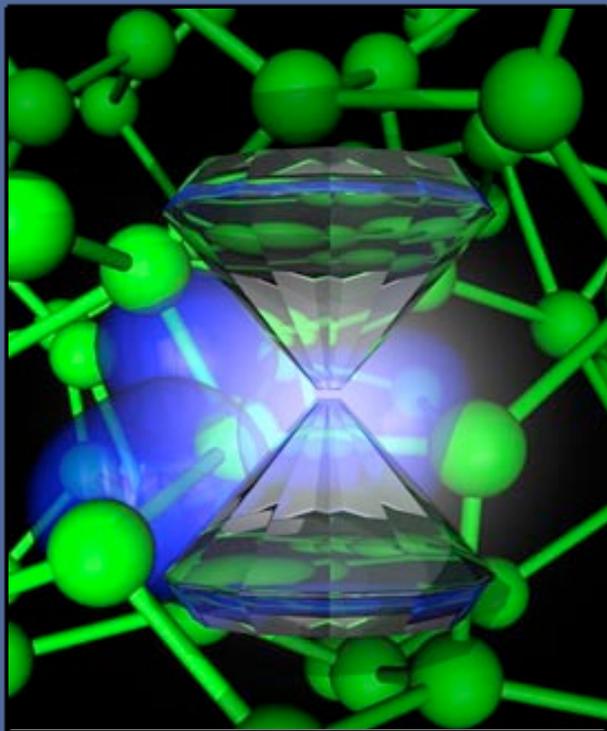


# Towards a multiphase equation of state for Carbon from first-principles



Physics and Advanced Technologies



ASC PI Meeting, Feb. 2007

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<sup>1</sup>Quantum Simulations Group  
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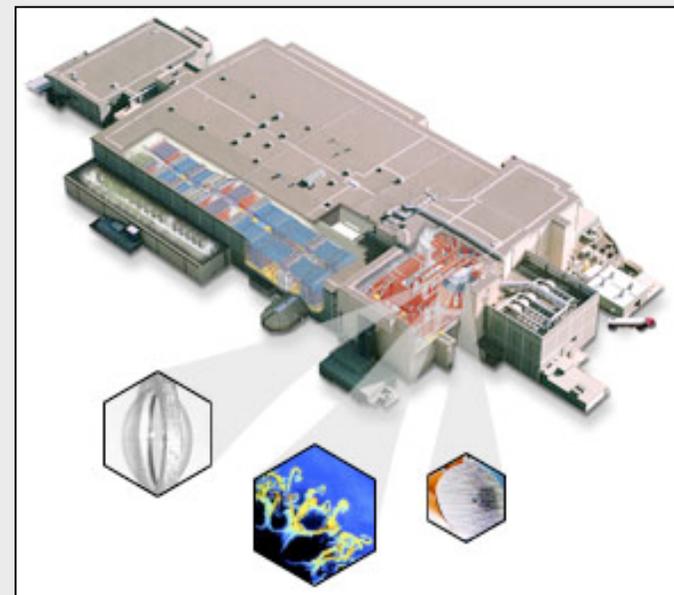
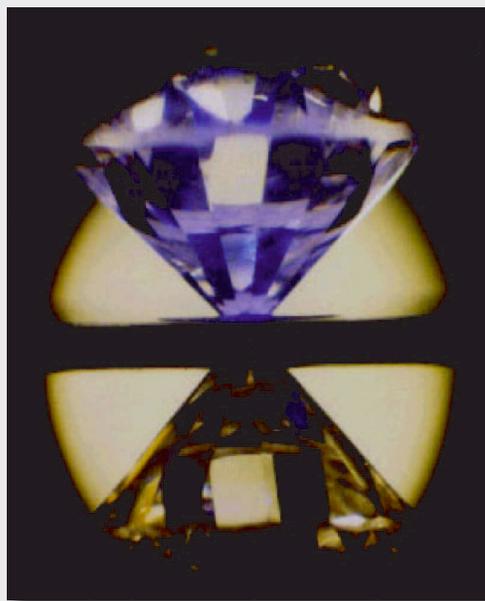
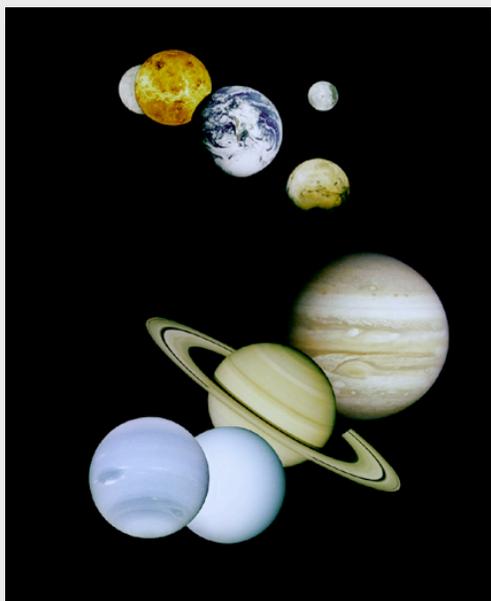
**Giulia Galli<sup>3</sup>, François Gygi<sup>4</sup>**  
<sup>3</sup>Department of Chemistry  
<sup>4</sup>Department of Applied Sciences  
UC Davis

<http://www.llnl.gov/qsg>

# Objective

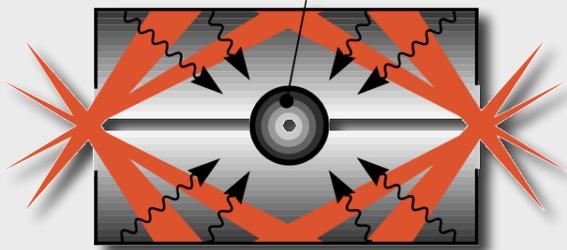
- **Accurate determination of the phase diagram of carbon**
  - **Solid-liquid phase boundaries -> melting lines**
  - **Relevant solid-solid phase boundaries**
- **Unified description**
  - **Entirely from first-principles based methods with reliable approximations and computational techniques**
- **Construction of a multiphase equation of state model**
  - **Broad range of validity**
  - **Appropriate for hydrodynamic simulations**
- **Comparison with experiments**
  - **Ongoing laser-shock experiments at Omega**

# Why study carbon at extreme conditions?

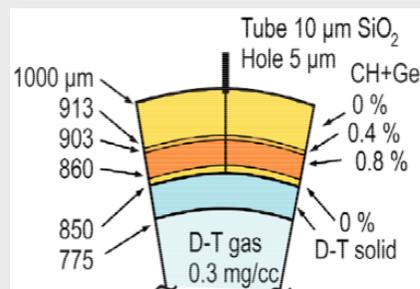
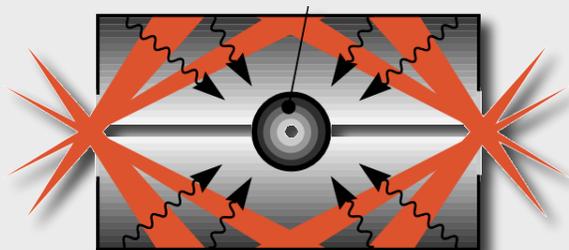


- **Astrophysics and planetary science**
- **High pressure research with diamond anvil cells**
- **ICF experiments at the National Ignition Facility**

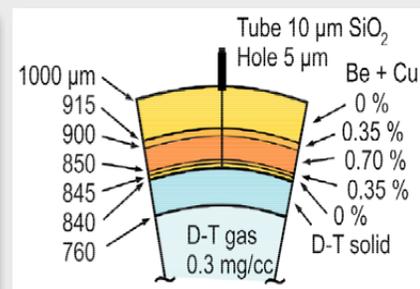
# Diamond capsules for ICF experiments on NIF



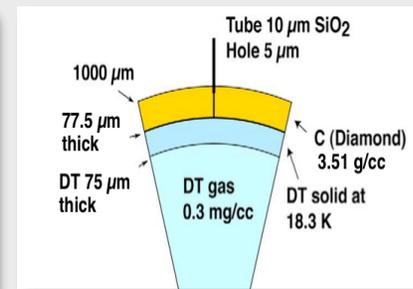
# Diamond capsules for ICF experiments on NIF



Plastics



Beryllium

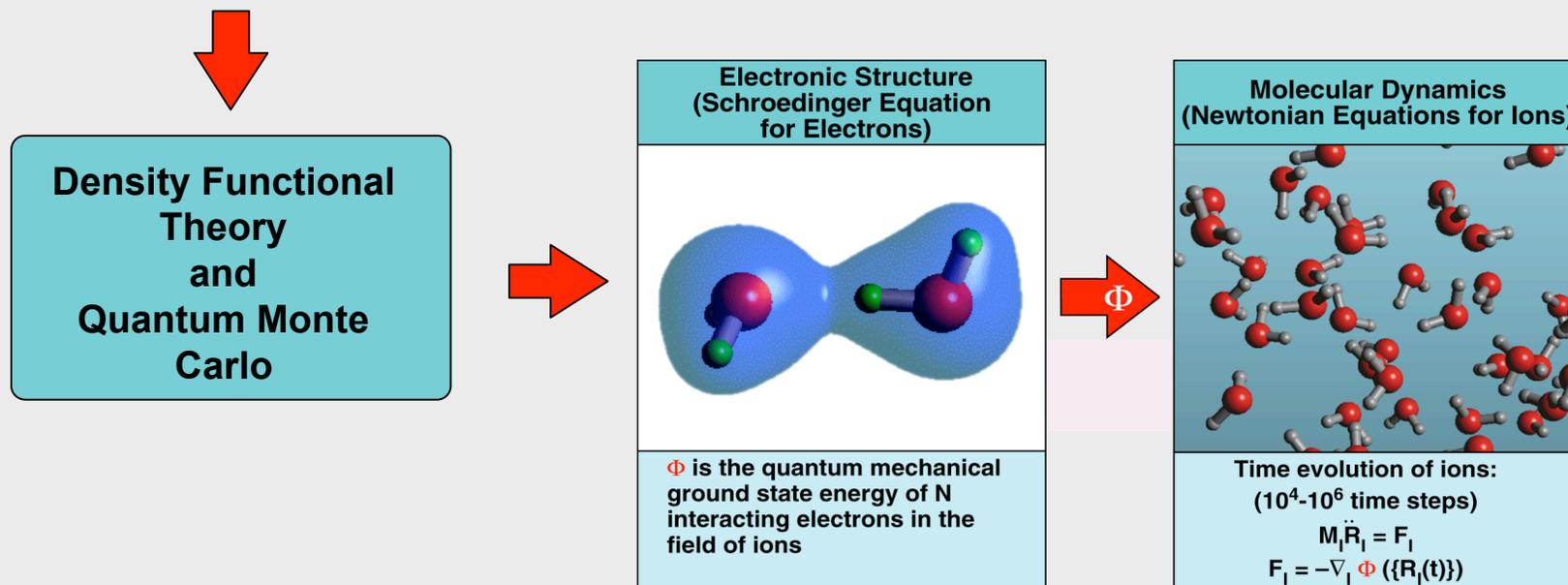


Carbon

- Ablator material candidates
  - Polyamide plastic
  - Beryllium
  - Carbon (diamond)
- Capsule design needs to be tested by hydrodynamic simulations, which require accurate (and smooth) multiphase equation of state tables

# Our main computational tool is first-principles molecular dynamics

$$i\hbar \frac{\partial}{\partial t} \Psi(\{r_i, s_i\}, \{R_j\}; t) = H \Psi(\{r_i, s_i\}, \{R_j\}; t)$$

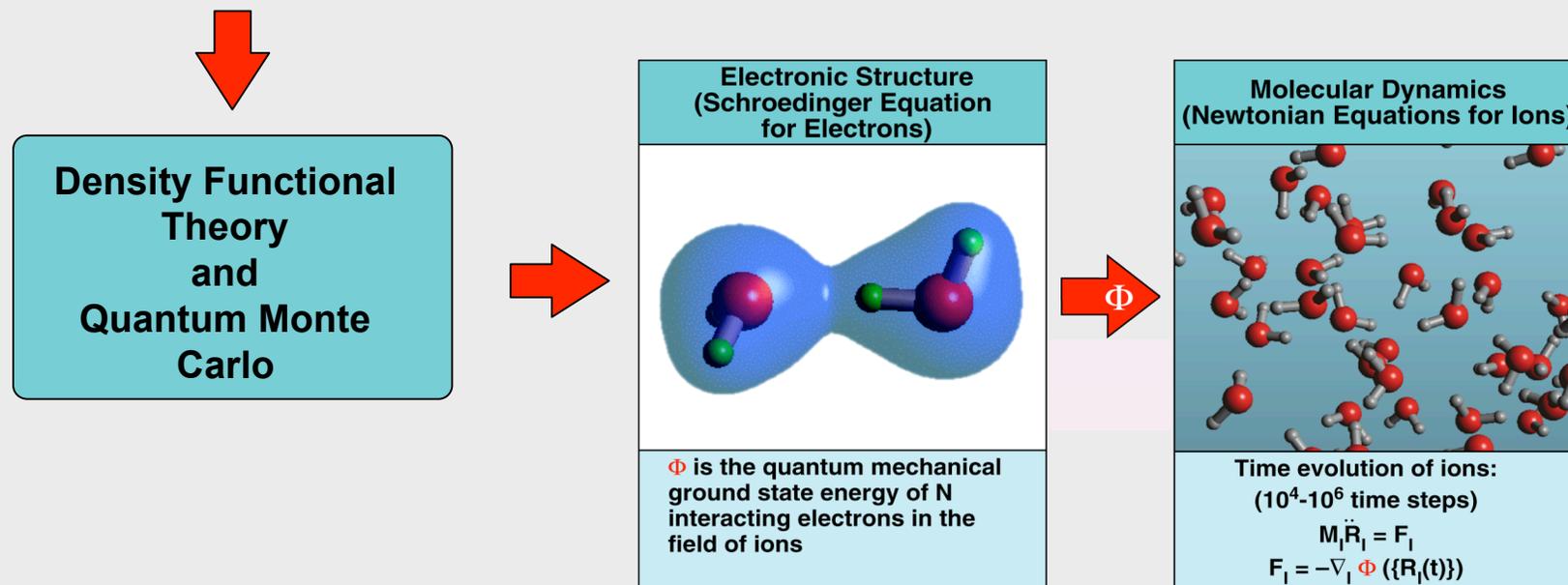


Predict the properties of low-Z materials under extreme conditions

- Structural and dynamical properties
- Phase boundaries
- Transport properties

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Predict the properties of low-Z materials under extreme conditions

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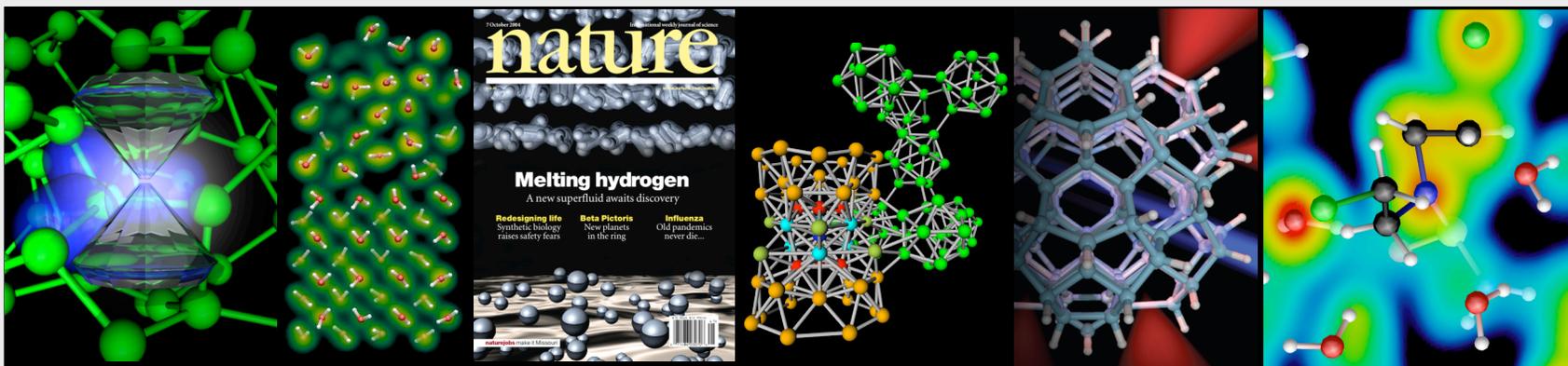
*"First-principles"* methods:

- Do not contain empirical parameters
- Do not require experimental input
- Are derived from the fundamental laws of quantum mechanics
- Involve approximations

# We have used the first-principles molecular dynamics code Qbox (F. Gygi and E. Draeger)

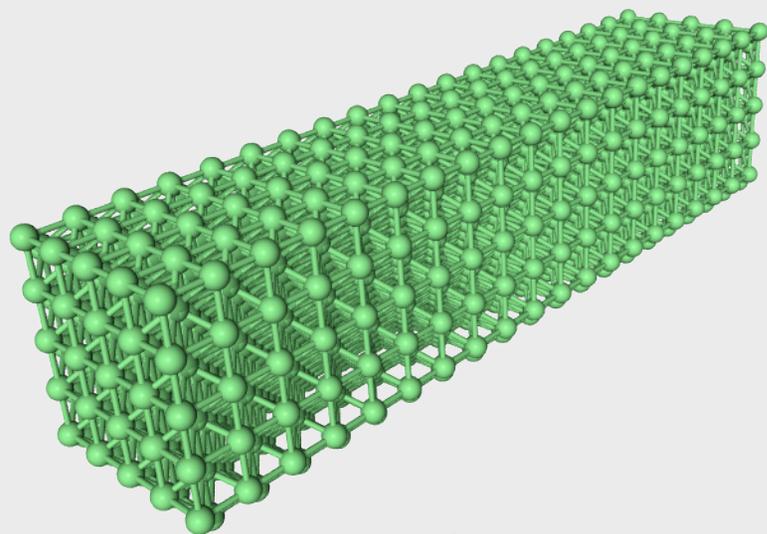
## Qbox, a C++/MPI implementation of first-principles molecular dynamics for massively parallel computers

- Complete rewrite (not a legacy code) specifically designed for massively parallel computers
- Parallelized over plane waves and electronic states
- Parallel linear algebra via ScaLAPACK and BLACS
- Fast fourier transforms via FFTW
- Norm conserving pseudopotentials
- Born-Oppenheimer or Car-Parrinello dynamics

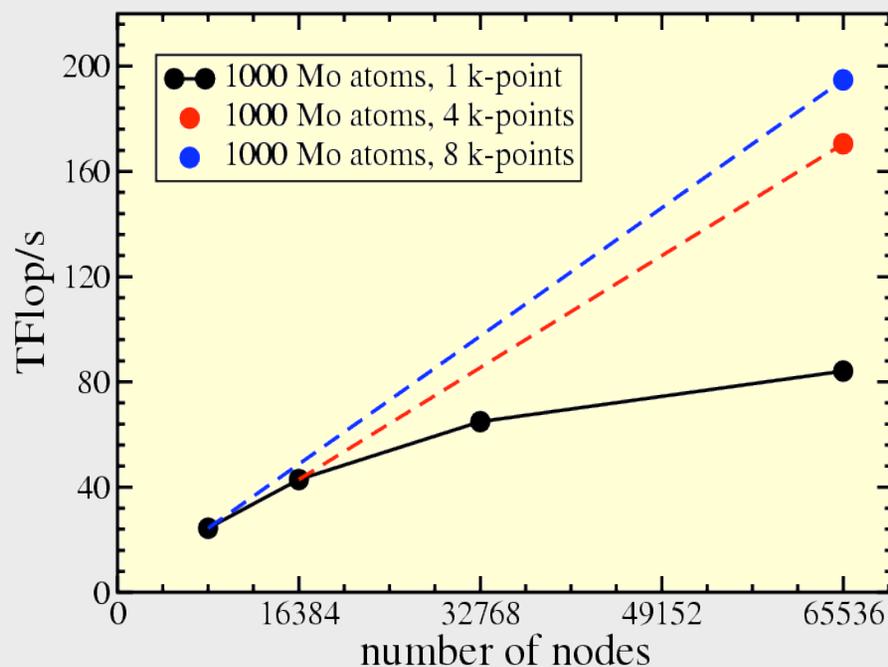


# Qbox has been successfully ported to all of the Labs parallel computing platforms, including BG/L

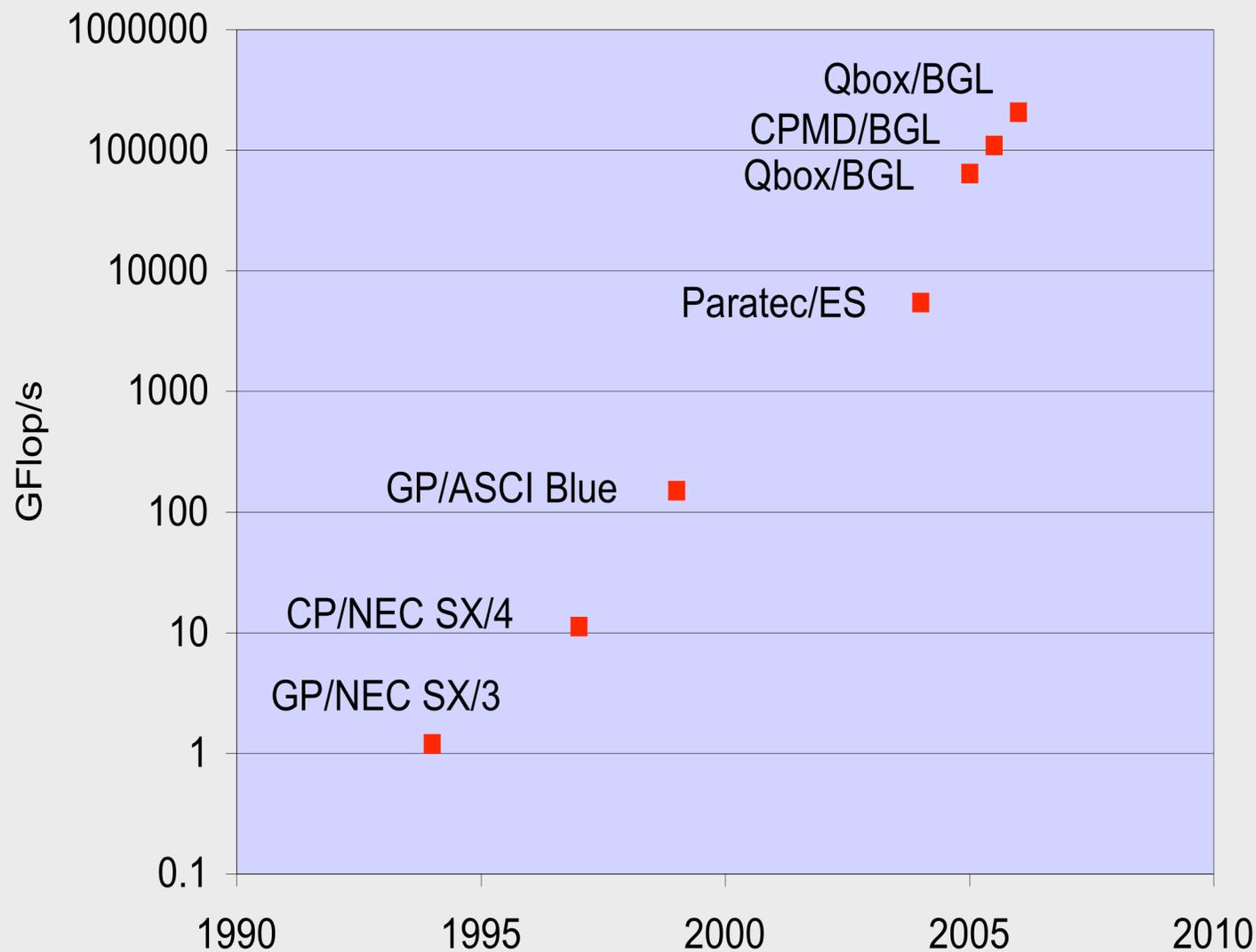
- **Test problem: 1000 molybdenum atoms**
- **12 valence electrons/atom: 12,000 electrons**
- **112 Ryd. cutoff: 33 million plane waves**
- **Norm conserving nonlocal pseudopotential with 32 semilocal projectors/atom**
- **Recent implementation of k-point sampling**



**2006 Gordon Bell Prize**



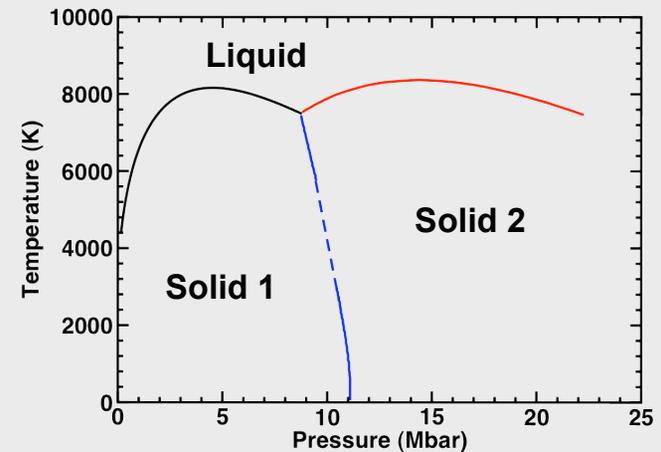
# History of first-principles MD performance



**The performance of first-principles MD codes has doubled every ~8 months**

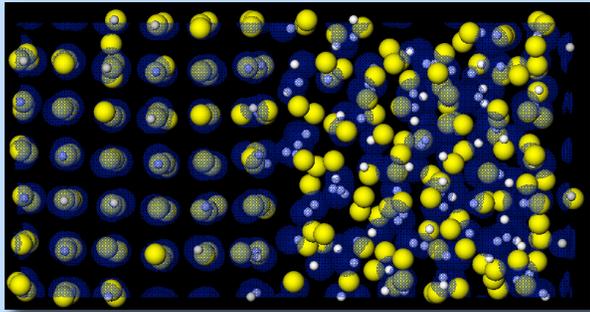
# The determination of phase boundaries

- **Single-phase “heat-until-it-melts” approaches are not appropriate for locating equilibrium phase boundaries**
  - **Superheating/cooling**
- **Single-phase free-energy matching**
  - + **Precise transition**
  - + **Good for low-T solid-solid phase boundaries**
  - **Difficult for solid-liquid phase boundaries**
- **Two-phase coexistence simulations**
  - + **Computationally efficient**
  - + **Good for solid-liquid phase boundaries**
  - **Not applicable for solid-solid phase boundaries**



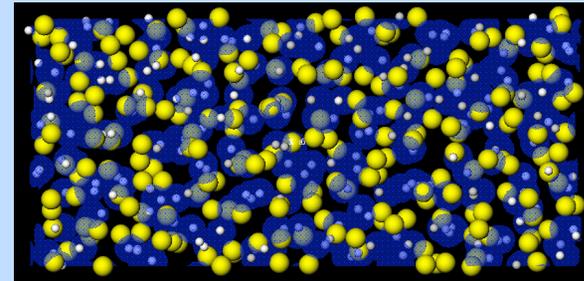
# Two phase simulation approach for determining melting temperatures

## Starting configuration

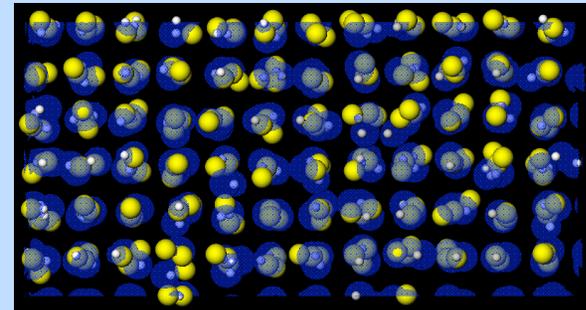


- Constant pressure MD for a set of (T,P)
- Stability of the solid and liquid phases directly compared

## Final configurations

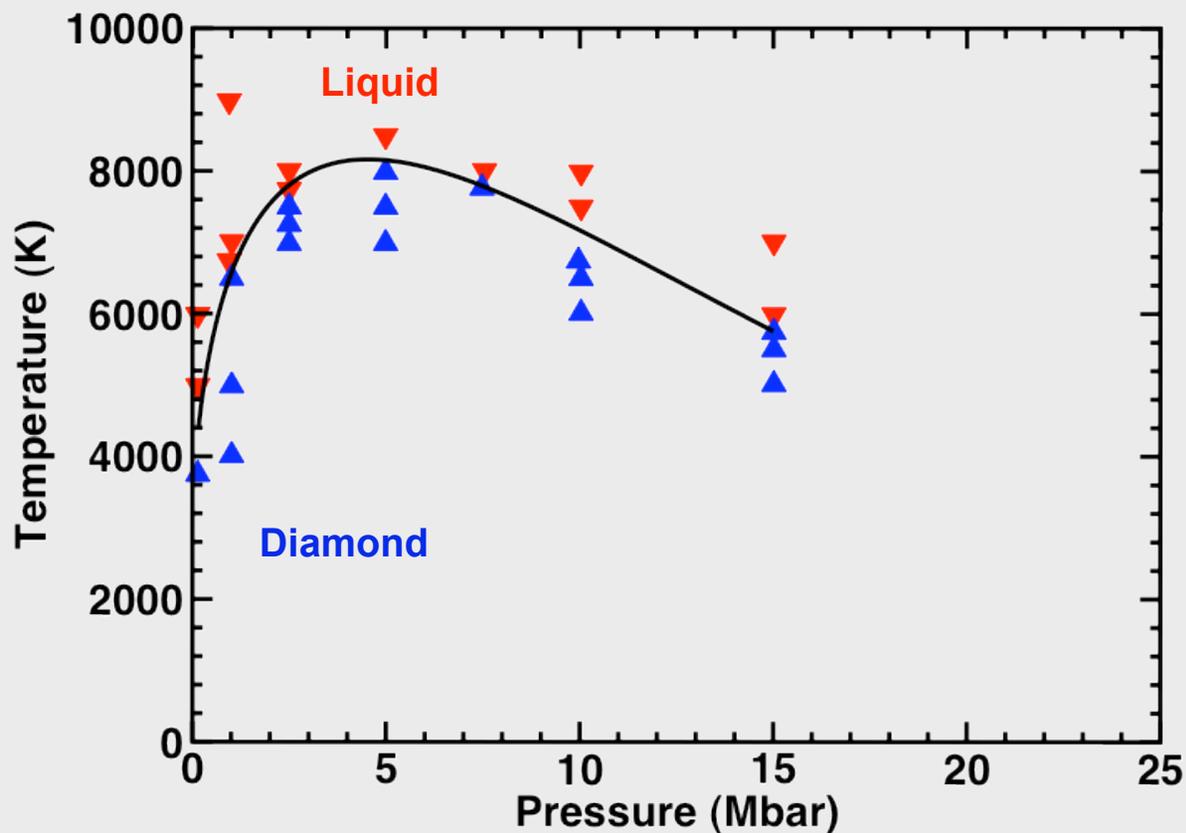


$$T > T_m$$



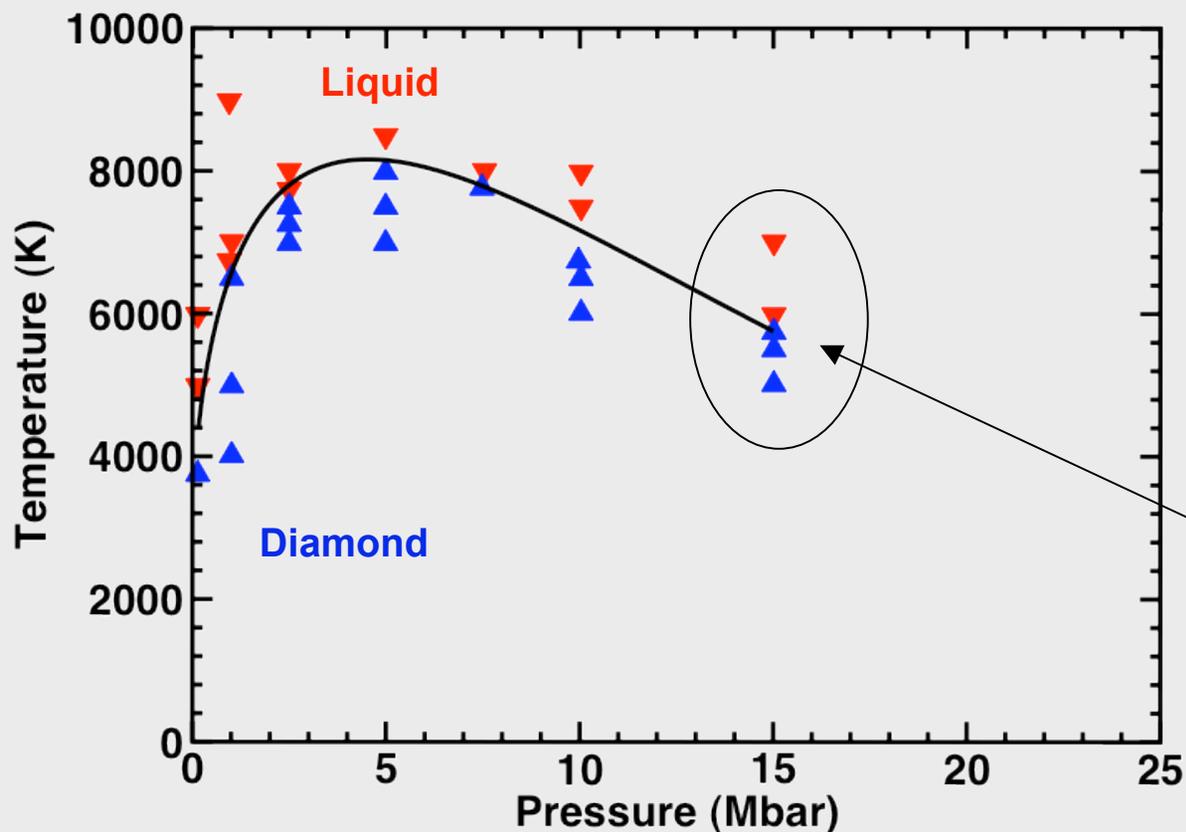
$$T < T_m$$

# The melting curve of diamond from two-phase simulations



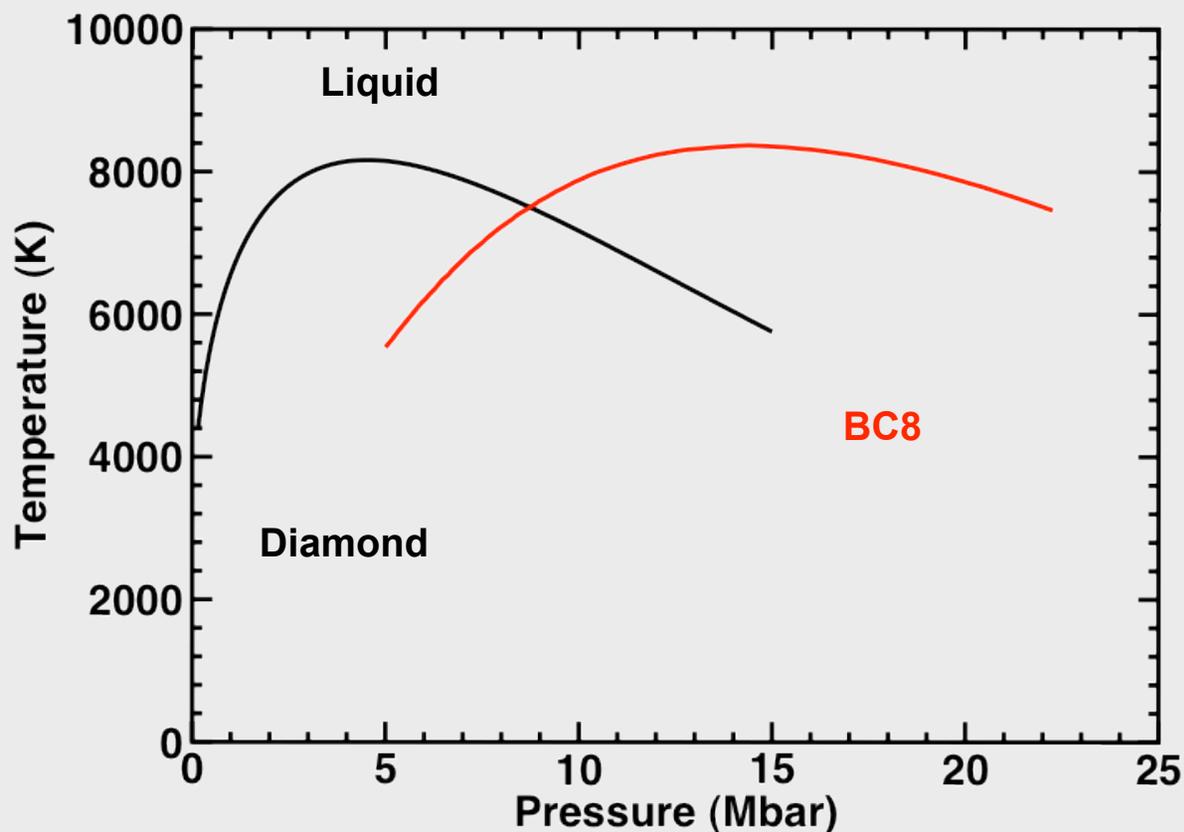
- First-principles two-phase simulations have been used to map out the diamond melting curve
- Maximum at  $P \sim 4.5$  Mbar

# The melting curve of diamond from two-phase simulations



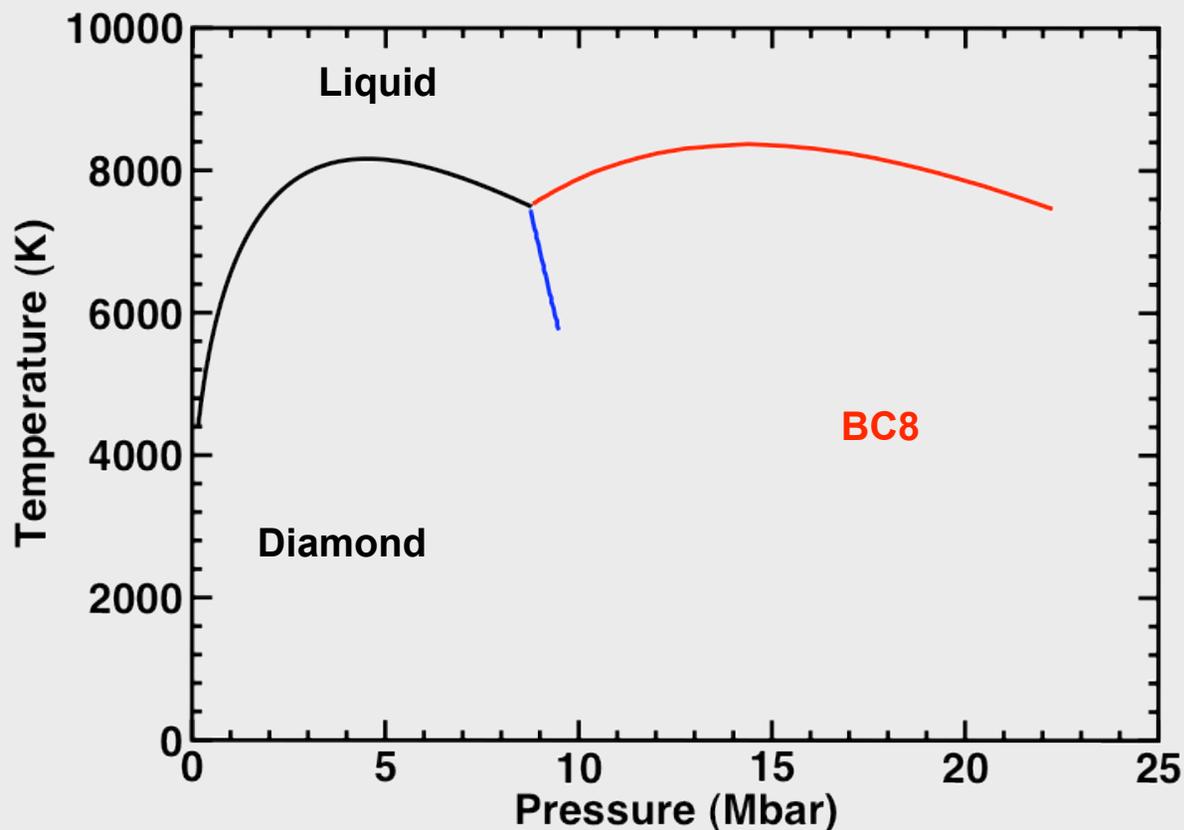
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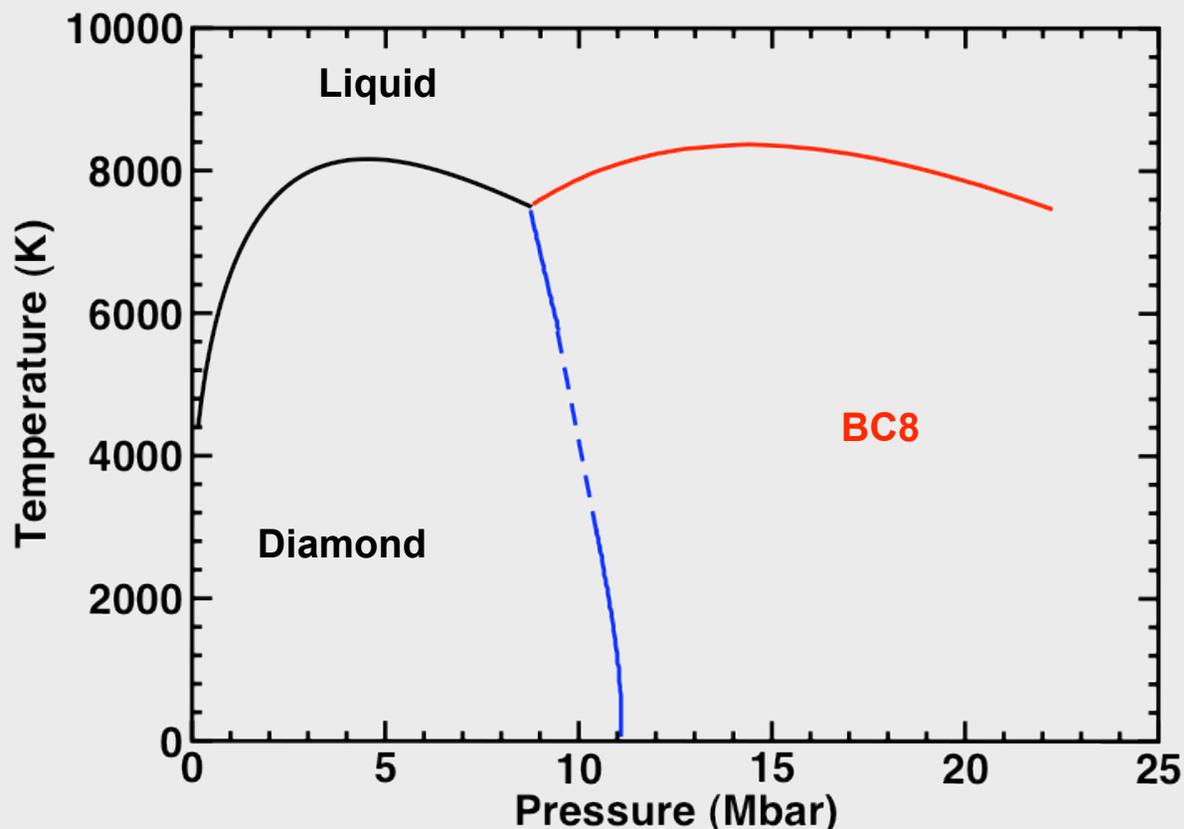
- We have carried out similar simulations with a BC8 solid structure
- BC8 also has a maximum
- Triple point located at  $P = 8.7$  Mbar and  $T = 7500$  K

# The melting curve of diamond from two-phase simulations



$$\left(\frac{dP}{dT}\right)_{DB} = \frac{\Delta S_{DB}}{\Delta V_{DB}} = \frac{\Delta V_{DL} \left(\frac{dP}{dT}\right)_{DL} - \Delta V_{BL} \left(\frac{dP}{dT}\right)_{BL}}{\Delta V_{DB}}$$

# The melting curve of diamond from two-phase simulations

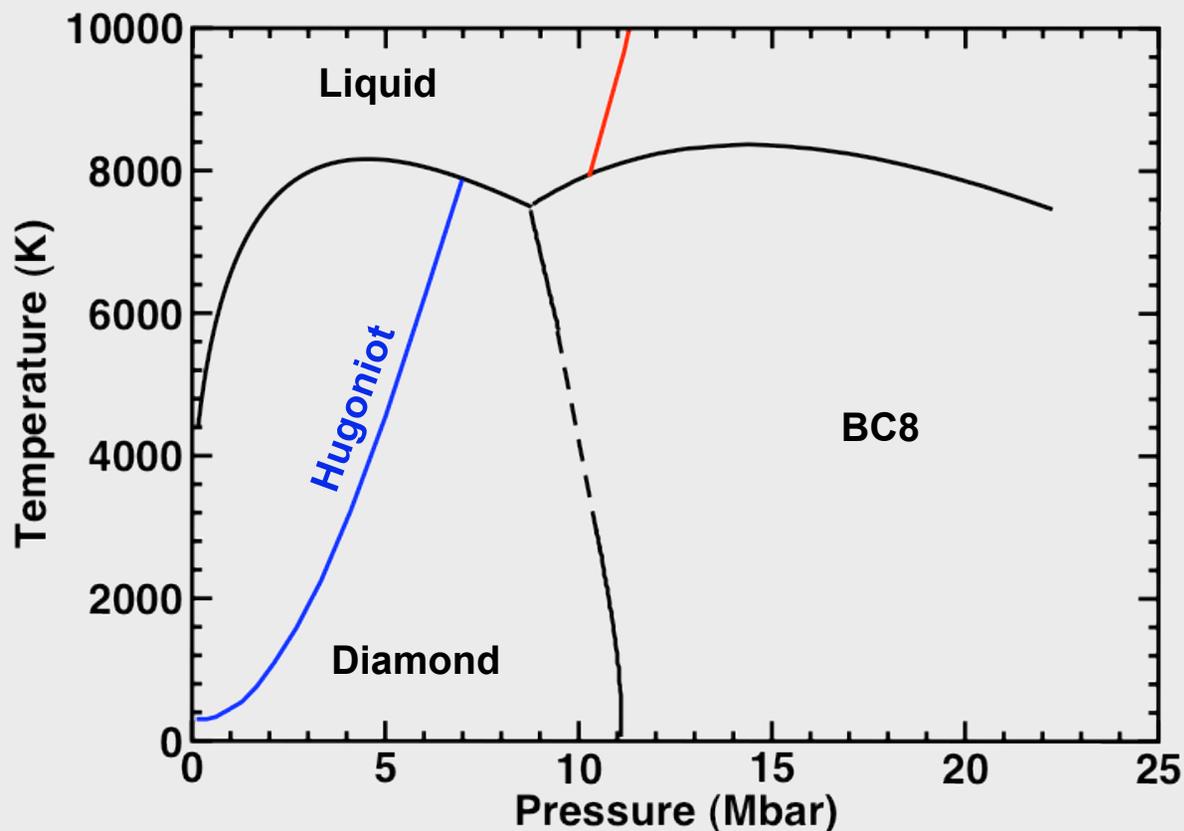


- Low T boundary between diamond and BC8 determined by free energy matching  $G_{\text{diamond}}(P, T) = G_{\text{BC8}}(P, T)$

- Quasiharmonic approximation

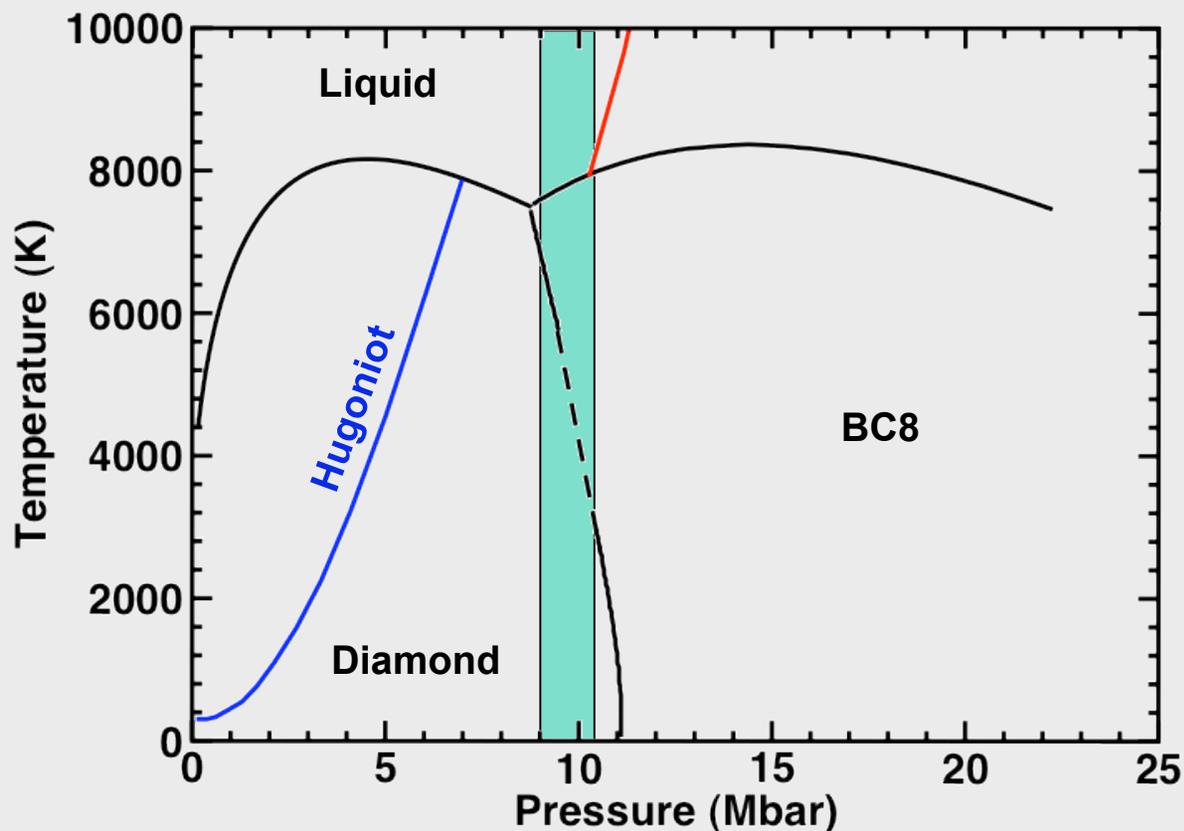
$$c_V = \sum_{\mathbf{q}\alpha} \frac{(\hbar\omega_{\mathbf{q}\alpha})^2 e^{\hbar\omega_{\mathbf{q}\alpha}/kT}}{(e^{\hbar\omega_{\mathbf{q}\alpha}/kT} - 1)^2 kT^2}$$

# The melting curve of diamond from two-phase simulations



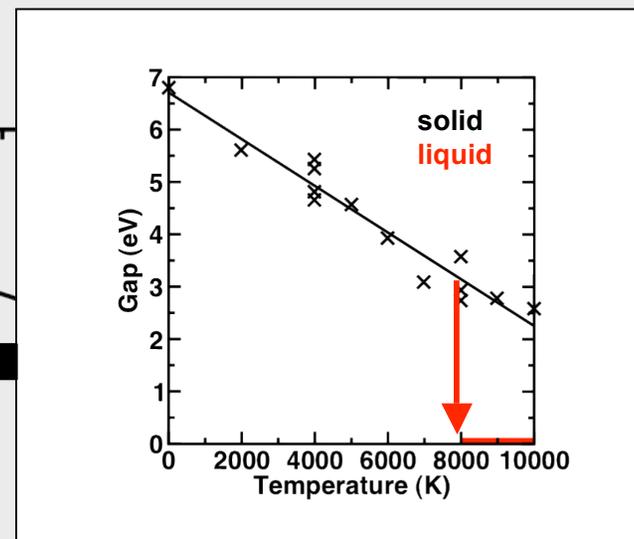
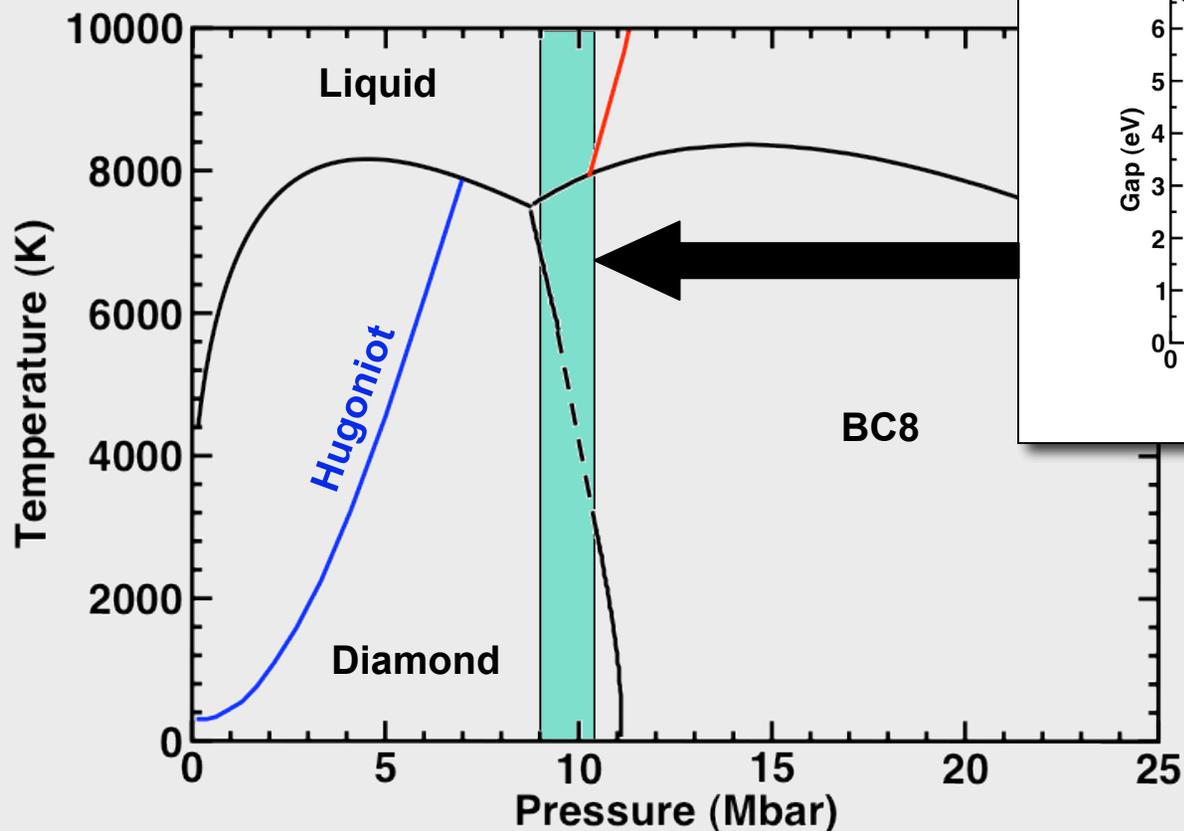
- Hugoniot calculations indicate shock melting between  $P = 6.7$  to  $10.5$  Mbar and  $T \sim 8000$  K.
- Diamond gap remains open until melting
- Good agreement with laser-shock experiments

# The melting curve of diamond from two-phase simulations



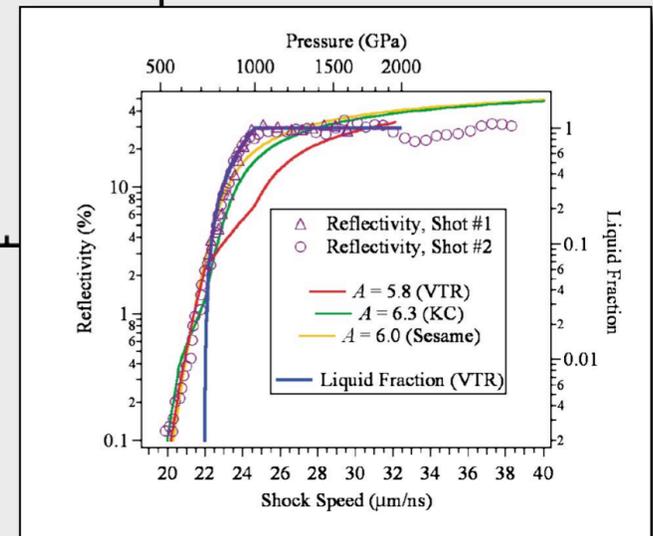
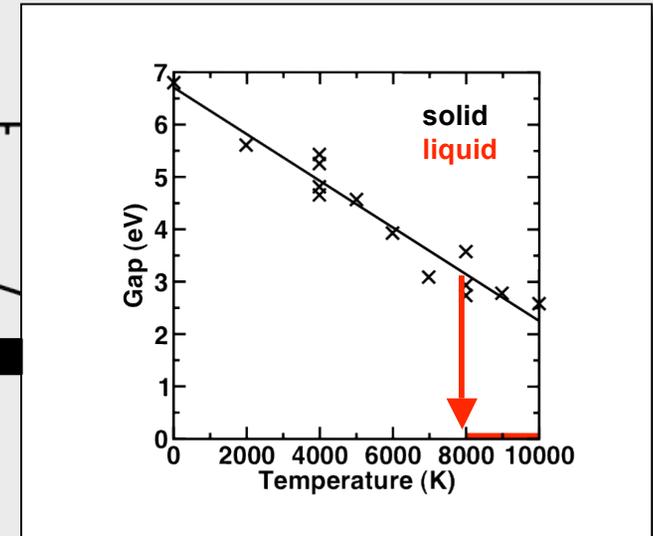
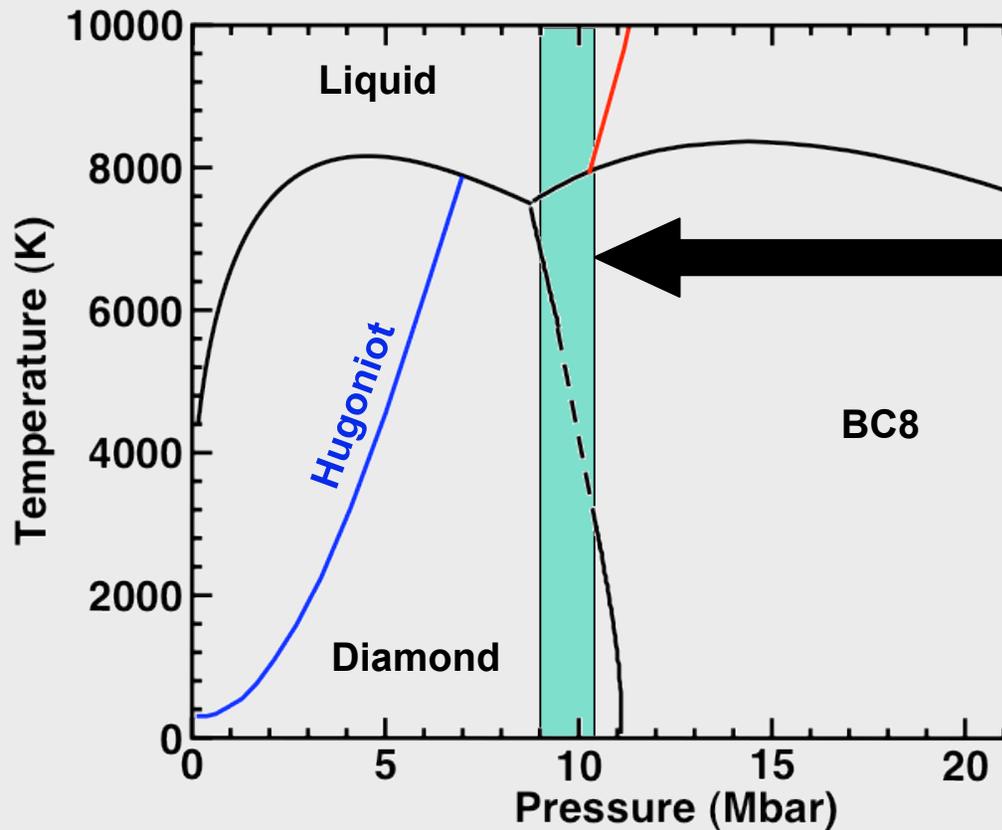
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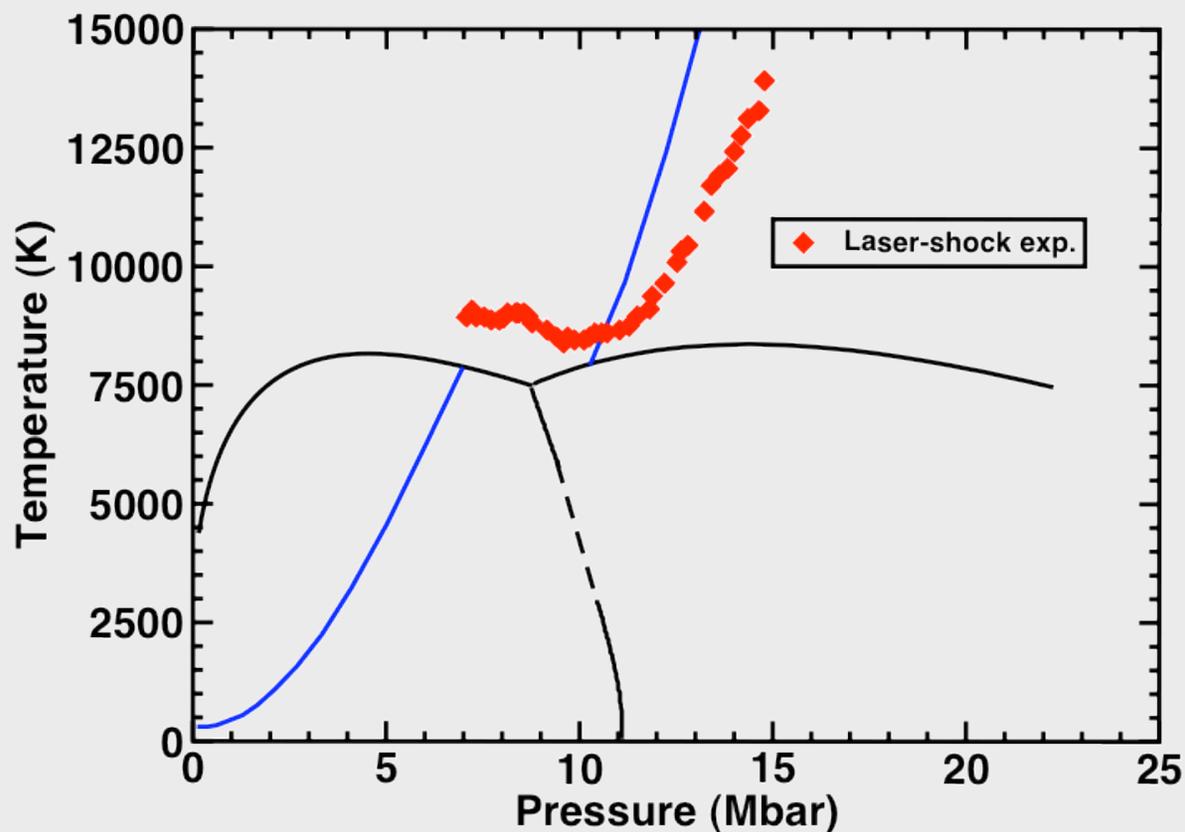
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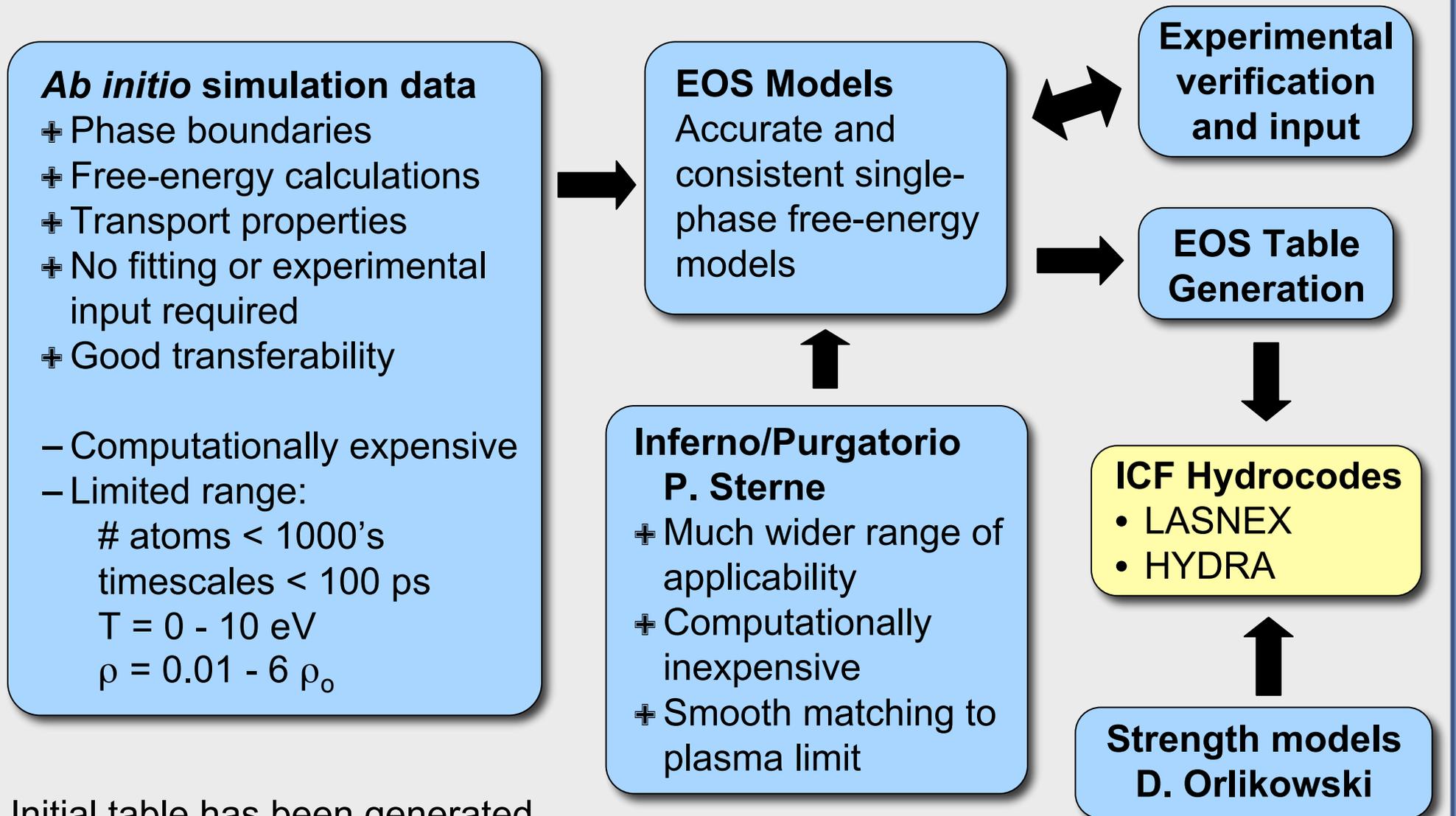
Bradley, et al. PRL 2004

# Comparison with recent laser-shock experiments



- Hugoniot calculations indicate shock melting between  $P = 6.7$  to  $10.5$  Mbar and  $T \sim 8000$  K.
- Simulations in good agreement with recent laser-shock measurements (Jon Eggert, et al. 2007)

# We are working to develop accurate EOS tables for materials relevant to ICF capsule designs



Initial table has been generated with this process (LEOS67) and is currently being used in LASNEX

# Analytic equation of state construction

- **Solids phases (Diamond and BC8)**

- $F(V, T) = E_0(V) + F_{\text{Debye}}(V, T) + F_{\text{anh}}(V, T)$
- Harmonic approximation at low temperatures
- Anharmonic corrections at higher temperatures
- For diamond we find that  $F_{\text{anh}}(V, T) \sim aT^2$

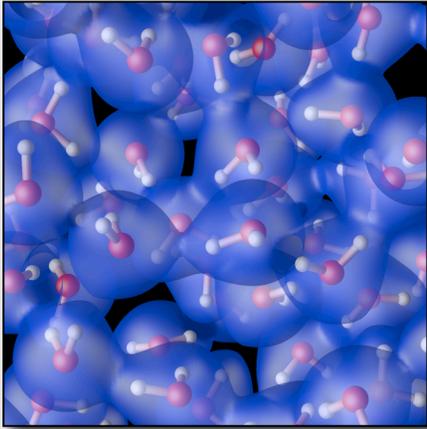
- **Liquid**

- $F(V, T) = E_0(V) + F_{\text{Debye}}(V, T) + F_{\text{elec}}(V, T)$
- Solid-like free energy (approximation validated by direct first-principles simulations)
- Gibbs free energy constrained to match the melting curve and first-principles liquid simulation [ $E(V, T)$  and  $P(V, T)$ ] data

- **Connection with a global EOS model**

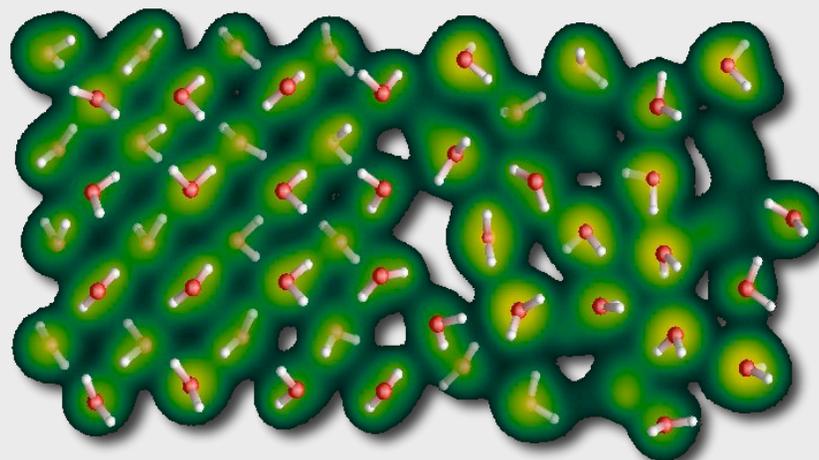
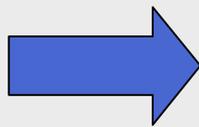
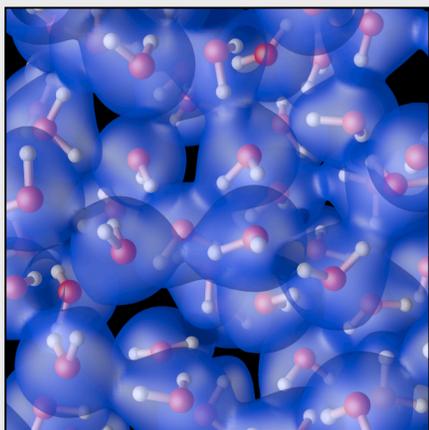
- Liquid EOS smoothly matched with QEOS

# What have you done for me lately?



- 144-processors of ASCI Blue, 1 iteration took 42 sec. (in 1999)
- 128-processors of ASC Purple, 1 iteration takes 1 sec
- Transition from computing “points” to “curves”

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**Now possible to assemble highly accurate first-principles based EOS tables for select materials**

# What are you doing for me tomorrow?

- **The current LEOS database is based on QEOS**
  - **Cold-curve, electron-thermal via modified Thomas-Fermi and ion-thermal via Debye-Grüneisen**
  - **Fast, smooth, many parameters to adjust**
- **Work underway at LLNL (P. Sterne) to rebuild the LEOS tables with electron-thermal component based on Purgatorio calculations (ion in jellium model)**
- **In the future, we will be able to routinely assemble EOS tables based entirely on first-principles methods**
  - **Complex mixtures**
  - **Beyond DFT**
  - **Realistic error bars**
  - **Transport properties**

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Phase diagram of lithium hydride

