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

Jeffrey M. McMahon

Department of Physics & Astronomy

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Phase Diagram of Hydrogen

Outline

• Background
  ▶ Structure-prediction methods
  ▶ Predicted crystal structures of atomic hydrogen

• Technical details
  ▶ Solid and liquid phases
  ▶ Thermodynamic conditions
  ▶ Calculation details

• Results
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Background

Outline:

- Structure-prediction methods
- Predicted crystal structures of atomic hydrogen
- Tetragonal structures: diamond, $\beta$-Sn, Cs-IV
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$^2$

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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\(^6\)

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

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

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

Technical Details

Outline:

- Solid and liquid phases
- Thermodynamic conditions
- Electronic structure details
- Nuclear quantum effects
Solid phases:
- Diamond: 216 atoms (3 $\times$ 3 $\times$ 3 supercell)
- $\beta$-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\textsuperscript{1} density-functional theory (DFT) code
- Perdew–Burke–Ernzerhof (PBE)\textsuperscript{2} exchange and correlation functional\textsuperscript{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 \textbf{k}-points (gives a similar convergence in energy and forces)
- Fermi–Dirac smearing
- Timestep of 8 a.u.
- 2000 – 5000 timesteps

\textsuperscript{1} P. Giannozzi \textit{et al.}, \textit{J. Phys. Condens. Matter} 21, 395502 (2009); http://www.quantum-espresso.org
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:

$$H = \sum_{s=1}^{P} \left\{ \sum_{l=1}^{N} \left[ \frac{(p_s^l)^2}{2m_l'} + \frac{1}{2} m_l \omega_p^2 (R_s^l - R_{s+1}^l)^2 \right] + \frac{1}{P} V(R_1^s, \ldots, R_N^s) \right\}$$

Often many replicas are needed to converge nuclear quantum effects.

Stochastic, frequency-dependent thermostats have recently been proposed\textsuperscript{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\textsuperscript{2}:

\textsuperscript{1} M. Ceriotti, D. E. Manolopoulos, and M. Parrinello, \textit{J. Chem. Phys.} \textbf{134}, 084104 (2011)

Results

Outline:

- Diffusion calculations (estimates)
- Free-energy calculations (rigorous)
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 \( \langle (\mathbf{r} - \mathbf{r}_0)^2 \rangle \):

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

\[
\gamma = \frac{\langle (\mathbf{r} - \mathbf{r}_0)^2 \rangle^{1/2}}{d} 
\]
Dynamical melting calculations suggest Cs-IV is stable to $T \approx 250$ K:
First-order phase transitions exhibit significant hysteresis. Thus, the solid may be stable well above the coexistence point, melting slowly, if at all:

![Diagram showing Lindemann Ratio over time](image-url)
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.
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:

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

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

\[
\frac{F(N, V, T_1)}{T_1} - \frac{F(N, V, T_0)}{T_0} = -\int_{T_0}^{T_1} \frac{U(N, V, T)}{T^2} dT \\
F(N, V_1, T) - F(N, V_0, T) = \int_{V_0}^{V_1} p(N, V, T) \, dV
\]

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:

\[
F_1(N, V, T) - F_0(N, V, T) = \int_0^1 \frac{\partial F(\lambda)}{\partial \lambda} d\lambda
\]

\[
= \int_0^1 \langle V_1 - V_0 \rangle_{T,V,N,\lambda} d\lambda,
\]

Reference States

\[ F_1(N, V, T) - F_0(N, V, T) = \int_0^1 \frac{\partial F(\lambda)}{\partial \lambda} d\lambda = \int_0^1 \langle V_1 - V_0 \rangle_{T,V,N,\lambda} d\lambda, \]

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:

\[ V^{\text{PIMD (DFT)}} \rightarrow V_{ij}^{\text{q}} \rightarrow V_{ij}^{\text{cl}} \rightarrow V_{ij}^{\text{cl}} + \frac{1}{2} k_i (\mathbf{r}_i - \mathbf{r}_{0,i})^2 \rightarrow \frac{1}{2} k_i (\mathbf{r}_i - \mathbf{r}_{0,i})^2 \]

(p, T)-points for EOSs

![Diagram showing (p, T) points for EOSs with symbols for liquid (bcc) and solid (Cs-IV)]
Solid hydrogen is stable at low temperatures!

Entropic stabilization of the liquid is important.
Free Energies Near Molecular Dissociation

![Graph showing free energies near molecular dissociation](image-url)
Discussion

Outline:

• Phase diagram of hydrogen
• Superconductivity in atomic hydrogen
• Approximations, and their impact
Phase Diagram of Hydrogen

Solid Hydrogen: Only a Superconductor?

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

- 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

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

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