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

WHO DID THE WORK?

Miguel Morales *Livermore*

Carlo Pierleoni *L'Aquila, Italy*

Jeff McMahon *Washington St.*

Markus Holzmann *Grenoble*

Ray Clay *Sandia*

Yubo Yang *Illinois*

DOE 0002911

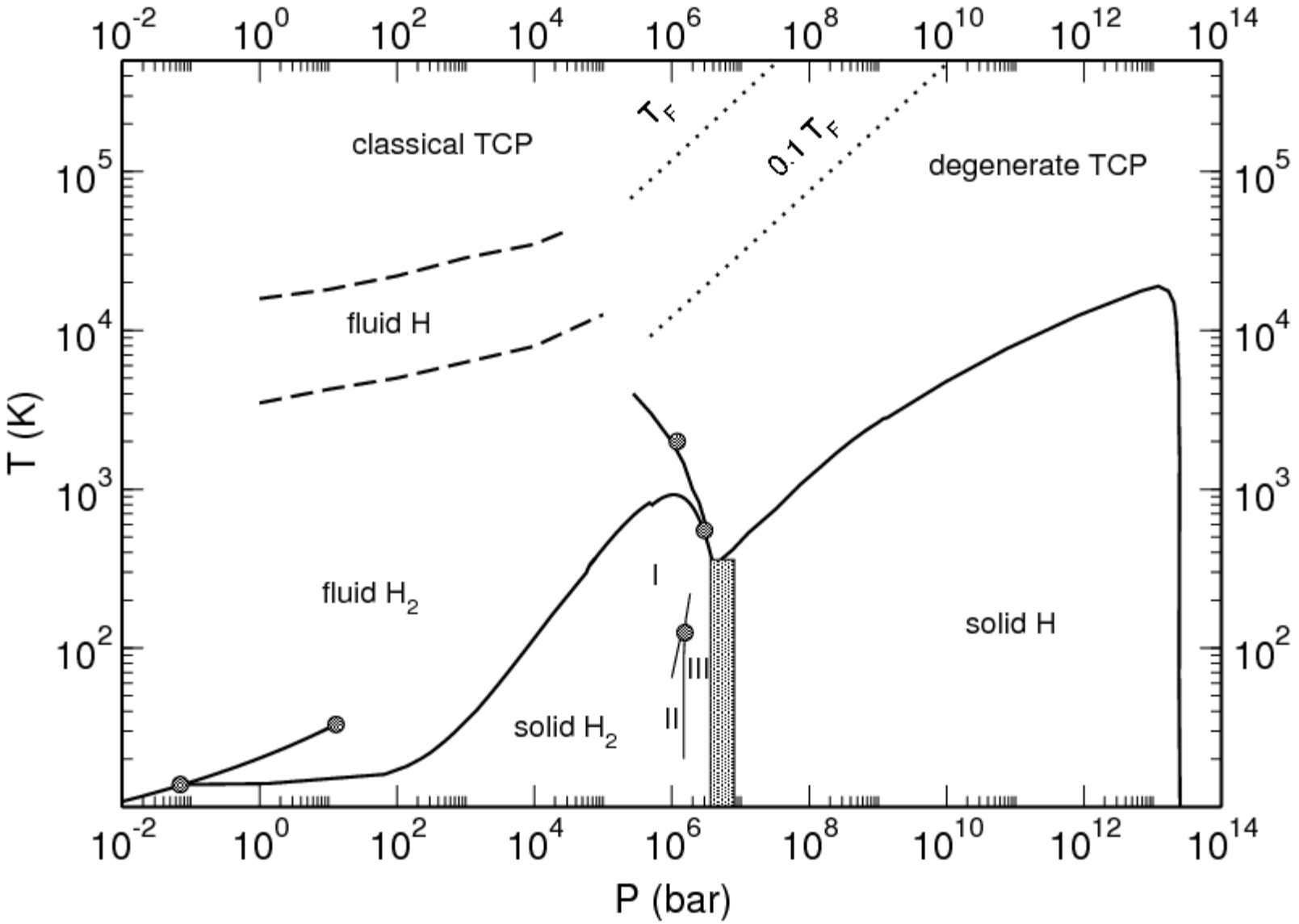
INCITE/Blue Waters award of computer time

For more information: see Rev. Mod. Phys. **84**, 1607 (2012)

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

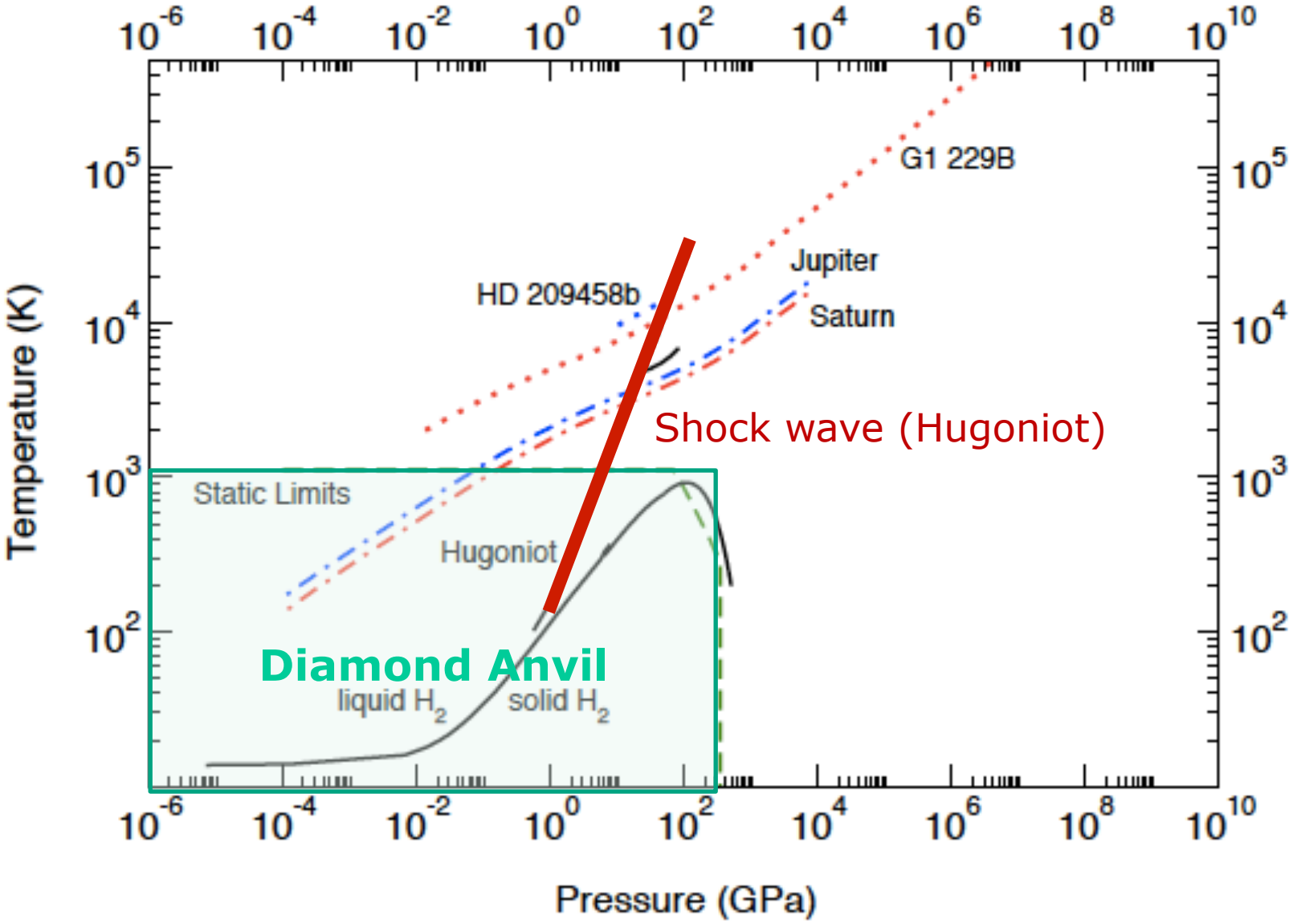
Simplified H Phase Diagram



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?

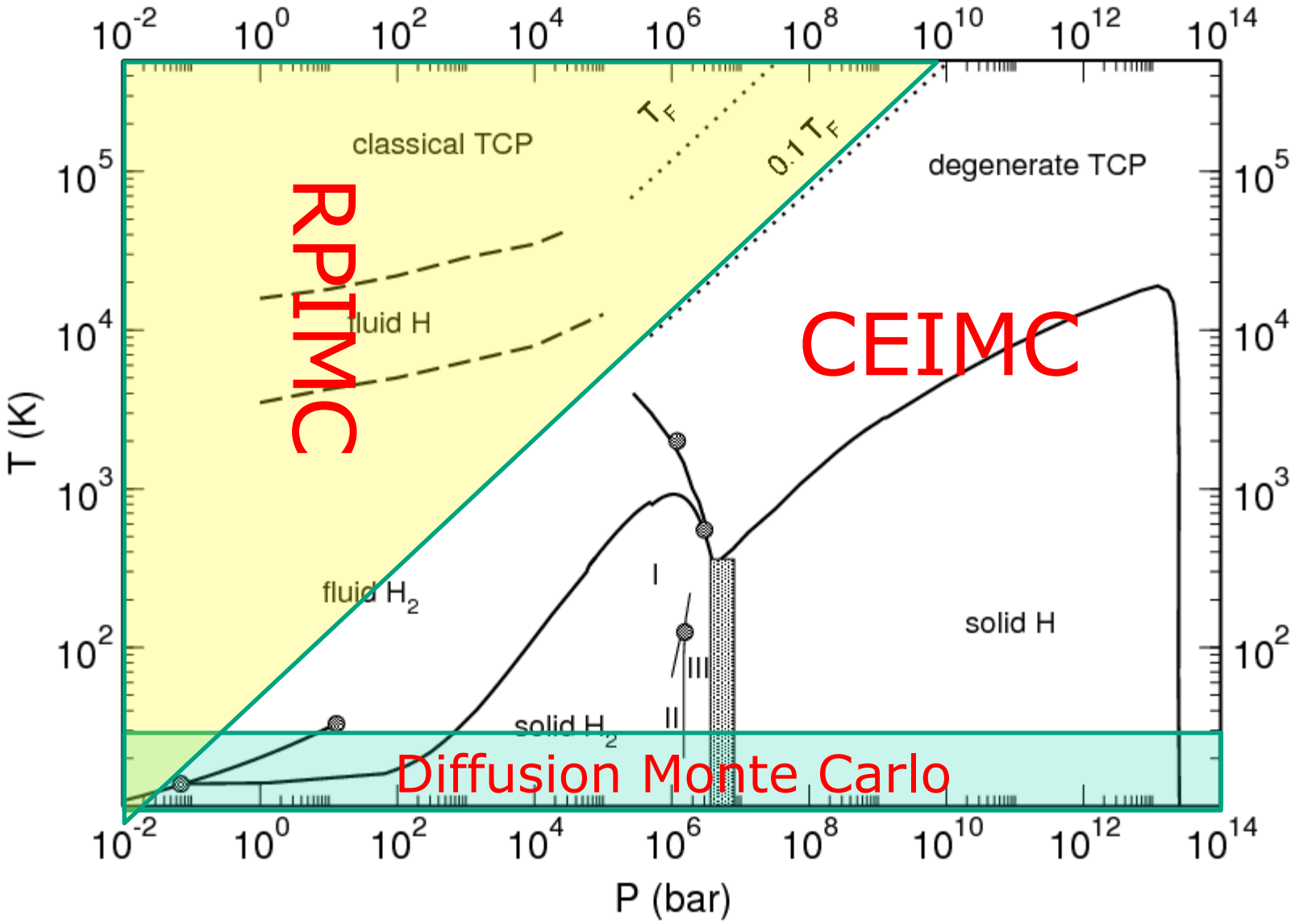
Experiments on hydrogen



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



New QMC Techniques

- Better algorithms, e.g. reptation
- 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

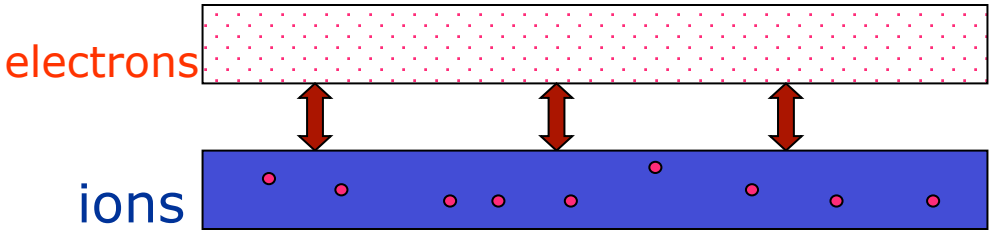
ab-initio with QMC
Coupled Electron-Ion MC (CEIMC)

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



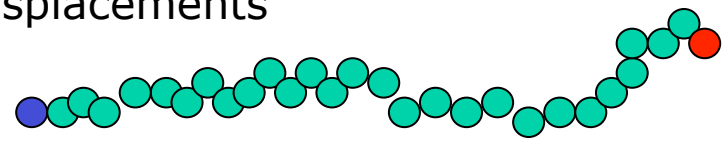
Reptation

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

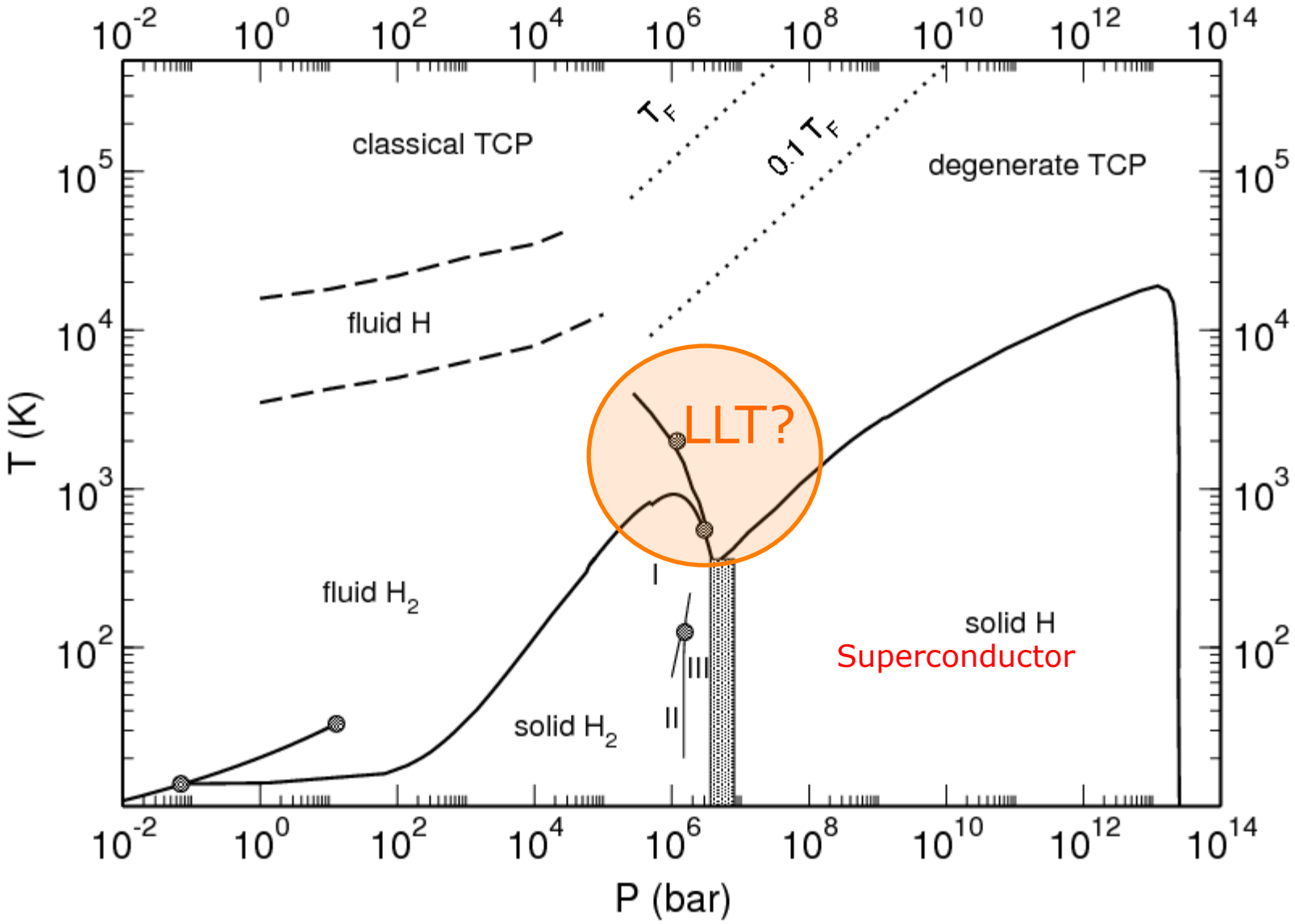
$$= \int dR' \quad dR \quad \Psi^*(R') \langle R' | e^{-\beta H} | R \rangle \Psi(R)$$

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

- 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



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.

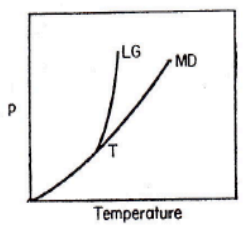


FIG 1.

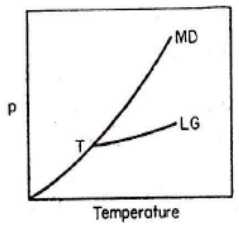
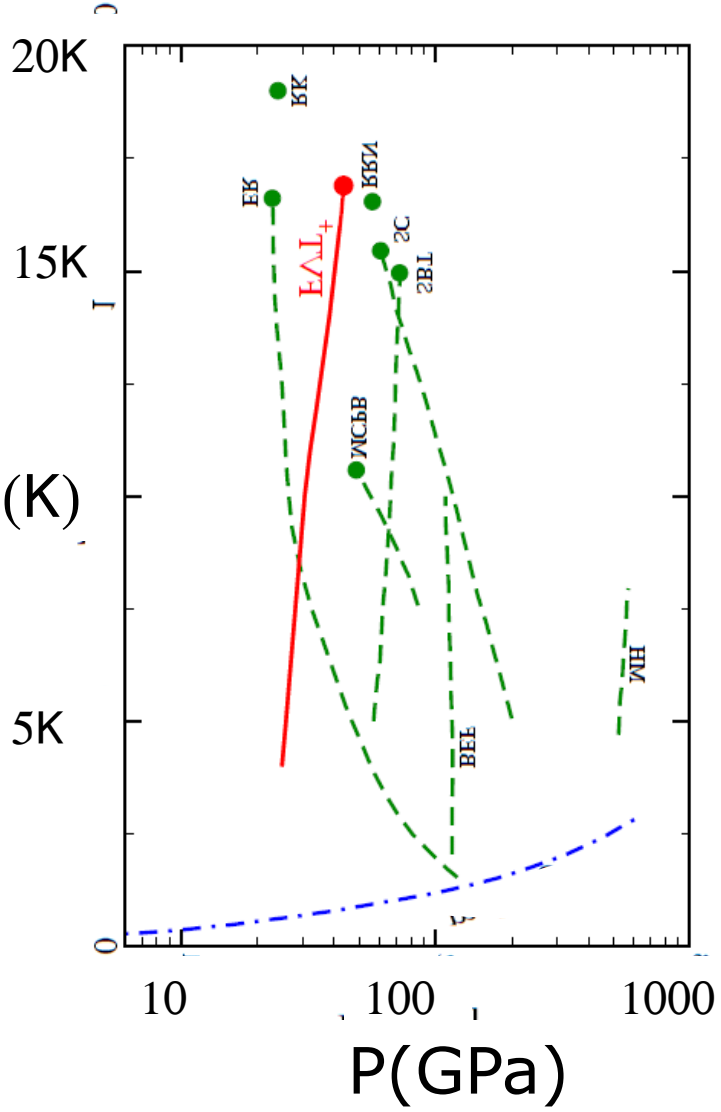


FIG. 2.

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

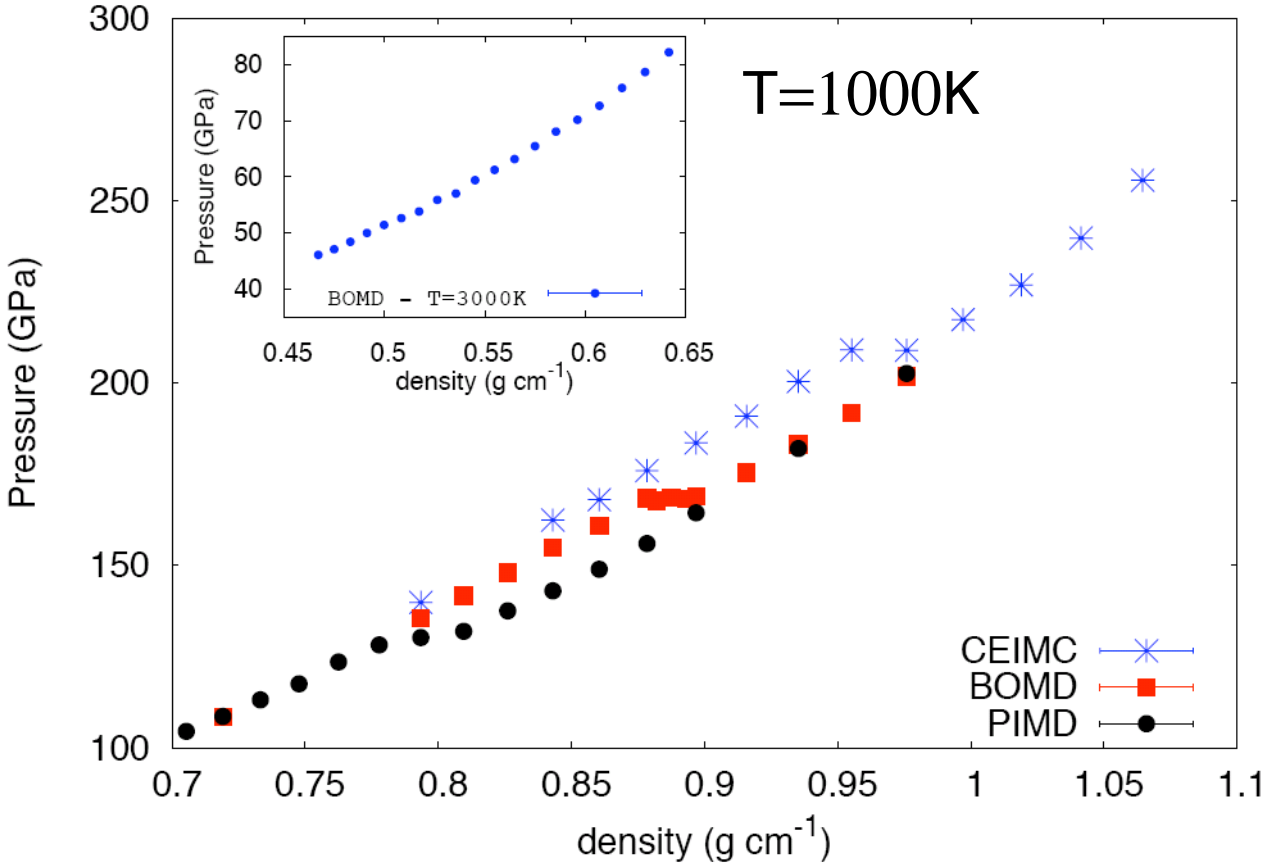
- How does an insulating molecular liquid become a metallic atomic liquid? Either a
  - Continuous transition or
  - First order transition with a critical point
- Zeldovitch and Landau (1944) *"a phase transition with a discontinuous change of the electrical conductivity, volume and other properties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



Liquid-Liquid Transition

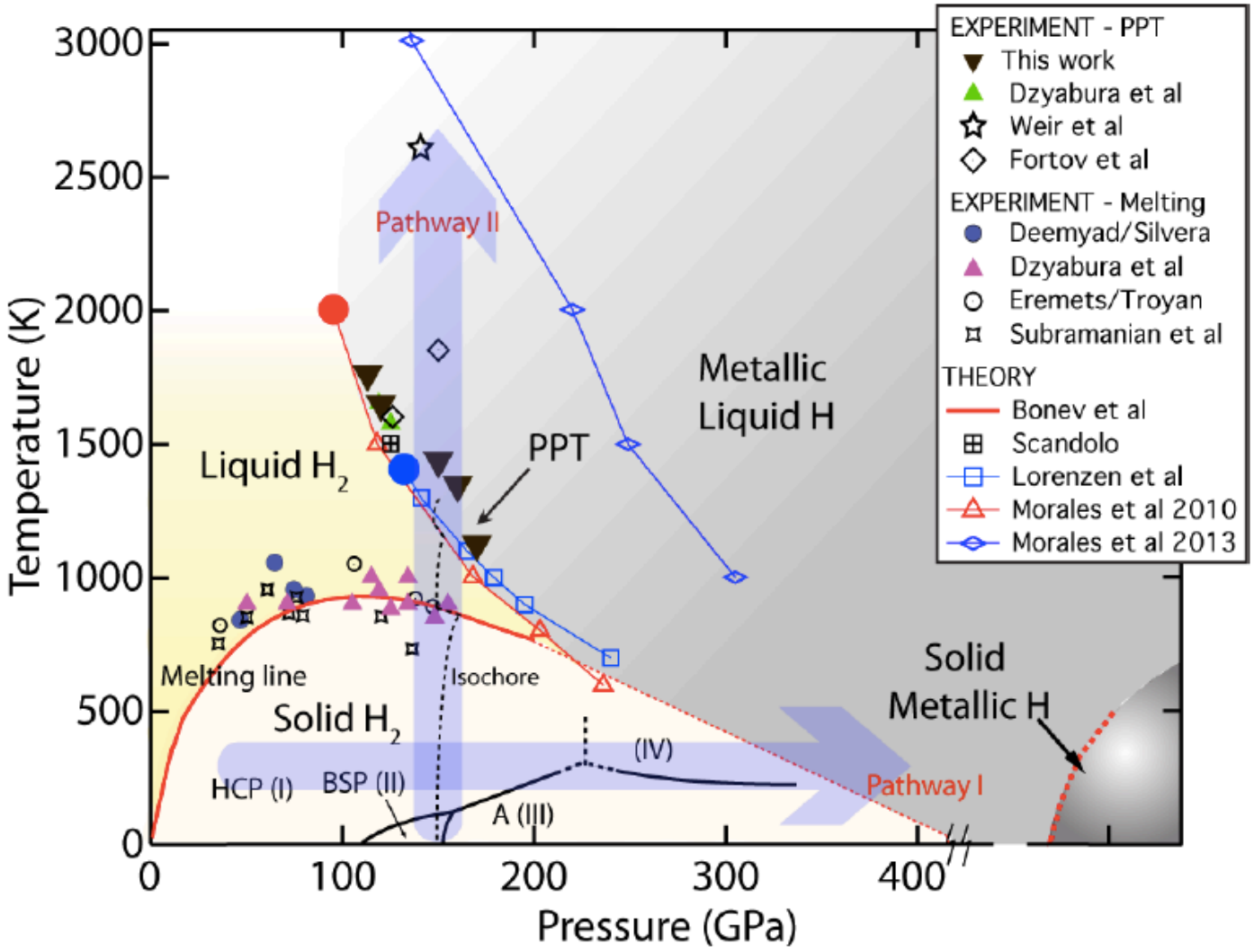
Morales,Pierleoni, Schwegler,DMC, PNAS 2010.

- 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



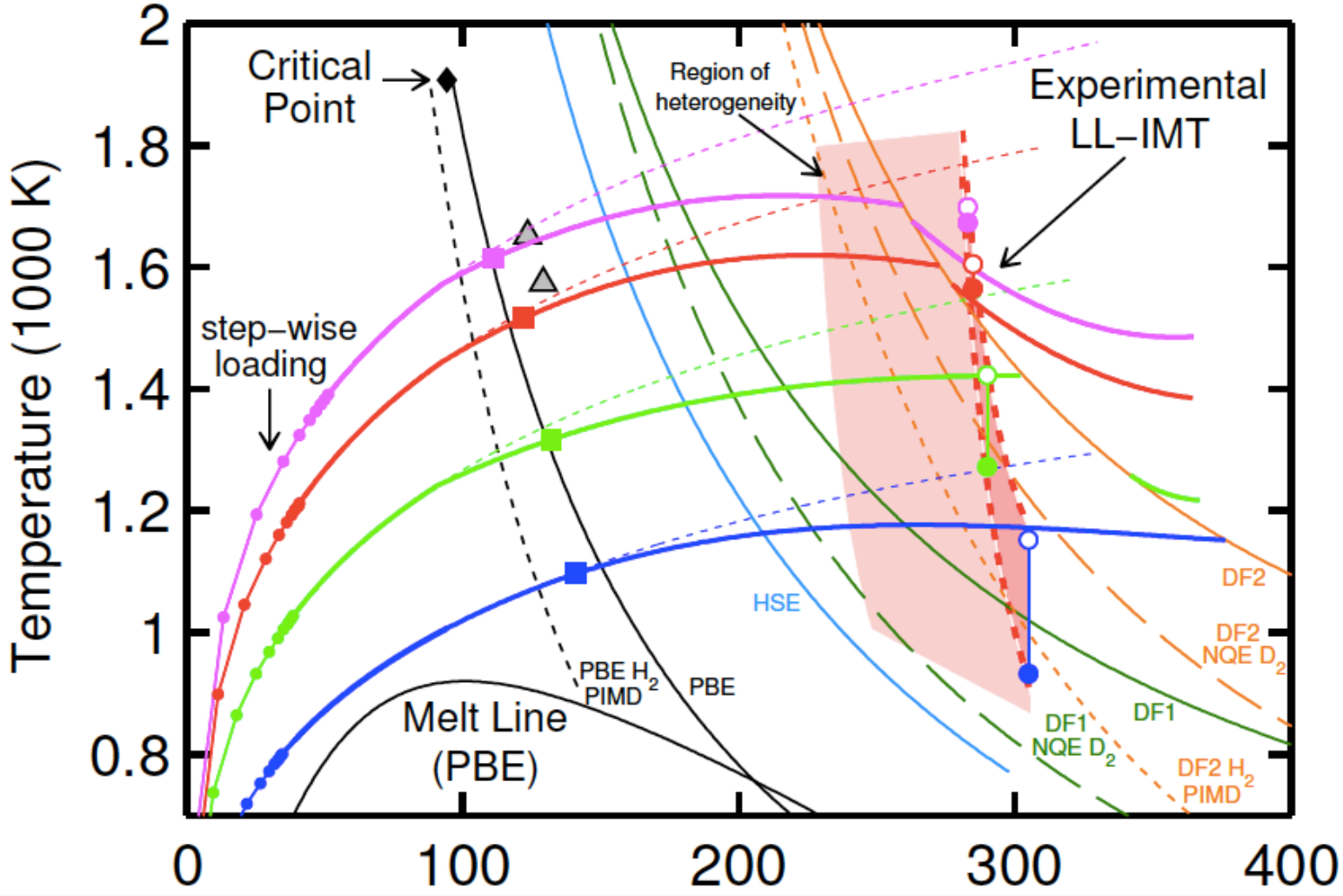
Three experimental confirmations!!

Dynamic heating within DAC (Harvard)



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

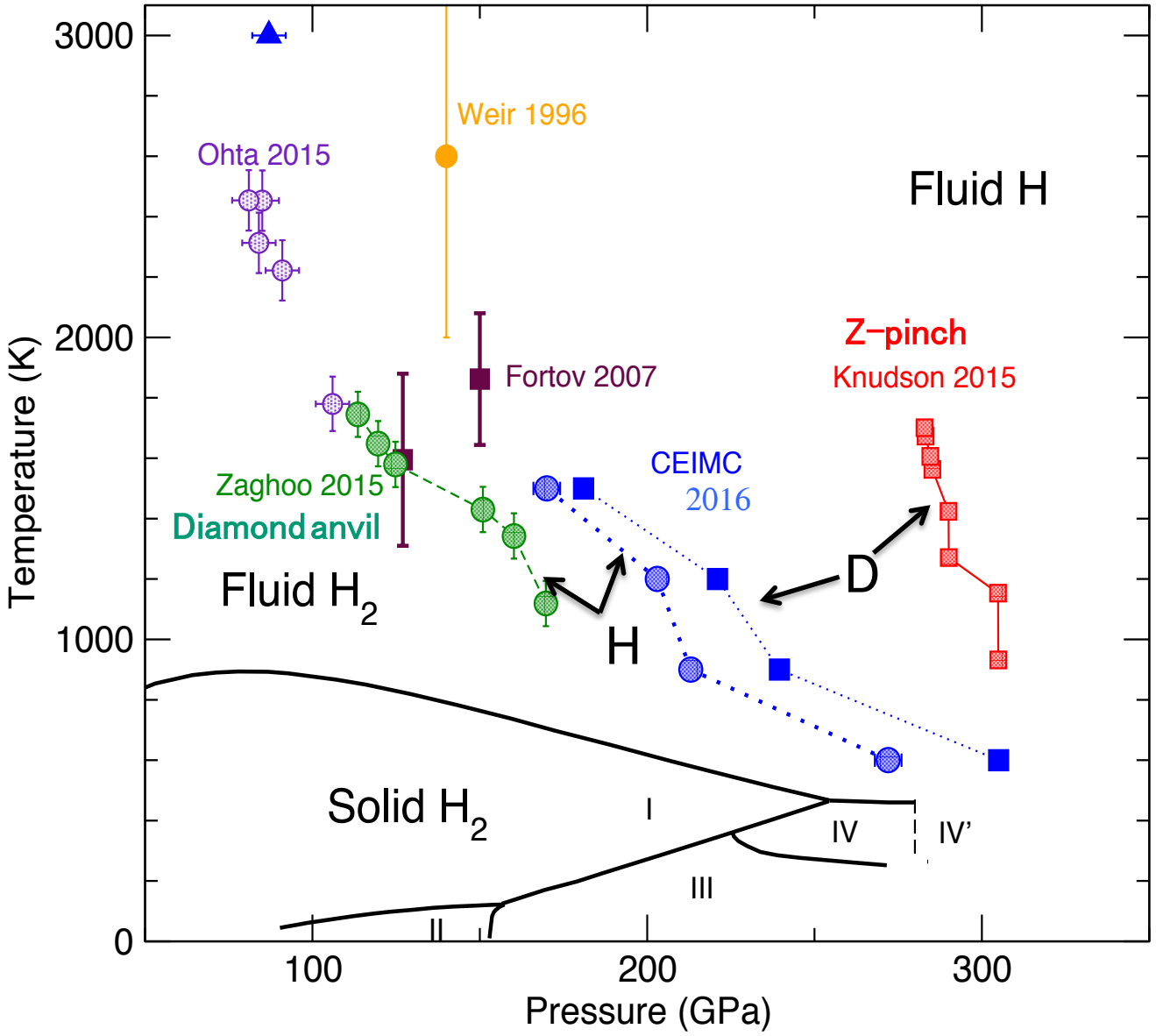
Ramp shock at Z-pinch (Sandia)



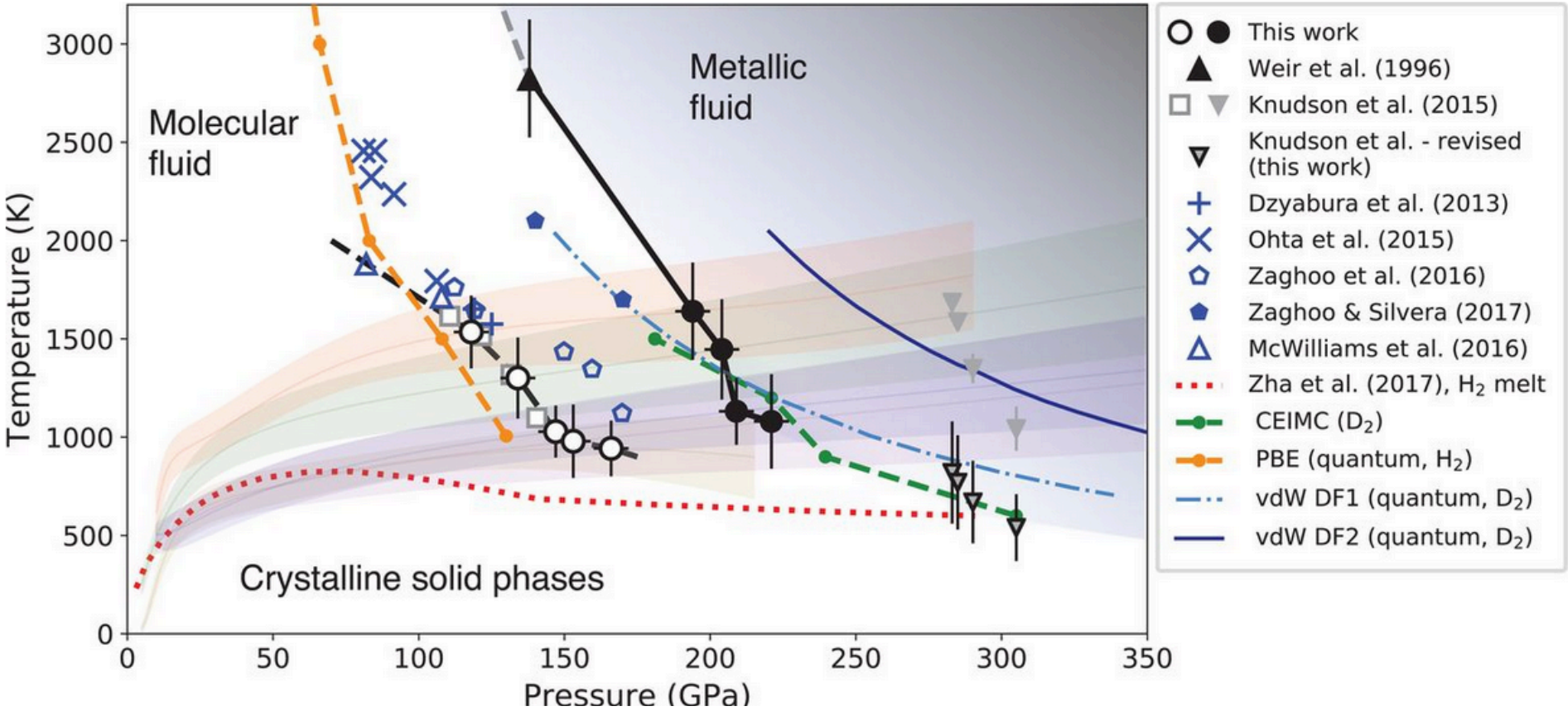
Knudson et al, Science (2015)

Experimental results differ by a factor 2!!

CEIMC is in the middle.



Resolution (NIF Livermore)

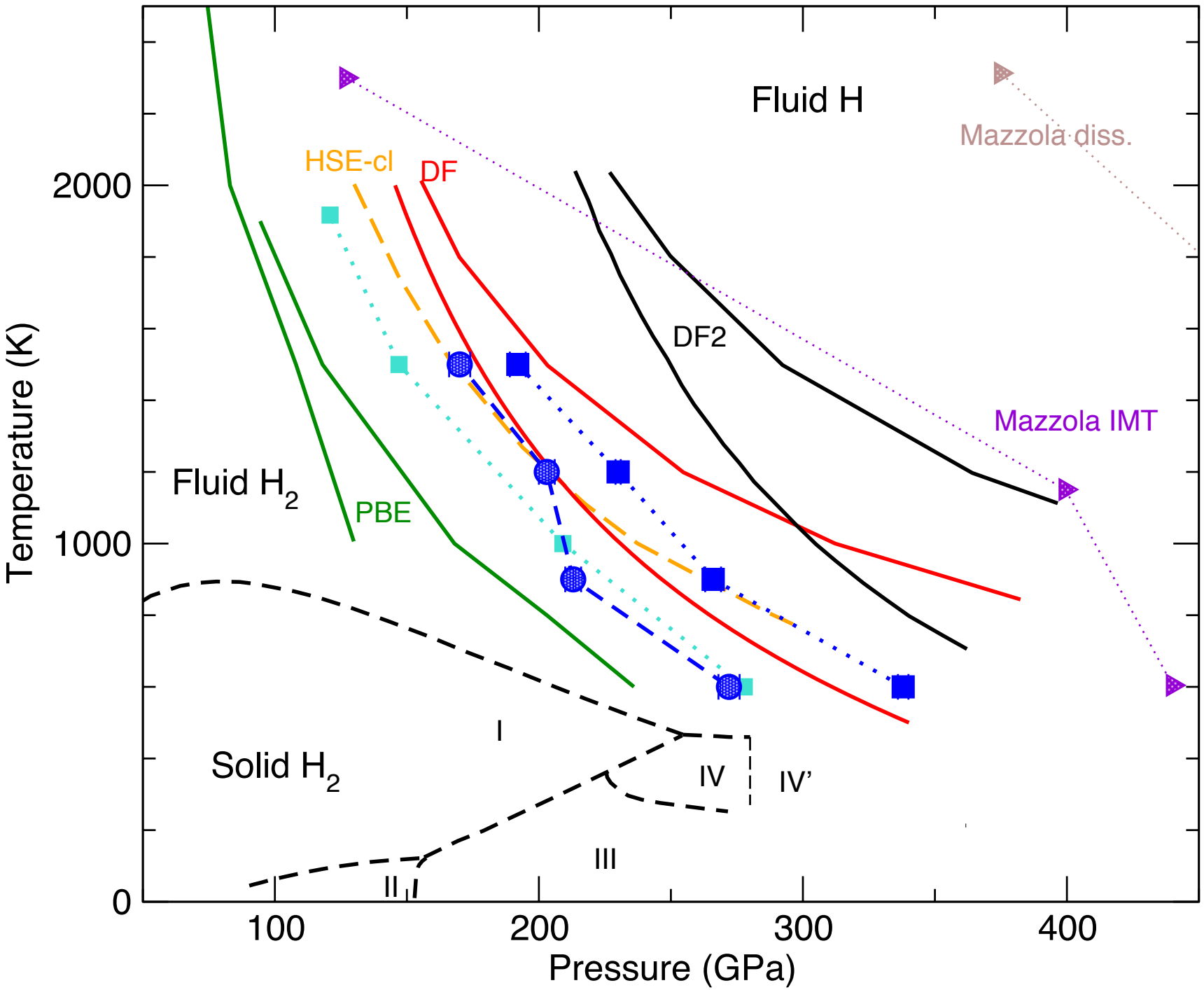


HIGH-PRESSURE PHYSICS

Insulator-metal transition in dense fluid deuterium

Science **361**, 677–682 (2018) 17 August 2018

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]

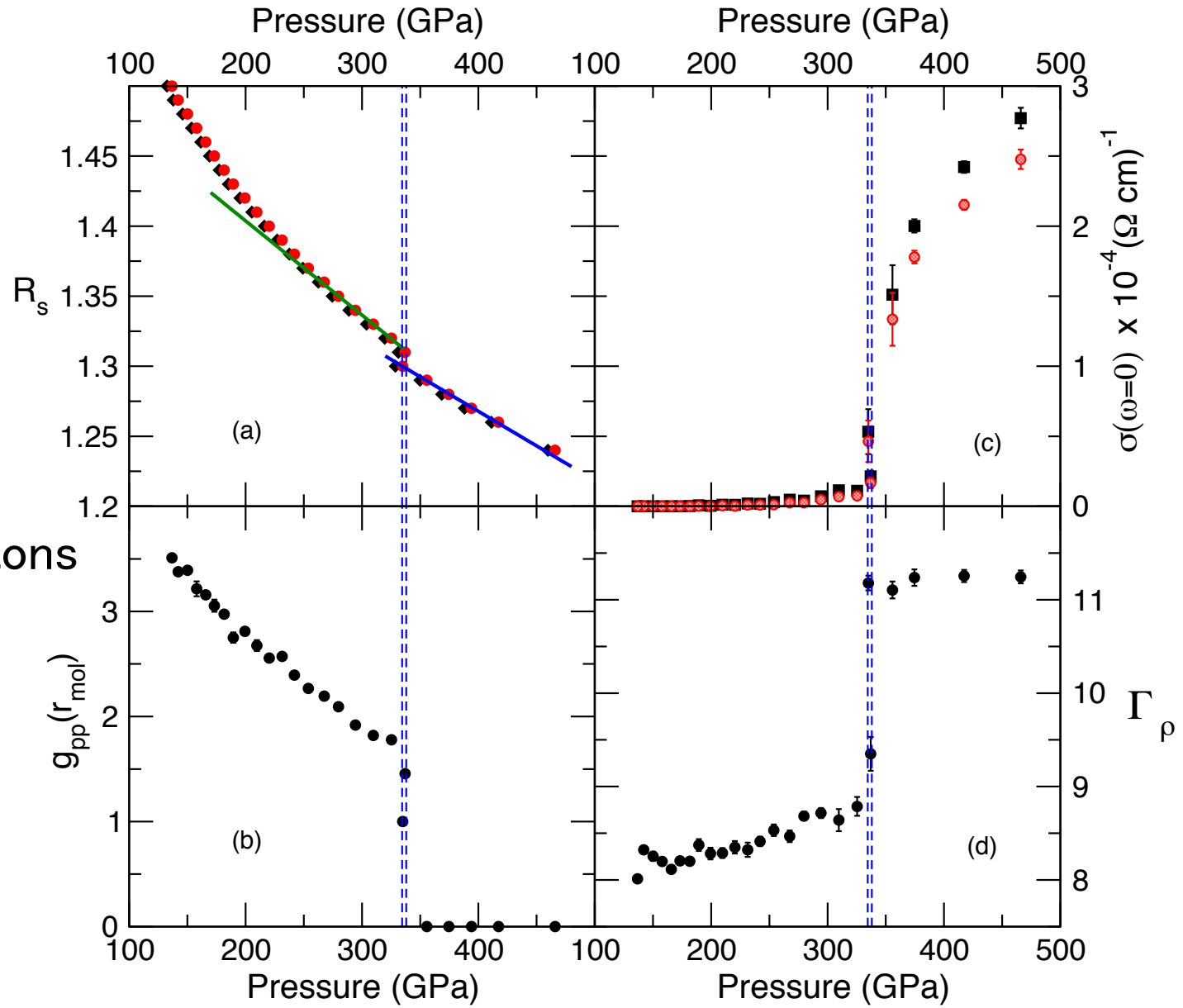

Fluid H
Mazzola diss.
HSE-cl
DF
DF2
Mazzola IMT
Fluid H2
PBE
Solid H2
I
II
III
IV
IV'
Temperature (K)
Pressure (GPa)
0
1000
2000
100
200
300
400

Signatures of the transition

atomic-molecular & metal-insulator

T=600K

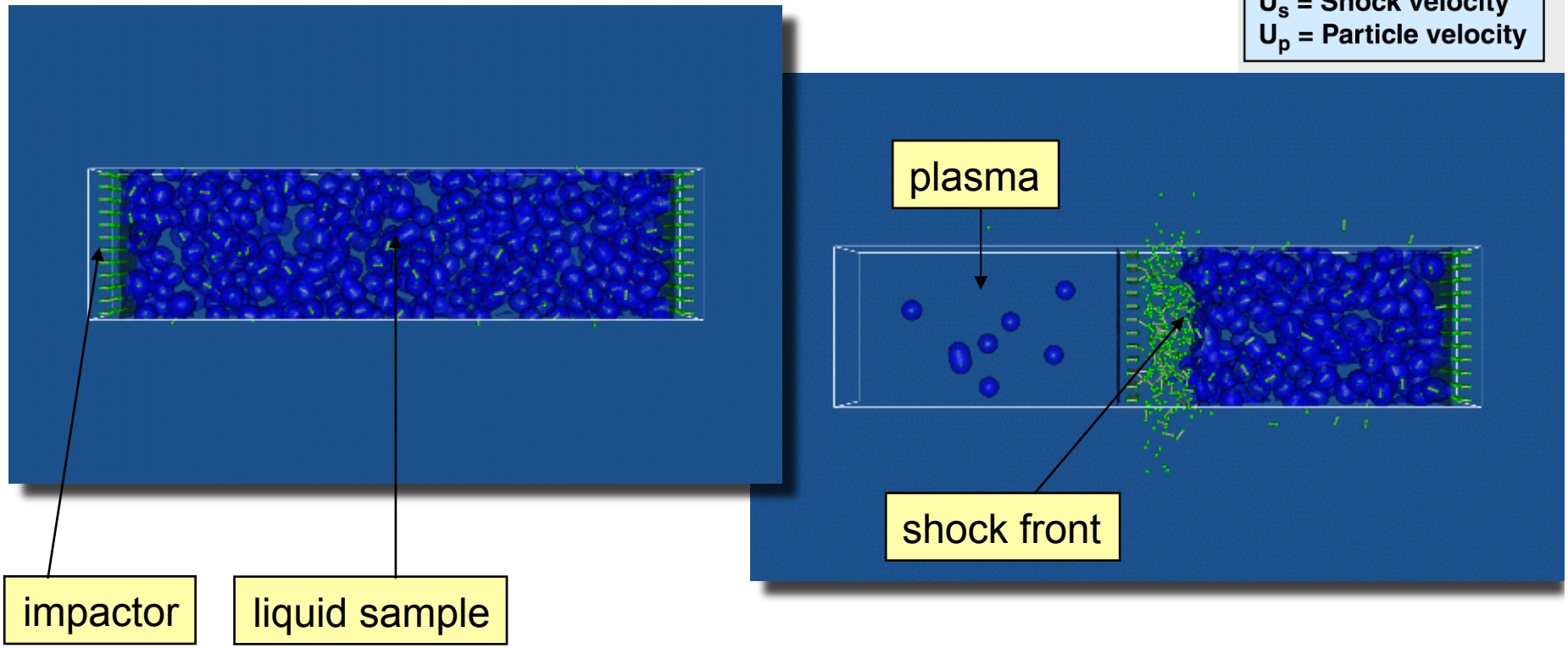
Classical protons



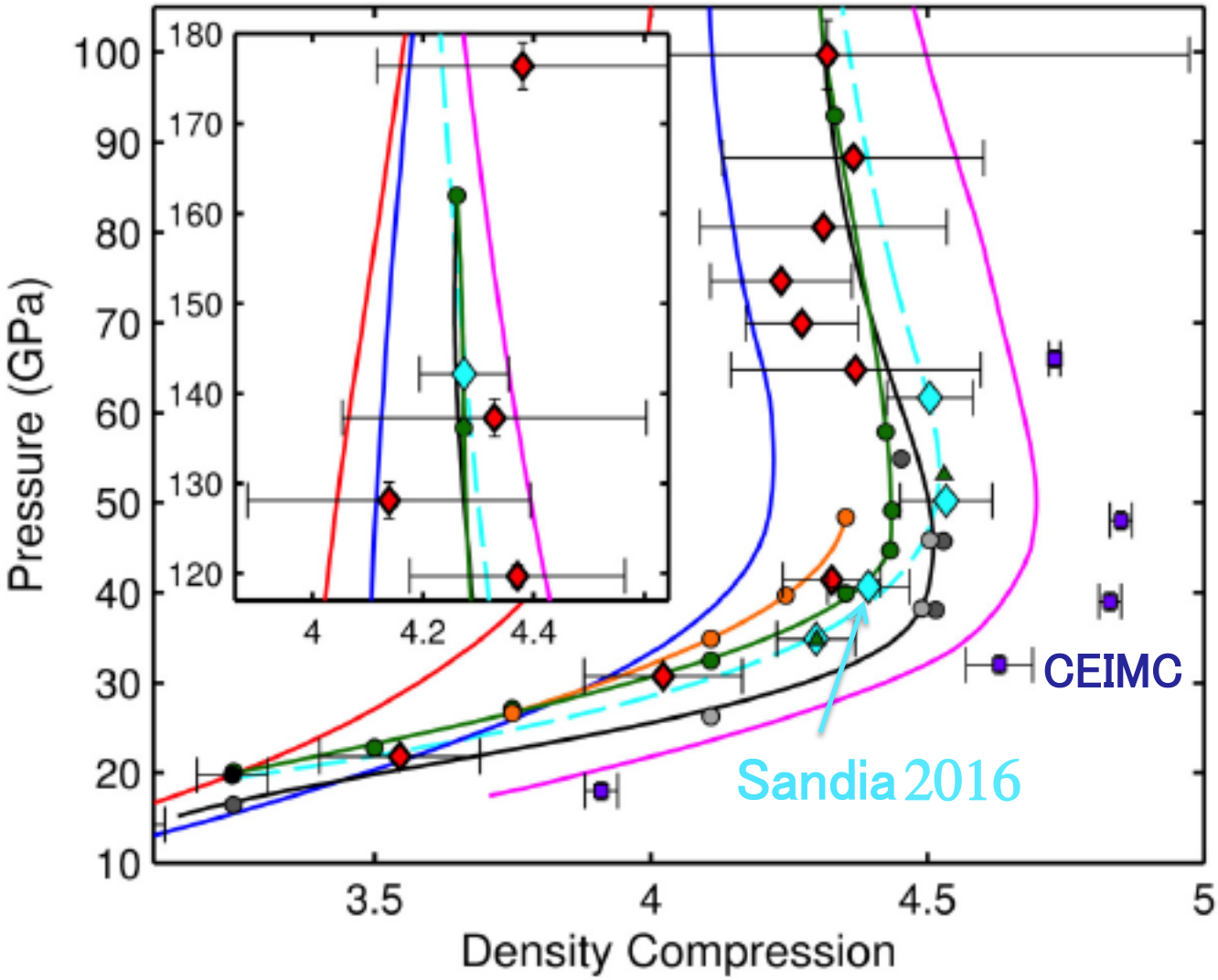
Shock wave experiments.

- 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

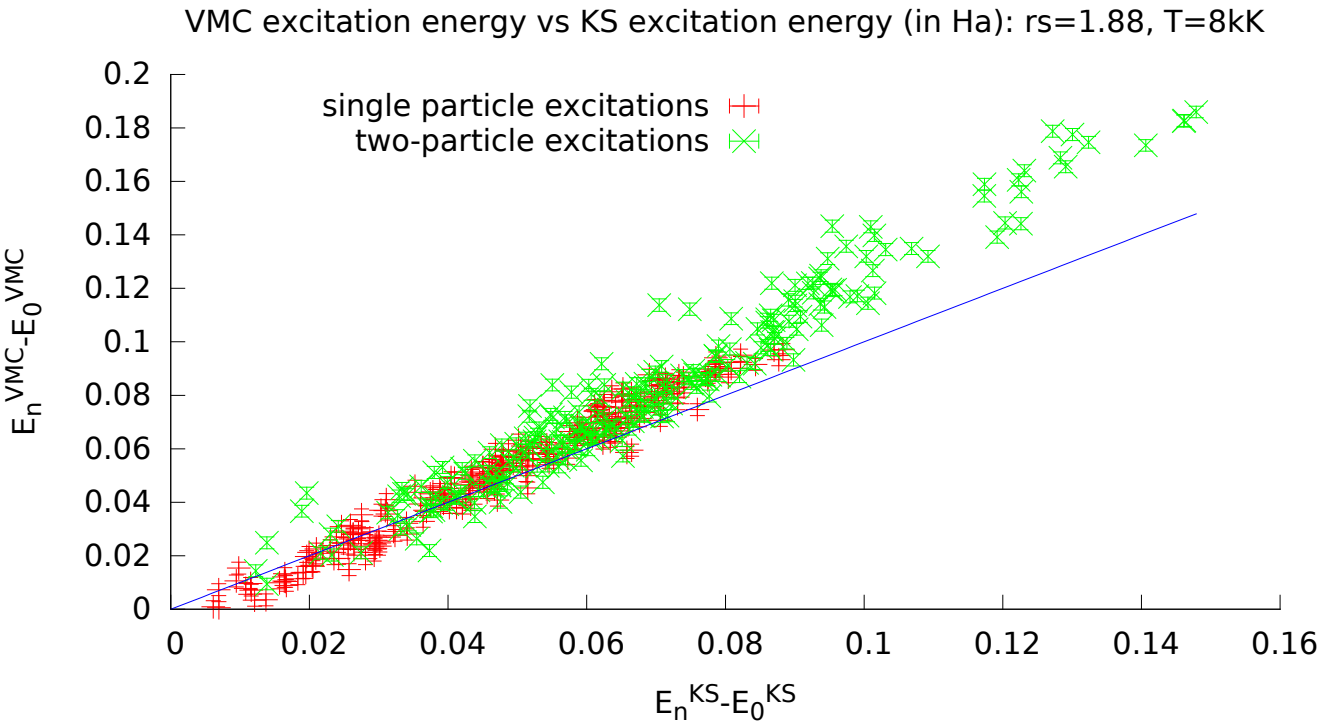
Conservation of Energy and Momentum
$E = E_o + \frac{1}{2}(P + P_o)(V_o - V)$
$P = \rho_o U_s U_p$ $\frac{U_p}{U_s} = 1 - \frac{\rho_o}{\rho}$
U_s = Shock velocity U_p = Particle velocity



Deuterium Hugoniot

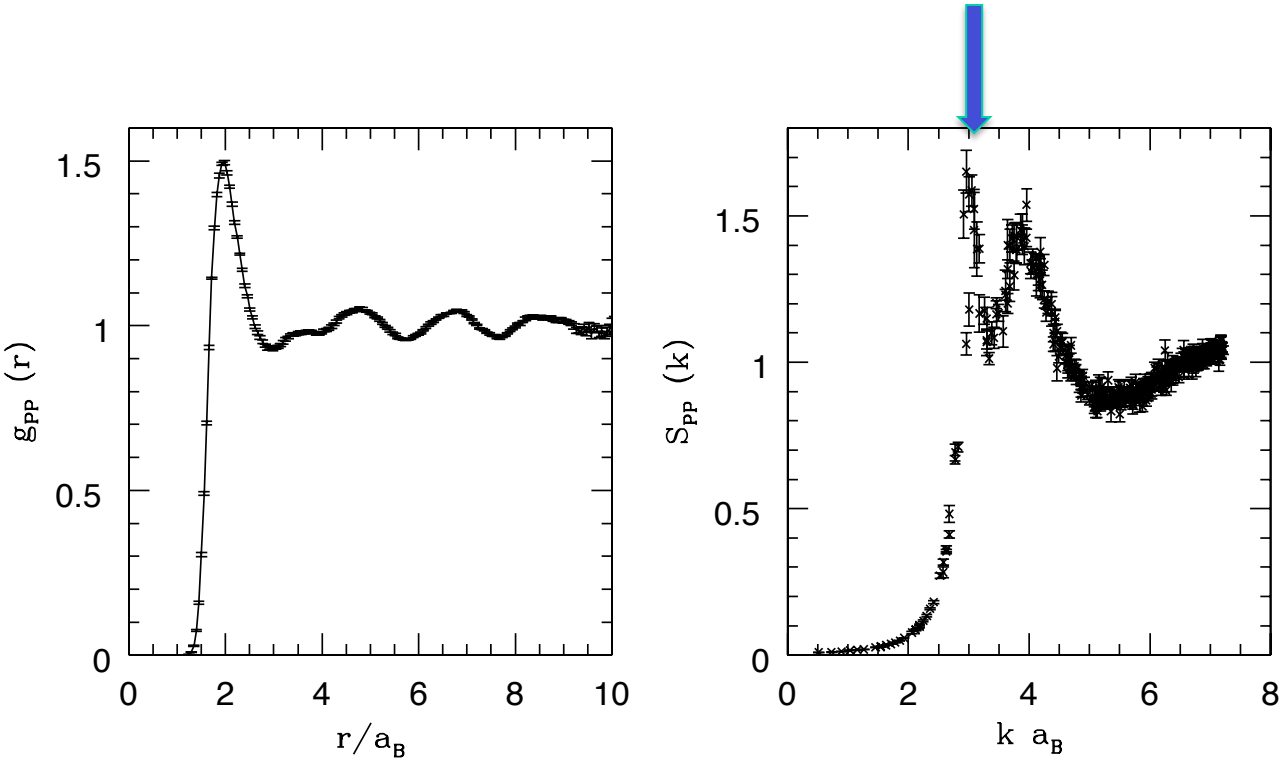


Thermal Excitations with QMC



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

Structure of the atomic liquid

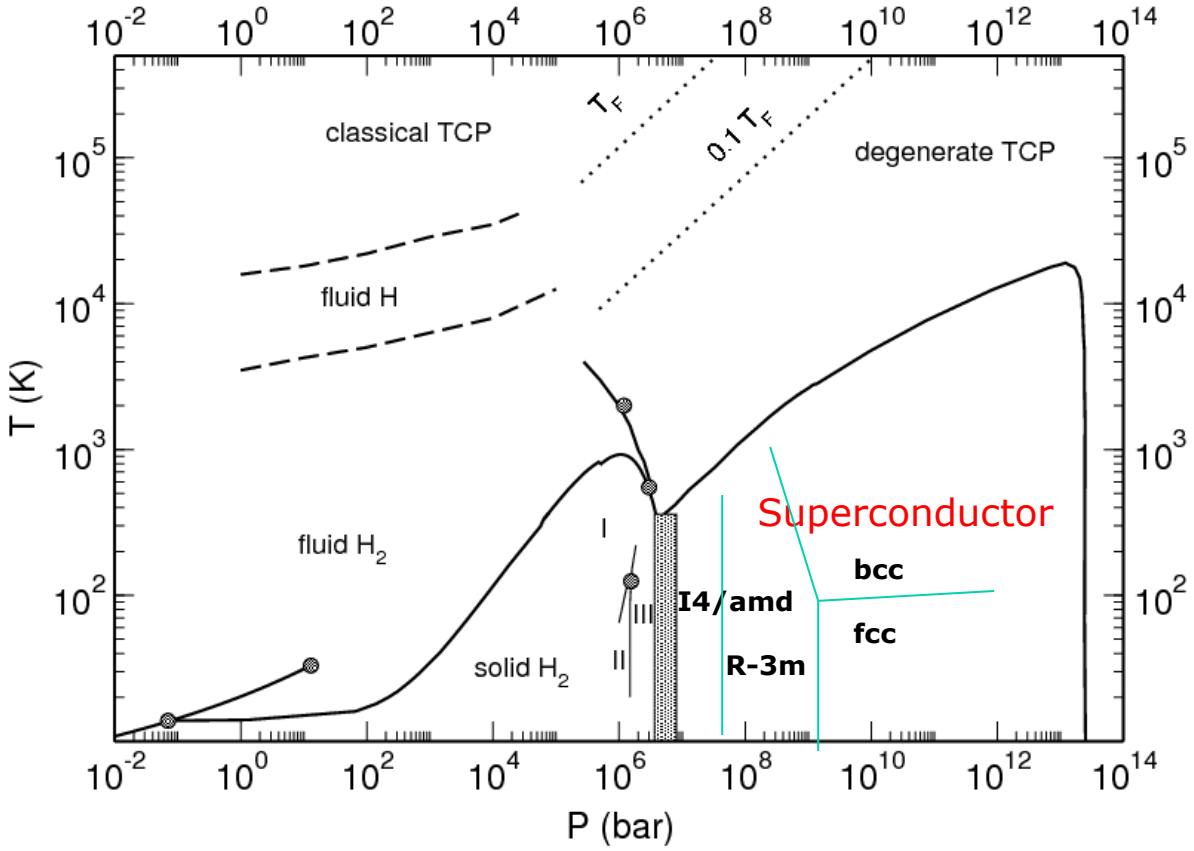


Unusual double peak structure factor for an atomic liquid

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

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

Hydrogen Phase Diagram



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

But at high pressure!

Conclusions

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

- DFT functionals give differing results especially near phase transitions.
- CEIMC allows one access to disordered $T>0$ systems.
- But CEIMC does not agree with experiments for the Hugoniot and LLPT (but experiments do not always agree)

There are many open questions with hydrogen:

- The sequence of molecular and atomic crystal structures
- Mechanism of metallization . Recent claim of its observation at 500GPa and 80K.
- High temperature superconductivity