Status of DMC for condensed phases

Luke Shulenburger
Acknowledgments

- Thomas Mattsson
- Jeongnim Kim
- Kyle Cochrane
- Mike Desjarlais
- DOE BES
- Sandia high performance computing and ACES
Goal is to understand properties of a wide variety of materials under pressure

- Van der Waals interactions
- Localization vs delocalization
- Kondo physics
- Charge transfer
- Chemical Reactions

Xe isosurfaces

Cerium Phase diagram

Elkin et al. PRB 84, 094120 (2011)

Localized d-orbital in FeO

e_g orbital with surrounding oxygen ions

Tkatchenko et al PRB 78, 045116 (2008)
Techniques to probe materials at extreme conditions
The Sandia Z Machine

16.5 m

Marx generator

laser-triggered gas switch

insulator stack

magnetically insulated transmission lines

Experiment

22 MJ stored energy
~26 MA peak current
~100-700 ns rise time
EOS poses a stringent challenge for calculations

- Calculate Be HCP-> BCC phase transition pressure with LDA+QHA
- What is sensitivity of transition?
  - Make constant shift of $E_{HCP}(V)$
- Transition pressure changes from 350 Gpa to 525 Gpa with a 1 kcal/mol shift
- Zero point energies were an order of magnitude larger
- Chemical Accuracy is not good enough!
DMC may allow required accuracy

- CASINO DMC (ADF QZ4P, dt → 0) [this work]
- CASINO DMC (old geometry, GTO 6-311G, dt=0.002) [this work]
- Grossman, DMC, pseudopotentials
- Feller et al., CCSD(T)

- from Nemec et al, JCP. 132, 034111 (2010)
QMCPACK – Massively Parallel QMC

- Quantum Monte Carlo code designed for massive parallelism
- Developed by J. Kim et al at Oak Ridge National Laboratory
- Hybrid MPI / OpenMP parallelism
  - Shared Memory on Nodes, Distributed between
- Can efficiently scale to more than 1,000,000 CPU cores
- CUDA port to GPUs with 15X speedup

Scaling on Jaguar_pf

![Graph showing speedup vs. number of cores]

- DMC
- DMC+Checkpoint
- 216K cores

Scaling on Sequoia

![Graph showing Monte Carlo moves per second vs. number of cores]

- Monte Carlo Moves per second / 1000
- Number of Cores / 1000
- 0 to 140
- 0 to 20
- 0 to 1600
DMC is not as mature as DFT

- Calculations of condensed phases involve a variety of approximations
  - Most approximations may be made arbitrarily small, but approaches to this are not standardized

- Finite size effects
  - One body effects -> DFT comparison or **twist averaging**
  - Two body effects -> Extrapolation, KZK functional or **MPC / Chiesa combination**

- Fixed node errors
  - **Slater jastrow wavefunction**, self healing, backflow, geminals, pfaffians, multideterminants

- Pseudopotentials
  - Only valence electrons simulated because of computational cost
  - In which approximation should core and valence be separated
  - Correction via all electron calculation or comparison with all electron DFT
Approximation methods can greatly affect results

- Case study on Si
- Total energies of diamond and beta-Sn phases calculated with DMC / LRDMC
- Quasiharmonic phonon corrections included

<table>
<thead>
<tr>
<th>Method</th>
<th>Raw (GPa)</th>
<th>Corrected (GPa) ($T = 300$ K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>7.21</td>
<td>6.34</td>
</tr>
<tr>
<td>PBE</td>
<td>9.87</td>
<td>8.99</td>
</tr>
<tr>
<td>VMC</td>
<td>15.48 ± 0.06</td>
<td>13.3 ± 1.0</td>
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<tr>
<td>LRDMC</td>
<td>16.65 ± 0.15</td>
<td>14.5 ± 1.0</td>
</tr>
<tr>
<td>DMC (Ref. 18)</td>
<td>19.0 ± 0.5</td>
<td>16.5 ± 0.5</td>
</tr>
<tr>
<td>DMC (Ref. 13)</td>
<td>16.5 ± 1.0</td>
<td>14.0 ± 1.0</td>
</tr>
<tr>
<td>AFQMC (Ref. 20)</td>
<td>15.1 ± 0.3</td>
<td>12.6 ± 0.3</td>
</tr>
<tr>
<td>Expt.</td>
<td>10.0 − 12.5</td>
<td>10.0 − 12.5</td>
</tr>
</tbody>
</table>

Sorella et al. PRB 83, 075119 (2011)
Test approximations on a suite of solids

- Binding is different
  - Far less effect from degenerate energy levels at highest energy states
  - More effect from relative energy levels

- Test should compare to easily measured experimental data
  - High pressure calculations to derive properties of ambient phase

- Previous calculations have required 1 year of time on NSF machines for a single solid

- Calculations performed on Cielo
Pseudopotential Details

- LDA pseudopotentials constructed with OPIUM
- Compared to either LAPW calculations with elk or LMTO calculations with RSPT (Mattsson et al. JCP 128, 084714 (2008))
- Bulk modulus and equilibrium volume nearly same to minimize corrections such as applied in Maezono et al. PRB 82, 184108 (2010)

![LDA vs Spacing for zincblende (SiC)](image)

- $V_0 = 68.43 \text{ bohr}^3$ (pseudo)
- $V_0 = 68.81 \text{ bohr}^3$ (RSPT from JCP 128, 084714 (2008))
- $K_0 = 226.89 \text{ GPa}$ (pseudo)
- $K_0 = 226 \text{ GPa}$ (RSPT from JCP 128, 084714 (2008))
Convergence of technical parameters

- Tests performed for moderate size supercell at 2 volumes
- Time step, b-spline spacing and twist averaging converged to within meV
- Finite size convergence achieved when change to larger supercell produced same energy shift in ambient and high pressure calculations
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<table>
<thead>
<tr>
<th>Timestep (Ha)</th>
<th>Energy (Ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-18.0775</td>
</tr>
<tr>
<td>0.005</td>
<td>-18.0765</td>
</tr>
<tr>
<td>0.01</td>
<td>-18.0755</td>
</tr>
<tr>
<td>0.015</td>
<td>-18.0745</td>
</tr>
<tr>
<td>0.02</td>
<td>-18.0735</td>
</tr>
</tbody>
</table>

![Graph showing timestep convergence of DMC](image_url)
Convergence of technical parameters

- Tests performed for moderate size supercell at 2 volumes
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![Diagram showing convergence of DMC energy with twist averaging.](image-url)
First ever extensive benchmarks of Quantum Monte Carlo for condensed matter

- Fit Vinet form to $E(V)$ and compare equilibrium volume (density) and bulk modulus (compressibility) to experiment

![Graph showing equilibrium volume (bohr$^3$) vs. DMC and Experiment](image)

- Materials span a factor of 10 in equilibrium volume
- Four types of bonding are included
  - Ionic
  - Covalent
  - Metallic
  - Van der Waals
- Lattice Constants within $\sim 0.9\%$
- This provides a new baseline procedure for a QMC calculations

Mean error: $-0.38 \pm 0.15$
Mean absolute error: $2.28 \pm 0.15$
RMS error: $-0.697 \pm 0.066\%$
Mean absolute relative error: $1.79 \pm 0.07\%$
First ever extensive benchmarks of Quantum Monte Carlo for condensed matter

- Fit Vinet form to E(V) and compare equilibrium volume (density) and bulk modulus (compressibility) to experiment

Bulk modulus spans over 3 orders of magnitude

This provides a new baseline procedure for a QMC calculations

Mean error: -0.07 +/- 0.42
Mean absolute error: 3.53 +/- 0.42
RMS error: 0.62 +/- 0.44%
Mean absolute relative error: 4.49 +/- 0.44%
Compare to DFT functionals

- Compare to various “good” DFT functionals
  - LDA
  - PBE
  - AM05
  - HSEsol
  - vdW-DF2
  - vdW-optB86b

- Non van der Waals functionals yield high quality results on many materials
  - But not noble gases

- van der Waals functionals are improving to wide applicability
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- van der Waals functionals are improving to wide applicability
Si Phase transition revisited:  
*Utilizing methodology from benchmark fares little better*

- Use DFT based pseudopotential
- Extensive twist averaging for Fermi surface
- Chiesa correction for kinetic energy and MPC for potential
- Equilibrium properties are worse than reported by other groups
  - Equilibrium density 2% too small
  - Bulk Modulus 5% too large
- Phase Transition pressure
  - 17.8 GPa (5-7.8 GPa too large!)

![Graph showing energy vs volume for Si](image_url)
Study simpler system to isolate errors:

*Be HCP -> BCC phase transition*

- Solid Be used in ICF
  - High strength, low Z material, Low x-ray absorption
- HCP at ambient temperature and pressure
- Phase transition to BCC at high pressure
- Simple but demanding computationally

Benedict et al. PRB 79, 064106 (2009)
Study simpler system to isolate errors:

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Study simpler system to isolate errors:

*Be HCP -> BCC phase transition*

- Equation of state is fit using Vinet form
  - More crucial because values have statistical errors
- Casula t-move formalism employed for pseudopotentials
- Phase transition occurs at > 635 GPa
  - Significantly higher than DFT result ~ 390 GPa

### HCP Equilibrium Parameters

<table>
<thead>
<tr>
<th></th>
<th>QMC</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c/a$</td>
<td>1.569 +/- 0.004</td>
<td>1.568</td>
</tr>
<tr>
<td>$V_0$ (angstrom$^3$)</td>
<td>7.746 +/- 0.078</td>
<td>8.117</td>
</tr>
<tr>
<td>Bulk Modulus (GPa)</td>
<td>124 +/- 2</td>
<td>116.8</td>
</tr>
</tbody>
</table>
Perform all electron calculation to eliminate pseudopotential errors

- Utilize hard pseudopotential with 4 electrons in valence for calculation of trial wavefunction
- Replace with $4/r$ for QMC
- All properties of HCP (ambient) phase agree with experiment
- Phase transition pressure shifts to 418 GPa, more in line with that inferred by shock experiments

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<th>Exp</th>
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<td>$c/a$ (Å)</td>
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<td>8.117</td>
</tr>
<tr>
<td>Bulk Modulus (GPa)</td>
<td>124 +/- 2</td>
<td>115.7 +/- 1.5</td>
<td>116.8</td>
</tr>
</tbody>
</table>
Accuracy of all electron methodology holds for another light nuclei phase transition

- Calculate LiH transition from B1 to B2 phase
- Ambient (B1) phase in excellent agreement with experiment
- Phase transition pressure 337 GPa
- DFT (LDA) calculations 308 Gpa
- Complements DAC experiments which top out near 250 GPa

<table>
<thead>
<tr>
<th>B1 Equilibrium Parameters</th>
<th>QMC</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Constant (angstrom)</td>
<td>4.074 +/- 0.002</td>
<td>4.08</td>
</tr>
<tr>
<td>Bulk Modulus (GPa)</td>
<td>32.2 +/- 0.4</td>
<td>33.1 +/- 0.3</td>
</tr>
<tr>
<td>B’</td>
<td>3.64 +/- 0.05</td>
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Lazicki et al. PRB, 85, 054103 (2012)
Minimizing the pseudopotential approximation will have the largest impact on DMC calculations of solids

- Phase transitions under pressure provide sensitive test of DMC
- Calculations using high quality DFT pseudopotentials have mediocre accuracy
- All electron calculations of Be and LiH give extremely accurate properties for equilibrium phases
- All electron phase transition pressures agree with available experiments and are comparable to best DFT based answers
- All electron calculations are not a feasible proposition for many applications
- Reducing the pseudopotential approximation should be the highest priority for the calculation of solids with DMC
Moving to higher temperatures

- High pressure low temperature conditions are quite rare in the universe
- Zero temperature behavior sets the foundation, but does not constrain all of an equation of state
- Melt boundaries, isentropes, adiabats, critical points etc are all of interest experimentally
- No general path for high temperature properties from DMC
  - Combine with another method
  - Free energy decomposition: $F(V,T) = F_c(V) + F_i(V,T) + F_e(V,T)$
  - Thermodynamic integration
Melt boundaries are particularly challenging

- Target recent discrepancies in melt curves under pressure
- Early DAC experiments may have encountered a variety of difficulties
  - Where available, shock determinations of melting often suggest a much steeper melt curve
  - Increased reactivity at high temperature and pressure can lead to chemical reactions that lower melt curve
  - Fast recrystallization caused by different absorption profiles of the solid and liquid can also lead to lowered determination of melting profile

![Ta melt curve](Ta melt curve)

Old Ta DAC Melt curve
Klug, Physics. 3, 52 (2010)

New Ta DAC Melt curve

![Fe melt curve](Fe melt curve)

Old Fe DAC Melt curve

New Fe DAC Melt curve

Klug, Physics. 3, 52 (2010)
Case Study: xenon melt transition

- Closed shell insulator at ambient conditions
- Under static compression
  - FCC -> HCP Phase transition
  - Isostructural insulator to metal transition
- Hugoniot well characterized
- Liquid phase may exhibit anomalous behavior
  - Very narrow temperature range at ambient pressure
  - Potentially flat melt curve at moderate pressures

Klug, Physics. 3, 52 (2010)

Root et al. PRL 105, 085501 (2010)
Pseudopotential poses a particular challenge for accurate DMC calculations

- Validated norm conserving Xe pseudopotentials not widely available
- D-states well removed from valence, but d-projector is crucial
  - Increasing d-hybridization suggested as cause of flat melt line
    - Ross et al. PRL 95. 257801 (2005)

\[ \sim 0.5 \text{ eV / Xe difference at 70GPa} \]
Fixed node approximation and DFT Functional

- **FCC equation of state**
  - LDA $\rightarrow$ no long range correlation, but self interaction in low density regions
  - AM05 $\rightarrow$ subsystem based functional, van der Waals is completely absent
Fixed node approximation and DFT Functional

- **FCC equation of state**
  - LDA $\rightarrow$ no long range correlation, but self interaction in low density regions
  - AM05 $\rightarrow$ subsystem based functional, van der Waals is completely absent
  - DMC with nodes and pseudopotentials taken from above calculations
    - *Very small dependence on DFT trial wavefunction*

![FCC energies of Xe using different methods](image-url)
Difficult to determine free energy directly:

*Determine relative free energy of phases within QMD*

- Place solid and liquid in contact with each other
- Run at different temperatures or starting energies and watch phase boundary
- Relative heat capacities and enthalpy of melting determine range of phase coexistence

- Melt at 5800 K
- Freeze at 5400 K
Thermodynamic integration to map to DMC free energies

- Calculate the change in free energy between different ensembles
- There are two approaches, a one shot formula or a perturbation series

\[ \Delta F = F_2 - F_1 \]
\[ = -k_B T \ln Z_2 + k_B T \ln Z_1 \]
\[ = -k_B T \ln \left( \sum_s e^{-\beta U^2_s} \right) / \left( \sum_s e^{-\beta U^1_s} \right) \]
\[ = -k_B T \ln \left( \sum_s e^{-\beta U^2_s - U^1_s} e^{-\beta U^1_s} \right) / \left( \sum_s e^{-\beta U^1_s} \right) \]
\[ = -k_B T \ln \left( e^{-\beta \Delta U} \right)_1 \]

\[ \Delta F = \sum_{n=1}^{\infty} \frac{(-\beta)^{n-1}}{n!} \kappa_n \]

Where the \( \kappa_n \) are cumulants of the energy

\[ \kappa_1 = \langle \Delta U \rangle_1 \]
\[ \kappa_2 = \langle \Delta U^2 \rangle_1 - \langle \Delta U \rangle_1^2 \]
\[ \kappa_3 = \langle \Delta U^3 \rangle_1 - 3 \langle \Delta U \rangle_1 \langle \Delta U^2 \rangle_1 + 2 \langle \Delta U \rangle_1^3 \]

- Comparison of the two approaches provides a rough idea of the rate of convergence of the series
- Need to calculate energy differences from snapshots
Trial wavefunctions used for QMC

- **Use a real space representation of the wavefunction**
  - Plane waves require evaluation of each basis element for every move
  - 3D b-splines require only 64 evaluations at each point
  - Very large amounts of memory required: 96 GB / wavefunction

- **Hybrid Representation**
  - Use coarse b-spline mesh in real space
  - Radial spline near atoms
  - Wavefunctions reduced to 24 GB
  - Conversion is expensive for large systems

- **GPU port of wavefunction conversions**
  - Massive parallelism available
  - Conversion Time reduced from 10 days on 16 CPU cores to 6 hours on 4 GPUs
Thermodynamic integration in practice

- 10 snapshots taken from a solid QMD calculations with LDA functional
- Free energy shift from exponential:
  - -0.05947 +/- 0.00085 eV / Xe
- Terms from the perturbation series
  - 1st order: -0.05818 +/- 0.00067 eV/Xe
  - 2nd order: -0.00158 +/- 0.00023 eV/Xe
  - 3rd order: -0.00030 +/- 0.00012 eV/Xe
- Fast convergence leads to confidence in closeness of ensembles
Two approaches to determine the shift of the melt line

- Determine the change in Gibbs free energy directly

\[ \Delta T_m \approx \frac{\Delta G^{ls}}{S_{DFT}^{ls}} \quad \Delta G \approx \Delta F - V \Delta p^2 / 2 K_T \]

  - Approach from Sola and Alfe PRL 130, 078501 (2009)
  - Some uncertainties in how to evaluate \( S_{DFT}^{ls} \) and \( \Delta p \)

- Alternative is to work with Helmholtz free energy

  - Calculate isotherm with DFT in each phase

\[ F = -PdV - SdT \quad \Rightarrow \quad dF = -\int P \, dv + C \]

  - Use pressure from two phase calculations to set relative shift between phases within DFT
  - Thermodynamic integration at multiple volumes allows for changes in slope of free energy
QMC correction on DFT melt line

- No evidence for low melt line found by experiment
- Shifts from DMC are a similar magnitude as those found in the iron paper

Melt line from various sources

- Boehler et al. 2001 (DAC)
- Ross et al. 2005 (DAC)
- Saija et al., 2005 (Calculation)
- Belonoshko et al. 2006 (Calculation)
- (QMC) T-shift
- (QMC) P-shift

Relative Helmholtz Free Energies from QMC

QMC Transition Pressure = 66.042 GPa
Validation of method: Melting of aluminum

- Shock and DAC melt exhibit a consistent trend
- DFT (2 phase approximation) accurately reproduces melt curve
- Thermodynamic integration from DFT to QMC gives a shift of only 18 K!

![Graph showing melting temperature vs. pressure]
Conclusions

- Diffusion Monte Carlo can accurately treat Xe under pressure
  - Pseudopotential Approximation is small
  - Fixed node approximation is likely a small error
- Accurate treatment of d-hybridization does not cause melt curve to flatten
- Relative energies from DFT within LDA appear to be accurate near 1 Mbar
- Errors in total energies from quantum MD calculations will increase melting temperature
- Flat melting curve from DAC should be revisited