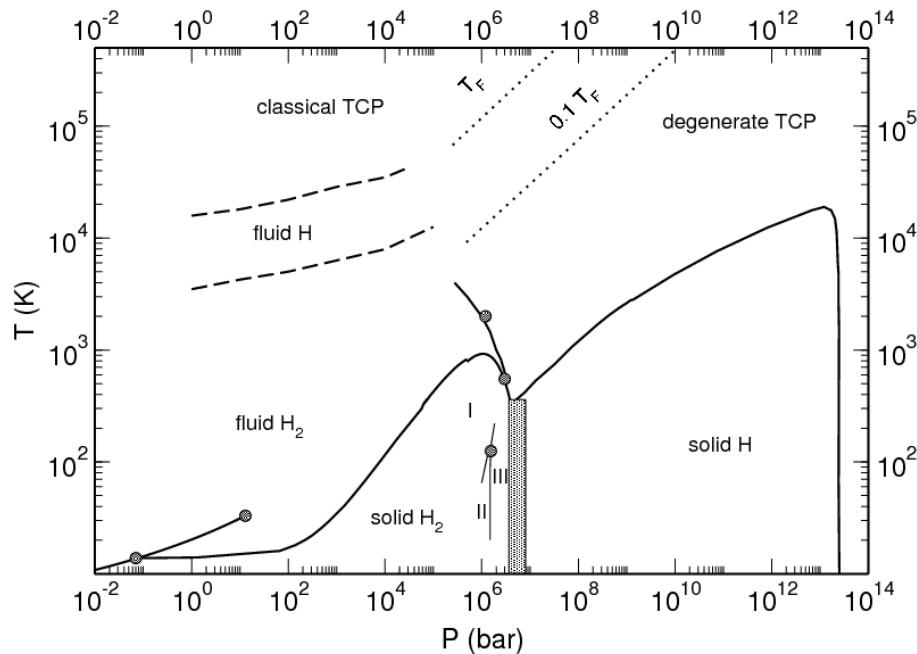


# Hydrogen under extreme conditions

D. Ceperley *University of Illinois Urbana-Champaign*



## WHO DID THE WORK?

*Carlo Pierleoni L'Aquila, Italy \*\**

*Miguel Morales Livermore*

*Markus Holzmann Grenoble*

*Giovanni Rillo Rome*

*Ray Clay UIUC/Livermore*

**DOE DE-NA0001789**

For more information:

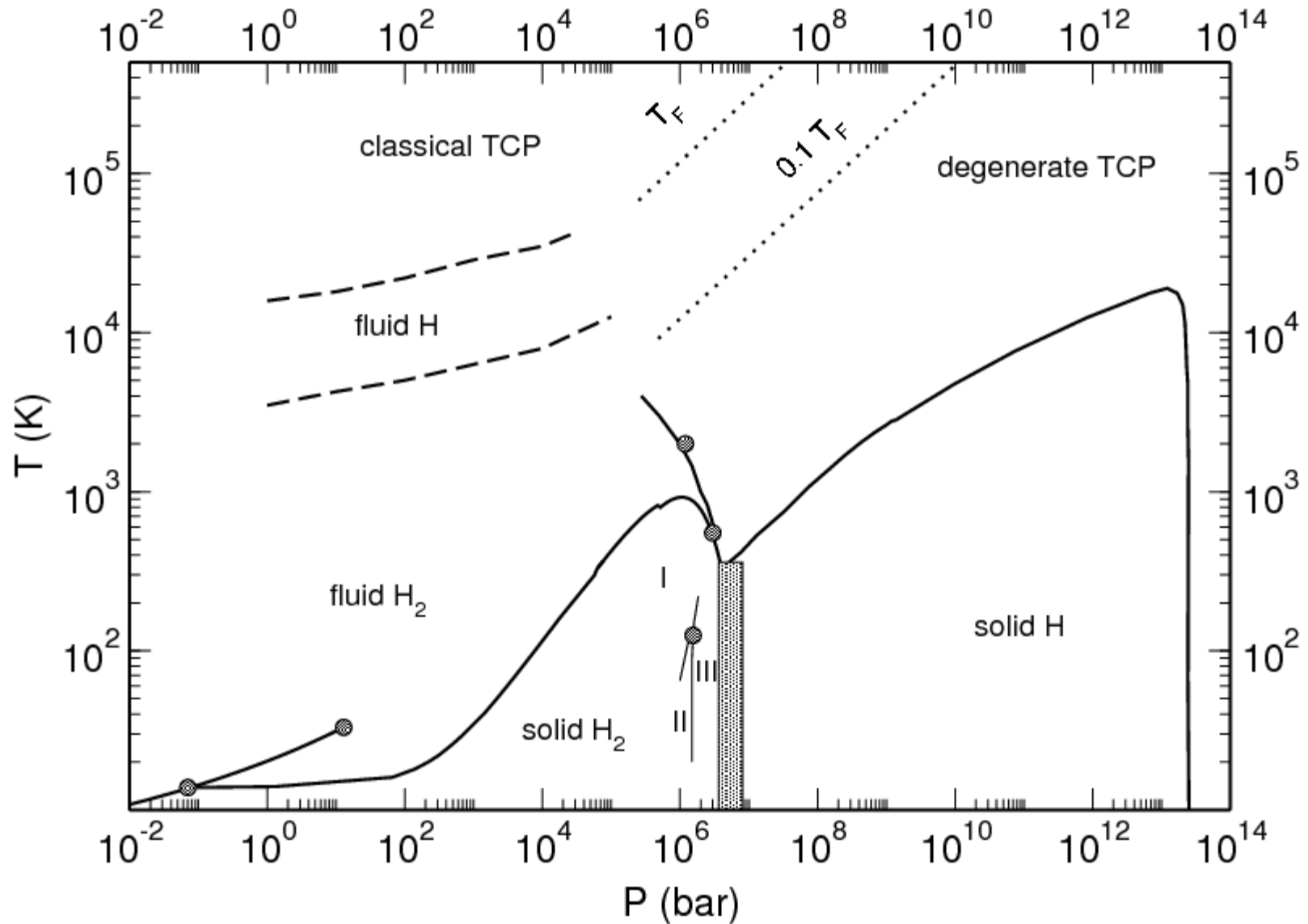
Rev. Mod. Phys. **84**, 1607 (2012)

C. Pierleoni, et al., Proc. Nat. Acad. Science (US), (2016).

# Why study dense Hydrogen?

- Applications:
  - Astrophysics: giant planets, exoplanets
  - Inertially confined fusion: NIF
- Fundamental physics:
  - Which 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

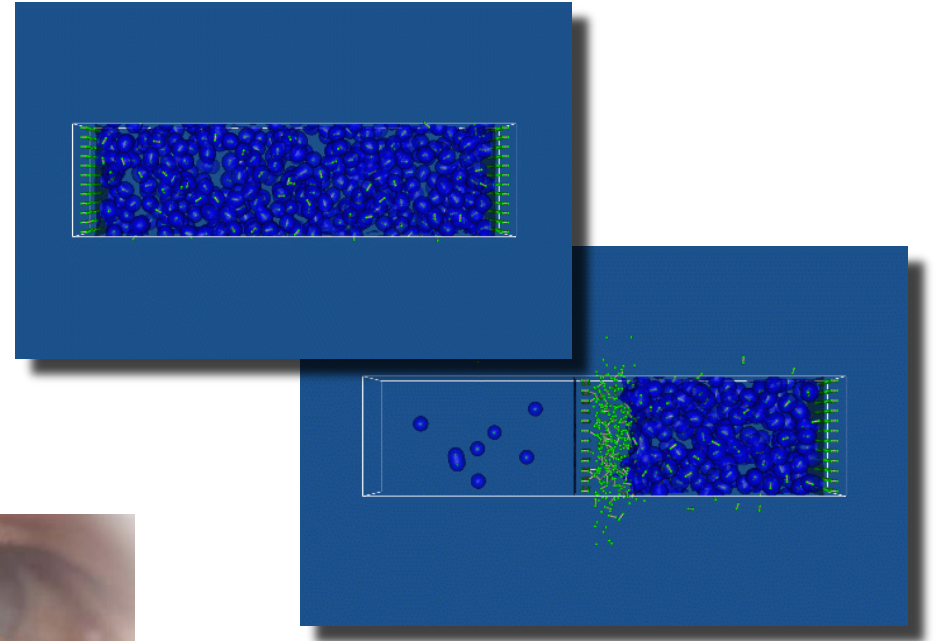
1. Is there a liquid-liquid transition in dense hydrogen?
2. How does the atomic/molecular or insulator/metal transition take place?
3. What are the crystal structures of solid H?
4. Could dense hydrogen be a quantum fluid? What is its melting temperature?
5. Are there superfluid/superconducting phases?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

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# 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

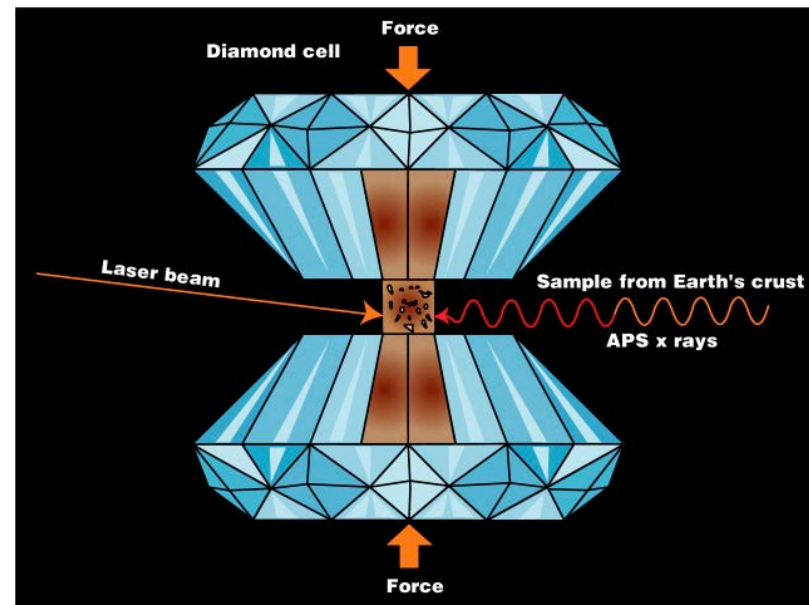
### Table-top experiment

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

### Static reproducible experiments

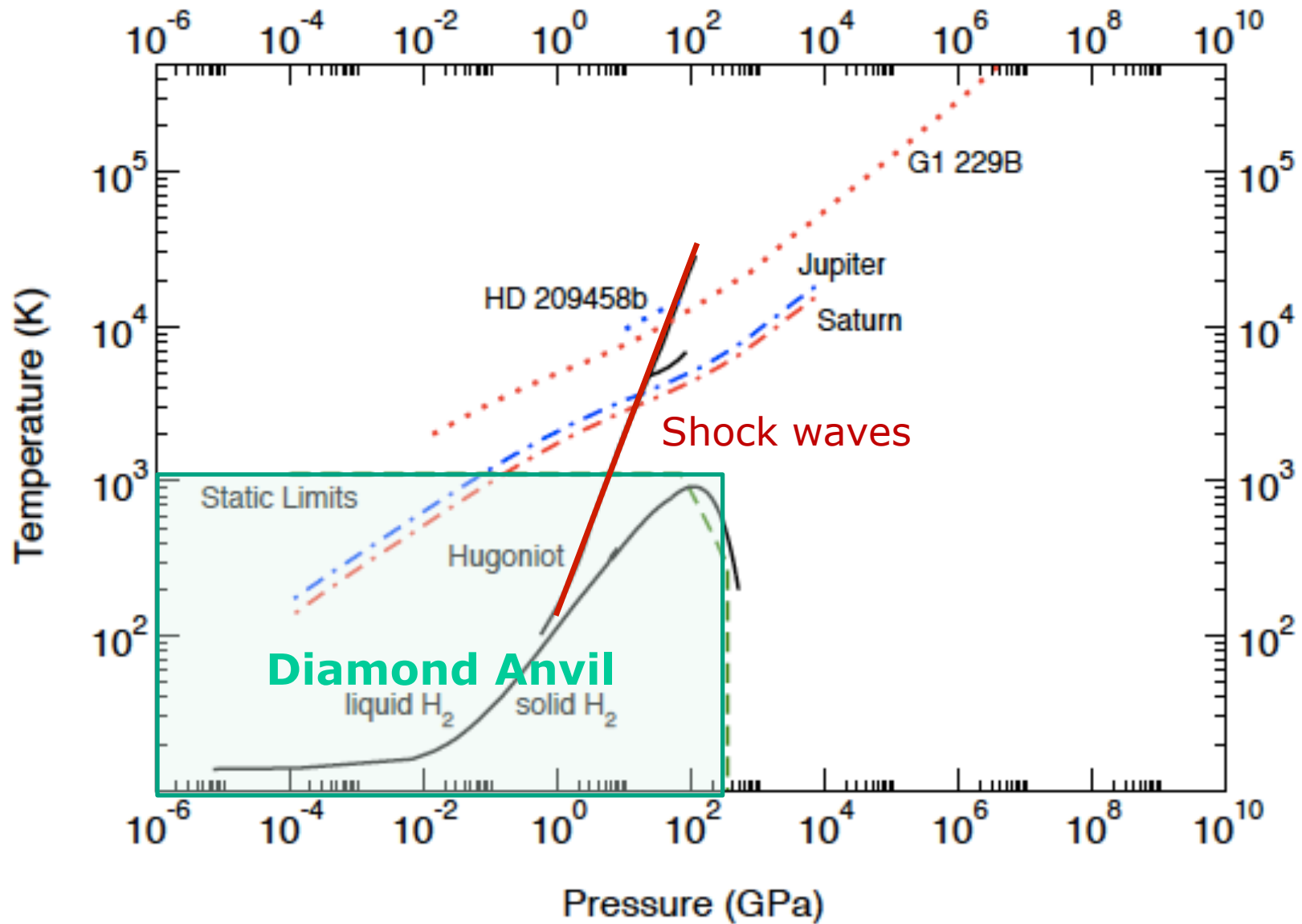
- Can get to 3MBar before diamond breaks
- $0 < T < 1000\text{K}$

Extend range of P,T by shocking compressed hydrogen



$$P = \textit{Force} / \textit{Area}$$

# Experiments on hydrogen

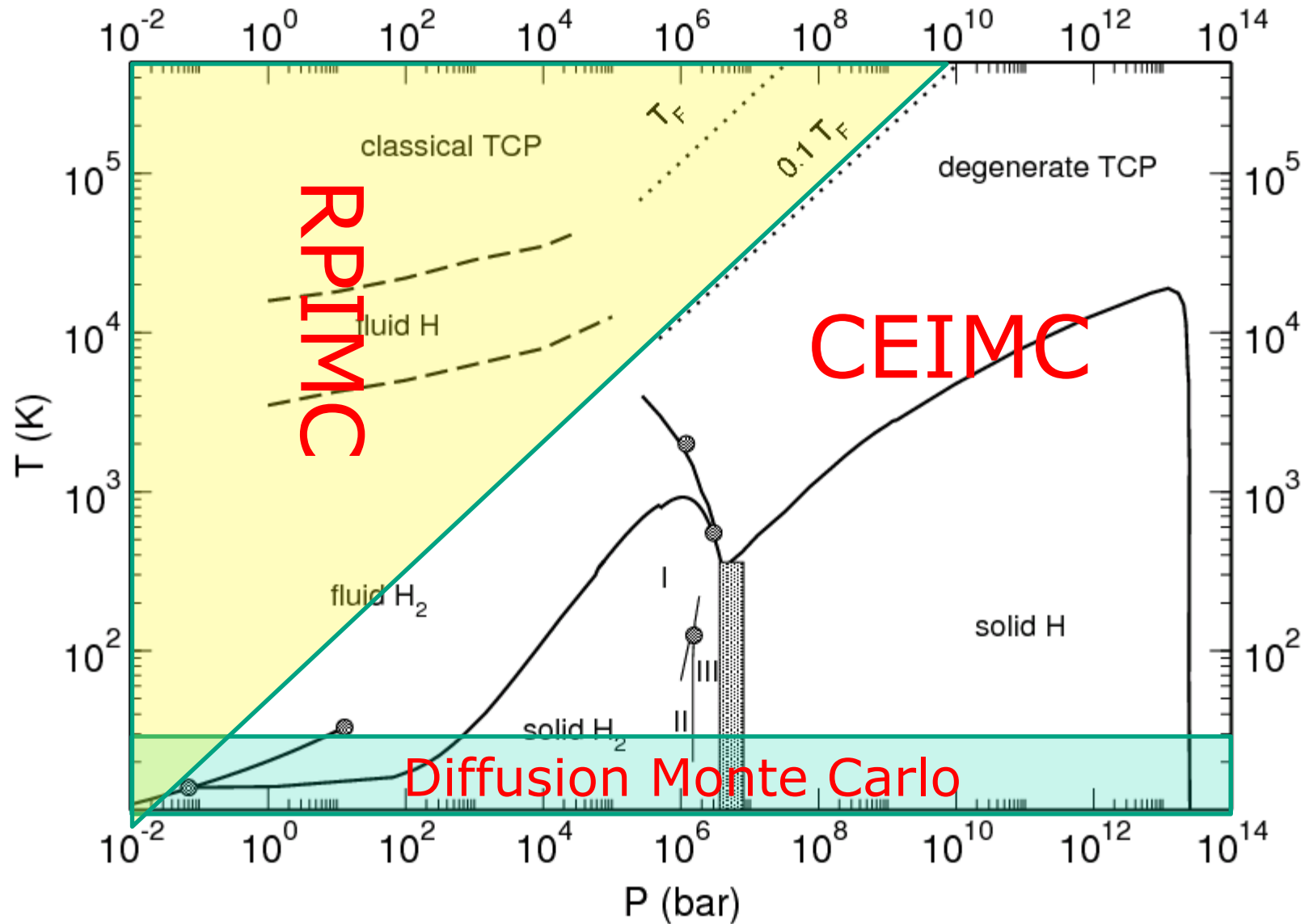




# Quantum Monte Carlo

- 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)
- Several different stochastic (QMC) methods used here:
  - **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



# ab-initio with QMC

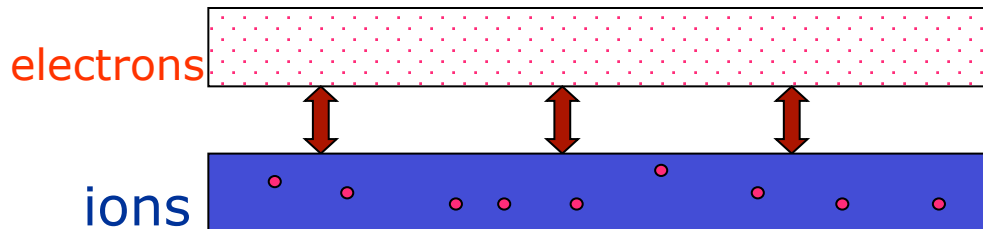
## Coupled Electron-Ion MC (CEIMC)

### 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



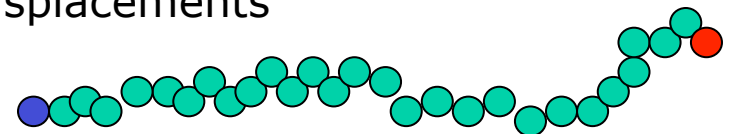
### Reptation

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

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

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

- 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



# 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 → better treatment of fermion statistics
- Coupled electron-ion Monte Carlo allows lower temperatures  $T \sim 300\text{K}$
- Optimization of trial function parameters
- Explicit calculation of entropy, free energy
- Computers/parallelization: Blue Waters

*Approximations can now be controlled*  
*Most older results were not converged*

# Twist averaged boundary conditions

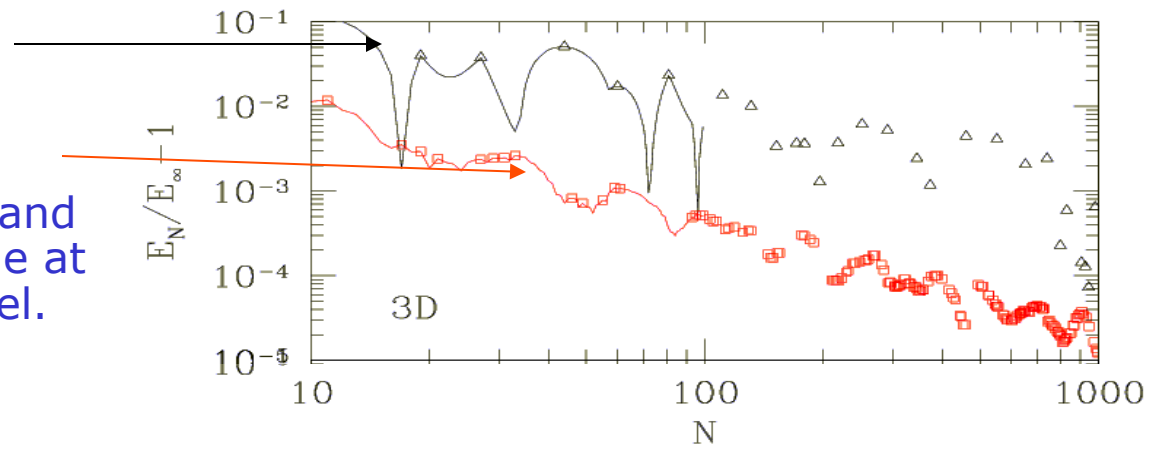
- In periodic boundary conditions, the wavefunction is periodic. Large finite size effects for metals because of fermi surface.
- In twist averaged BC, we use an arbitrary phase  $\theta$  as  $r \rightarrow r+L$
- Integrate over all phases, i.e. Brillouin zone integration.
- Momentum distribution changes from a lattice of k-vectors to a fermi sea.
- Eliminates single-particle finite-size effects.

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

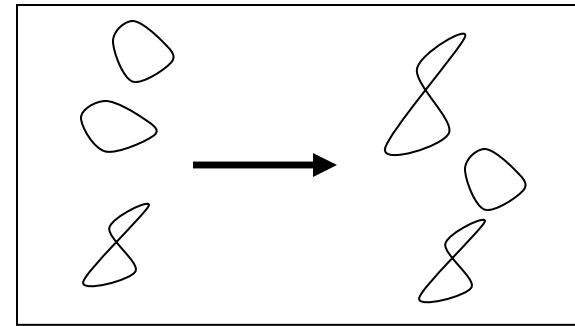
$$\bar{A} = \frac{1}{(2\pi)^3} \int_{-\pi}^{\pi} d^3\theta \langle \Psi_{\theta} A \Psi_{\theta} \rangle$$

Error with PBC  
Error with TABC

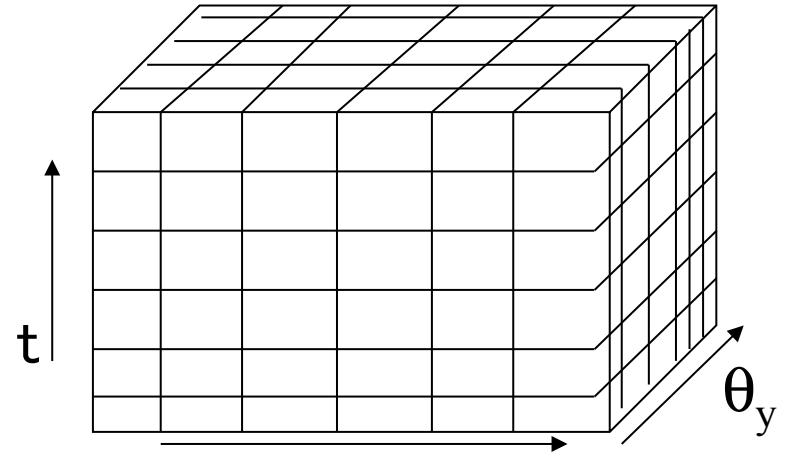
Error is zero in the grand canonical ensemble at the mean field level.



- Make a move of the protonic paths
- Set up a 4D lattice of twisted boundary conditions ( $\theta_x$   $\theta_y$   $\theta_z$ ) and imaginary times ( $t$ )
- Send them all out to  $M$  separate processes
- Do QMC to get energy differences and variances
- Combine to get global difference and variance.
- Path Integrals and twist averaging are almost free.



$$R_\tau \rightarrow R'_\tau$$



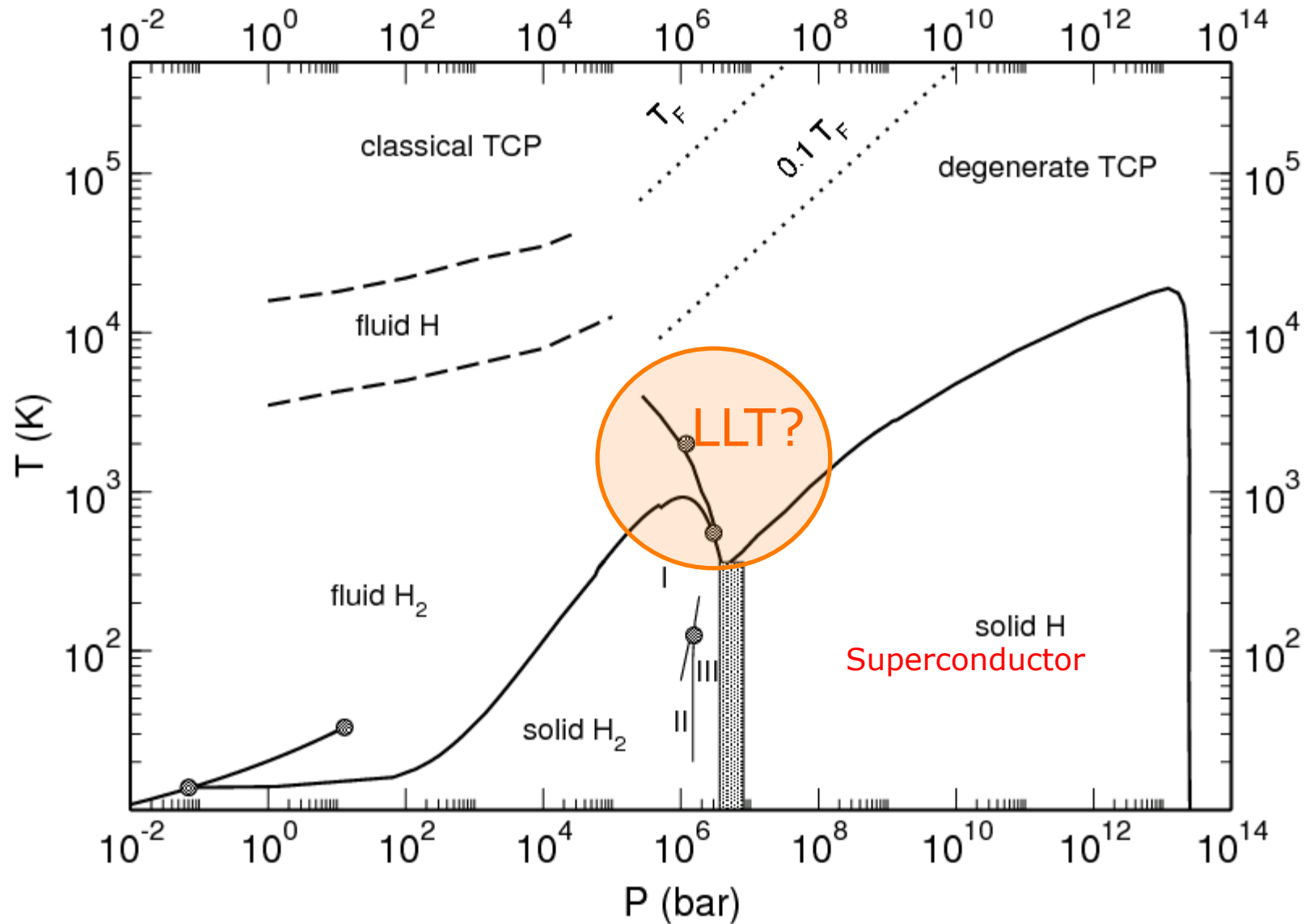
$$\Delta E_{BO} = \frac{1}{M} \sum_{\theta, \tau} E_{\theta, \tau}$$

$$\sigma^2 = \frac{1}{M^2} \sum_{\theta, \tau} \sigma_{\theta, \tau}^2$$

# Code Development

- We used 3 codes during this calculation
  - BOPIMC: Fortran/MPI code used to develop method
  - Quantum Espresso. DFT code to generate orbitals as protons are moving around
  - QMCPACK. C++ code developed by J. Kim that uses MPI, Open-MP, CUDA, will be used next year
- We have exploited several levels of parallelism
  - twist averaging
  - Path integrals
  - Multiple state points
  - Anticipating future moves

# 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.

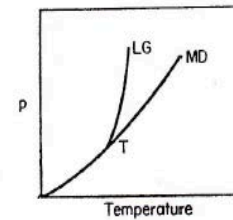


FIG. 1.

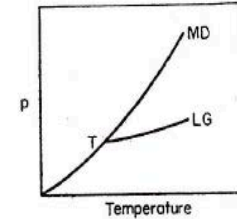


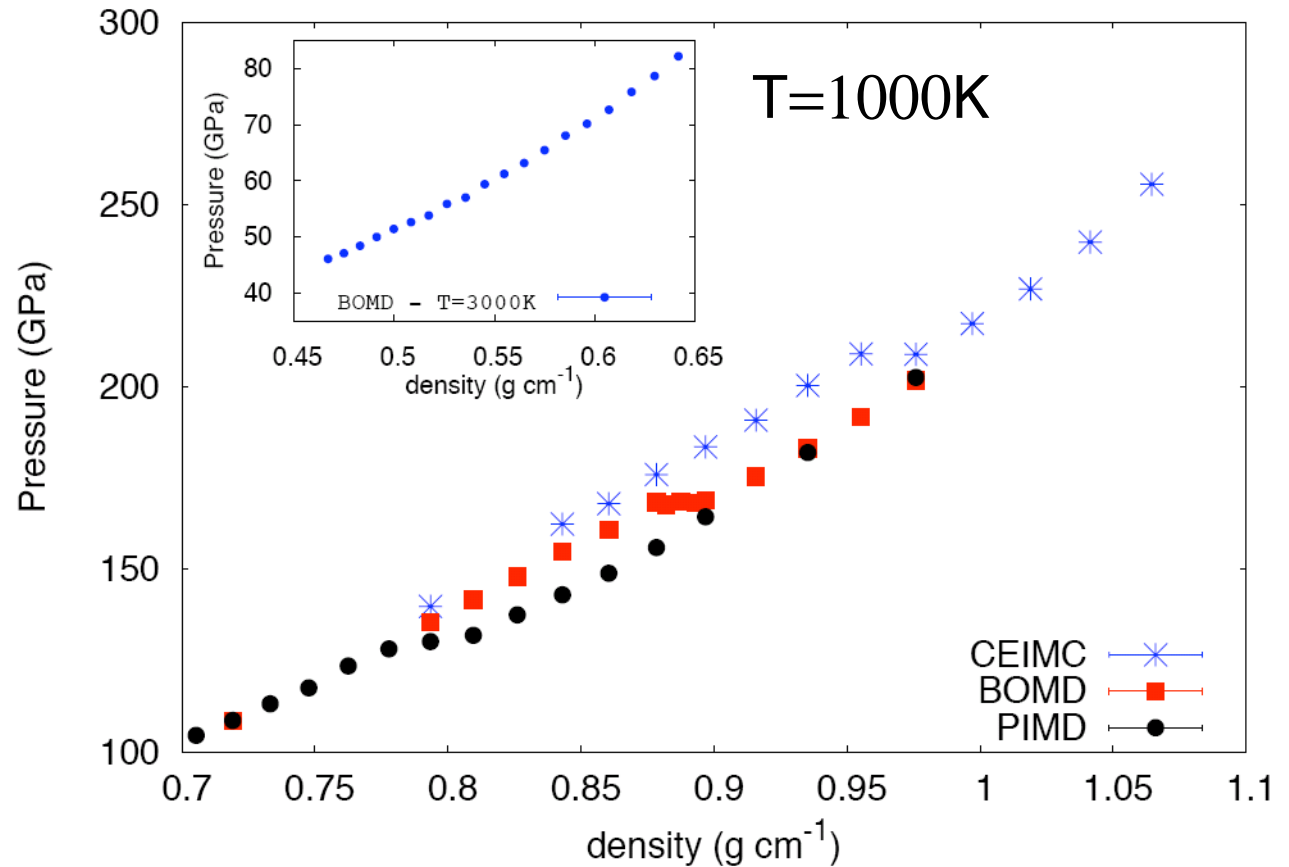
FIG. 2.

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.

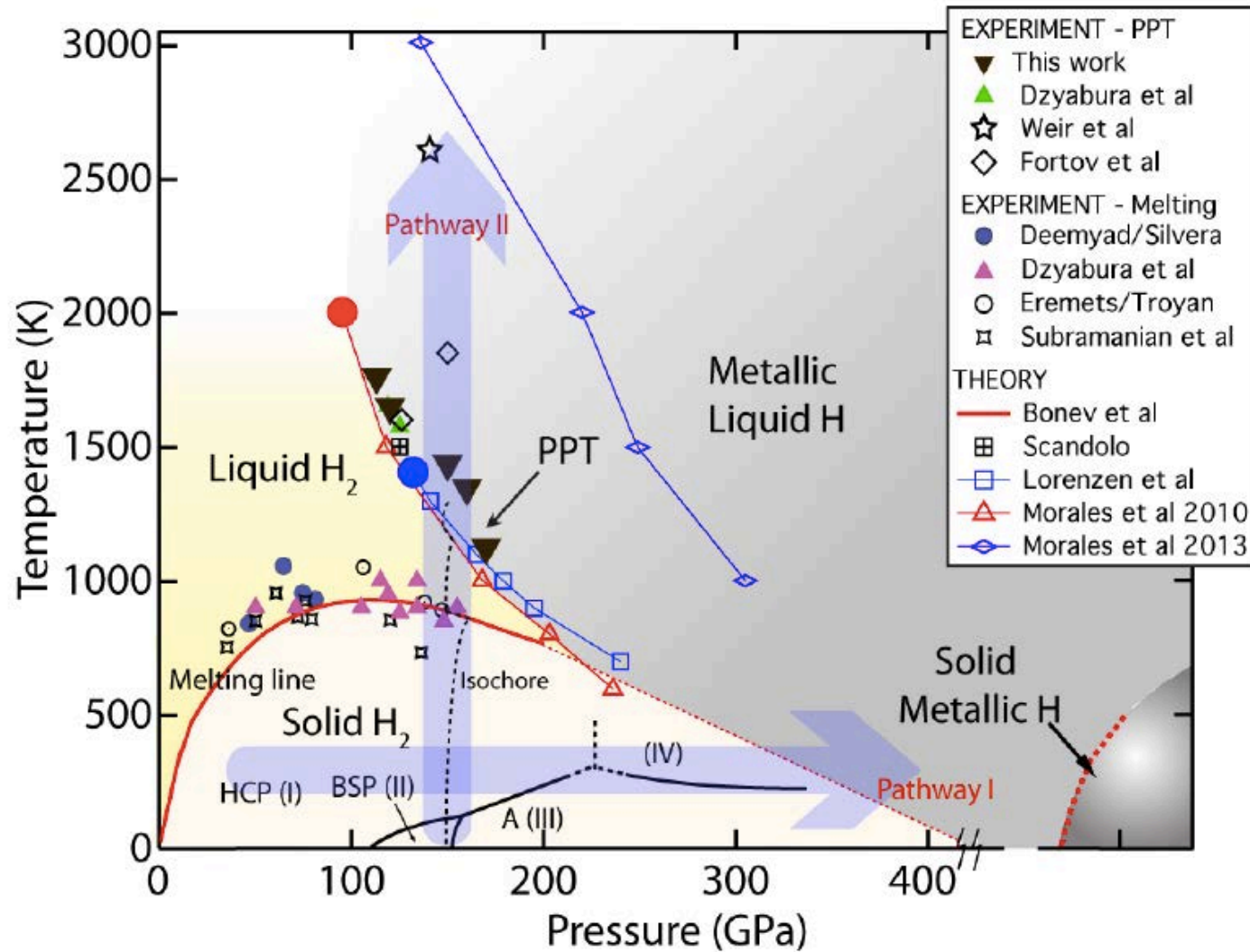
# Liquid-Liquid Transition

*Morales, Pierleoni, Schwegler, DMC, PNAS 2010.*

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

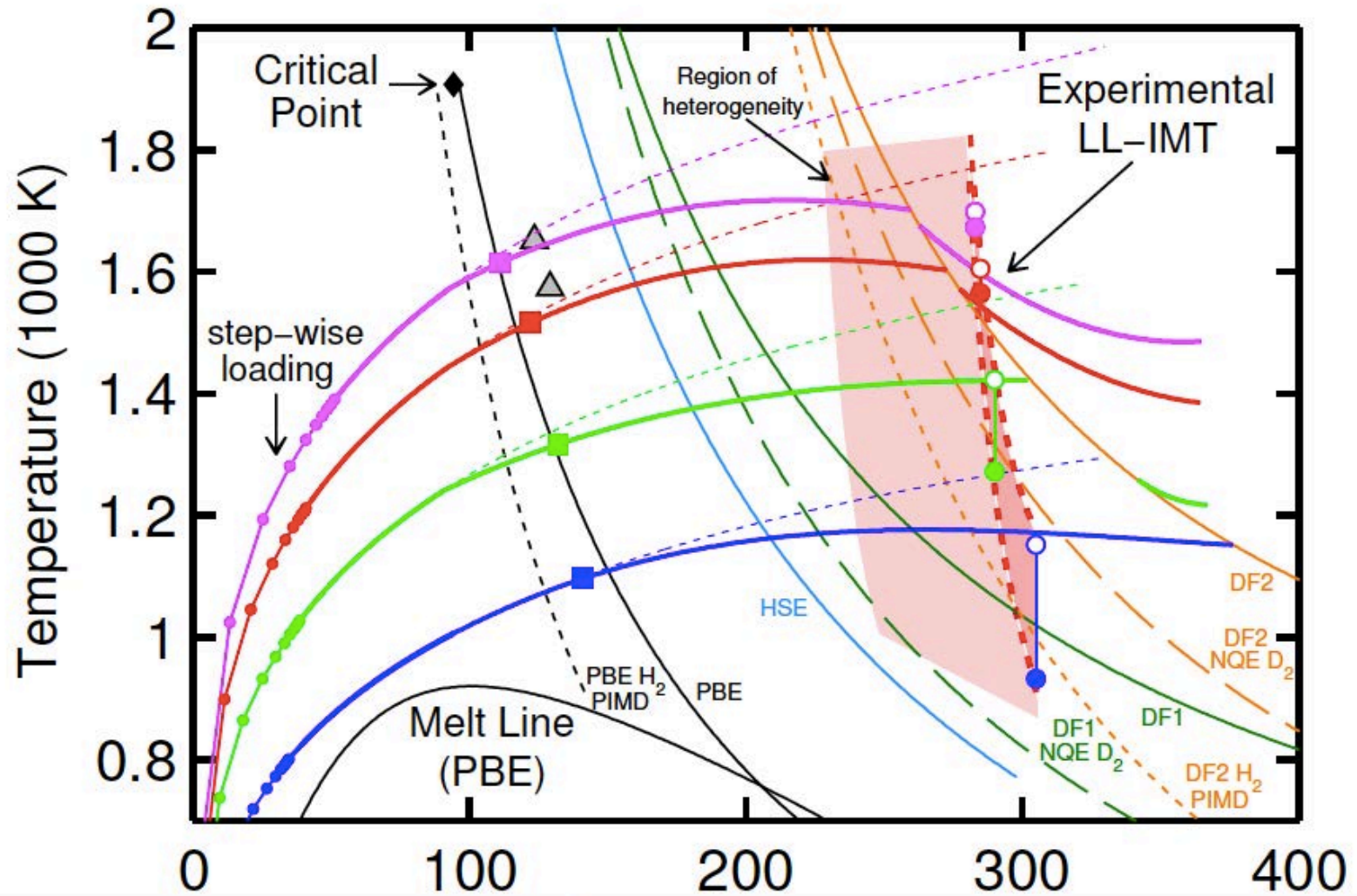


# Dynamic heating within DAC



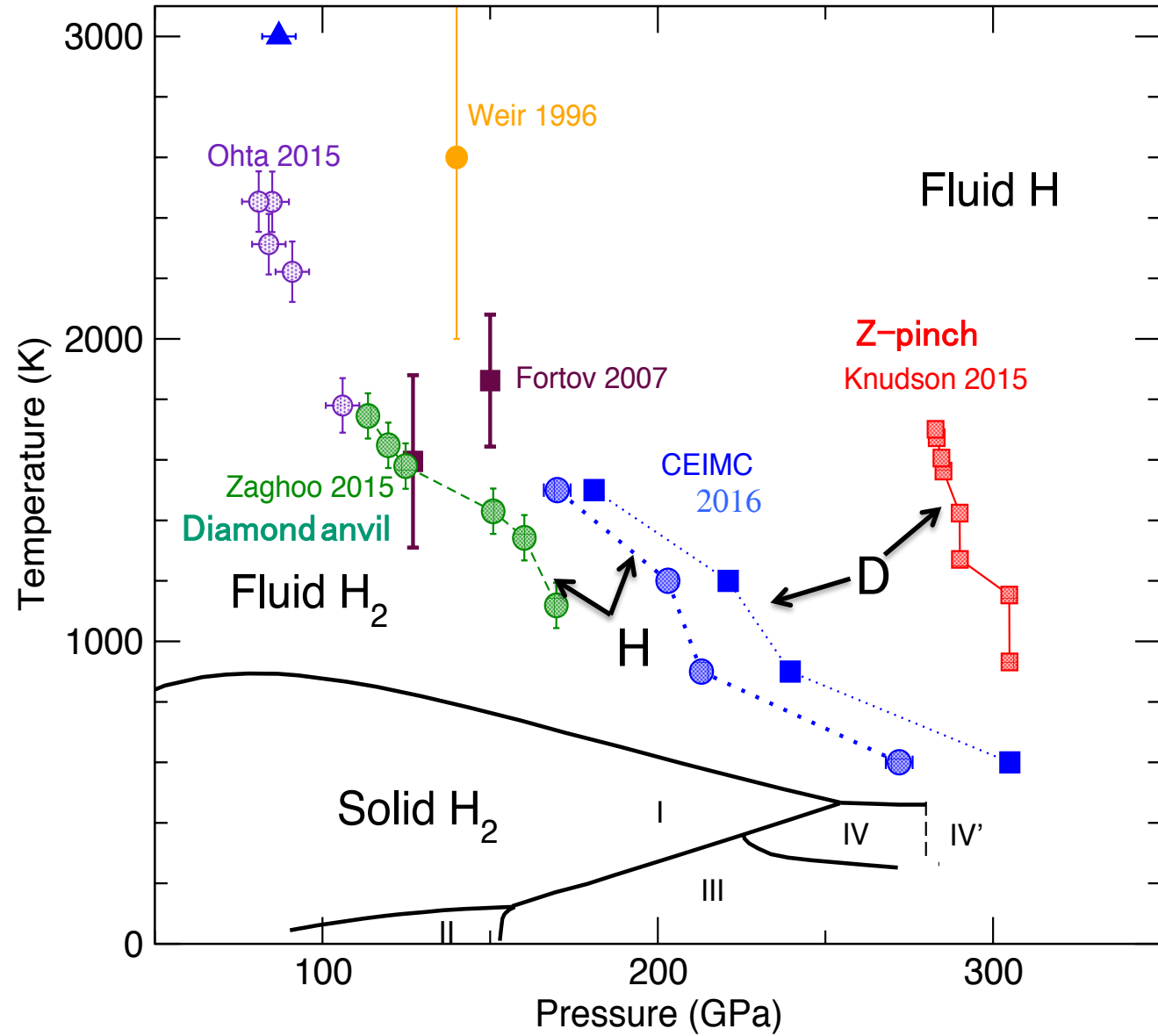
*M. Zaghou, A. Salamat, and I. Silvera (2015)*

# Ramp shock at Z-pinch

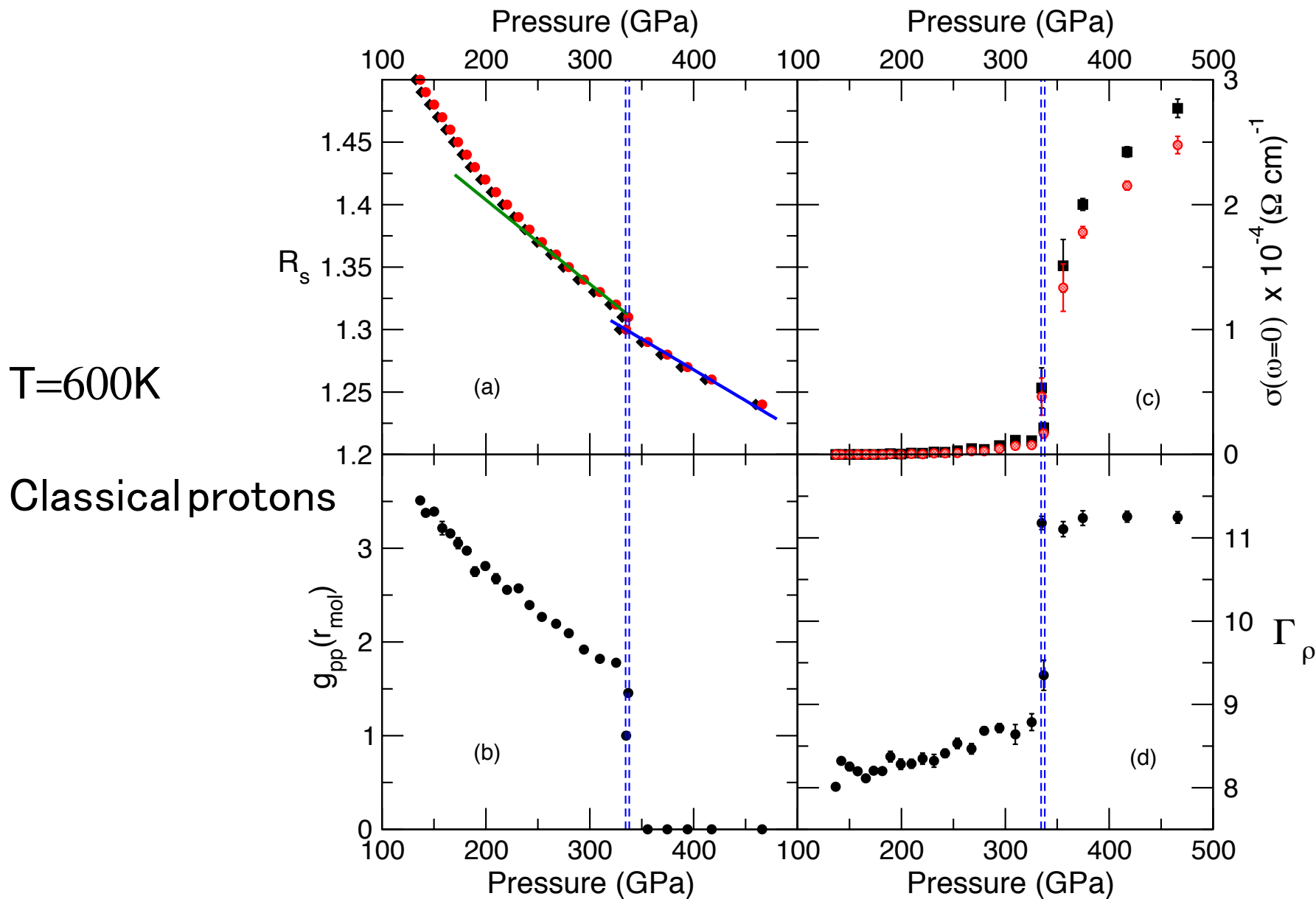


Knudson et al, Science (2015) Pressure (GPa)

# Experimental results differ by a factor 2!!



# Transitions all happen together



# OUTLOOK

- Rich, subtle phase diagram of hydrogen.
  - 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 (potentially) much more accurately because:
  - Availability of Blue Waters.
  - Algorithmic progress gives us much better methods.
- QMC can be used tailor functionals and “force fields”, which can be used on much larger systems with MD.
- Our goal is to do much more accurate simulations of all sorts of materials.