On the Molecular Dissociation of Dense Hydrogen and the Finite-temperature Stability of the Atomic Phase

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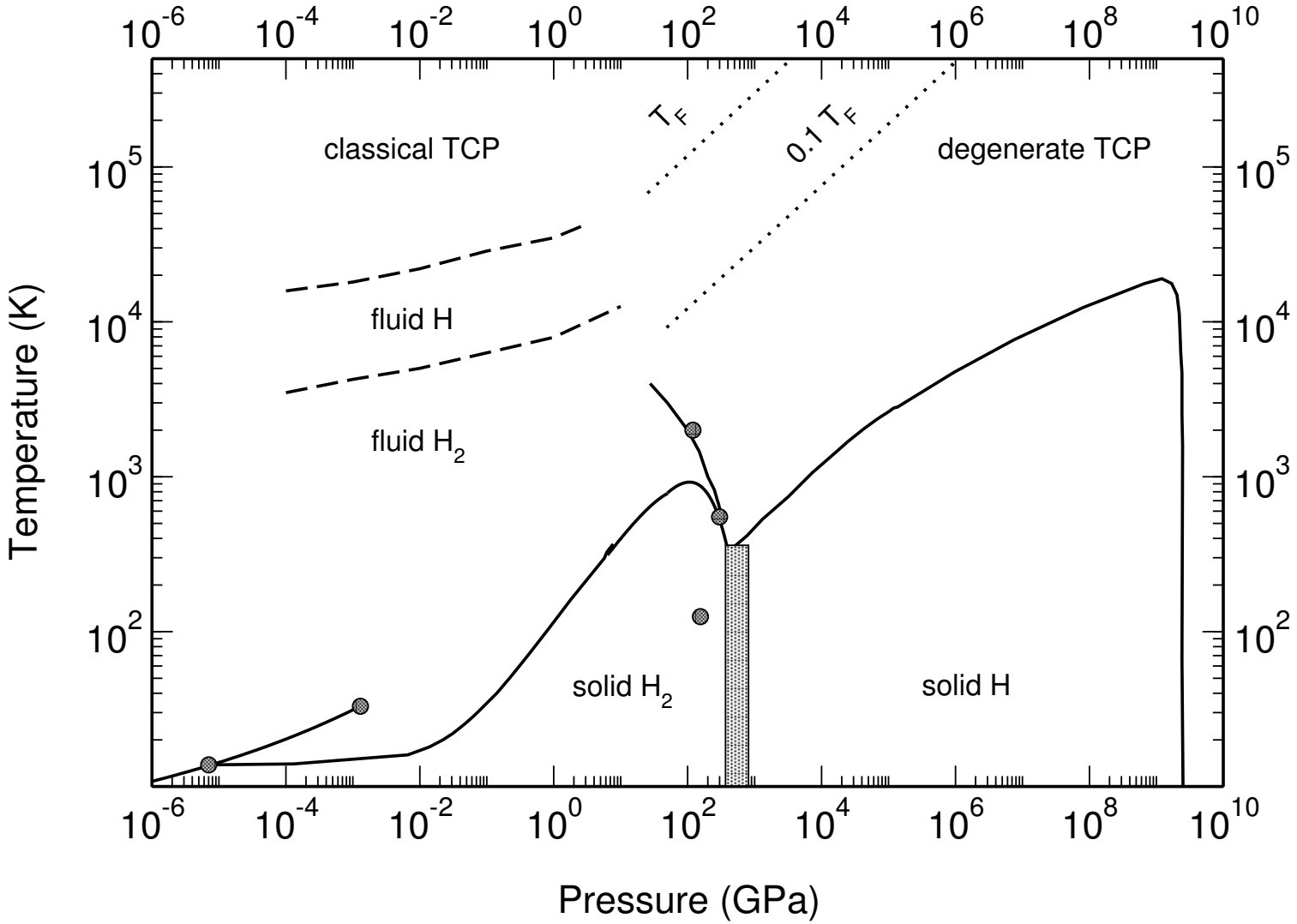
Phase Diagram of Hydrogen



J. M. McMahon, M. A. Morales, C. Pierleoni, and D. M. Ceperley, *Rev. Mod. Phys.* **84**, 1607 (2012)

E. Wigner and H. B. Huntington, *J. Chem. Phys.* **3**, 1748 (1935)

Outline

- Background
  - Structure-prediction methods
  - Predicted crystal structures of atomic hydrogen
- Technical details
  - Solid and liquid phases
  - Thermodynamic conditions
  - Calculation details
- Results
  - Diffusion calculations
  - Free-energy calculations
- Discussion
  - Phase diagram of hydrogen
  - Approximations, and their impact
- Concluding remarks

Background

Outline:

- Structure-prediction methods
- Predicted crystal structures of atomic hydrogen
- Tetragonal structures: diamond, β-Sn, Cs-IV

Structure-Prediction Methods

Structure-prediction methods are revolutionizing our understanding of condensed-phase systems, allowing us to:

- Reliably predict the ground- and metastable-state structure(s) of a system, with little to no *a priori* information
- Simulate challenging experimental conditions

Such methods can also be used to design novel materials:

- Study promising chemical compositions
- Use evolutionary techniques to optimize the fitness of a structure

Various algorithms exist:

- *Ab initio* random structure searching[1]
- Evolutionary algorithms[2]

[1] C. J. Pickard and R. J. Needs, *Phys. Rev. Lett.* **97**, 045504 (2006)

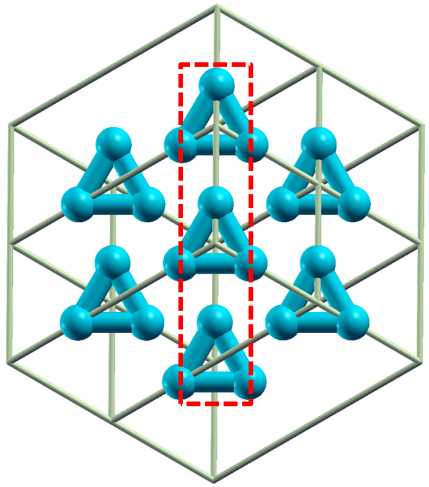
[2] A. R. Oganov and C. W. Glass, *J. Chem. Phys.* **124**, 244704 (2006)

Structure-Prediction: Successes and Novel Predictions

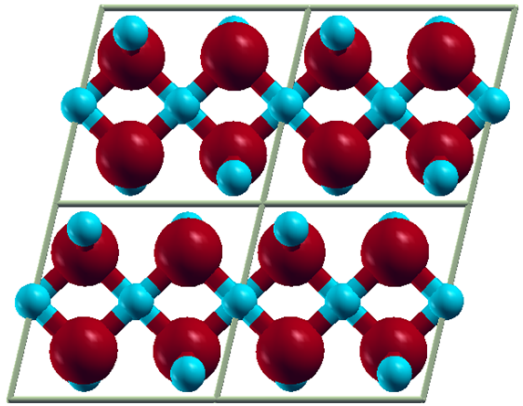
The reliability of such methods is well-summarized by the opening session at the 2012 High-pressure Gordon Research Conference[1]: *Structure Prediction at Extreme Conditions: Are Experiments Still Necessary?*

Successes and novel predictions:

- Triatomic and superconducting phases of H[2,3]
- A metal–semiconductor–metal transition in Li[4]
- A dense insulating phase of Na[5]
- A metallic phase of water-ice[6]



Triatomic H

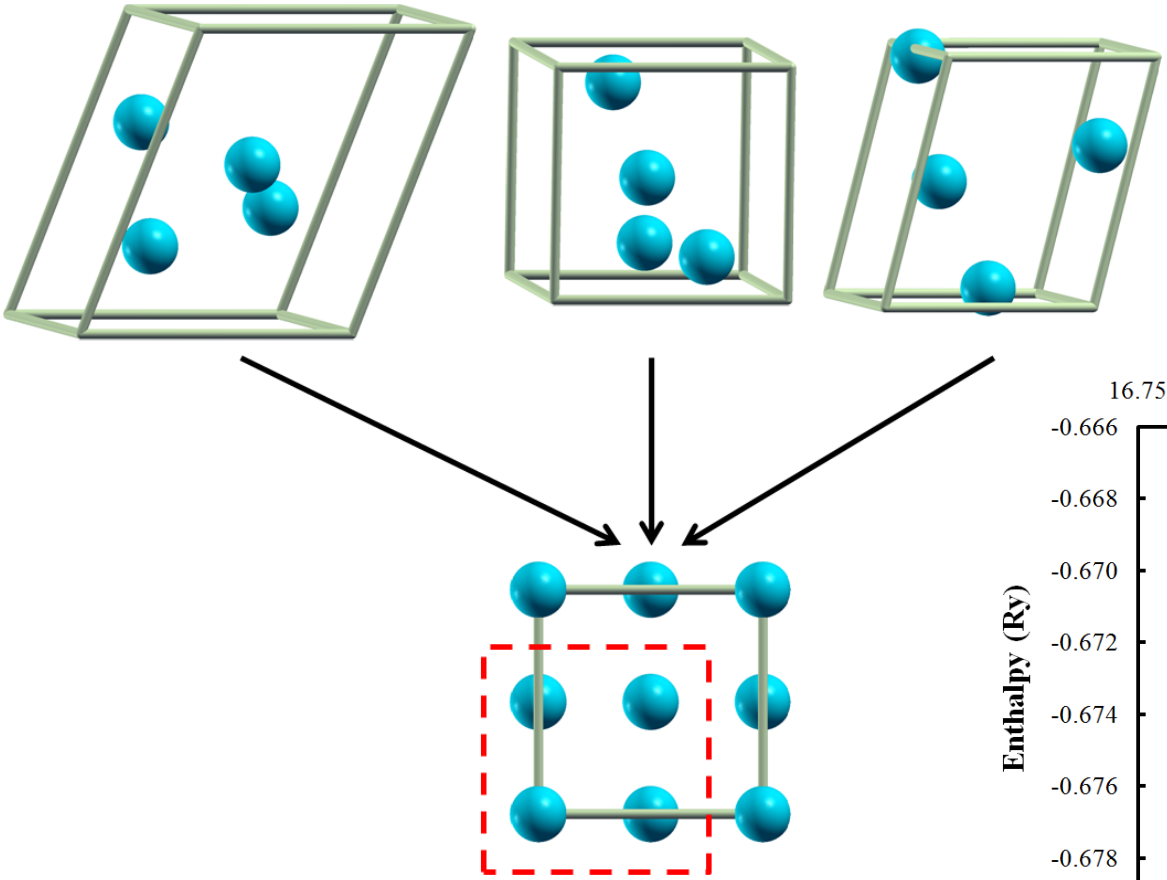


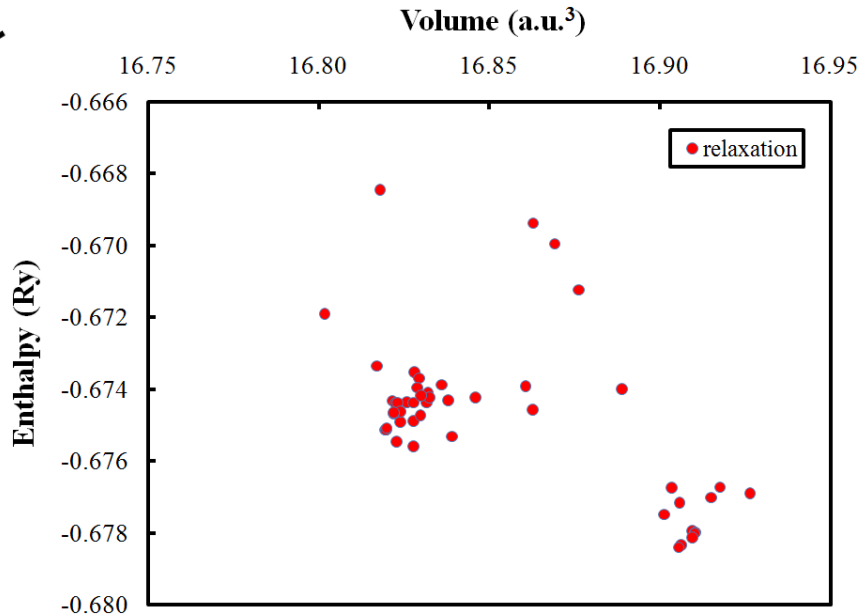
Metallic water-ice

[1] http://www.grc.org/programs.aspx?year=2012&program=highpress
[2] J. M. McMahon and D. M. Ceperley, *Phys. Rev. Lett.* **106**, 165302 (2011)
[3] J. M. McMahon and D. M. Ceperley, *Phys. Rev. B* **84**, 144515 (2011)
[4] M. Marqués *et al.*, *Phys. Rev. Lett.* **106**, 095502 (2011)
[5] Y. Ma *et al.*, *Nature* **458**, 182 (2009)
[5] J. M. McMahon, *Phys. Rev. B* **84**, 220104(R) (2011)

Ab Initio Random Structure Searching

Relax a number of random configurations at constant pressure, and pick out the lowest enthalpy ($H = U + pV$) one(s):

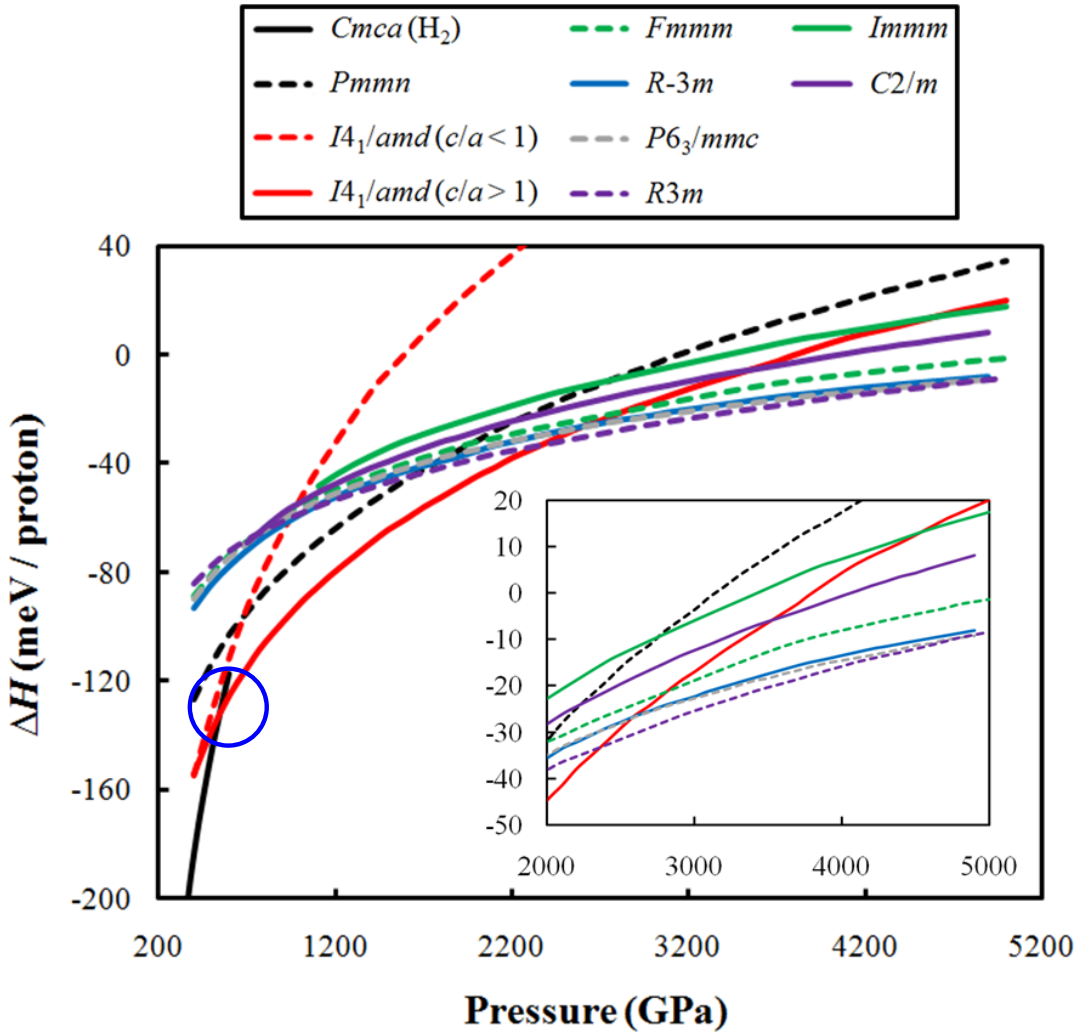




C. J. Pickard and R. J. Needs, *Phys. Rev. Lett.* **97**, 045504 (2006)

Crystal Structures of Atomic Hydrogen

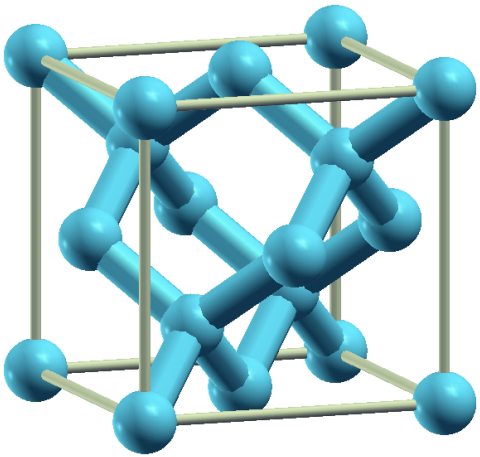
We have applied structure prediction to the atomic phase of hydrogen, finding a number of structures:



J. M. McMahon and D. M. Ceperley, *Phys. Rev. Lett.* **106**, 165302 (2011)

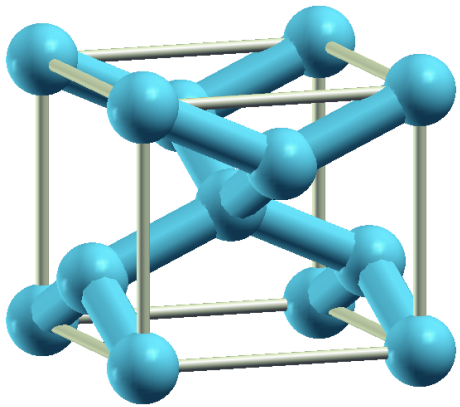
Tetragonal Structures of Atomic Hydrogen

The tetragonal structures Fd-$3m$ and $I4_1/amd$ are all comparatively stable near molecular dissociation, differing only in their lattice parameter c/a:



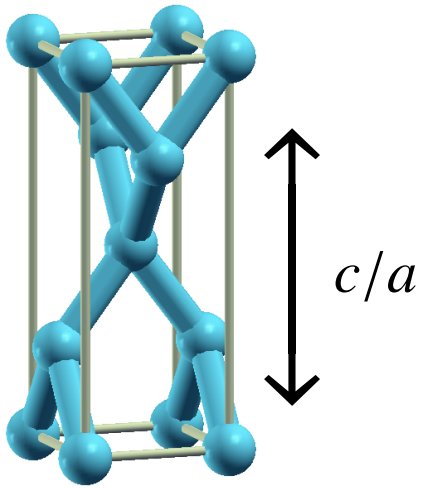
Diamond

Fd-$3m$
($c/a = 1.414$)



β-Sn

$I4_1/amd$
($c/a \sim 0.55 < 1$)



Cs-IV

$I4_1/amd$
($c/a \sim 3.73 > 1$)

J. M. McMahon and D. M. Ceperley, *Phys. Rev. Lett.* **106**, 165302 (2011)
V. Natoli, R. M. Martin, and D. M. Ceperley, *Phys. Rev. Lett.* **70**, 1952 (1993)

Technical Details

Outline:

- Solid and liquid phases
- Thermodynamic conditions
- Electronic structure details
- Nuclear quantum effects

Solid and Liquid Phases, and Thermodynamic Conditions

Solid phases:

- Diamond: 216 atoms ($3 \times 3 \times 3$ supercell)
- β-Sn: 256 atoms ($4 \times 4 \times 4$ supercell)
- Cs-IV: 288 atoms ($6 \times 6 \times 2$ supercell)

Liquid phase:

- Melted bcc lattice: 250 atoms ($5 \times 5 \times 5$ supercell)

Thermodynamic conditions:

- Pressures from $\sim$300–800 GPa
- Temperatures from 100–1000 K

Electronic-Structure Details

- Quantum ESPRESSO[1] density-functional theory (DFT) code
- Perdew–Burke–Ernzerhof (PBE)[2] exchange and correlation functional[3]
- Norm-conserving pseudopotential with $r_c = 0.65$ a.u.
- 70 Ry cutoff (ensures an accuracy in energy to $\sim$3.5 mRy/proton and negligible error in the forces)
- 2^3 shifted **k**-points (gives a similar convergence in energy and forces)
- Fermi–Dirac smearing
- Timestep of 8 a.u.
- 2000 – 5000 timesteps

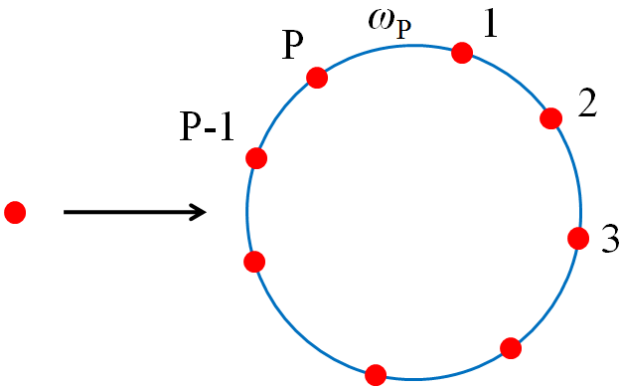
[1] P. Giannozzi *et al.*, *J. Phys. Condens. Matter* **21**, 395502 (2009); http://www.quantum-espresso.org
[2] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996)
[3] R. C. Clay, III, J. McMinis, J. M. McMahon, C. Pierleoni, D. M. Ceperley, and M. A. Morales, *Phys. Rev. B* **89**, 184106 (2014)

Nuclear Quantum Effects

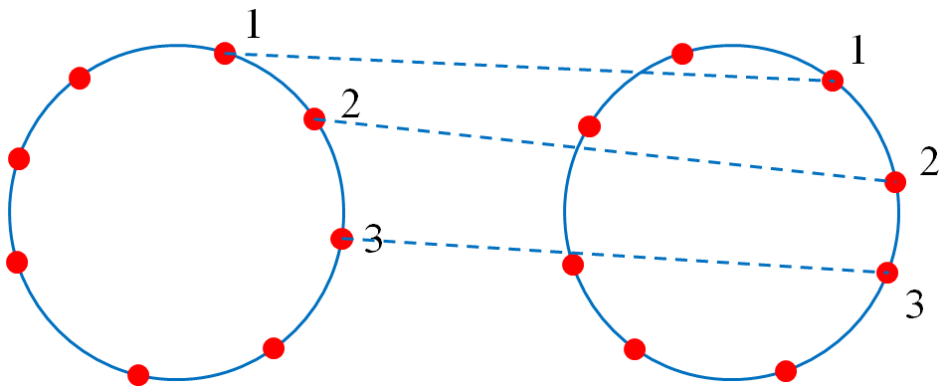
Nuclear quantum effects are essential to consider in hydrogen, which we can treat using path integrals.

The path integral for a N-particle system is isomorphic to an extended system consisting of N ring-polymers each with P classical particles (as $P \to \infty$) with the Hamiltonian:

$$H = \sum_{s=1}^{P} \left\{ \sum_{I=1}^{N} \left[\frac{\left(\mathbf{p}_I^s\right)^2}{2m_I'} + \frac{1}{2} m_I \omega_{\mathrm{P}}^2 \left(\mathbf{R}_I^s - \mathbf{R}_I^{s+1}\right)^2 \right] + \frac{1}{\mathrm{P}} V\left(\mathbf{R}_1^s, ..., \mathbf{R}_N^s\right) \right\}$$



Single Particle



Two Particles

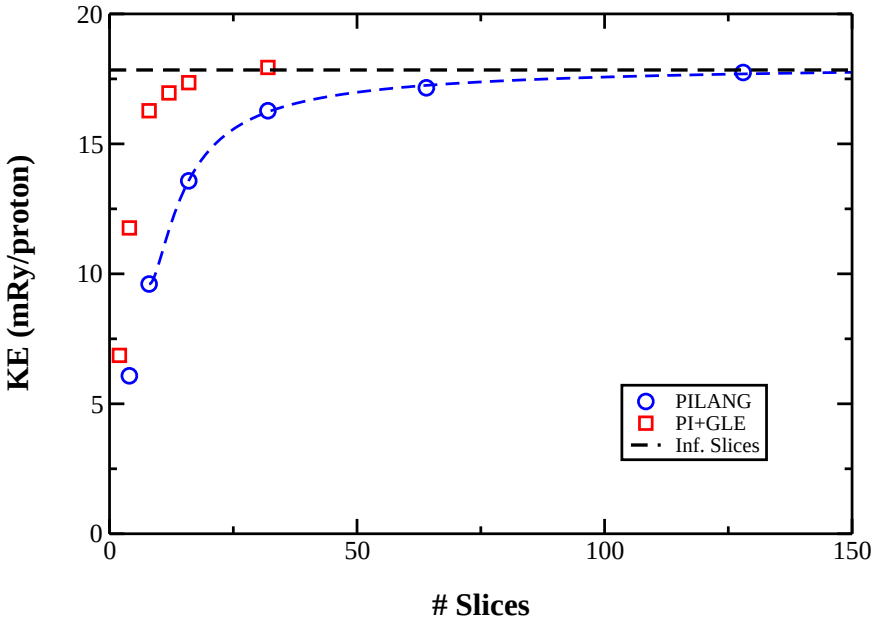
D. Chandler and P. G. Wolynes, *J. Chem. Phys.* **74**, 4078 (1981)

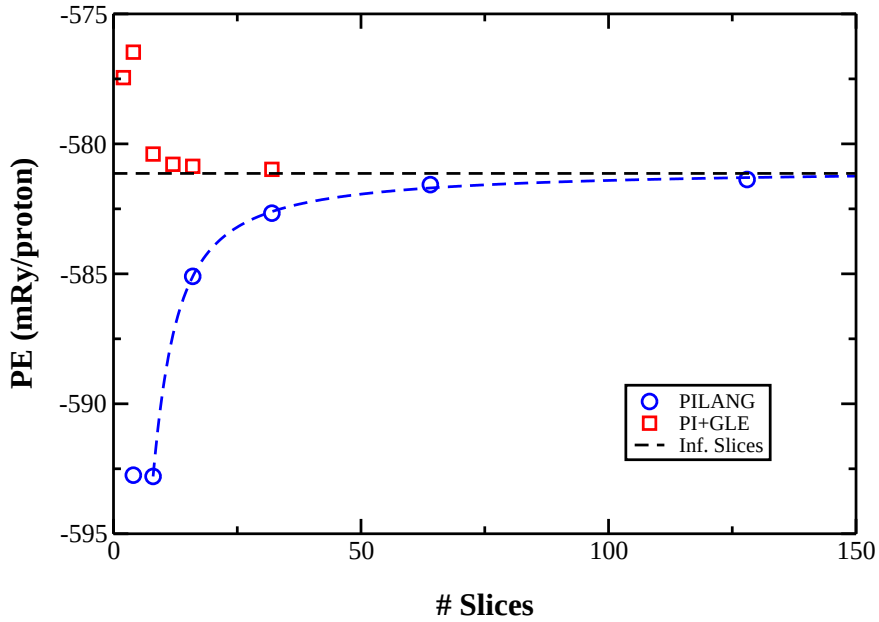
Accelerated Path-Integral Molecular Dynamics

Often many replicas are needed to converge nuclear quantum effects.

Stochastic, frequency-dependent thermostats have recently been proposed[1] that enforce quantum mechanical position and momentum distributions, accelerating convergence with P.

Example of P-convergence for 250 bcc hydrogen atoms at 3 TPa and 200 K[2]:





[1] M. Ceriotti, D. E. Manolopoulos, and M. Parrinello, *J. Chem. Phys.* **134**, 084104 (2011)

[2] J. M. McMahon, M. A. Morales, R. C. Clay III, C. Pierleoni, and D. M. Ceperley, *Submitted* (2016)

Results

Outline:

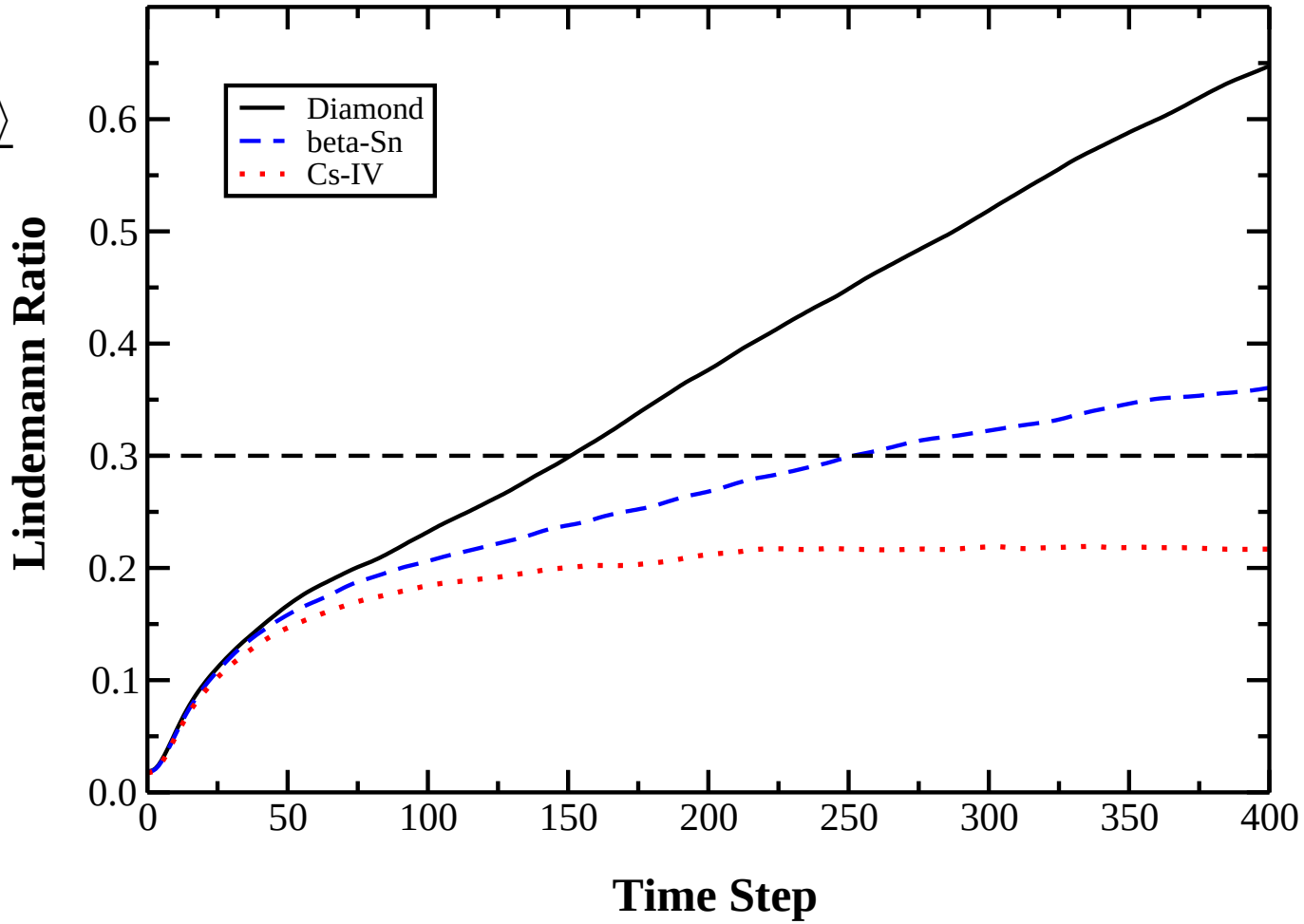
- Diffusion calculations (estimates)
- Free-energy calculations (rigorous)

Diffusion Calculations (Near Molecular Dissociation)

The simplest way to *estimate* the finite-T stability of a solid is to heat it and wait for it to melt – e.g., by monitoring $\langle(\mathbf{r}-\mathbf{r}_0)^2\rangle$:

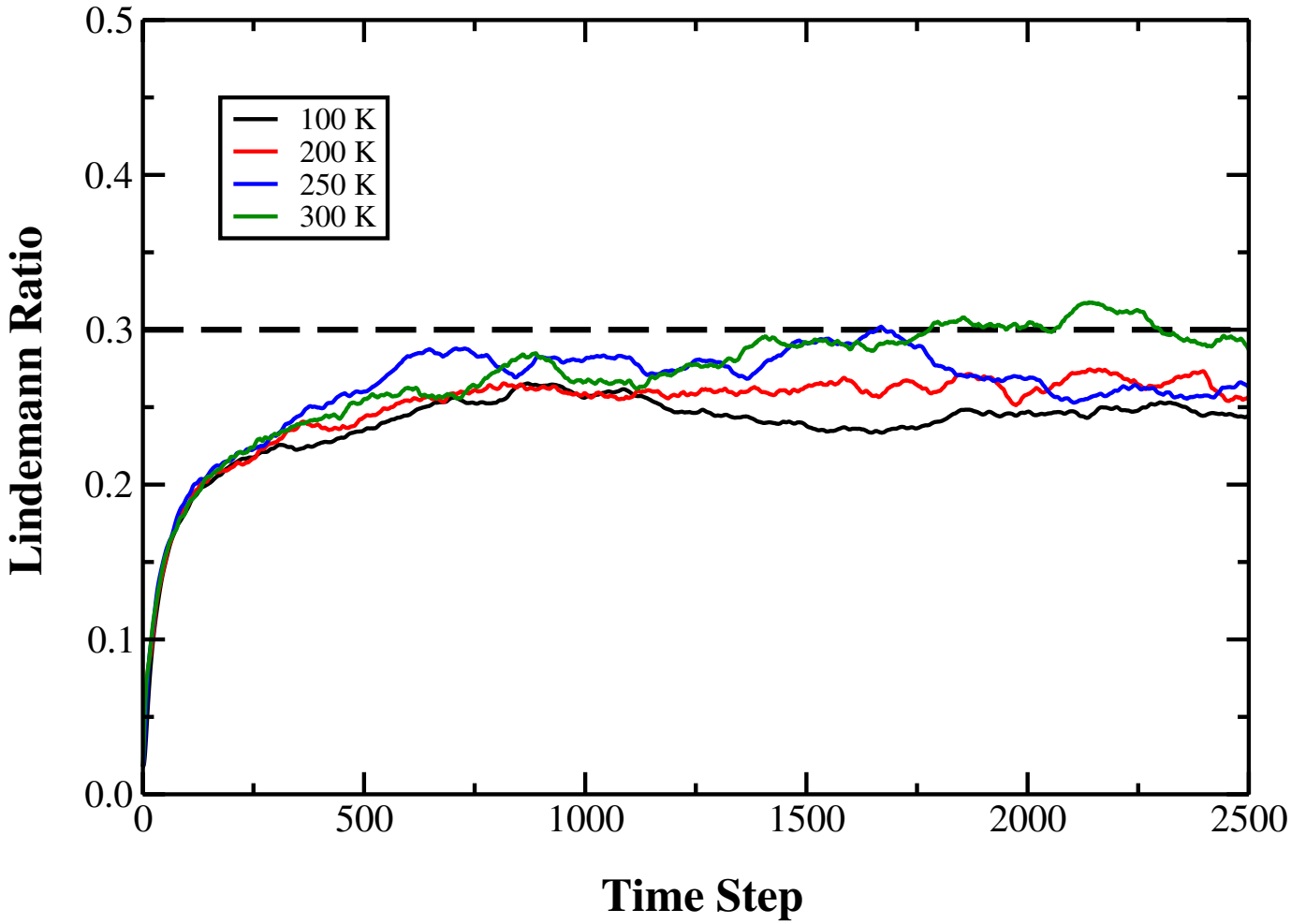
$$\mathrm{D} = \frac{1}{6}\lim_{t\to\infty}\frac{\partial\langle[\mathbf{r}(t)-\mathbf{r}_0]^2\rangle}{\partial t}$$

$$\gamma = \frac{[\langle(\mathbf{r}-\mathbf{r}_0)^2\rangle]^{1/2}}{d}$$



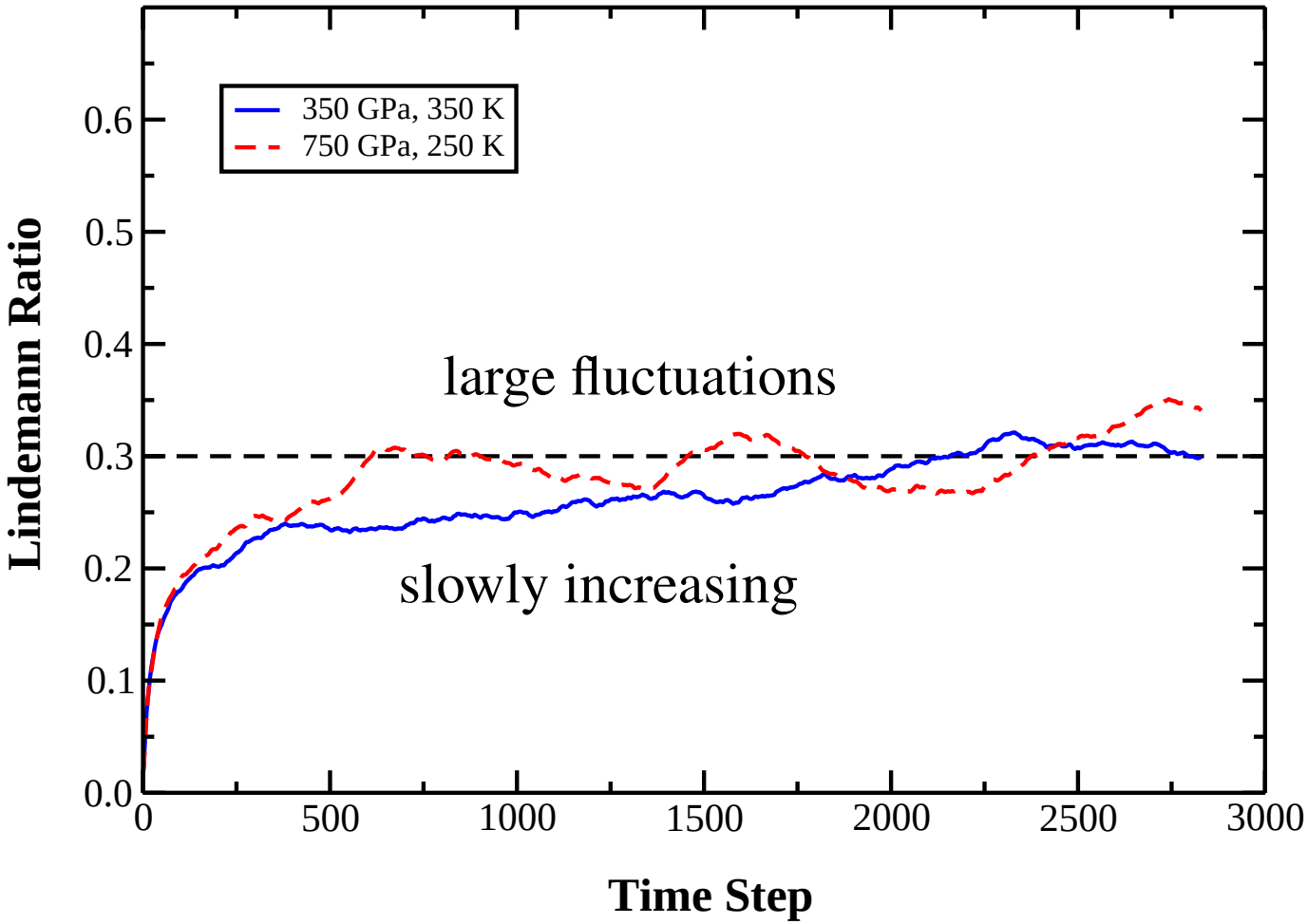
Cs-IV (Near Molecular Dissociation)

Dynamical melting calculations suggest Cs-IV is stable to $T \approx 250$ K:



Does Cs-IV Melt?

First-order phase transitions exhibit significant hysteresis. Thus, the solid may be stable well above the coexistence point, melting slowly, if at all:



Free-energy Calculations: Gibbs Free Energy

We can get a more accurate assessment of the solid/liquid coexistence by using **the second law of thermodynamics**.

For a constant particle number (N), the thermodynamic potential with T and p as natural variables is the Gibbs free energy:

$$G = H - TS$$

with the fundamental thermodynamic relation:

$$dG = -SdT + Vdp$$

Unfortunately, we can't get thermal quantities (e.g., S) *directly*.

Thermodynamic Integration

Although, if we were to know the free energy at any point in phase space, we could calculate the (Helmholtz) free-energy difference at any other point using **thermodynamic integration**:

$$F\left(\xi_1, \Omega\right) - F\left(\xi_1, \Omega\right) = \int_{\xi_0}^{\xi_1} \left(\frac{\partial F(\xi)}{\partial \xi} \right)_{\Omega} d\xi$$

The simplest application is by considering variations in the natural variables of the ensemble. For example, in the canonical ensemble:

$$\frac{F(N, V, T_1)}{T_1} - \frac{F(N, V, T_0)}{T_0} = -\int_{T_0}^{T_1} \frac{U(N, V, T)}{T^2}\, dT$$

$$F(N, V_1, T) - F(N, V_0, T) = \int_{V_0}^{V_1} p(N, V, T)\, dV$$

D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications* (2002)

Coupling-Constant Integration

To obtain an absolute free-energy, one must reach a limiting state where it is known exactly (e.g., $V \to \infty$) — *computationally expensive!*

A variant of thermodynamic integration allows us to calculate the free-energy difference described by different Hamiltonians. For two systems with potentials V_0 and V_1, we can define a linear combination $V(\lambda) = \lambda V_1 + (1 - \lambda)V_0$, and in the canonical ensemble we have:

$$\begin{aligned} F_1(N,V,T) - F_0(N,V,T) &= \int_0^1 \frac{\partial F(\lambda)}{\partial \lambda} d\lambda \\ &= \int_0^1 \langle V_1 - V_0 \rangle_{T,V,N,\lambda} \, d\lambda, \end{aligned}$$

D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications* (2002)

Reference States

$$
\begin{aligned}
F_1(N,V,T) - F_0(N,V,T) &= \int_0^1 \frac{\partial F(\lambda)}{\partial \lambda} d\lambda \\
&= \int_0^1 \langle V_1 - V_0 \rangle_{T,V,N,\lambda} \, d\lambda,
\end{aligned}
$$

For computational efficiency, we used a multistep approach:

For the **liquid**: our reference state is non-interacting particles:

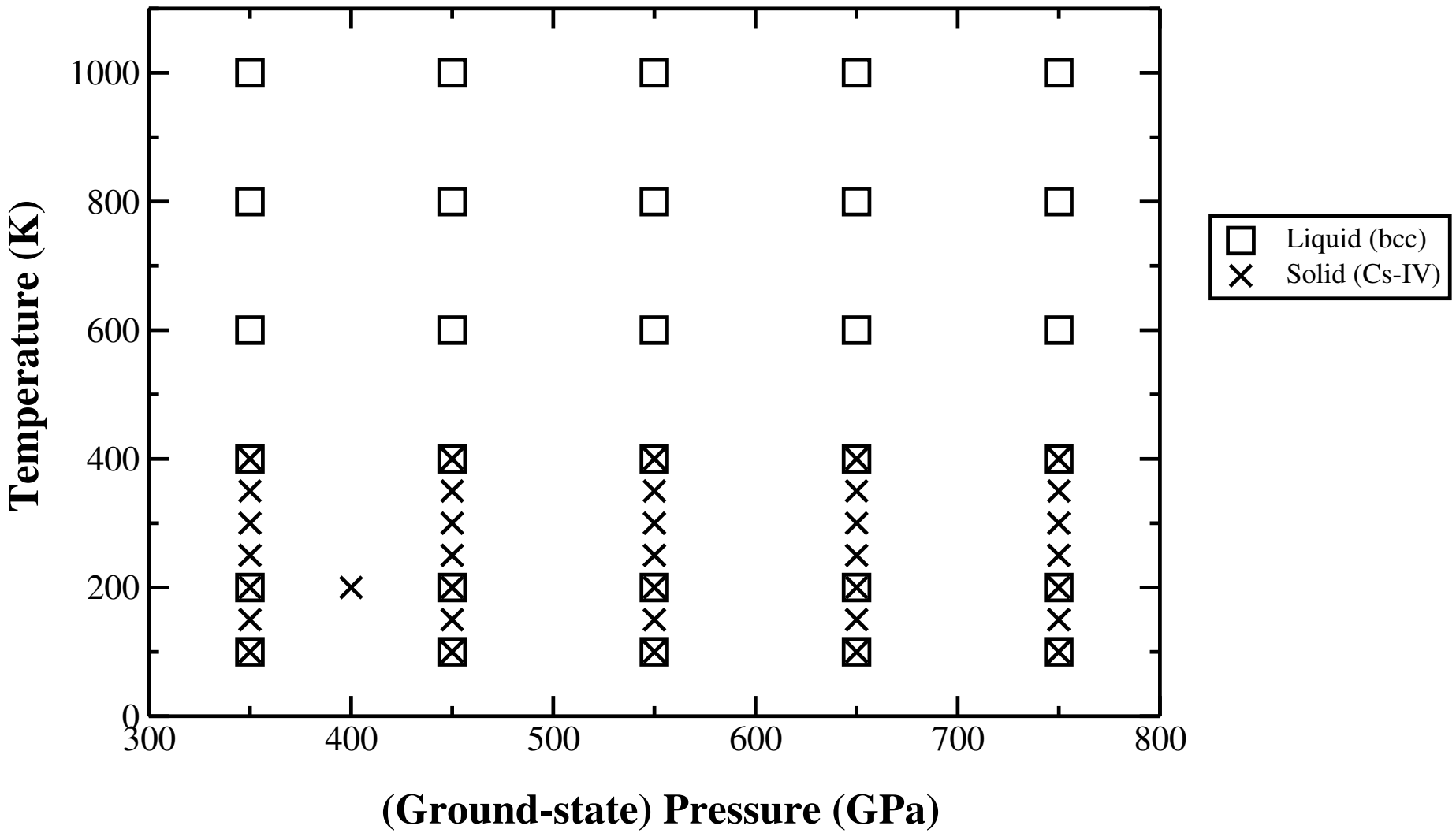
$$V^{\text{PIMD (DFT)}} \rightarrow V_{ij}^{\text{q}} \rightarrow V_{ij}^{\text{cl}} \rightarrow 0$$

For the **solid**: our reference state is a harmonic crystal:

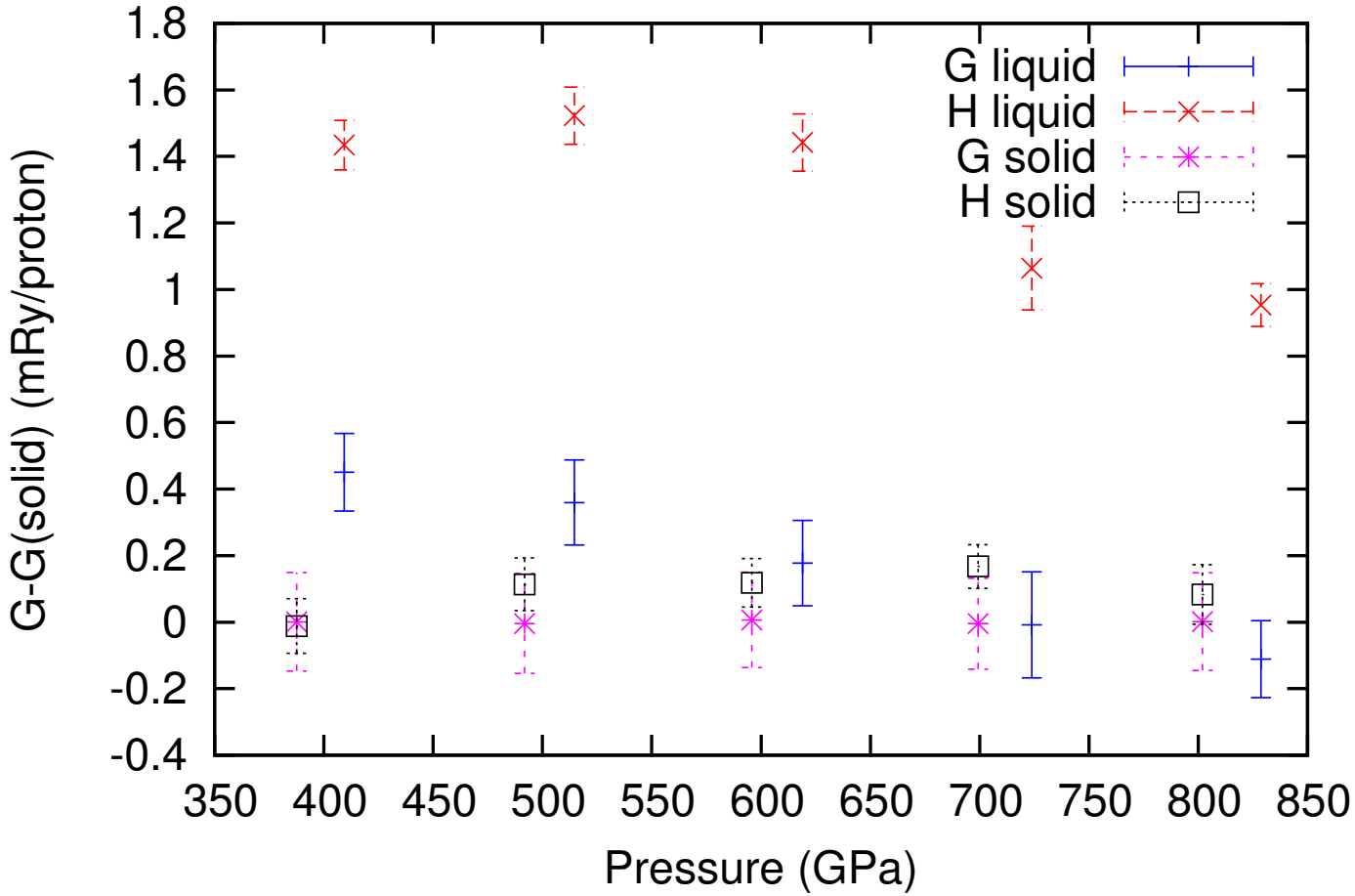
$$V^{\text{PIMD (DFT)}} \rightarrow V_{ij}^{\text{q}} \rightarrow V_{ij}^{\text{cl}} \rightarrow V_{ij}^{\text{cl}} + \tfrac{1}{2} k_i \left(\mathbf{r}_i - \mathbf{r}_{0,i}\right)^2 \rightarrow \tfrac{1}{2} k_i \left(\mathbf{r}_i - \mathbf{r}_{0,i}\right)^2$$

D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications* (2002)

(p, T)-points for EOSs



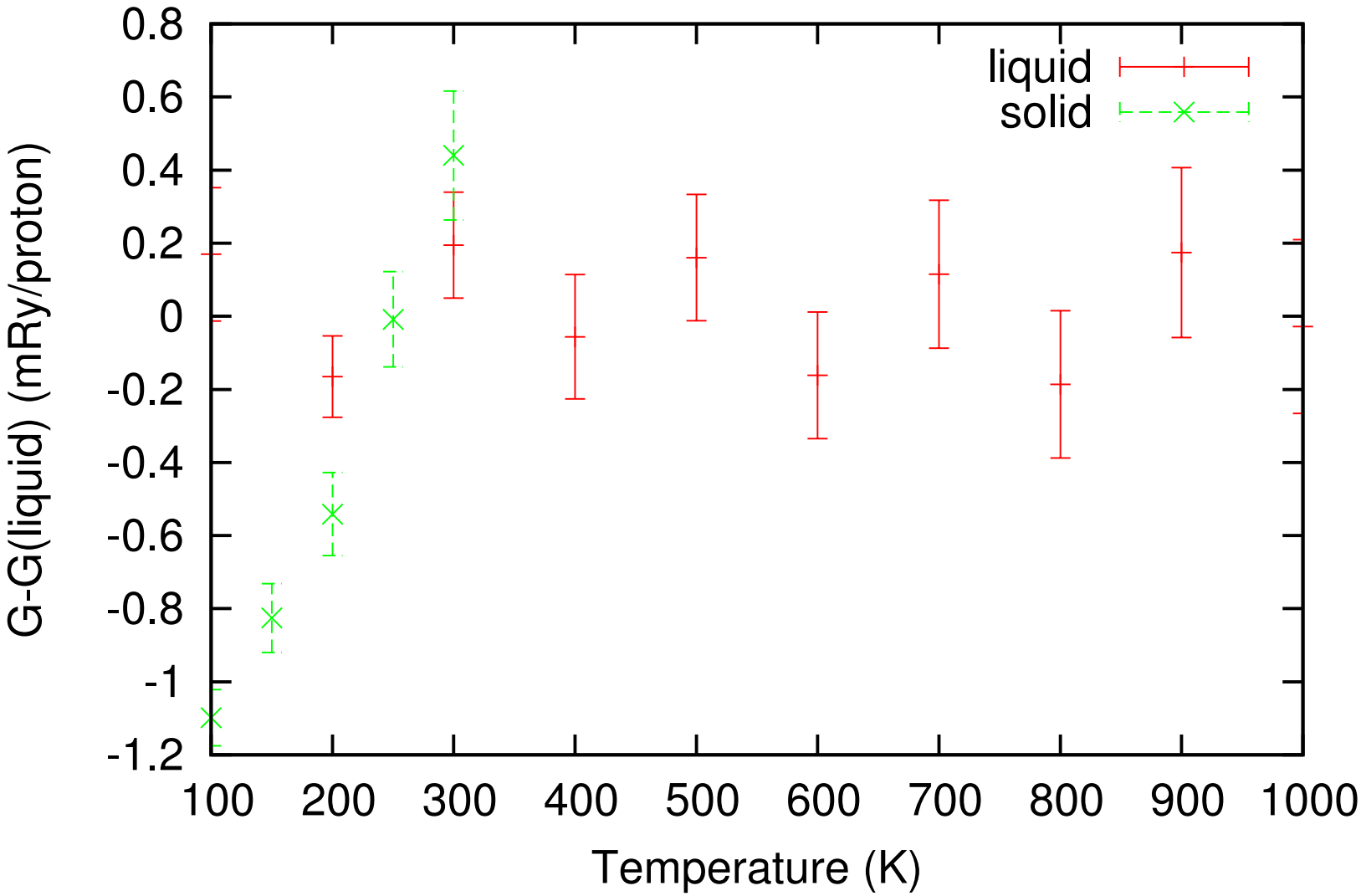
Free Energies Near Molecular Dissociation



Solid hydrogen is stable at low temperatures!

Entropic stabilization of the liquid is important.

Free Energies Near Molecular Dissociation

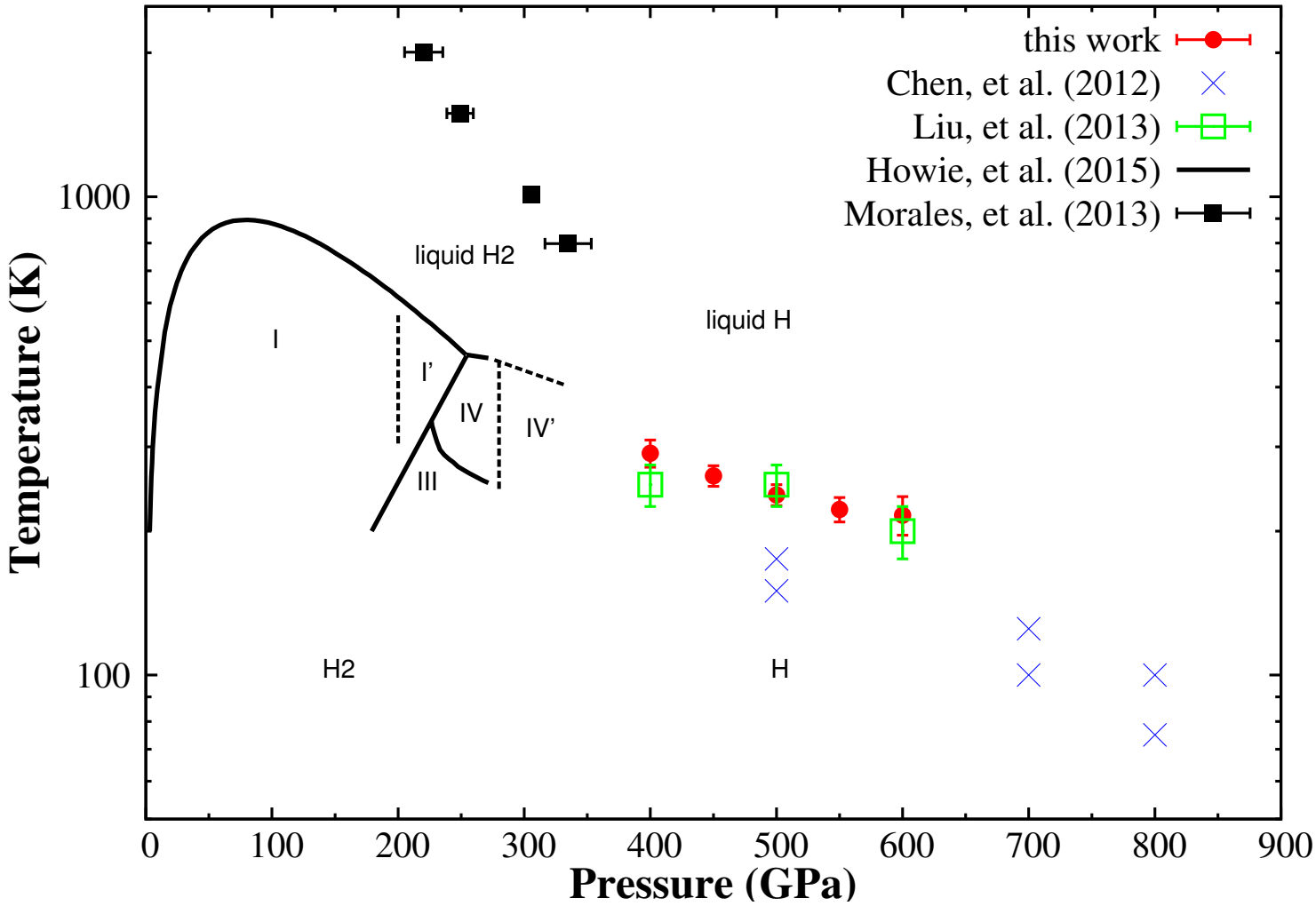


Discussion

Outline:

- Phase diagram of hydrogen
- Superconductivity in atomic hydrogen
- Approximations, and their impact

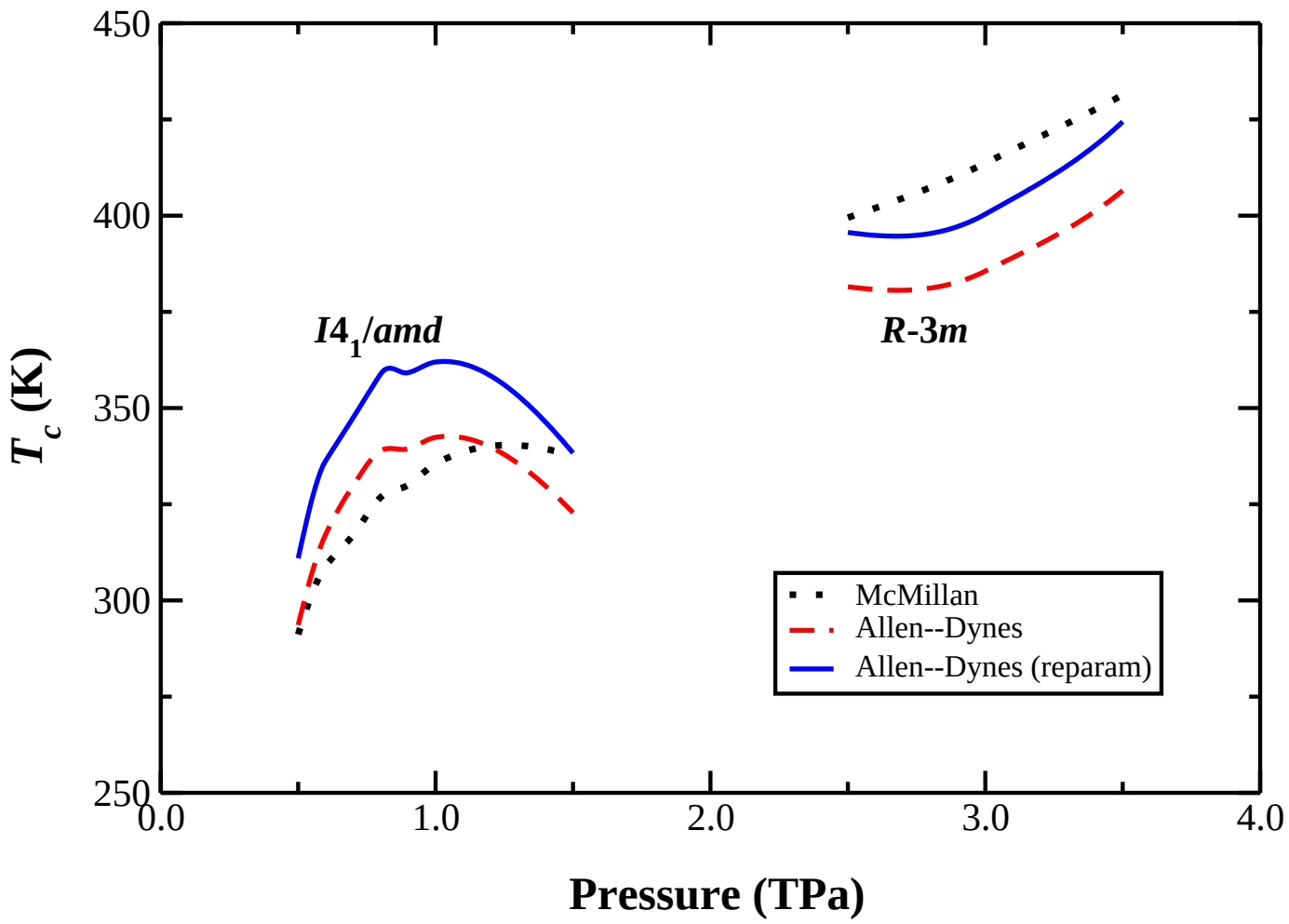
Phase Diagram of Hydrogen



J. M. McMahon, M. A. Morales, R. C. Clay III, C. Pierleoni, and D. M. Ceperley, *Submitted* (2016)

M. A. Morales, J. M. McMahon, C. Pierleoni, and D. M. Ceperley, *Phys. Rev. Lett.* **110**, 065702 (2013)

Solid Hydrogen: Only a Superconductor?



J. M. McMahon and D. M. Ceperley, *Phys. Rev. B* **84**, 144515 (2011); *ibid.* **85**, 219902(E) (2012)

N. W. Ashcroft, *Phys. Rev. Lett.* **21**, 1748 (1968)

M. Borinaga, I. Errea, M. Calandra, F. Mauri, and A. Bergara, arXiv:1602.06877 (2016)

Approximations

Most significant approximations of prior calculations were removed.

Remaining approximations:

- Crystal structures:
  - Assumed from structure-searching calculations ...
  - ... *but*: any more stable structure will have a lower free energy (by definition), and thus a higher melting temperature
- Quantum statistics:
  - Protons are fermions, yet were treated as distinguishable particles ...
  - ... *but*: this should also increase the melting temperature (by $\sim$200 K), since the free energy of the Fermi liquid is higher than that of distinguishable particles, while the energies of the solids are similar

Concluding Remarks

Summary and Open Questions

Summary

- Cs-IV is the only stable solid phase of hydrogen above molecular dissociation ...
- ... but the melting temperature is low, with a negative slope
- Atomic hydrogen likely exists entirely in a superconducting state

J. M. McMahon, M. A. Morales, R. C. Clay III, C. Pierleoni, and D. M. Ceperley, *Submitted* (2016)

Open Questions

- Does a 0 K liquid exist at TPa pressures?
- Are our predicted structures of atomic hydrogen correct?
- Are proton exchange and/or electron–phonon coupling important?
- How does the melting line connect to the molecular phase? ...
- ... and a lot more recent results in the molecular phase

Acknowledgments

- David M. Ceperley (University of Illinois at Urbana–Champaign)
- Members of the Ceperley research group
- Miguel A. Morales (Lawrence Livermore National Laboratory)
- Carlo Pierleoni (University of L'Aquila, Italy)

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Department of Physics & Astronomy