Path Integral Monte Carlo for Fermions

Summer school “QMC Theory and Fundamentals”

Burkhard Militzer
University of California, Berkeley
militzer@berkeley.edu
http://militzer.berkeley.edu
PIMC is the best simulation method for fermions in moderately and highly excited states: Hydrogen plasma in the sun, some giant planets and for simulation of fusion processes.
NASA’s Kepler Mission

- Determine the frequency of Earth-size and larger planets in the habitable zone of sun-like stars
- Determine the size and orbital period distributions of planets
Pre-Kepler Transiting Planets - 2009

Size Relative to Earth

Orbital Period in days
Kepler Candidates as of February 1, 2011

Size Relative to Earth

Orbital Period in days
Ab initio Simulations to Characterize of the Interiors of Giant Planets

![Graph showing temperature and density relationships for giant planets](image)

- **Diagonal Lines:**
  - Light Red: Sun
  - Green: Molecular Fluid
  - Blue: Metallic Fluid
  -粉红色: ICF path

- **Equilateral Triangles:**
  - Yellow: Molecular Hydrogen (helium & neon depleted)
  - Pink: Metallic Hydrogen (helium & neon rich)

- **Layers:**
  - Helium-poor envelope
  - Helium droplets

- **Density Levels:**
  - $n=10^{18}$ cm$^{-3}$
  - $n=10^{26}$ cm$^{-3}$
Use analytical (chemical) models at low density and very high temperature

Free energy model to describe weakly interacting chemical species:

- $H_2$, $H$, $H^+$, $e^-$
- $He$, $He^+$, $He^{++}$, $e^-$

Free energy is constructed but it contains free parameters to describe the interaction.

- Saumon and Chabrier model ($H+He$)
- Sesame data base (many substances)

$n=10^{18}$ cm$^{-3}$

$n=10^{26}$ cm$^{-3}$
Density functional molecular dynamics (DFT-MD)
Couple Ion-Electron Monte Carlo (CEIMC) for lower temp.

Born-Oppenheimer approx.
MD with classical nuclei:
\[ F = m \ a \]
Forces derived DFT with electrons in the instantaneous ground state.
Path integral Monte Carlo for higher temperatures where electronic excitations are present.

Temperature (K) vs. Density (g/cm³)

- Plasma
- Atomic Fluid
- Molecular Fluid
- Metallic Fluid
- Molecular Solid
- Metallic Solid
- Sun
- Laser Shock
- Gas Gun
- PIMC

PIMC applicable at: $T > 5000K$

$n=10^{18} \text{ cm}^{-3}$

$n=10^{26} \text{ cm}^{-3}$
I. Fermion PIMC with and without nodes
Fermions lead to Permutations that Carry a Negative Sign

Fermionic density matrix:
Sum over all antisymmetric eigenstates.

\[
\rho_F(R,R',\beta) = \sum_i e^{-\beta E_i} \Psi_{AS}^*(R) \Psi_{AS}^i(R')
\]

Project out the antisymmetric states:

\[
\rho_F(R,R',\beta) = \sum_P (-1)^P \rho_D(R,PR',\beta)
\]

\[
\langle R | \hat{\rho}_{FB} | R' \rangle = \sum_P (\pm 1)^P \int dR_1... \int dR_{M-1} \langle R | e^{-\tau \hat{H}} | R_1 \rangle...\langle R_{M-1} | e^{-\tau \hat{H}} | PR' \rangle
\]

D:

\[
\begin{align*}
R' = & \{r_1, r_2\} \\
R = & \{r_1, r_2\}
\end{align*}
\]

 Imaginary time

B: (+1)P

F: (-1)P
“Direct” Fermion Path Integrals

The fermion sign problem poses a major challenge.

\[ \langle R | \hat{\rho}_F | R' \rangle = \sum_P (-1)^P \int dR_1 \ldots \int dR_{M-1} \langle R | e^{-\tau \hat{H}} | R_1 \rangle \ldots \langle R_{M-1} | e^{-\tau \hat{H}} | PR' \rangle \]

How do we evaluate an integral with negative and positive contributions with MC?

→ Let us try the “direct” fermion method first:

- Sample all path with the bosonic action including permutations, \( P \)
- Add a weight factor of \((-1)^P\) when the observables are computed.

\[ \langle O \rangle_F = \frac{\langle \sigma(P)O(R) \rangle_B}{\langle \sigma(P) \rangle_B}, \quad \sigma(P) = (-1)^P \]

- This is exact, but positive and negative contributions cancel to a large extent

→ Fermion sign problem

- The efficiency of the algorithm scale like (Ceperley 1995)

\[ \xi = \left[ \frac{M_+ - M_-}{M_+ + M_-} \right]^2 = \left[ \frac{Z_F}{Z_B} \right]^2 = \exp[-2\beta (F_F - F_B)] = \exp[-2\beta N(\mu_F - \mu_B)] \]
Fixed-Node Method for Fermion PIMC

• Get rid of negative walks by canceling them with some of the positive walks. We can do this if we know where the density matrix changes sign. Restrict walks to those that stay on the same side of the node.

• Fixed-node identity. Gives exact solution if we know the places where the density matrix changes sign: the nodes.

\[
\rho_F(R_\beta, R_*; \beta) = \frac{1}{N!} \sum_{P} (-1)^P \int_{\rho_F(R_t, R_*; t) > 0} dR_t e^{-S(R(t))} \quad \text{with } R_0 = PR_*
\]

• Classical correspondence exists!!
• Problem: fermion density matrix appears on both sides of the equation. We need nodes to find the density matrix.
Proof of the fixed node method for path integrals

1. The density matrix satisfies the Bloch equation with initial conditions.
\[
\frac{\partial \rho(R,t)}{\partial t} = \hat{H} \rho(R,t) = \lambda \nabla^2 \rho(R,t) - V(R) \rho(R,t) \quad \rho(R,0) = \frac{1}{N!} \sum_P (-1)^P \delta(R - P R_0)
\]

2. One can use more general boundary conditions, not only initial conditions, because solution at the interior is uniquely determined by the exterior-just like the equivalent electrostatic problem.

3. Suppose someone told us the surfaces where the density matrix vanishes (the nodes). Use them as boundary conditions.

4. Putting an infinite repulsive potential at the barrier will enforce the boundary condition.

5. Returning to PI’s, any walk trying to cross the nodes will be killed.

6. This means that we just restrict path integrals to stay in one region.
What nodes shall we used in PIMC?

- To get around the sign problem, why not just use the fixed-node method from T=0 calculation?
- What nodes? The ground state nodes are not necessarily the correct ones at T>>0.
- The nodes of the density matrix have an imaginary time dependence: \( \rho_F(R,R_0;t) = 0 \) with \( R_0,t \) fixed.

High temperature

Low temperature

Slide - David Ceperley
Simplest type of nodes: **Free particles nodes**
they are exact at high temperature

Construct a *fermionic trial density matrix*
in form of a Slater determinant of
single-particle density matrices:

\[
\rho_T(R, R', \beta) = \begin{pmatrix}
\rho_0(r_1, r'_1, \beta) & \cdots & \rho_0(r_1, r'_N, \beta) \\
\vdots & \ddots & \vdots \\
\rho_0(r_N, r'_1, \beta) & \cdots & \rho_0(r_N, r'_N, \beta)
\end{pmatrix}
\]

Enforce the following nodal condition
for all time slices along the paths:

\[
\rho_T\left[ R(t), R(0), t \right] > 0
\]

This 3N-dimensional conditions eliminates
all negative and some positive contribution to the path [Ceperley et al. 1995]
⇒ “Solves” the fermion sign problem.

Free particle density matrix:

\[
\rho_0(r, r', \beta) = \frac{1}{V} \int d^3k \ e^{-\beta \lambda k^2} e^{-ikr} e^{ikr'}
\]

\[
\rho_0(r, r', \beta) = (4\pi\lambda\beta)^{-D/2} \ exp\left[ -\frac{(r-r')^2}{4\lambda\beta} \right]
\]

\[
\lambda = \frac{\hbar^2}{2m}
\]

\[
\beta = \frac{1}{k_b T}
\]

---

**Burkhard Militzer, UC Berkeley:** “Path Integral Monte Carlo”, 2012
Nodal action

- Principal rule: simply reject paths if they cross a node.
- Will lead to an error proportional to $\sqrt{\lambda \tau / r_{nn}}$
- Improved nodal action: solve for a particle next to a planar node. Use method familiar from electrostatics, the method of images:

$$\rho(r', r; t) = e^{-\frac{(r-r')^2}{4\lambda \tau}} - e^{-\frac{(r-r^*)^2}{4\lambda \tau}} = r^* = -r'$$

$$\delta S(r', r; t) = -\ln \left(1 - e^{\frac{dd'}{\lambda \tau}}\right)$$

$d$=distance to node $\approx |\nabla \ln \left(\rho(R, R'; \tau)\right)|^{-1}$

- Determine nodal distance using "Newton estimate."
- As paths approach within a thermal wavelength of the node, we get a repulsion, to account for the probability that a path could have crossed and recrossed within $\tau$. 

---

**Slide - David Ceperley**
II. Better nodes: Variational Density Matrix
Derivation of a Variational Density Matrix
(see Militzer, Pollock, Phys. Rev. E 61 (2000) 3470)

Bloch equation: \[ -\frac{\partial \rho}{\partial \beta} = \mathcal{H}_\rho \]

**Ansatz** for density matrix
\[ \rho(\mathcal{R}, \mathcal{R}'; \beta) = \rho(\mathcal{R}, q_1, \ldots, q_m) \quad q_k = q_k(\mathcal{R}', \beta) \]

**Variational principle:** \( \delta I = 0 \)
\[ I \left( \frac{\partial \rho}{\partial \beta} \right) = \int d\beta \int d\mathcal{R} \left( \frac{\partial \rho}{\partial \beta} + \mathcal{H}_\rho \right)^2 \]
\( \Rightarrow \) ordinary differential equations for \( q_k \) in imaginary time

Slater determinant: \( \rho(\mathcal{R}, \mathcal{R}'; \beta) = \| \rho^{[1]}(r_i, r_j'; \beta) \|_{ij} \)

**Gaussian Ansatz:**
\[ \rho^{[1]}(r, r', \beta) = (\pi w)^{-3/2} \exp \left\{ -\frac{1}{w} (r - m)^2 + d \right\} \]

**Variational parameters:**
- \( m \ldots \) mean position (\( = r' \))
- \( w \ldots \) squared width (\( = 4\lambda_\beta \))
- \( d \ldots \) amplitude (\( = 0 \))
Derivation of a Variational Density Matrix
(see Militzer, Pollock, Phys. Rev. E 61 (2000) 3470)

Gaussian Ansatz:

\[ \rho^{[1]}(r, r', \beta) = (\pi w)^{-3/2} \exp \left\{ -\frac{1}{w} (r - m)^2 + d \right\} \]
Comparison: T=0 and T>0 Fermion Methods

Analogy to Ground State Methods

\[ T = 0 \]
\[ \Psi_{GS}(\mathbf{R}) \]
\[ E \leq \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle \]

\[ T > 0 \]
\[ \rho(\mathbf{R}, \mathbf{R}'; \beta) = \sum_s e^{-\beta E_s} \Psi_s(\mathbf{R}) \Psi_s(\mathbf{R}') \]
\[ F \leq \text{Tr}[\tilde{\rho}H] + kT \text{Tr}[\tilde{\rho} \ln \tilde{\rho}] \quad \tilde{\rho} = \rho / \text{Tr}[\rho] \]

1. Effective Single Particle Level

\[ \Psi_{KS}(\mathbf{R}) = \begin{pmatrix} \phi_1(r_1) & \ldots & \phi_N(r_1) \\ \cdots & \cdots & \cdots \\ \phi_1(r_N) & \ldots & \phi_N(r_N) \end{pmatrix} \]
\[ \rho(\mathbf{R}, \mathbf{R}'; \beta) = \begin{pmatrix} \rho^{[1]}(r_1, r_1'; \beta) & \ldots & \rho^{[1]}(r_N, r_1'; \beta) \\ \cdots & \cdots & \cdots \\ \rho^{[1]}(r_1, r_N'; \beta) & \ldots & \rho^{[1]}(r_N, r_N'; \beta) \end{pmatrix} \]

LDA: \[ \epsilon_s \phi_s = -\frac{\nabla^2}{2} \phi_s + V_{\text{eff}} \phi_s \]

Variational solution of many-body Bloch Equation

2. Correlations beyond LDA or Mean Field

\[ \Psi_{\text{Jastrow}}(\mathbf{R}) = \Psi_{KS}(\mathbf{R}) \prod_{i,j} f(r_{ij}) \]

\[ \rho(\mathbf{R}, \mathbf{R}'; \beta) = \rho_{\text{MF}}(\mathbf{R}, \mathbf{R}'; \beta) \prod_{i,j} f(r_{ij}, r_{ij}'; \beta) \]

3. Diffusion QMC

Restricted PIMC
III. Example: Paths of two free particle
Fermionic Path Integrals
Example: 2 free particles

Distinguishable particles:
Consider path types: $A + B$

Bosons:
Consider path types: $A + B + C$

Direct fermions:
Consider path types: $A + B - C$

Restricted fermions:
Consider only path type: $A$
IV. Application to hot, dense hydrogen and Shock Wave Experiments
Molecular Hydrogen
Snapshot from a PIMC simulation with 32 protons and electrons

2 protons (pink spheres) and spin-up and one spin-down electron form one H₂ molecule.

Burkhard Militzer, UC Berkeley: “Path Integral Monte Carlo”, 2012
Molecular Hydrogen
Snapshot from a PIMC simulation with 32 protons and electrons

2 protons (pink spheres) and spin-up and one spin-down electron form one H₂ molecule.

- strongly interacting molecules, close to pressure dissociation
- Electrons are degenerate, partially delocalized
- Electron paths are permuting

Burkhard Militzer, UC Berkeley: “Path Integral Monte Carlo”, 2012
Metallic Hydrogen
Snapshot from a PIMC simulation with 32 protons and electrons

Free protons (pink spheres) and delocalized electrons.

Burkhard Militzer, UC Berkeley: “Path Integral Monte Carlo”, 2012
Recent **PIMC** work provides EOS for ICF conditions (FPEOS table constructed)

Hydrogen


For hydrogen, **PIMC** and **DFT-MD** Simulations Predict Consistent Shock Properties

Study planetary interiors in the laboratory: shock wave experiments

1) Two-stage gas gun (Livermore)  
   20 GPa in deuterium

2) Nova laser (Livermore) 340 GPa

3) Z capacitor bank (Sandia) 175 GPa

4) NIF…
Shock wave measurements determine the EOS on the Hugoniot curve

Conservation of mass, momentum and energy yields:

\[
\frac{\rho}{\rho_0} = \frac{u_s}{u_s - u_p}
\]

\[P - P_0 = \rho_0 u_s u_p\]

\[E - E_0 = \frac{1}{2}(V_0 - V)(P + P_0)\]

Gas gun (LLNL), Sesame model (Kerley), linear mixing model (M.Ross)
Deuterium Hugoniot
Nova laser shock wave experiments reached 3.4 Mbar

Why is the compressibility so high?
What does this imply for the dissociation of molecules?
Are electronic excitations important?

Nova laser results predict a 50% higher compressibility.
Deuterium Hugoniot
Path integral Monte Carlo results

- Accuracy increases with T
- Small size dependence
- Comparison of VDM and free particle nodes

Discrepancy:
\[ \Delta E/N = 3 \text{ eV} \]
\[ \Delta PV/N = -2 \text{ eV} \]

Good agreement between all \textit{ab initio} methods.

Militzer and Ceperley,
PIMC predicts low compressibility and agrees with more recent experiments.

Recent measurements agree reasonably well with first principle methods but need to be verified.

Militzer, Ceperley et al. 

- Predict low compressibility!

Good agreement with:

- Magnetic shocks waves
  [Knudson et al., *PRL* **87** (2001) 225501]

- Spherical converging shock waves
  [Belov et al, Boriskov et al.]

- DFT results (e.g. Bonev et al.)
V. Application to hot, dense helium
Helium DFT calculations agree well with gas gun shock experiment [Nellis PRL (1984)]
DFT-MD and classical MC simulation yield less than 4-fold compression

Classical MC simulation using the Aziz pair potential track the DFT-MD data reasonably well ⇒ compression less than 4-fold the initial density.
PIMC results yield more than 5-fold compression.

This high precompression is surprising because both PIMC and DFT-MD gave about 4-fold compression for hydrogen.
Add electronic excitations to DFT-EOS improves agreement with PIMC results.

For a number of MD configurations, quasi-static finite-temperature electronic corrections to the EOS increase the compressibility.
Laser and Z-machine can probe regime of 5-fold compression

Livermore gas gun:
Deuterium: 23.4 GPa
Helium: 15.6 GPa

Livermore Nova laser:
Deuterium: 340 GPa
Helium: 270 GPa

Sandia Z-machine:
Deuterium: ~175 GPa
Helium: ~124 GPa
The pressure is severely underestimated by the SC model.
For Helium, PIMC and DFT-MD Simulations have been combined to make one consistent EOS table


For Helium, **PIMC** and **DFT-MD** Simulations have been combined to make one consistent **EOS** table

$$\frac{(P-P_0)}{P_0}$$

**Temperature (K)**

- **$r_s=1.25$**
- **$r_s=1.86$**
- **$r_s=2.4$**

New Experimental Technique: Combination of Static and Dynamic Compression

1) Static compression
   Diamond anvil cell

2) Dynamic shock comp.
   Laser shocks

- LLNL-CEA collaboration
- Samples are precompressed in modified diamond anvil cell
- Precompression up to 1.5 GPa = 15 kbar
Comparison of PIMC Simulations with Laser Shock Experiments on Helium

Comparison of PIMC Simulations with Laser Shock Experiments on Helium

Comparison of PIMC Simulations with Laser Shock Experiments on Helium

Comparison of PIMC Simulations with Laser Shock Experiments on Helium

Principal Hugoniot:

Shock Compression of Quartz to 1.6 TPa: Redefining a Pressure Standard

M. D. Knudson and M. P. Desjarlais
Sandia National Laboratories, Albuquerque, New Mexico 87185-1195, USA
(Received 25 June 2009; published 24 November 2009)

VI. PIMC of Carbon and Water Plasmas
Regime of Warm Dense Matter requires new simulation techniques – Application ICF experiments

Effects of bonding, ionization, exchange and correlation, and quantum degeneracy all important.
Carbon is a promising ablator for Inertial confinement fusion (ICF).
We are working with LLNL on carbon EOS.
Why were there no PIMC calculations for elements heavier than helium until 2012?

Problem 1: **Nonlocal pseudopotentials** in fermionic path integrals

\[
\langle R | \hat{\rho}_{n,l} | R' \rangle = \langle R | e^{-\tau[\hat{T} + \hat{V}_{n,l}]} | R' \rangle
\]

→ Sign problem even for the 1-particle scattering problem.

Problem 2: **More accurate nodes** needed at low temperature.

Problem 3: Acceptance ratio of **reference point moves** decreases at low temperature. Low sampling efficiency.

Hydrogen: \(T > 0.1 \times T_{\text{fermi}}\)

Alternative: Coupled Electron-Ion Monte Carlo (Delaney, Pierleoni, Ceperley)

Reintroduce Born-Oppenheimer approximation:

- Classical MC for the ions \((T_{\text{ion}} > 0)\)
- QMC for the electrons \((T_{\text{el}} = 0)\)
First Path Integral Monte Carlo Simulations for Heavier Elements Fill this Gap in Temperature

Water
Density=3.18 g/cm$^3$
24-atom cell

Water
Density=11.18 g/cm$^3$
24-atom cell

- Plot showing the ratio $(P-P_0)/P_0$ vs. Temperature (K) for two different densities of water.
- The x-axis represents the temperature in Kelvin, ranging from $10^4$ to $10^8$.
- The y-axis represents the ratio $(P-P_0)/P_0$, ranging from -0.8 to 0.
- The graph includes data points for PIMC, DFT-MD, and a Debye model.
Again **Path Integral Monte Carlo** bridges the Gap in $T$ between DFT-MD and the Debye Model.
Path Integral Monte Carlo bridges the Gap in Internal Energy vs Temperature for Water and Carbon Plasmas.

![Graph showing the internal energy vs temperature for water and carbon plasmas. The graph compares the results between PIMC, Debye model, and DFT-MD simulations. The graphs show the relative energy change ($\frac{E-E_0}{E_0}$) for different densities of water and carbon. The densities and temperatures are indicated on the graph.]

- Water: $11.18 \text{ g/cm}^3$ with $E_0$ at $10^4$ K.
- Carbon: $12.64 \text{ g/cm}^3$ with $E_0$ at $10^4$ K.
- Carbon: $3.18 \text{ g/cm}^3$ with $E_0$ at $10^4$ K.
Study Structural Properties: **Pair Correlation Functions for Water and Carbon Plasmas**

Carbon Density = 12.64 g/cm$^3$

Water Density = 11.18 g/cm$^3$

$T = 750,000$ K

![Graph showing pair correlation functions for Carbon and Water]
Path Integral Monte Carlo and DFT-MD are in very good agreement

Carbon Density = 12.64 g/cm$^3$
Water Density = 11.18 g/cm$^3$
T = 750,000 K

Why do free-particle nodes work for PIMC simulations of first-row elements?

Core electrons are fully ionized. Free-particles nodes are ideal!

1s state doubly occupied. Others ionized. Free-particles nodes should still work.

1s 100% occupied, 2s less than 60% occupied Free-particles nodes in PIMC are accurate for $T > 250,000$ K for carbon and water plasmas.

2s 100% occupied. Free-particles nodes do no longer work but KS-DFT works!
Summary

• Presented new path integral Monte Carlo simulations for heavier elements (all-electron simulations, free particles nodes).
• Very good agreement with DFT for carbon and water plasmas.
• No insufficiencies in the ground-state exchange-correlation functionals.
• We constructed again consistent EOS table for C and H₂O.
• More materials to be studied. Please make suggestions!

The End