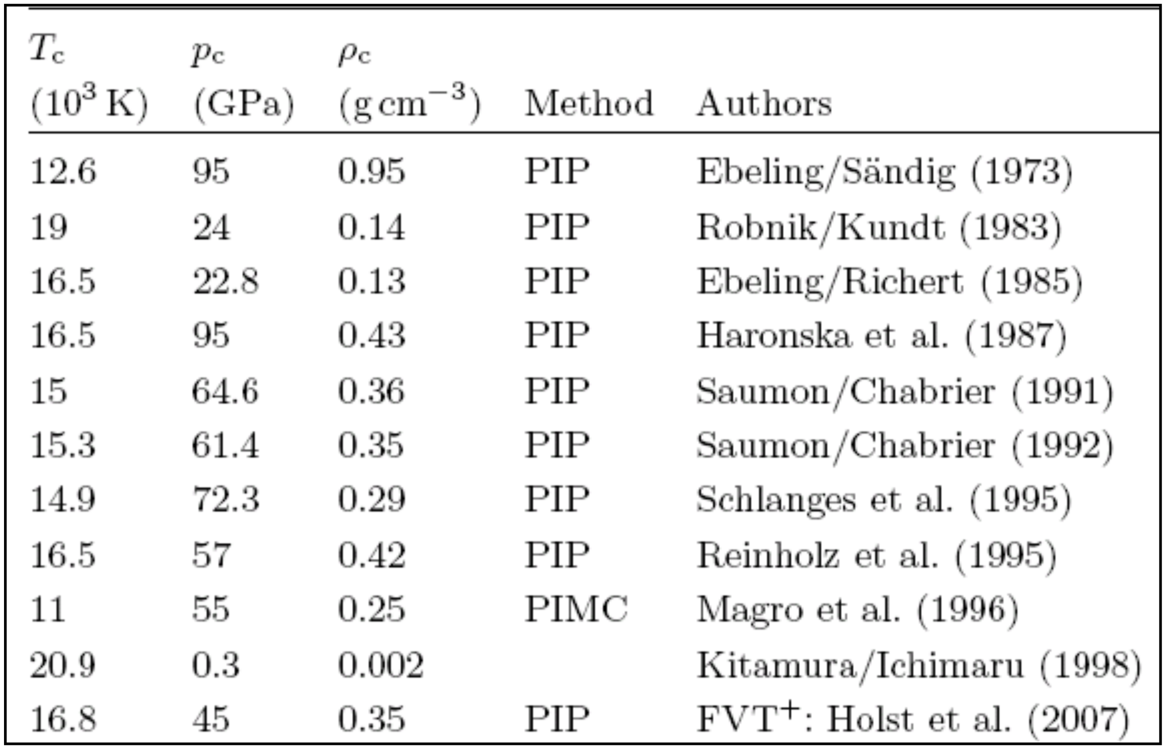
$$w_i(S^*) = \frac{\left|\psi_T(R_i;S^*)\right|^2}{P(R_i)}$$

$$p(s) \propto \left|\Psi_1(s)^2 \Delta E_{L1} - \Psi_2(s)^2 \Delta E_{L2}\right|$$

$$p(s) \sim \left|\Psi_1(s)\right|^2 + \left|\Psi_2(s)\right|^2$$

Liquid-Liquid transition

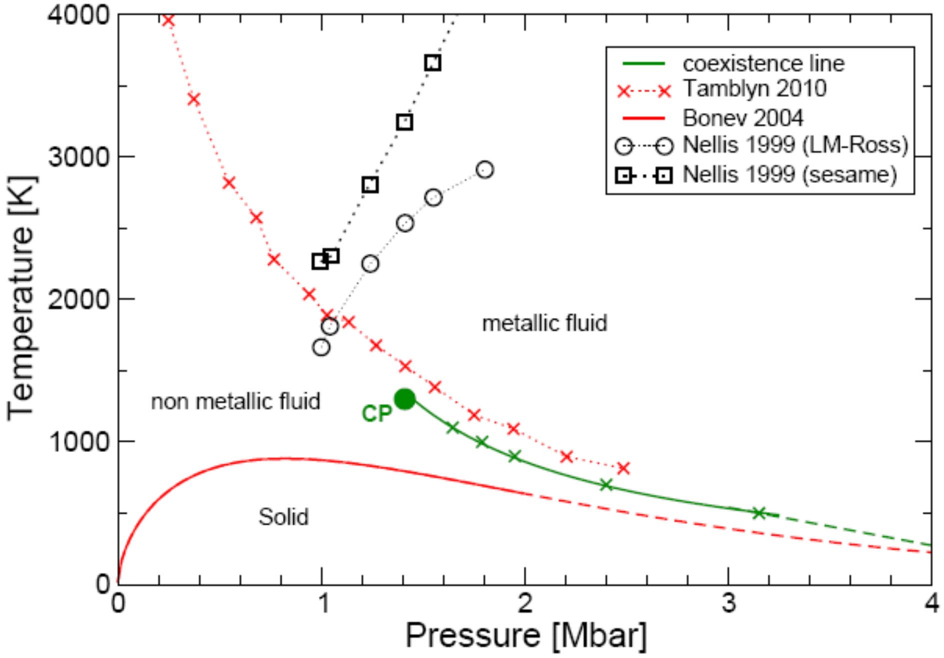
- How does an insulating molecular liquid become a metallic atomic liquid? Either a
  - Continuous transition or
  - First order transition with a critical point
- Zeldovitch and Landau (1944) *"a phase transition with a discontinuous change of the electrical conductivity, volume and other properties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

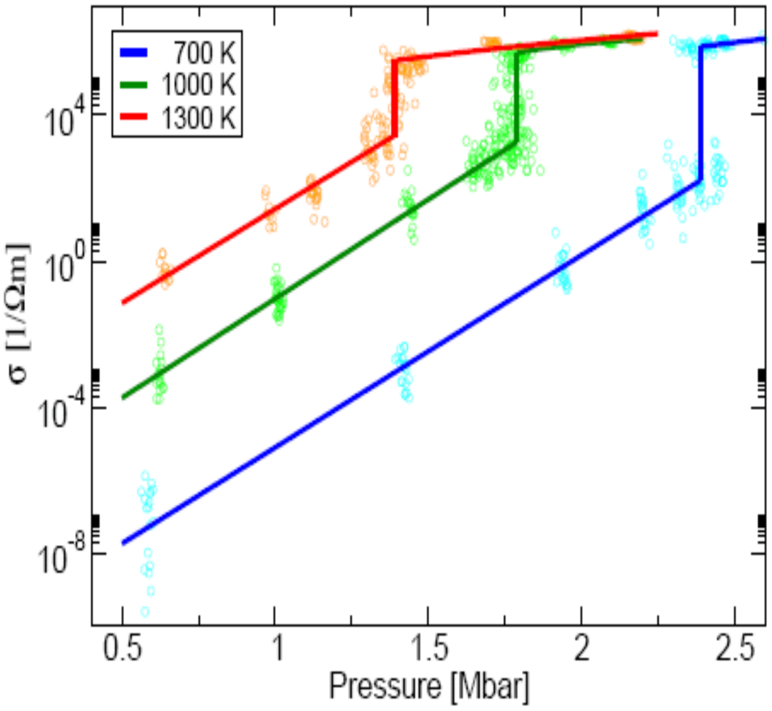


T_c (10^3 K)	p_c (GPa)	ρ_c ($\mathrm{g\,cm^{-3}}$)	Method	Authors
12.6	95	0.95	PIP	Ebeling/Sändig (1973)
19	24	0.14	PIP	Robnik/Kundt (1983)
16.5	22.8	0.13	PIP	Ebeling/Richert (1985)
16.5	95	0.43	PIP	Haronska et al. (1987)
15	64.6	0.36	PIP	Saumon/Chabrier (1991)
15.3	61.4	0.35	PIP	Saumon/Chabrier (1992)
14.9	72.3	0.29	PIP	Schlanges et al. (1995)
16.5	57	0.42	PIP	Reinholz et al. (1995)
11	55	0.25	PIMC	Magro et al. (1996)
20.9	0.3	0.002		Kitamura/Ichimaru (1998)
16.8	45	0.35	PIP	$\mathrm{FVT^{+}}$: Holst et al. (2007)

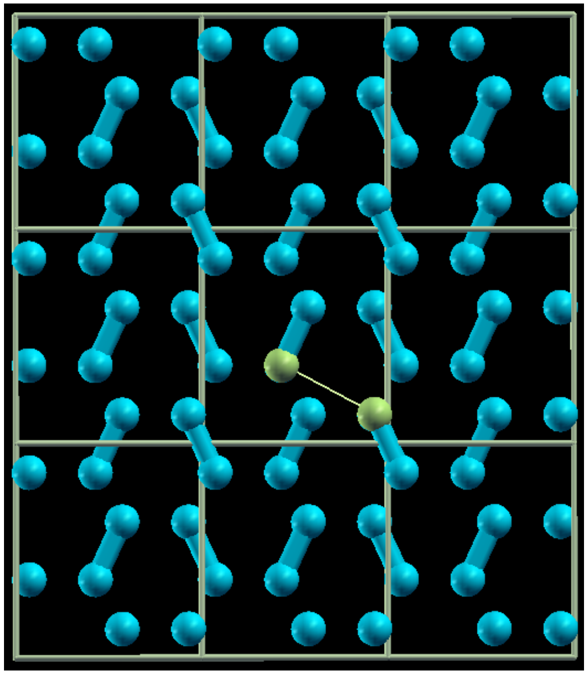
Confirmation of DFT results

W. Lorenzen, B. Holst, and R. Redmer, PRL 2010.

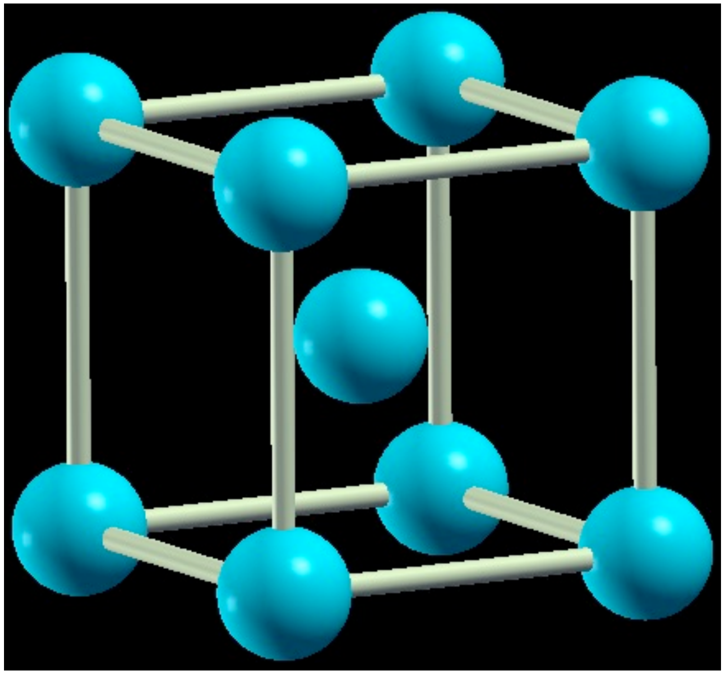




Highest Pressure Molecular and Atomic Phases



Cmca (H_2)



Im-3m (H)

(bcc; Wigner crystal)

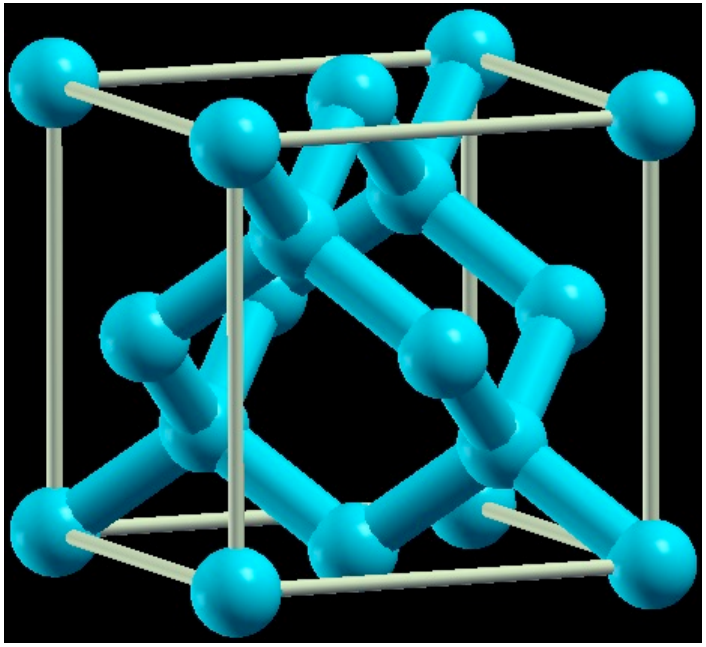
K. A. Johnson and N. W. Ashcroft, *Nature* **403**, 632 (2000)

C. J. Pickard and R. J. Needs, *Nature Phys.* **3**, 473 (2007)

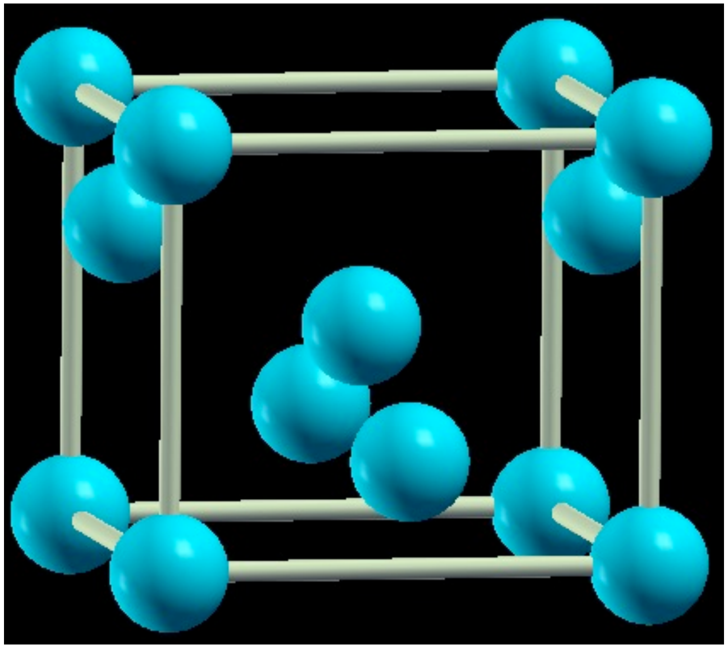
Common Approach: Candidate Structures

The standard approach for “determining” the high pressure atomic structures is to propose some likely candidate ones.

Two likely candidates are Fd-3m and I4$_1$/amd (c/a ~ 0.9):



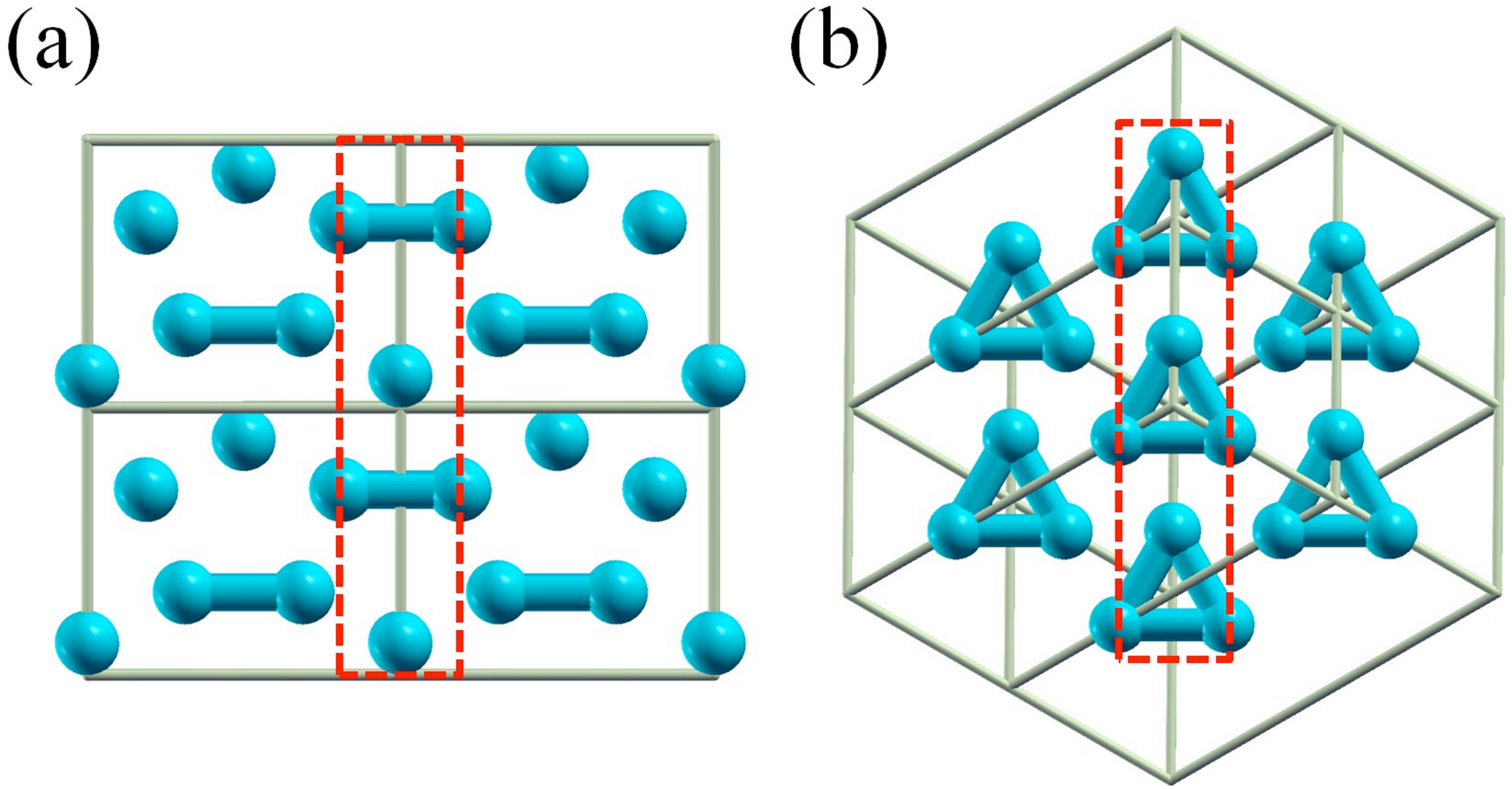
Fd-3m
(diamond)



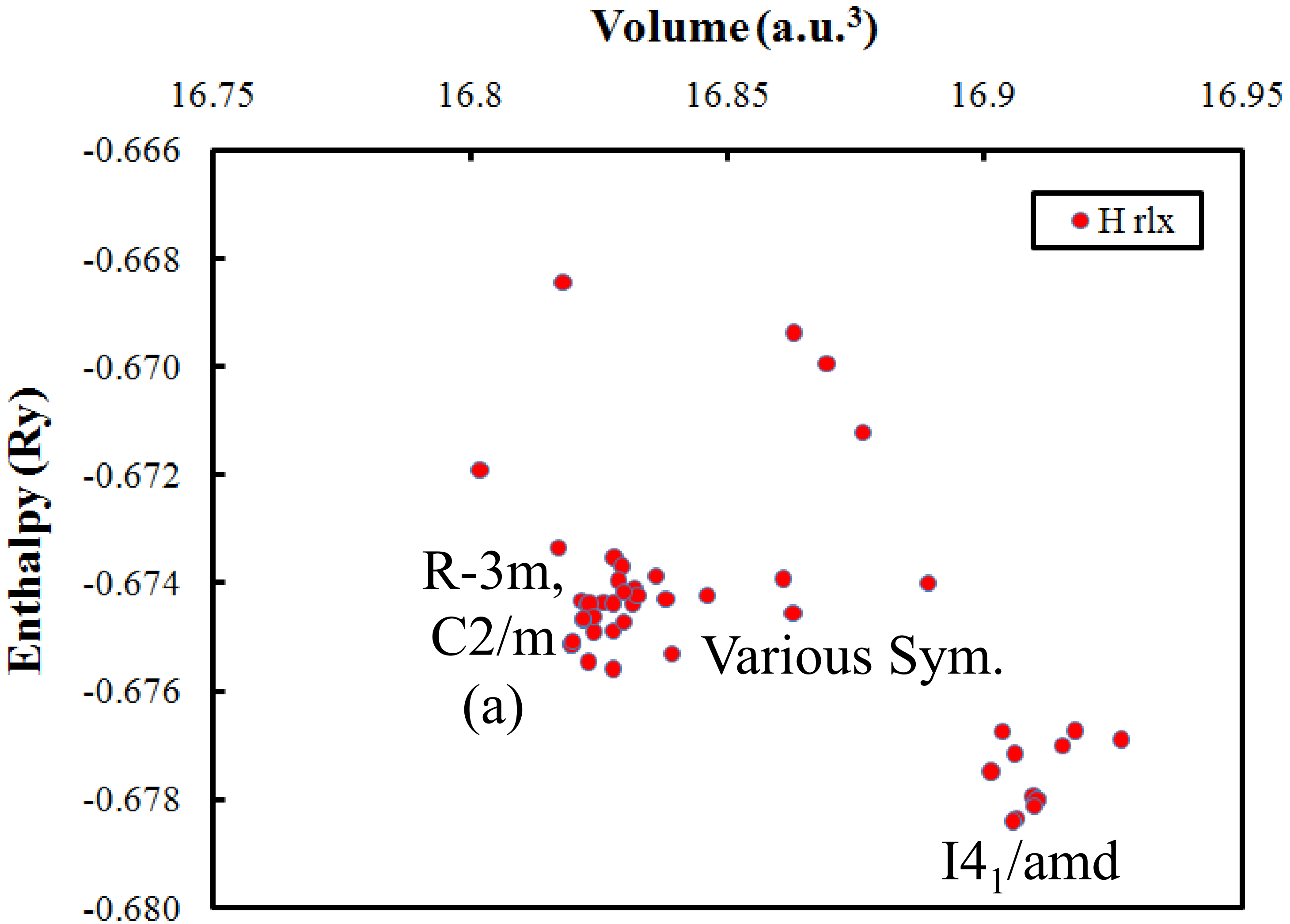
I4$_1$/amd (c/a < 1)
(β-Sn)

V. Natoli, R. M. Martin, and D. M. Ceperley, *Phys. Rev. Lett.* **70**, 1952 (1993).

***Pmmn* and *R3m*:**

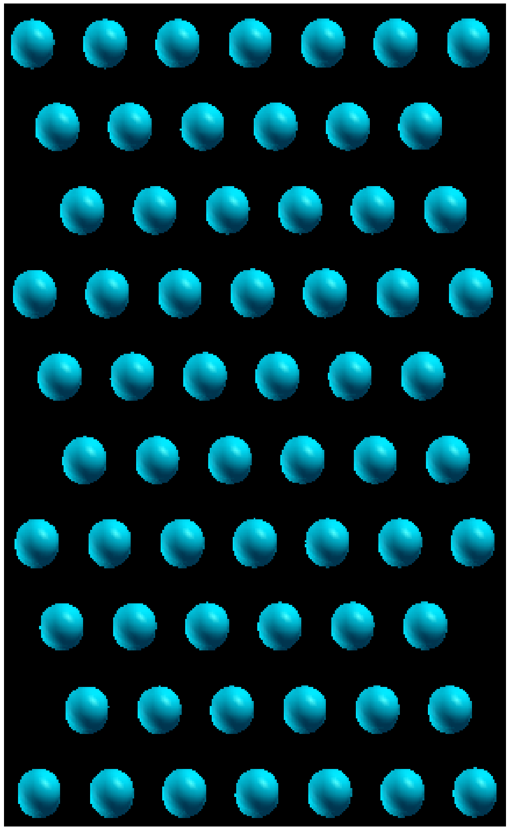


4 Atom Rand. Struct. Rlx. at 2 TPa

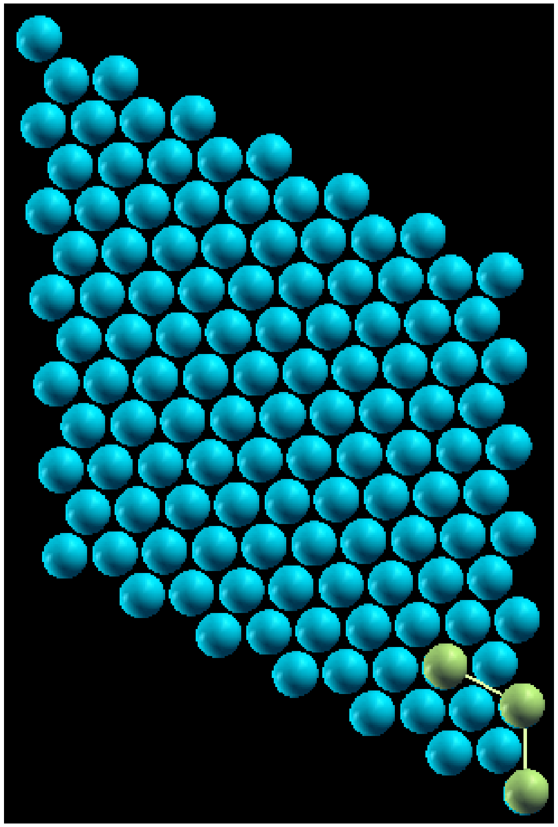


C2/m (a) is a slight distortion and subgroup of R-3m.
6 atom relaxations at 2TPa reveal similar results.

R-3m



Side View



Top Down

(highlighted atoms are in-plane)

R-3m forms an ABCABC… layered structure with c/a ~ 2

SUMMARY

- Liquid-Liquid transition predicted in pure hydrogen
  - Critical point at T~1700K
  - Intersects melting line T~250K, 400 GPa.
- Low temperature (100K) solid phase
- Simulation methods can now predict properties of dense hydrogen & helium much more accurately because:
  - Computer power is still increasing!
  - Algorithmic progress: better trial functions, methods.
- Overall good agreement between DFT and QMC away from critical region.

OUTLOOK

- Rich phase diagram of hydrogen. More phases to come.
  - Liquid-Liquid transition predicted in pure hydrogen
  - Experiments are now addressing this question
  - Crystal structures, melting temperatures predicted at higher pressures.
- Simulation methods can now predict properties of dense hydrogen and helium much more accurately because:
  - Computer power is still increasing.
  - Algorithmic progress gives us much better methods.
- The goal is to do much more accurate simulations of all sorts of materials.

Concluding Remarks

QMC is arguably the most accurate computational method to make predictions about properties of hydrogen under extreme conditions.

- DFT functionals give differing results especially near the phase transitions.
- DMC is most accurate for the ground state.
- CEIMC allows one access to disordered $T>0$ systems with control of correlation effects
- CEIMC does not agree with experiments for the Hugoniot, but experiments do not always agree.
- PIMC is best for $T>1$ ev.

There are many open questions with hydrogen:

- The sequence of molecular and atomic crystal structures
- Mechanism of metallization in the solid
- High temperature superconductivity in LaH_{10} and SH_3.