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

Alfredo A. Correa
Department of Physics
UC Berkeley

Eric Schwegler, Lorin Benedict

1 Quantum Simulations Group
2 EOS and Materials Theory Group
Lawrence Livermore National Laboratory

Giulia Galli, François Gygi

3 Department of Chemistry
4 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
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- 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

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

Density Functional Theory and Quantum Monte Carlo

Electronic Structure (Schroedinger Equation for Electrons)

Molecular Dynamics (Newtonian Equations for Ions)

\( \Phi \) is the quantum mechanical ground state energy of N interacting electrons in the field of ions

Time evolution of ions:
- \( 10^3 - 10^6 \) time steps
- \( M_i \dot{R}_i = F_i \)
- \( F_i = -\nabla_i \Phi(\{R_j(t)\}) \)

Predict the properties of low-Z materials under extreme conditions

- Structural and dynamical properties
- Phase boundaries
- Transport properties
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“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
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

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

Starting configuration

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
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Each $T_m$ point requires $\sim 120K$ cpu hours to compute
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

\[
c_V = \sum_{q\alpha} \frac{(\hbar \omega_{q\alpha})^2 e^{\hbar \omega_{q\alpha}/kT}}{(e^{\hbar \omega_{q\alpha}/kT} - 1)^2 kT^2}
\]
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
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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 ~ 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.

**Ab initio simulation data**
+ Phase boundaries
+ Free-energy calculations
+ Transport properties
+ No fitting or experimental input required
+ Good transferability
  - Computationally expensive
  - Limited range:
    - # atoms < 1000’s
    - timescales < 100 ps
    - T = 0 - 10 eV
    - ρ = 0.01 - 6 ρ₀

**EOS Models**
Accurate and consistent single-phase free-energy models

**Inferno/Purgatorio P. Sterne**
+ Much wider range of applicability
+ Computationally inexpensive
+ Smooth matching to plasma limit

**Experimental verification and input**

**EOS Table Generation**

**ICF Hydrocodes**
- LASNEX
- HYDRA

**Strength models D. Orlikowski**

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 \( F_{\text{anh}}(V,T) \sim a T^2 \)

• 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 \([E(V,T) \text{ and } P(V,T)]\) 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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