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Advancing Frontiers of Condensed Matter Physics**

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# First Principles Simulations of Dense Hydrogen and other Light Elements

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# First Principles simulations of dense hydrogen and other light elements

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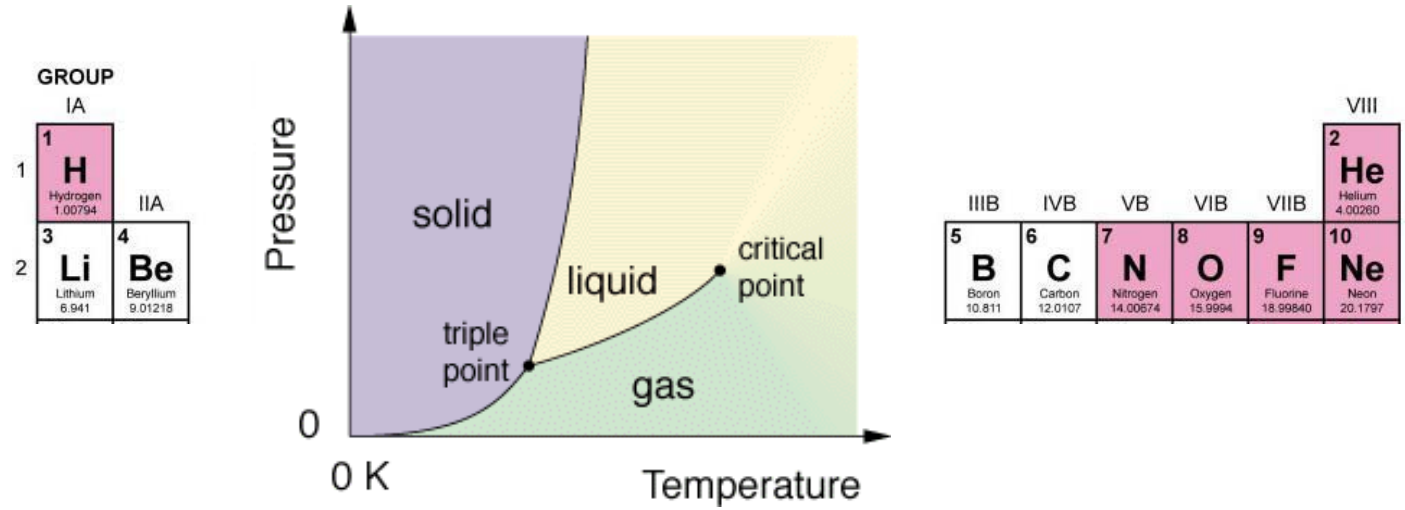
**In collaboration with Stanimir Bonev (Dalhousie Univ., Canada), Eric Schwegler, Tadashi Ogitsu (LLNL) and F.Gygi (UCD)**

Work supported by DOE

Stig Lundqvist Conference, Trieste, July 5th, 2006

# Some contributions to the understanding of elemental phase diagrams

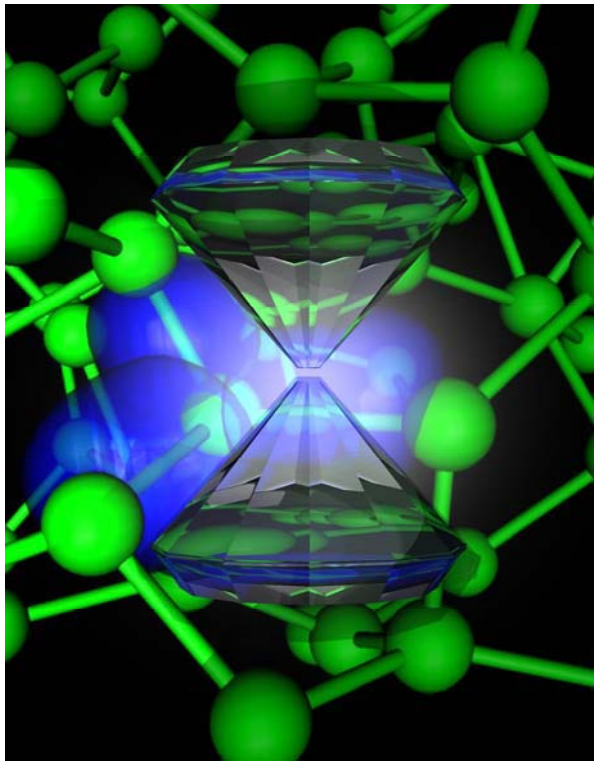



- Hydrogen: a liquid ground state at zero T and high P?
- Difficult to tame: Does diamond melt?
- A spin glass of oxygen molecules at high-P?
- Beryllium melting: a mixture of metallic phases?
- Boron: is there a crystalline ground state?

# We have used first principles MD to investigate EOS, melting lines and shock experiments

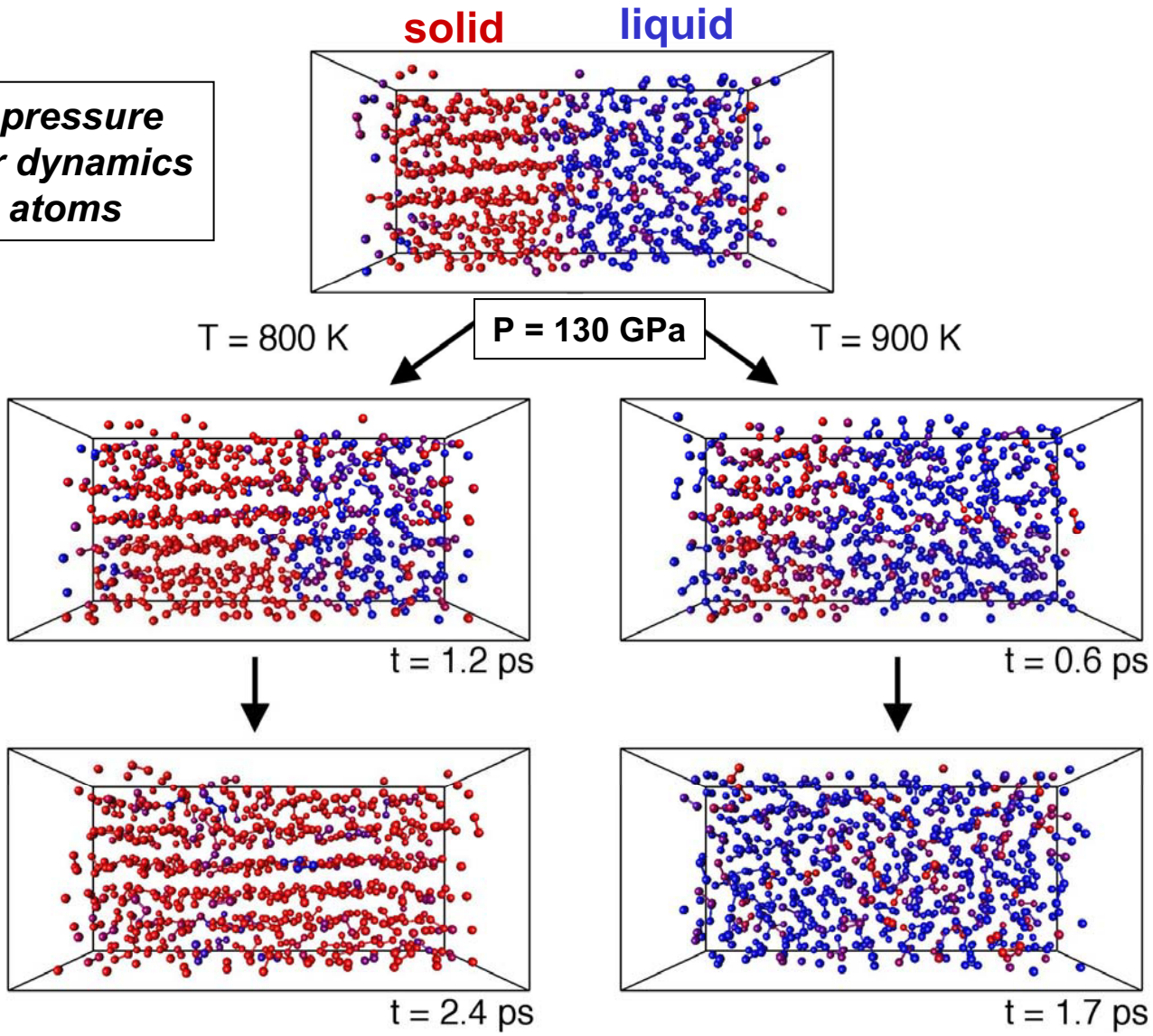
- Two phase simulation method
- Direct and indirect shock simulations
- Presence of magnetic fields

- DFT/GGA (PBE)
- Plane waves and pseudo-potentials
- Born-Oppenheimer and Car-Parrinello simulations
- Qbox code (F.Gygi, UCD)

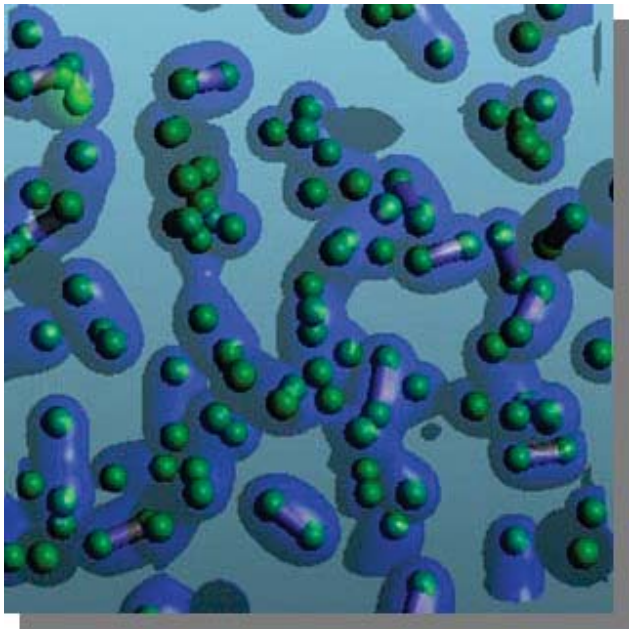


# We computed melting T as a function of P using an *ab-initio* two-phase technique

***Constant pressure molecular dynamics***
***N = 720 H atoms***



# Comparison between simulations and final states of shock experiments



Simulations at constant volume & temperature

$p_1, V_1, E_1$

Hugoniot relations satisfied?

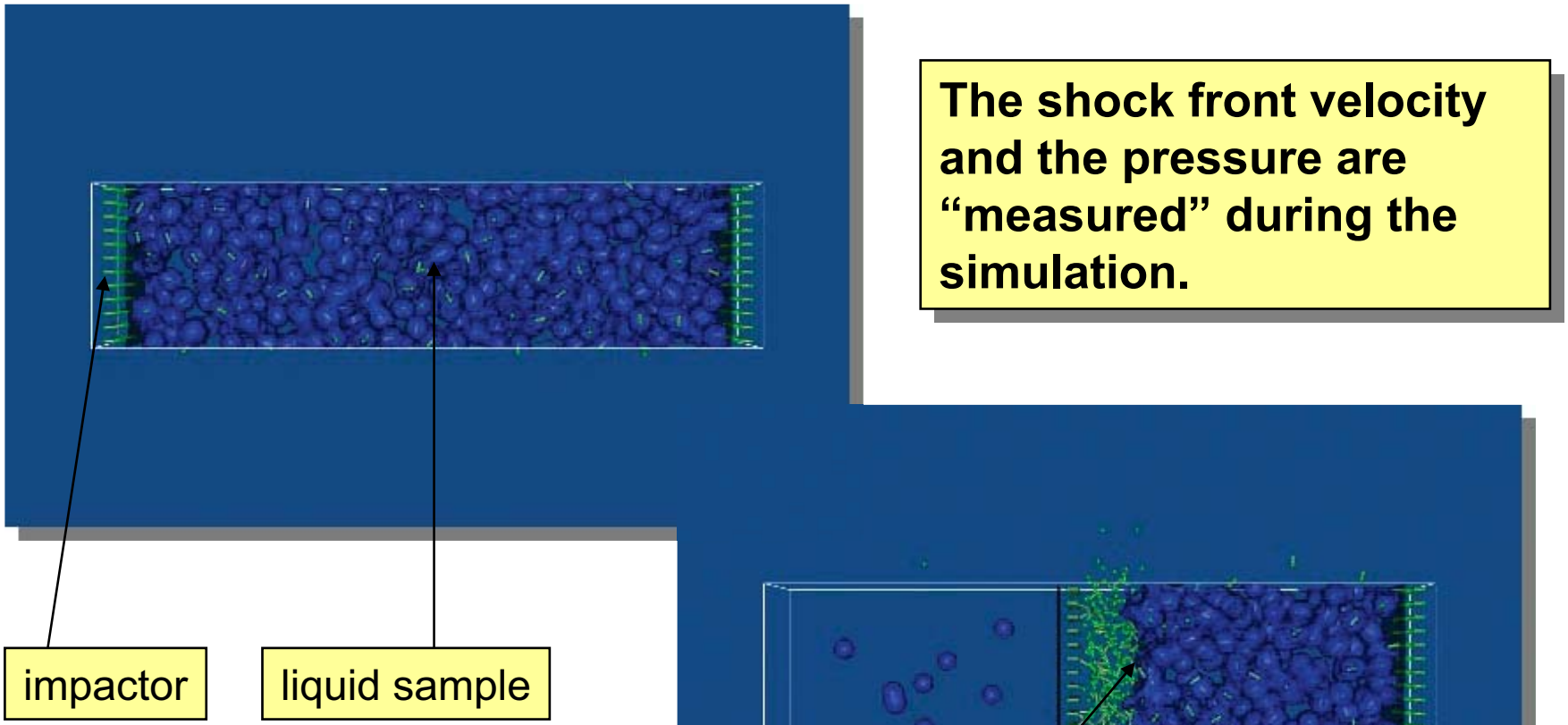
$E_1 - E_0 = \frac{1}{2}(p_1 + p_0)(V_1 - V_0)$

$p_1, \rho_1$

**Compare with experiment**: comparison at given thermodynamic conditions

Dynamical processes occurring during **shock propagation**, and the microscopic structure of **shock fronts** are ignored in simulations of shocked states.

# *Direct ab initio* simulations of shock propagation

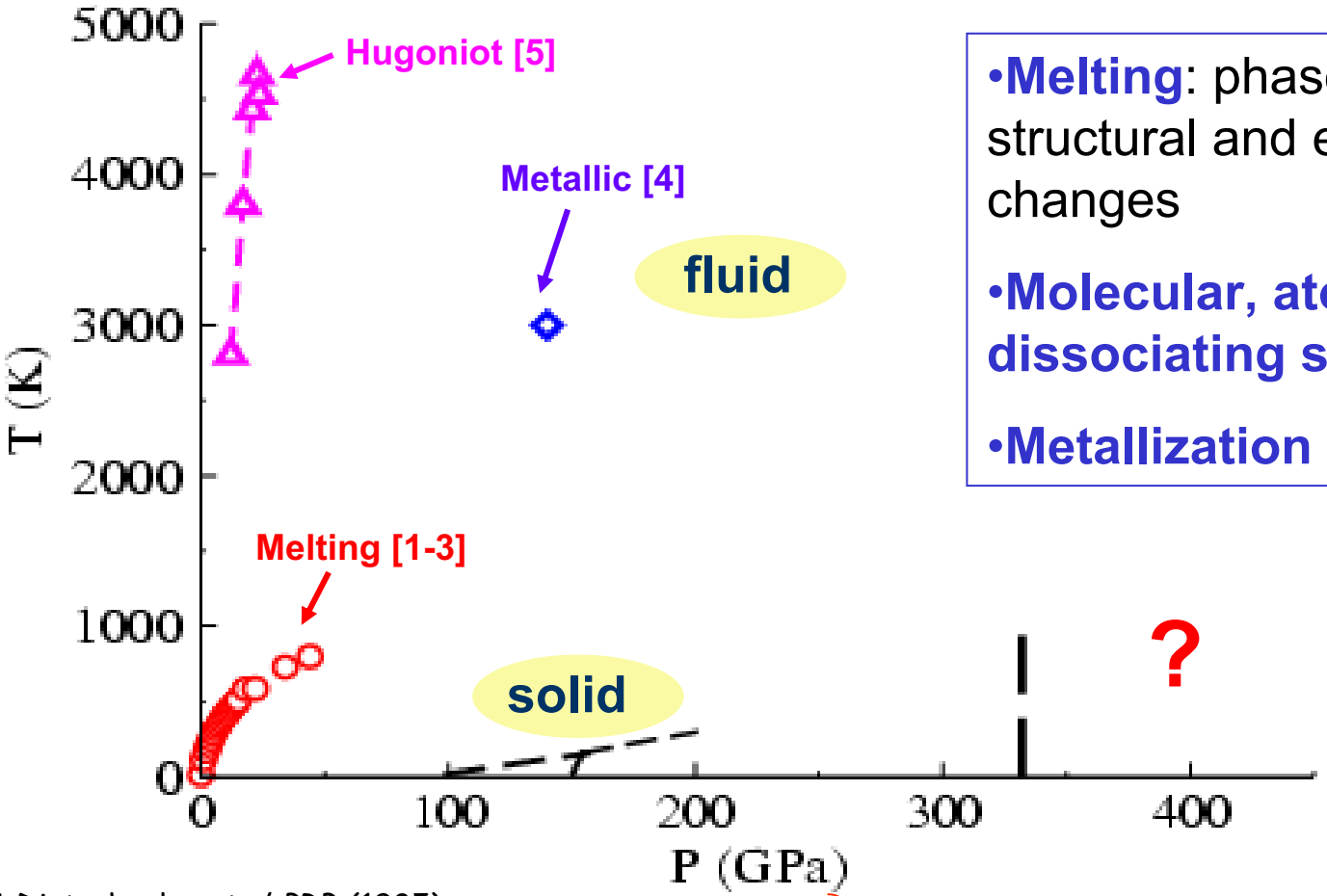



**The shock front velocity and the pressure are "measured" during the simulation.**

•1320 D atoms arranged in a periodically repeated MD cell; the liquid sample is represented by 744 D atoms

F.Gygi and G.G., PRB-RC 2002

# The high-pressure phase diagram of hydrogen at low temperature



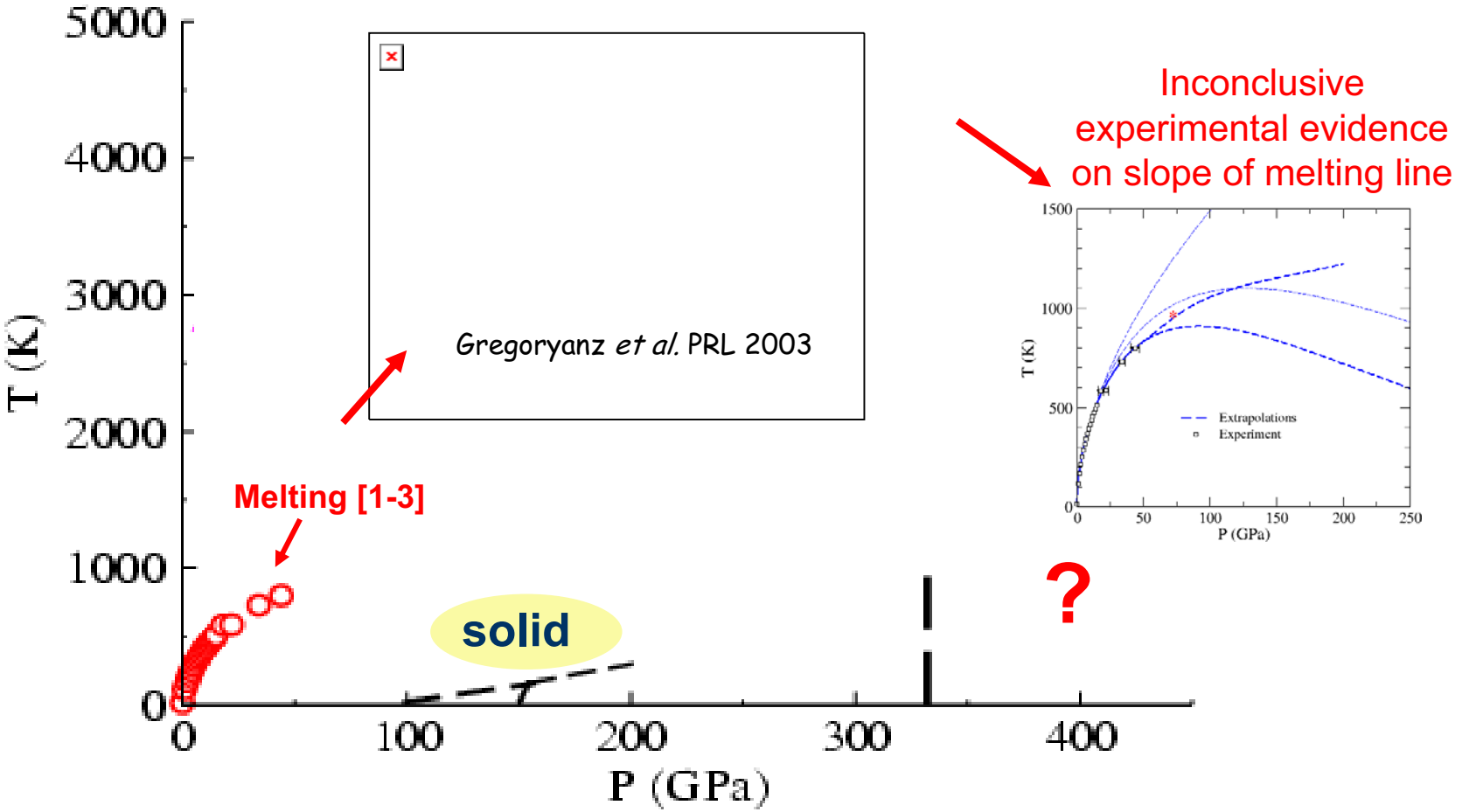

- **Melting**: phase boundaries; structural and electronic changes
- **Molecular, atomic or dissociating states**
- **Metallization**


[1] Diatschenko *et al* PRB (1985).
[2] Datchi, Loubeyre, and LeToullec, PRB 61, 6535 (2000).
[3] Gregoryanz *et al*. PRL (2003).
[4] Weir, Mitchell, and Nellis PRL 76, 1860 (1996).
[5] Holmes, Ross, and Nellis, PRB 52, 15835 (1995).


← Diamond Anvil Cell experiments

← Shock wave experiments

# The high-pressure phase diagram of hydrogen at low temperature

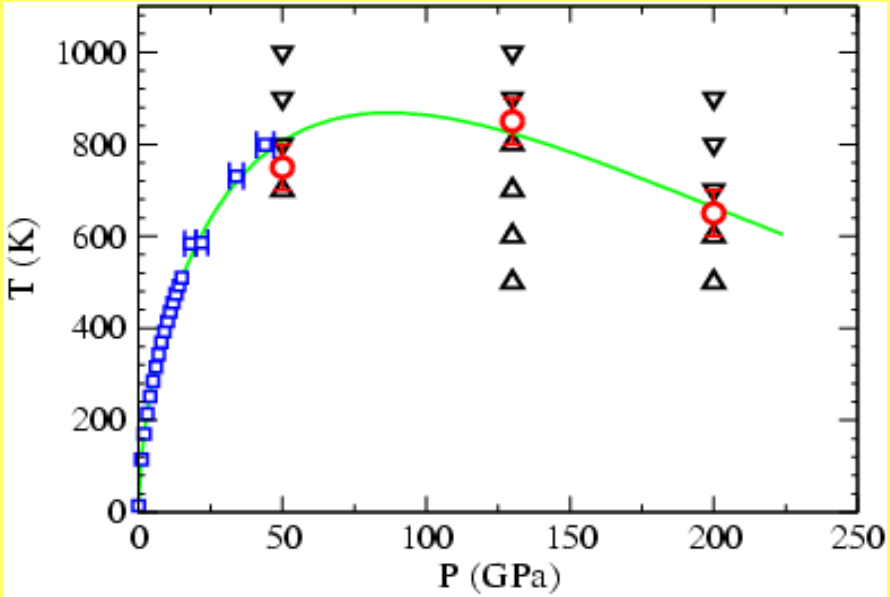




[1] Diatschenko *et al* PRB (1985).
[2] Datchi, Loubeyre, and LeToullec, PRB 61, 6535 (2000).
[3] Gregoryanz *et al.* PRL (2003).


← Diamond Anvil Cell experiments

# The predicted melting curve of deuterium has a maximum at ~ 900 K and ~ 90 GPa




S.Bonev, E.Schwegler, T.Ogitsu and G.G, Nature 2004

Experimental melting points

**Computations**

Solidification

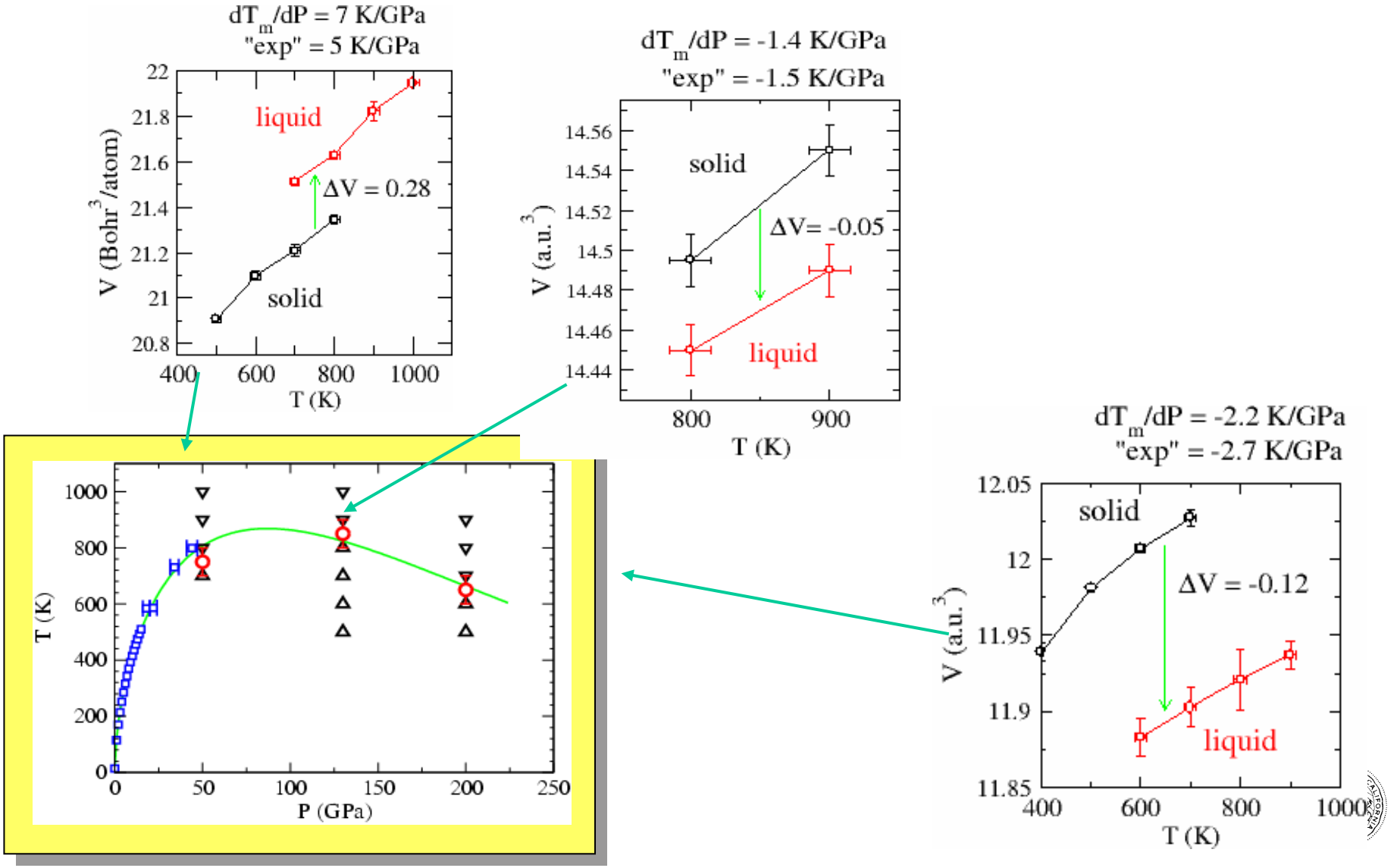
Melting

Coexistence

Kechin fit to experiment and theory

$$T_m = T_0\left(1+\Delta P/a\right)^b \exp\left(-c\Delta P\right)$$

# Volume and structural changes have been monitored as a function of T and P



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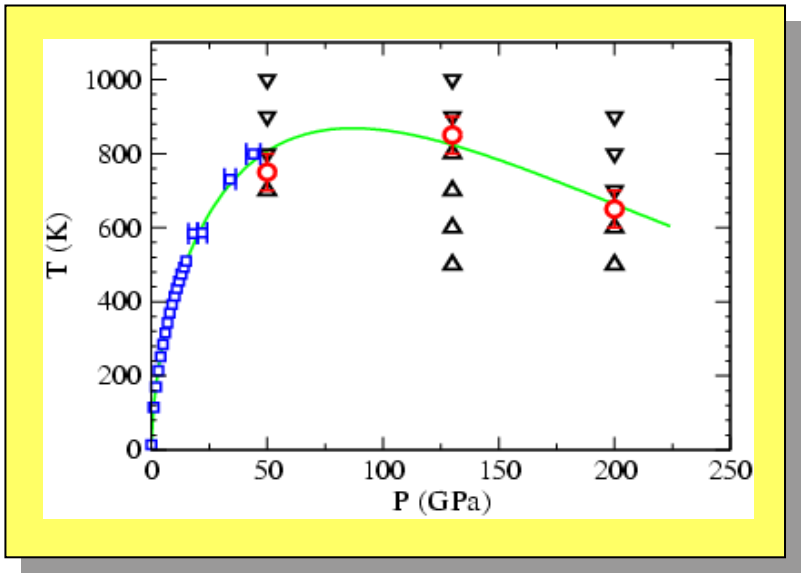
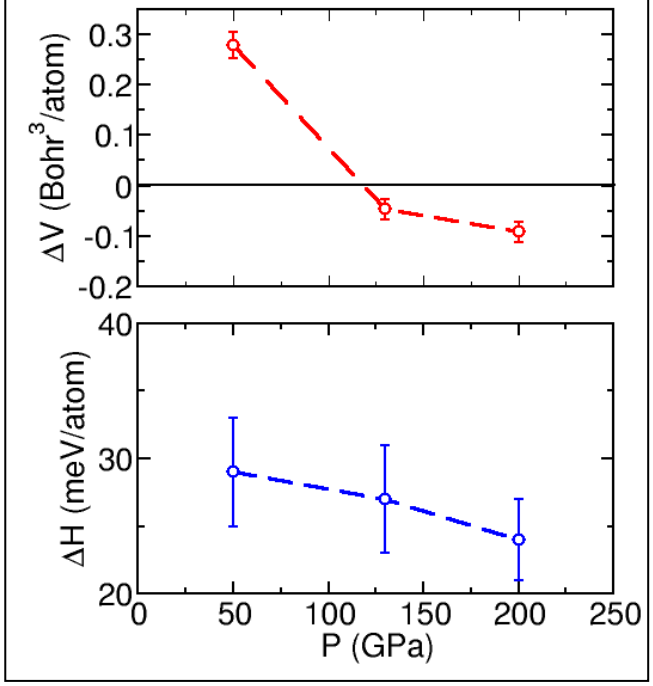



**Differences in volumes and enthalpies between the liquid and solid phases at coexistence**



# Thermodynamic consistency has been checked

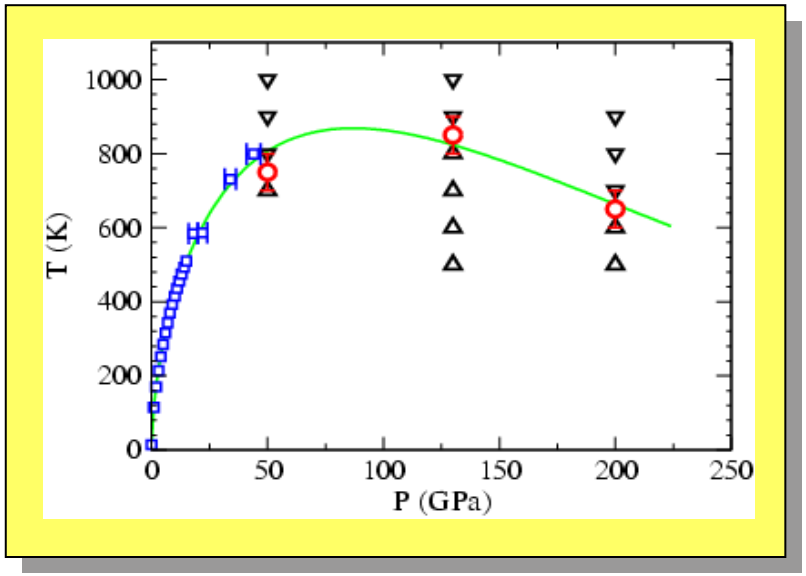
**Comparison of slopes obtained from from one- and two-phase simulations**

**Clausius-Clapeyron equation:**

$$\frac{dT_m}{dP} = T_m \frac{\Delta V}{\Delta H}$$

From 2-phase

From 1-phase



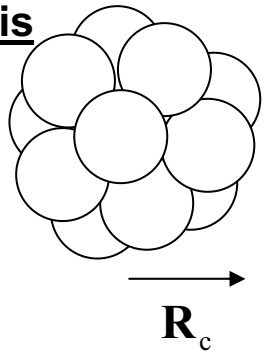

| $dT_m/dP$ (K/GPa) from | | |
|---|---|---|
| P(GPa) | Melt line fit | Clausius-Clapeyron |
| 50 | 3.9* | 6.5(12) |
| 130 | -2.2 | -1.4(4) |
| 200 | -2.7 | -2.3(6) |

*Weighted by the experimental points

# The liquid freezes as an *hcp* (rotational) crystal

**Local order analysis**

Cluster of molecules

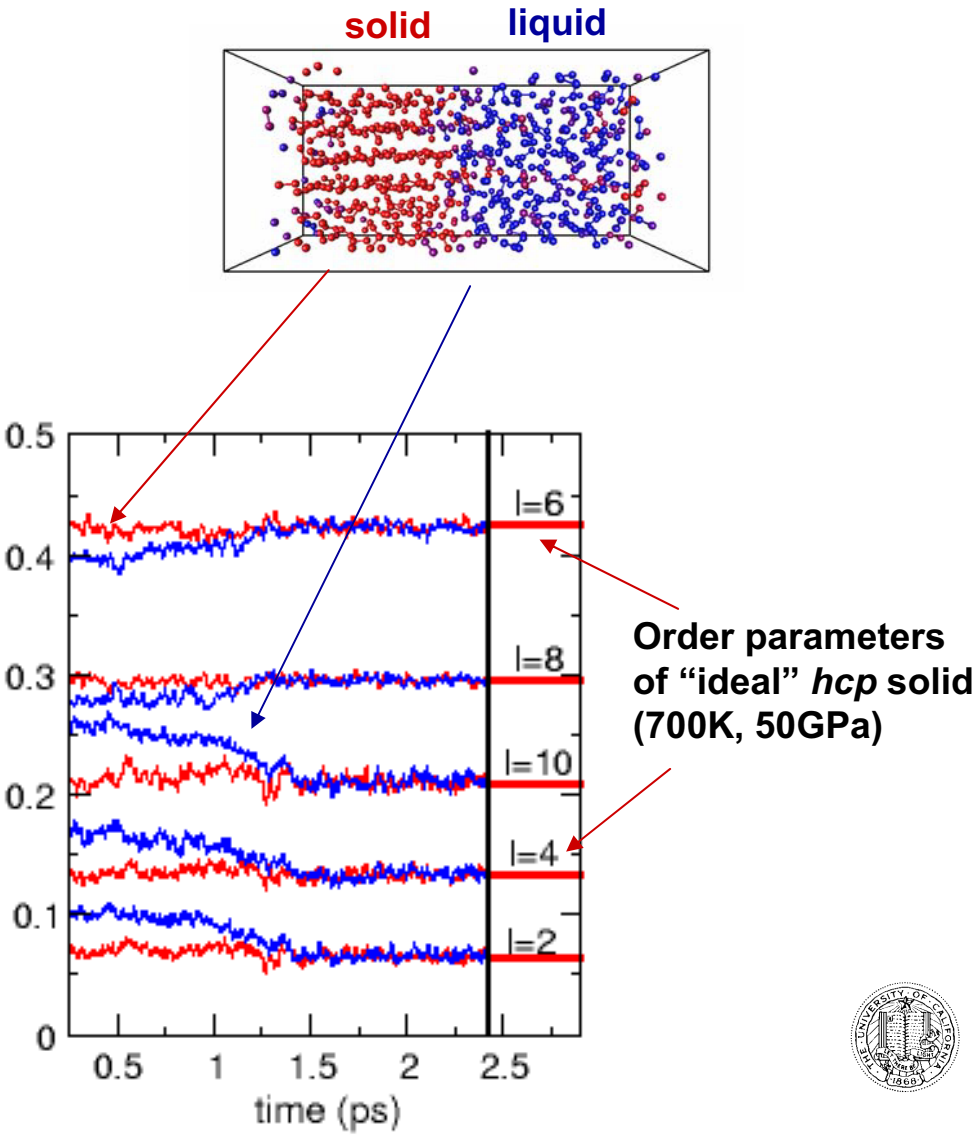



**A unique set of rotationally invariant local order parameters**

$$\overline{Q}_{lm} = \frac{1}{N_b} \sum_{ij} Y_{lm}\left(\theta_{ij}, \phi_{ij}\right)$$

$$Q_l = \left[ \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \left| \overline{Q}_{lm} \right|^2 \right]^2$$

Steinhardt *et al.* PRB (1983).




**Order parameters of "ideal" *hcp* solid (700K, 50GPa)**

# Classical and adiabatic approximations

## Classical ion motion

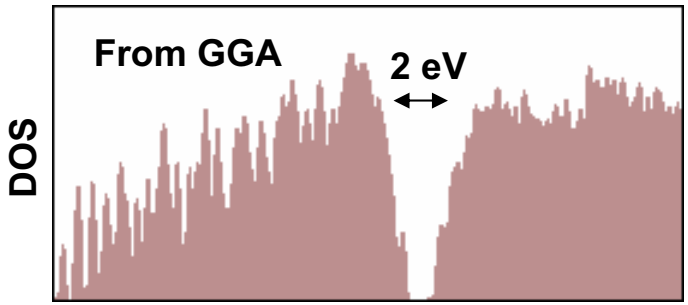
**Quantum correction to the classical ion free energies:**

$$\Delta F = \frac{\hbar^2}{24 k_B^2 T^2} \left\langle \sum_i \frac{\mathbf{F}_i^2}{m_i} \right\rangle_C$$

Wigner-Kirkwood formula

**Up to 200 GPa, the difference in $\Delta F$ between solid and liquid is less than 2 meV/atom at $T$ near the melt curve**

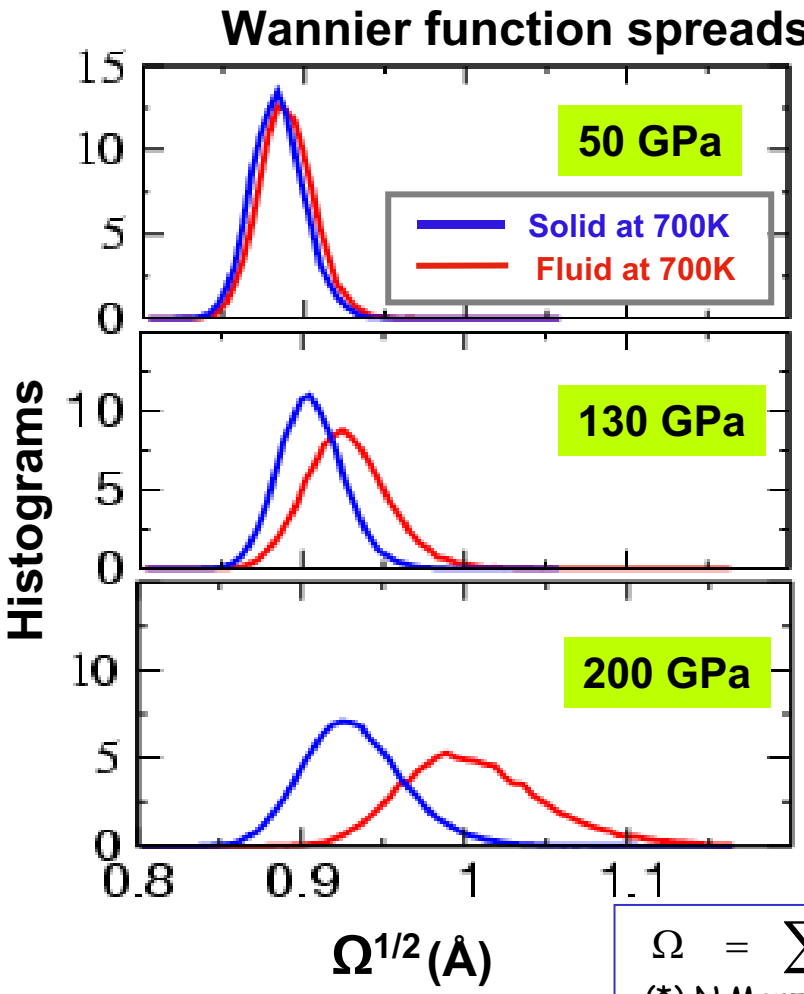
## Adiabatic interactions




**At 200 GPa, the band gap in the solid is still > 2 eV. Therefore, electron-phonon interactions are expected to be negligible.**

# Deuterium melts before dissociating and the fluid close to the melt line is semi-conducting

*Maximally localized Wannier functions* → *"Molecular orbitals" in the condensed phase (*)*



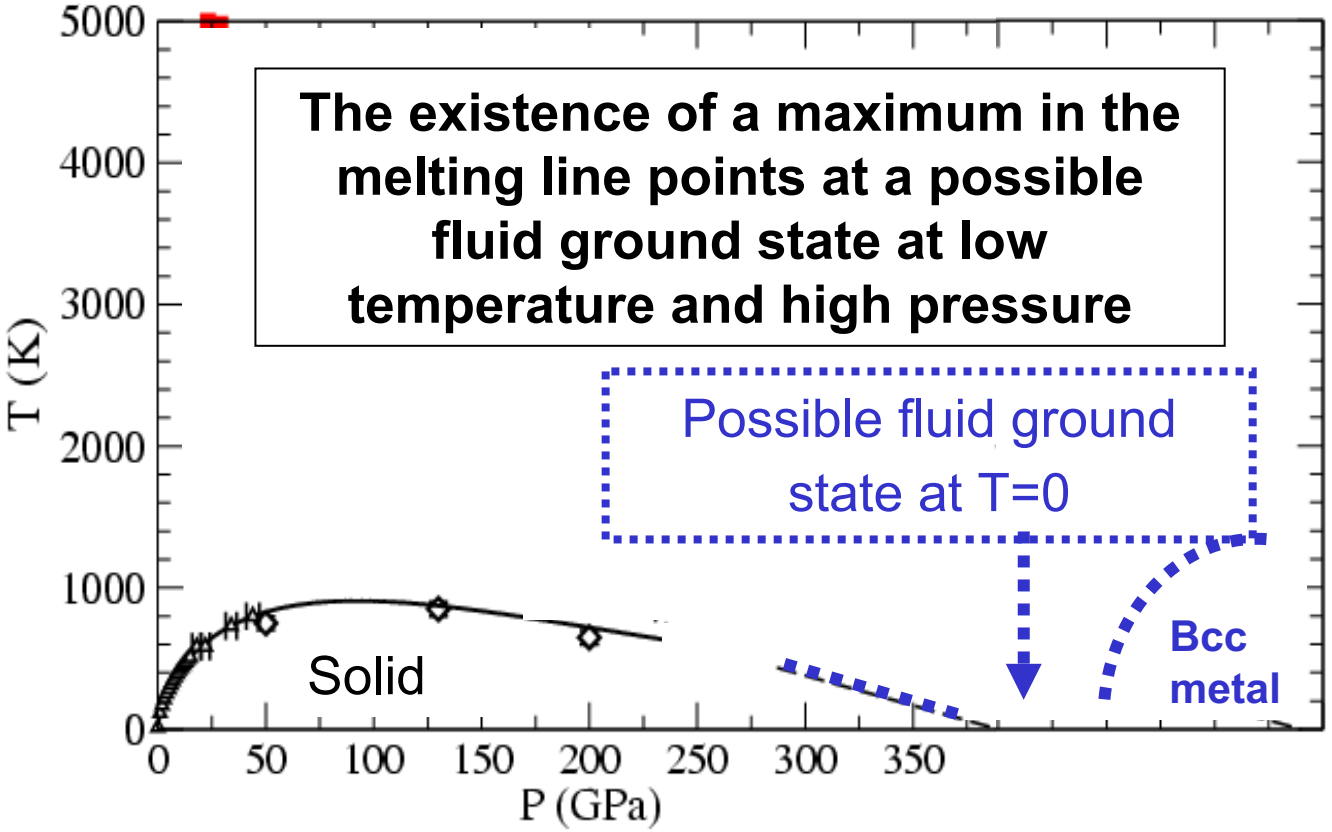

**Presence of maximum in the melting line is related to change in intermolecular interaction, not to molecular dissociation**

**Asymmetry in MLWF tails → effective intermolecular charge transfer in the fluid → enhanced infrared activity which may be detected experimentally**

$$\Omega = \sum_n \left( \langle r^2 \rangle_n - \langle \mathbf{r} \rangle^2_n \right) \quad \langle \mathbf{r} \rangle_n = \langle w_n | \mathbf{r} | w_n \rangle$$

(*) N.Marzåri and D.Vanderbilt; R.Resta; I.Souza and R.M.Martin

# A quantum fluid at low T and high P ?

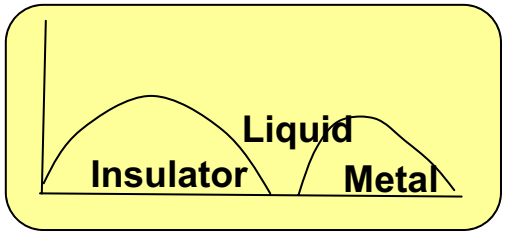


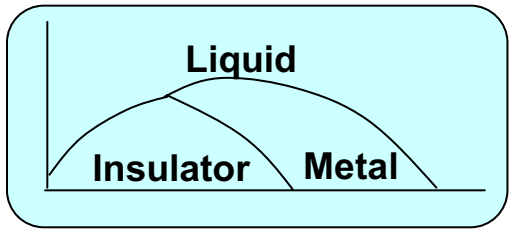

**The existence of a maximum in the melting line points at a possible fluid ground state at low temperature and high pressure**

Possible fluid ground state at T=0

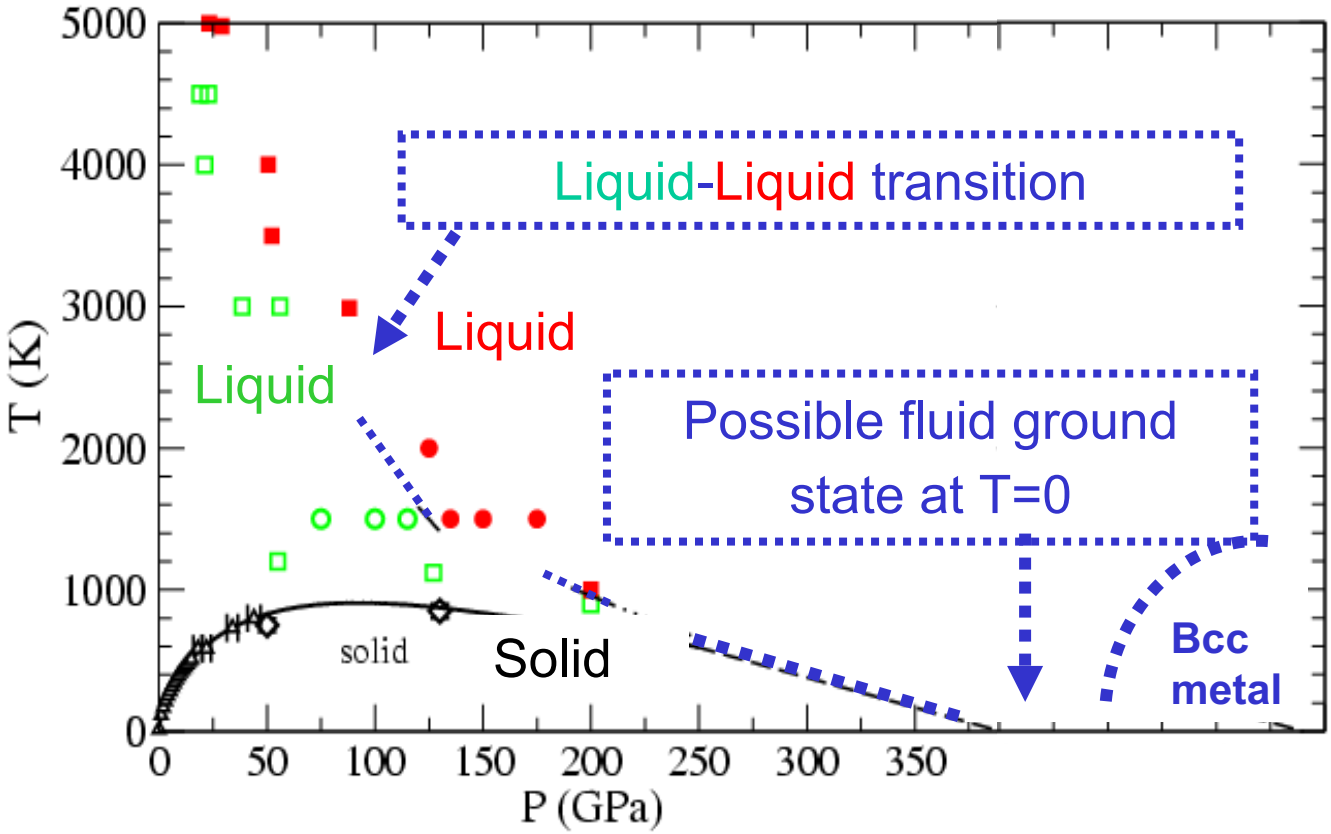
**If low-temperature liquid metallic hydrogen exists, it would be a novel state of matter – a two-component quantum fluid with long-range interactions**

**This quantum fluid may exhibit phase transitions, from superconductors to superfluid** (Babaev et al. Nature, 2004)




# Extensive *ab-initio* simulations point at a liquid-liquid transition (from molecular to a dissociated fluid)




Location of liquid-liquid transition is relevant to the formation of Saturn and Jupiter

Results include S.Scandolo's simulations (●), PNAS (2002).

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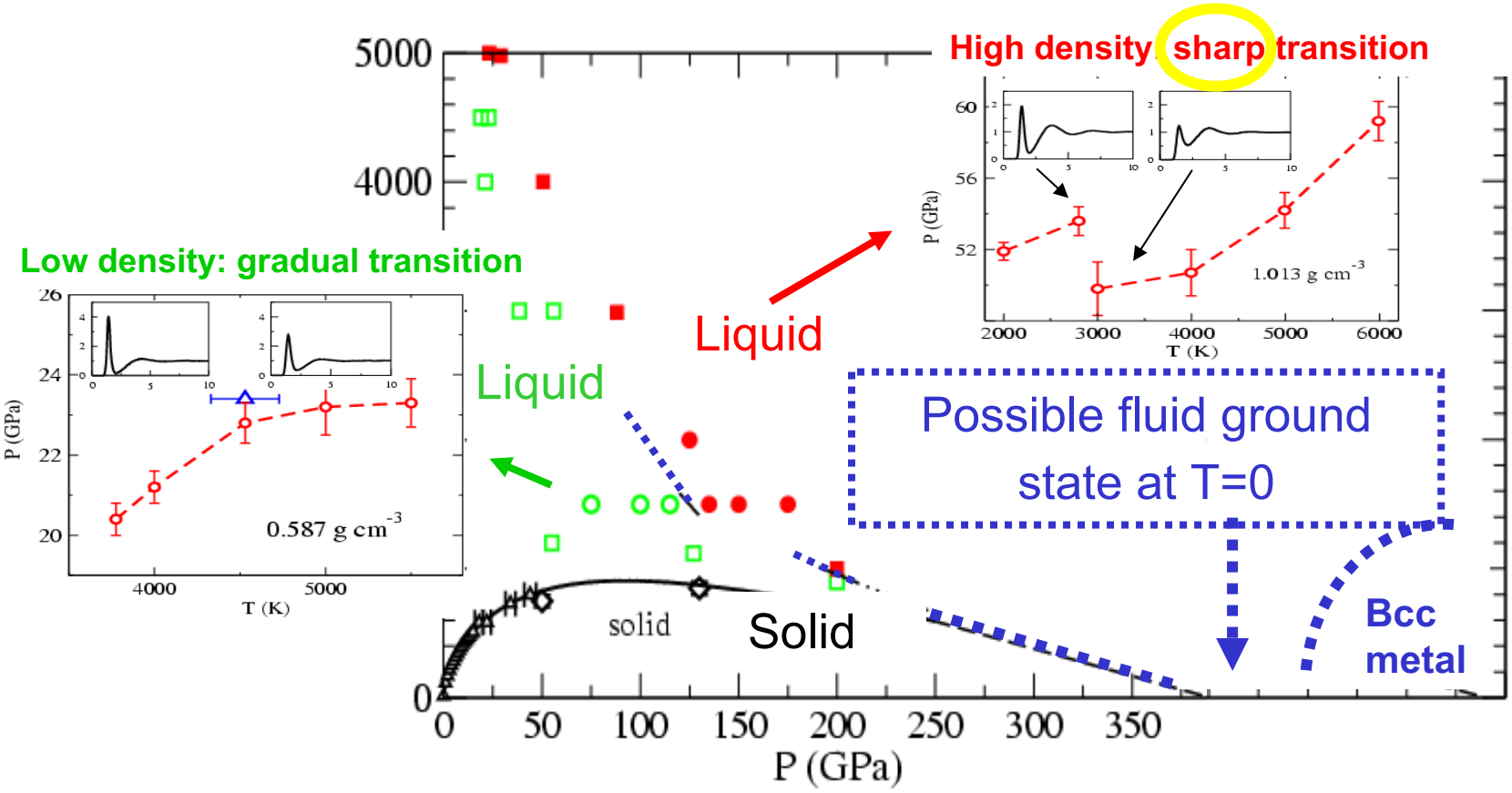
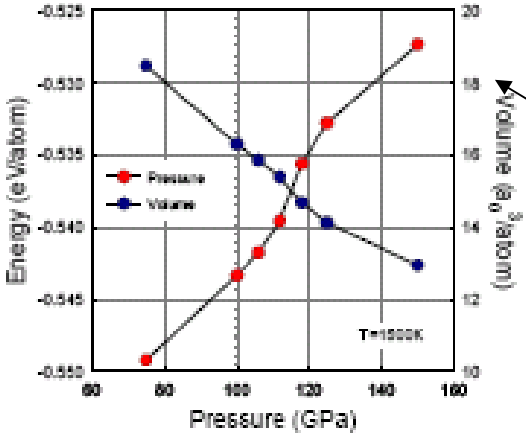



Location of liquid-liquid transition is relevant to the formation of Saturn and Jupiter

(*) S.Bonev, B.Militzer, G.G., PRB 2004

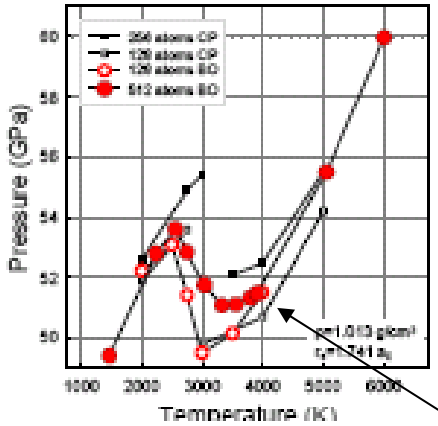
# A closer look at the liquid-liquid transition

Isotherm (1500K)

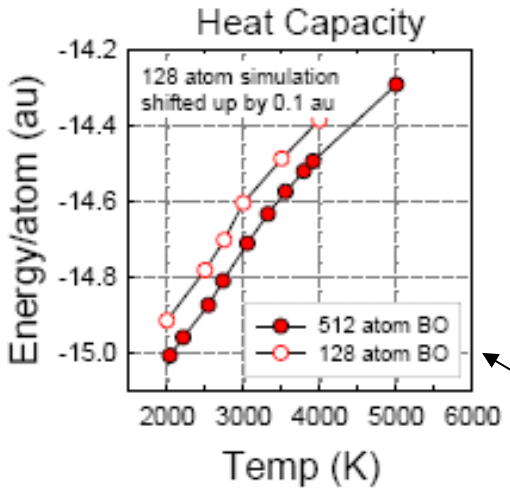



Continuous behavior of E(P) and V(P)

Isocore (1.013 g/cm3)




**No indication of a first order liquid-liquid phase transition, based on BO simulations**

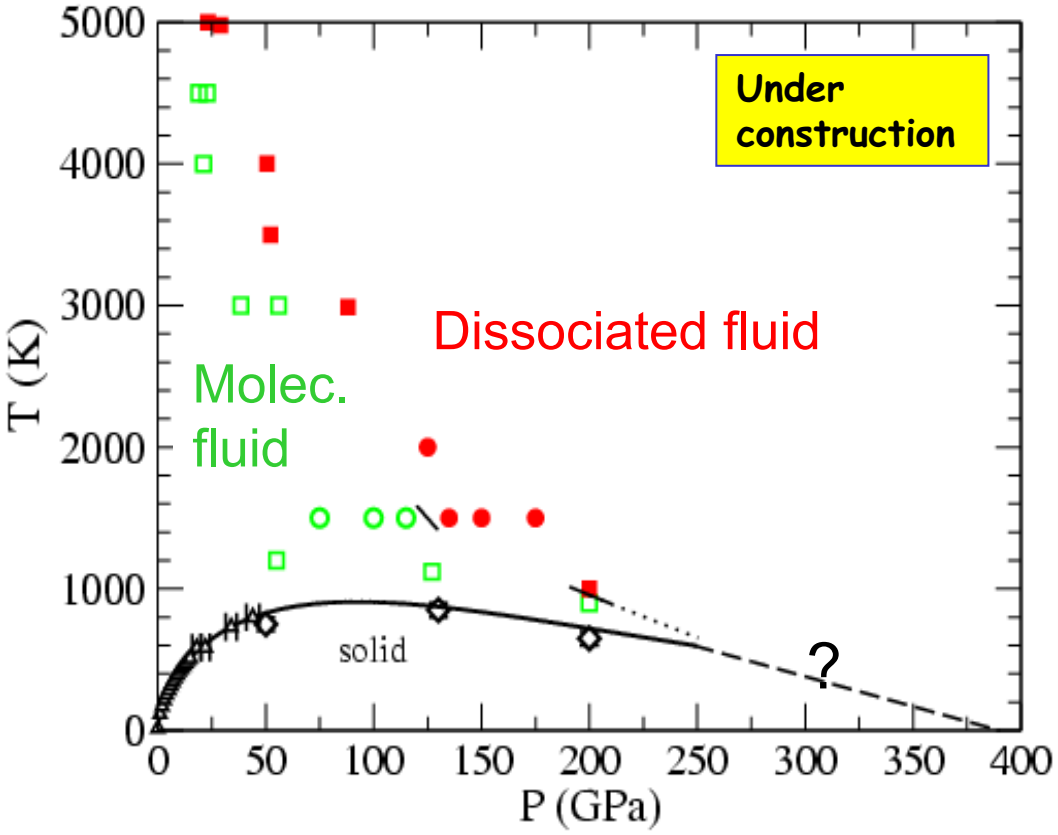



BO simulations with 512 atom cells: **Non monotonic behavior of P(T), however no discontinuity in P(T).**

**No discontinuity in E(T)**

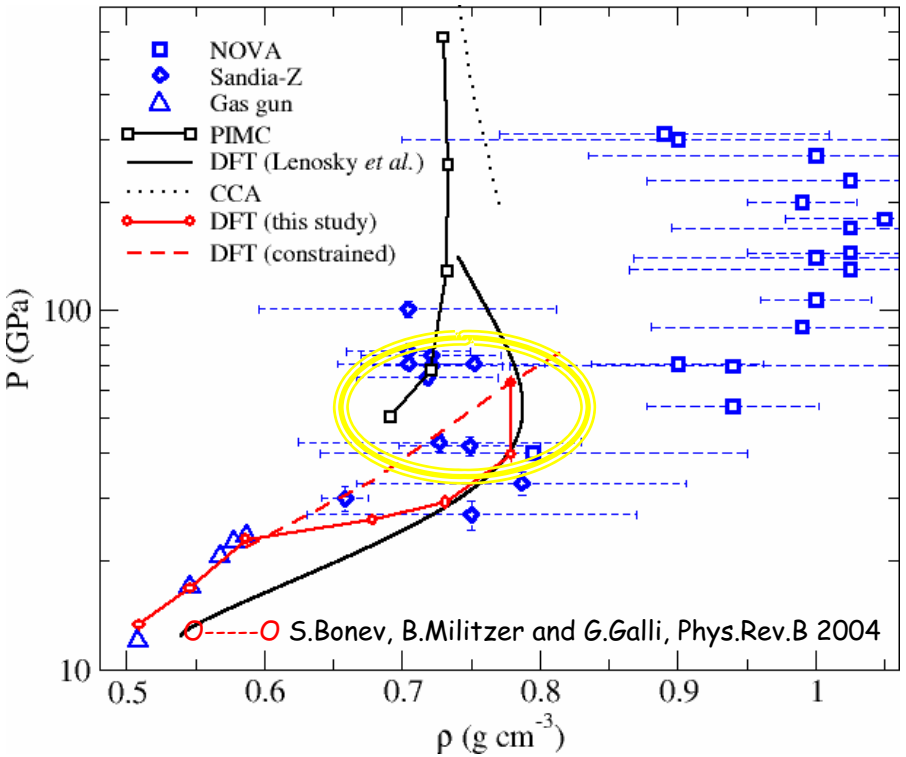
K.Carpensen et al. 2006

# We have elucidated several portions of the hydrogen phase diagram




- **Melt curve maximum at ~ 90 GPa and 900 K**
- **Melting before dissociation for P < 200 GPa**
- **Possible fluid ground state at ~ 400 GPa (?)**
- **Liquid-Liquid transition below the primary Hugoniot: not a first order transition**

# *Ab-initio* Simulations for Deuterium Hugoniot




(*) F.Gygi and G.Galli, PRB-RC 2002

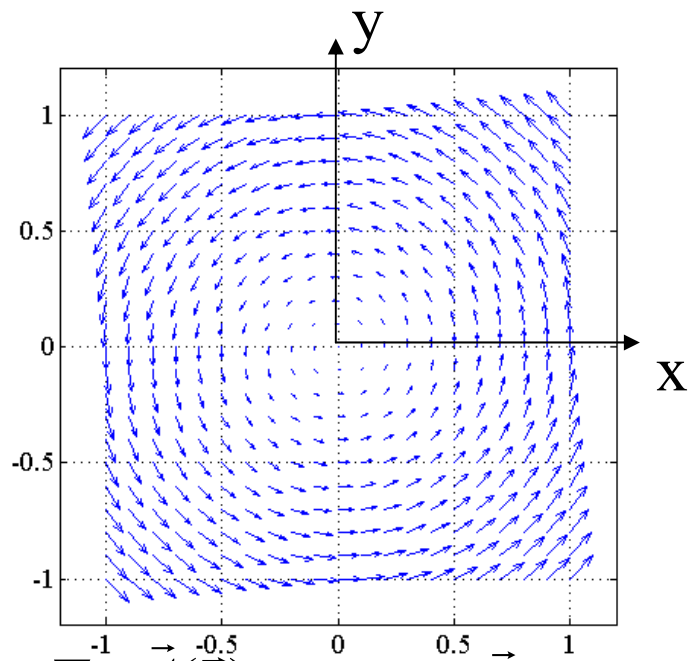
- Computed maximum compression (~ 4.6) at equilibrium:
  - slightly smaller with Density Functional Theory than found in Pat Integral Monte Carlo simulations (~ 4.3)
  - consistent with Sandia and Omega impedance matching data and with Russian data (Trunin)
- Non equilibrium electronic, adiabatic effects proposed (*) to explain:
  - Recent LLNL re-shock data
  - Nova Data

# Intense magnetic fields can substantially change properties of compressed hydrogen

**Apply uniform (strong) magnetic field B and carry out plane wave total energy calculations and *ab-initio* MD of condensed systems**

$$H = \frac{1}{2m}[\hat{p} + e\vec{A}(\vec{r})]^2 + V(\vec{r})$$

$$\vec{A}(\vec{r}) = (0, Bx, 0)$$




$$\vec{B} = \nabla \times \vec{A}(\vec{r}) \qquad \vec{B} = (0,0,B)$$

Symmetric gauge: $\vec{A}(\vec{r}) = (-By, Bx, 0)/2$

$$\psi(\vec{r} - \vec{c}) = \exp[i\frac{e}{h}\vec{A}(\vec{c}) \cdot \vec{r} - i\vec{k} \cdot \vec{c}] \cdot \psi(\vec{r})$$

W.Cai and G.Galli, PRL 2004; E.Lee, W.Cai and G.Galli (in preparation)

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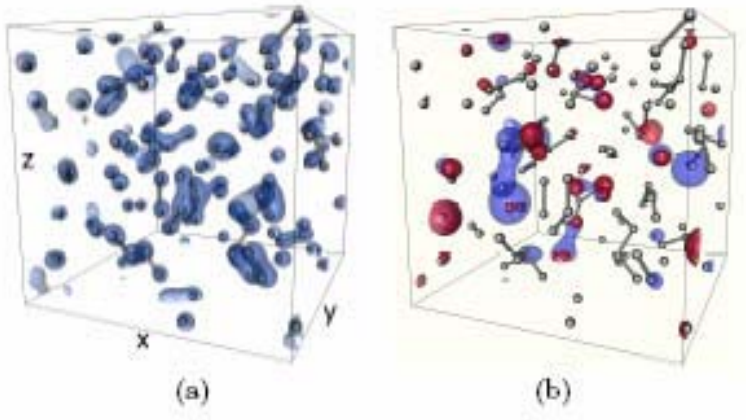
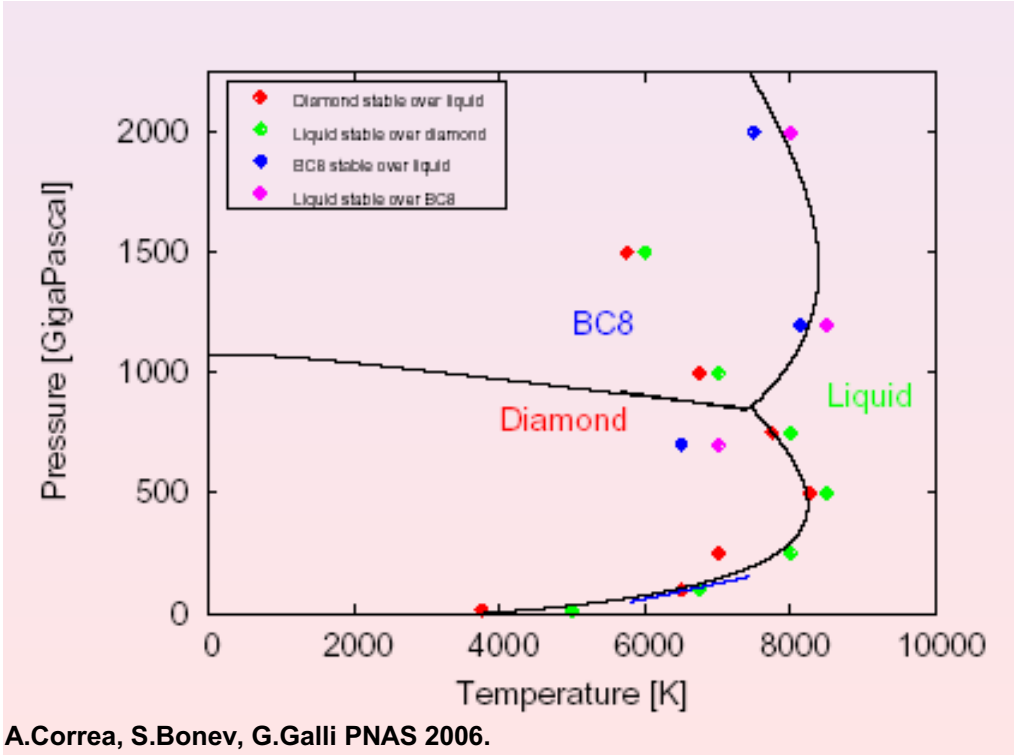



**Compressed hydrogen in a intense magnetic field**: minimal changes in charge density*; changes in HOMO-LUMO localization*; *changes in magnitude of electronic gap*

W.Cai and G.Galli, PRL 2004; E.Lee, W.Cai and G.Galli (in preparation)

# Proposed phase diagram of carbon at high pressure




**A.Correa, S.Bonev, G.Galli PNAS 2006.**

- The **liquid** is a metal retaining **covalent features** in its bonding up to extreme conditions.
- **Coordination** of the liquid is **higher than 4** above the max. of D melting line, and **higher than 6** above the max of BC8 melting line.
- Metallization on the Hugoniot line consistent with recent shock wave experiments.
- **No L/L phase transition** in I-C over a wide pressure range (*) (contrary to claims based on empirical potentials).

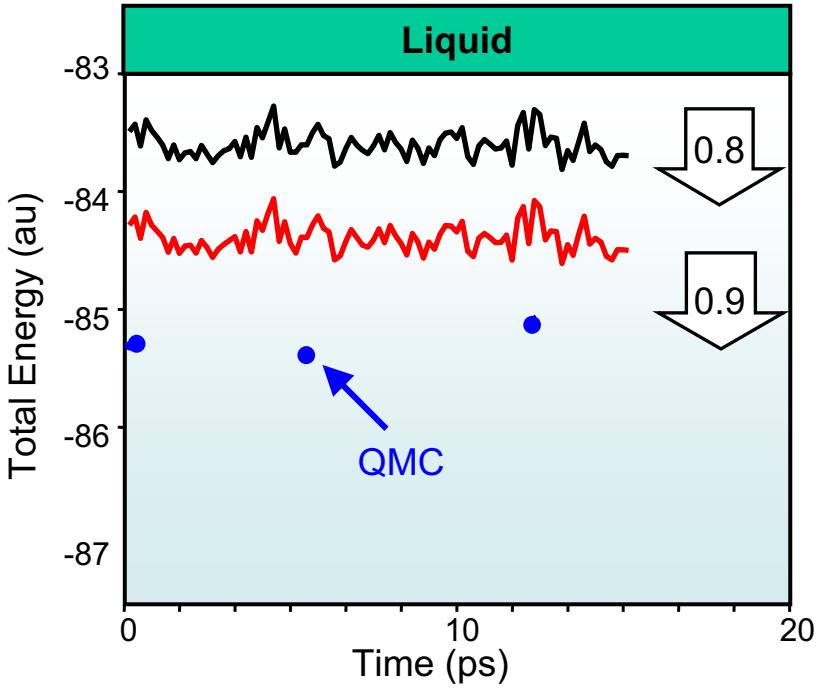
(*) C.Wu, J.Glosli,G.G. and F.Ree, PRL 02

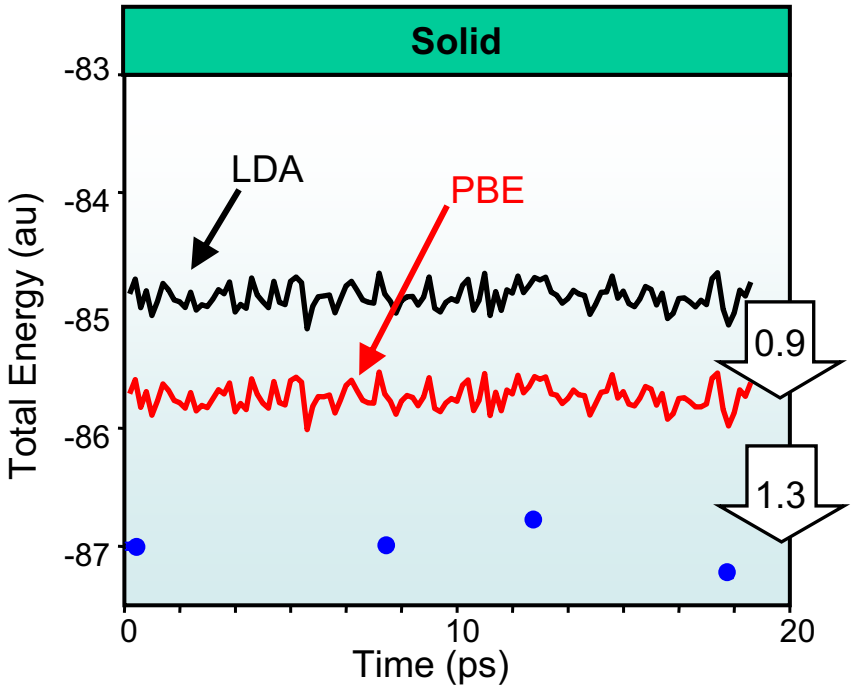
Present results:

- consistent with *ab-initio* calculations of Grumbach and Martin (PRB 1996) in the diamond region (not above).
- consistent with model potential calculations of Ghiringhelli et al (PRL05) at low pressure; however in disagreement on maximum existence.
- in agreement with free-energy calculations by X.Wang, R.Car and S.Scandolo (PRL 2005) for diamond melting, however some minor quantitative discrepancies need further investigation.

# Energy differences between solid and liquid phases may be corrected by “rigid shifts”

100GPa 2250K Solid and Liquid LiH  LDA, PBE and DMC



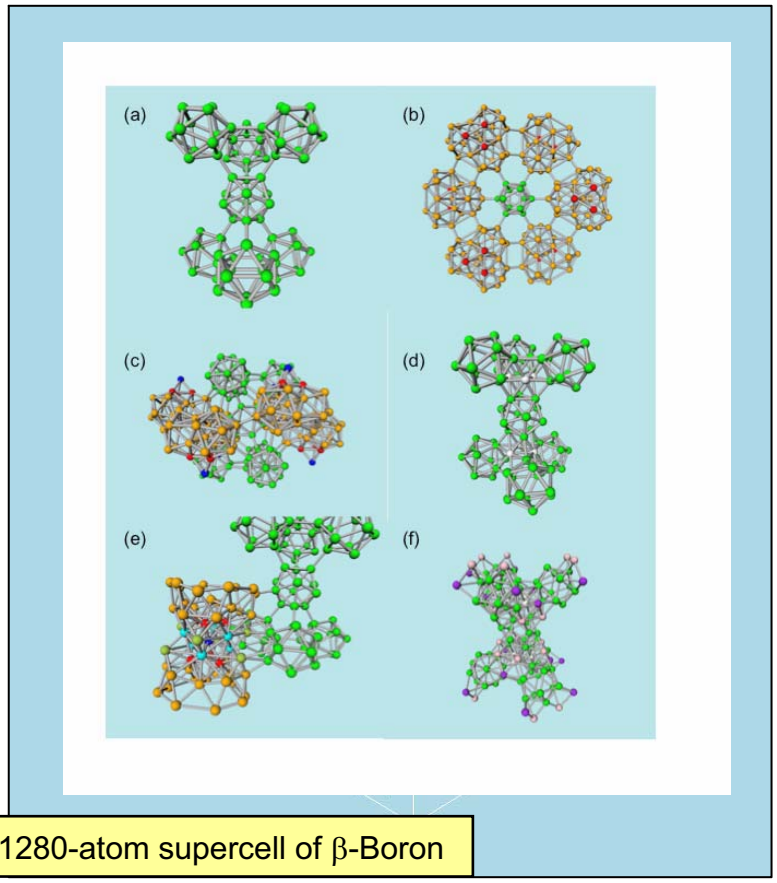

**The error of LDA/GGA on the solid phase energies is larger than that on the liquid phase energies.**

A.Williamson and T. Ogitsu et al.

# The ground state structure of elemental boron is not yet known

- Boron has the most complex geometry of all `stable` elements in the Periodic Table (with more than 300 atoms/cell).
- Under pressure, reported amorphization (~ 100 GPa) and superconducting transition are puzzling.

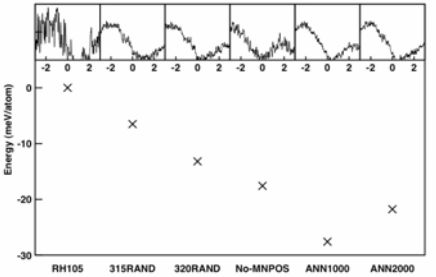
- Many proposed structures (315 atoms/cell) are in principle half filled metals, yet conductivity data show semi-conducting behavior.
- Is there a crystalline order (and what is the # atom/unit cell)? Is it compatible with electronic structure data?
- How does pressure induced amorphization occur?

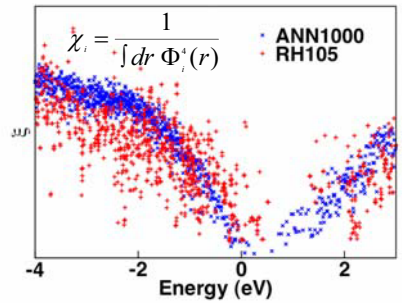



1280-atom supercell of β-Boron

# Imperfect crystal and unusual semiconductor: Boron a frustrated element

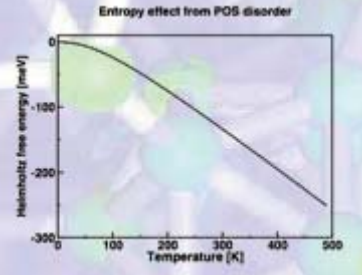
- At zero T and P *ab-initio* calculations including partially occupied sites –POS-- (1280 atoms) favor 320 atoms/cell (*even* $N_{el}$) and correlated configuration of POS.
- At zero P, the electronic structure of crystalline B resembles that of a disordered semiconductor, with a small, finite density of non-conductive, localized states at the Fermi level.




- Inclusion of configurational entropy is key to `reproduce` experimental data.
- MC simulations with `cluster-expanded` Hamiltonian (from fit to *ab-initio* data) allowed us to determine finite T model of elemental boron, and eventually to include phonon contributions. We also understand why β, not α, is Boron ground state.

$$F(T) = -kT \log[\sum_i \exp\{-\beta(E_i - E_0)\}]$$



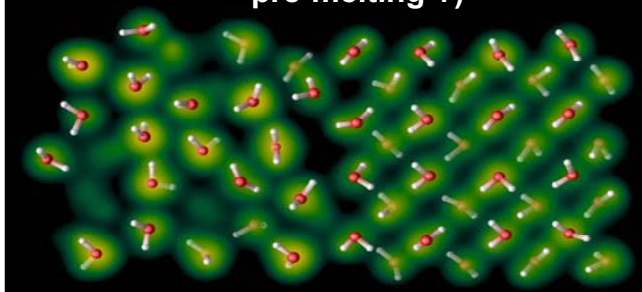

T.Ogitsu, F.Gygi, J.Reed and G.G. 2006

# Some open questions

Phase boundaries of low-Z elements with quantum corrections and improved correlation effects

Conductivity and transport properties as a function of time

**Ice melting line(s) under pressure are not yet known and melting process is controversial (super-ionic phases or pre-melting ?)**



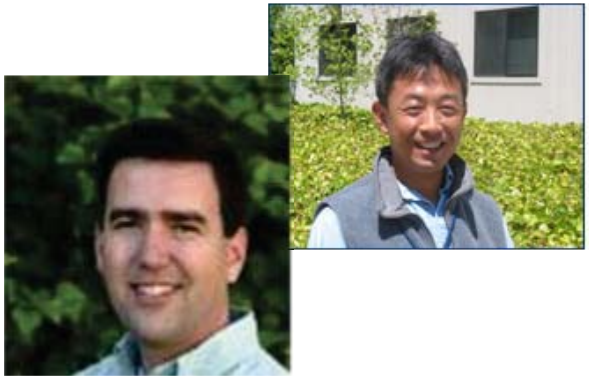
**256 water molecules, 2-phase quantum simulations on Thunder (E.Schwegler et al.)**

# Many thanks to my collaborators

Stanimir Bonev (Dalhousie Univ., Canada)

Tadashi Ogitsu (LLNL)

Eric Schwegler (LLNL)



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