Recent Progress in QMC

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New techniques allowing us to do new problems:

- Effective mass of the 2DEG
- The metal-insulator transition in liquid hydrogen

Support from NSF, CNRS, CNR and DOE (SCIDAC & NNSA)

Computer time from NCSA and ORNL

New QMC Techniques

- Better Finite-Size scaling methods
  - Twist averaging for kinetic energy
  - Coulomb correction for potential energy
- Better trial wavefunctions -> better nodes
  - Backflow
  - Iterated backflow
  - Direct coupling to DFT
- Coupled Electron-Ion Monte Carlo
- Optimization
- Computers/parallelization
- Algorithms (e.g. reptation, AFQMC)

Fermi Liquid parameters in the 2DEG

Kwon, Y., Ceperley, D. M. and Martin, R. M., PRB50, 1684 (1994).

Effective mass computed from the energy of particle-hole excitations about the Fermi surface.

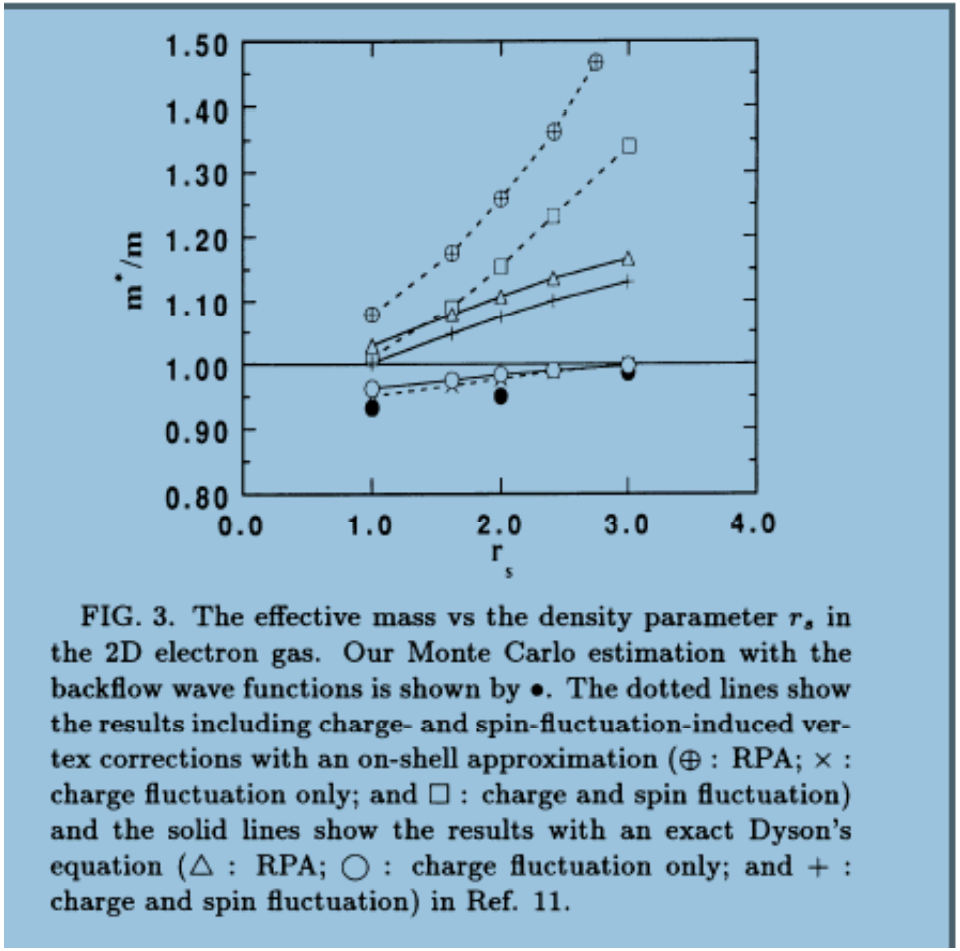


FIG. 3. The effective mass vs the density parameter r_s in the 2D electron gas. Our Monte Carlo estimation with the backflow wave functions is shown by •. The dotted lines show the results including charge- and spin-fluctuation-induced vertex corrections with an on-shell approximation (⊕ : RPA; × : charge fluctuation only; and □ : charge and spin fluctuation) and the solid lines show the results with an exact Dyson's equation (△ : RPA; ○ : charge fluctuation only; and + : charge and spin fluctuation) in Ref. 11.

Substantially different from theory!

New Finite size methods

S. Chiesa, DMC, R.M. Martin, M. Holzmann, PRL **97, 076404 (2006)**

Consider the energy in a finite system in PBC and in the thermodynamic limit:

$$E(L) = \sum_k \frac{k^2}{2m} n_k^L + \sum_k v(k)[S^L(k) - 1]$$

$$\frac{E(\infty)}{V} = \int \frac{d^D k}{(2\pi)^D} \frac{k^2}{2m} n_k^\infty + \int \frac{d^D k}{(2\pi)^D} v(k)[S^\infty(k) - 1]$$

- finite size errors are integration errors
- singularities/non-analytic points dominate size errors
  - k=0 in potential energy
  - $k=k_F$ in kinetic energy

Twist averaged boundary conditions

- In periodic boundary conditions, the wavefunction is periodic⇒Large finite size effects for metals because of fermi surface.
- In twist averaged BC, we use an arbitrary phase θ as r →r+L
- Integrate over all phases, i.e. Brillouin zone integration.
- Momentum distribution changes from a lattice of k-vectors to a fermi sea.
- Eliminates single-particle finite-size effects.

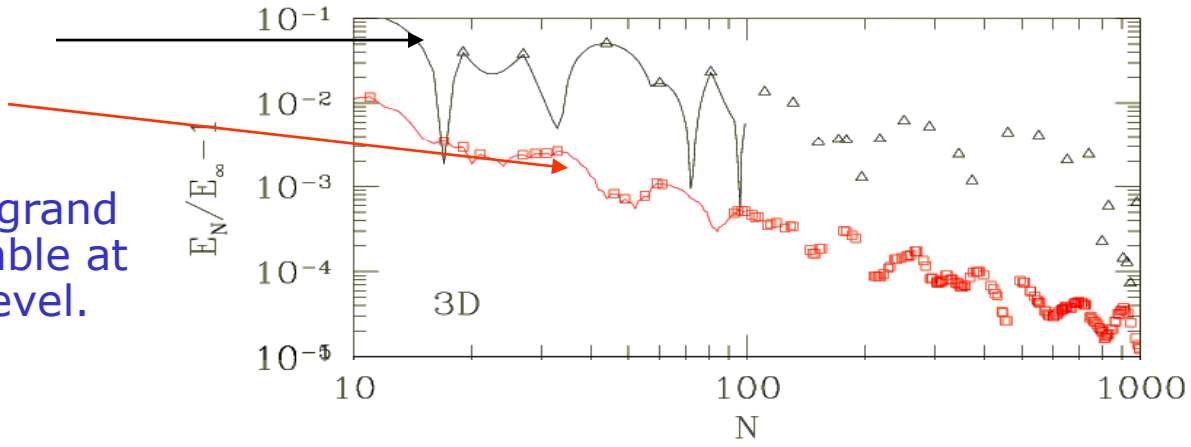
$$\Psi(x+L) = e^{i\theta}\Psi(x)$$

$$\bar{A} = \frac{1}{(2\pi)^3}\int_{-\pi}^{\pi} d^3\theta \left\langle \Psi_\theta A \Psi_\theta \right\rangle$$

Error with PBC

Error with TABC

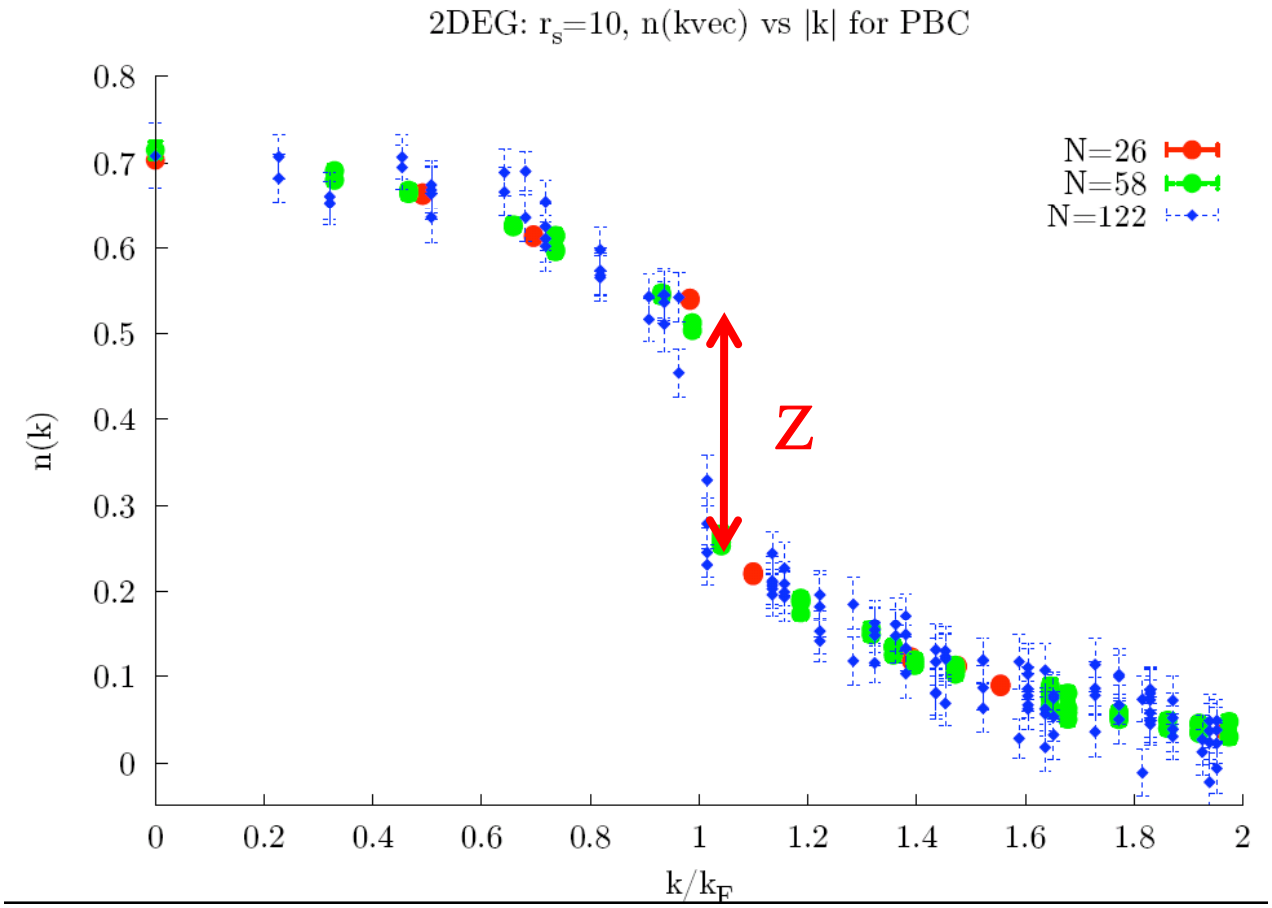
Error is zero in the grand canonical ensemble at the mean field level.



Excitations in the 2DEG

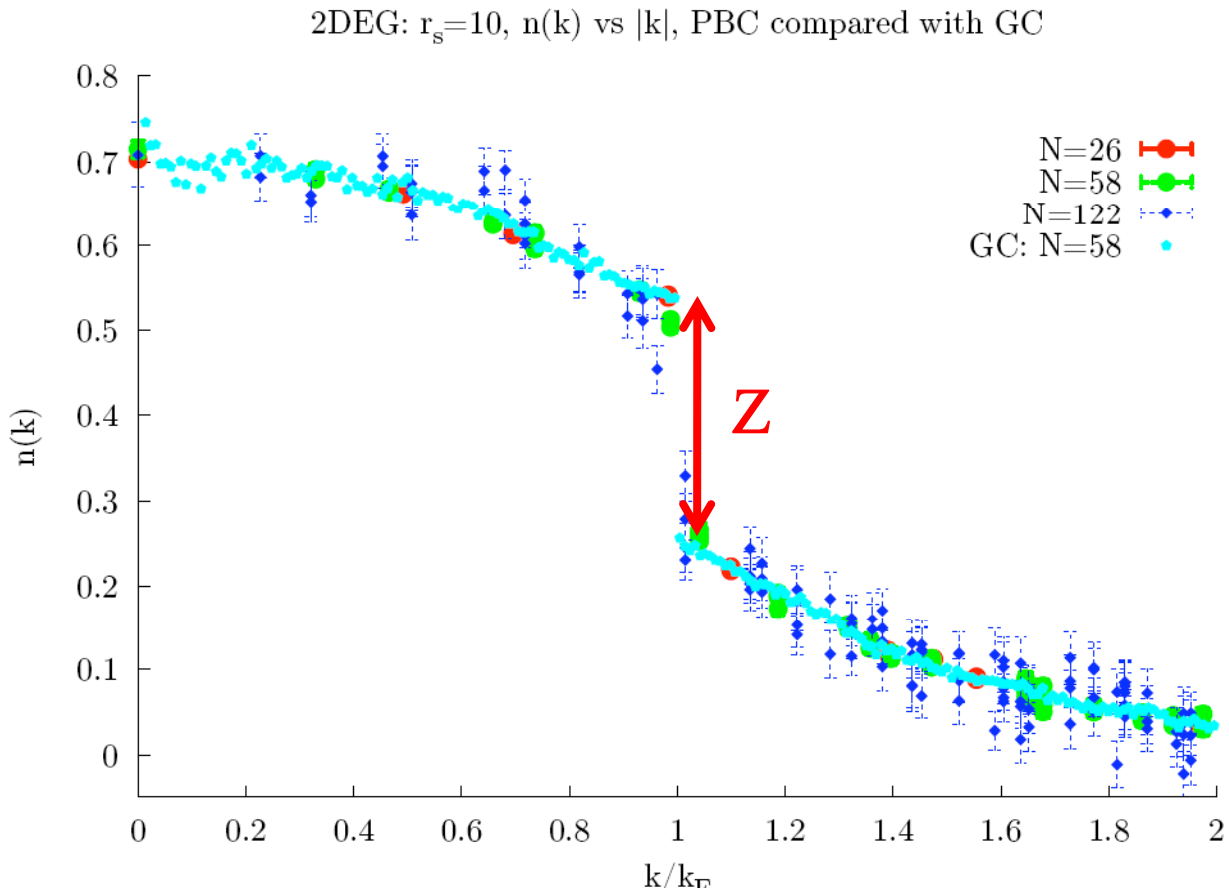
M. Holzmann, B. Bernu, V. Olevano, R. M. Martin and DMC, PRB 79, 041308 (2009)

The quasiparticle strength is determined by the jump of the momentum distribution at the fermi level:

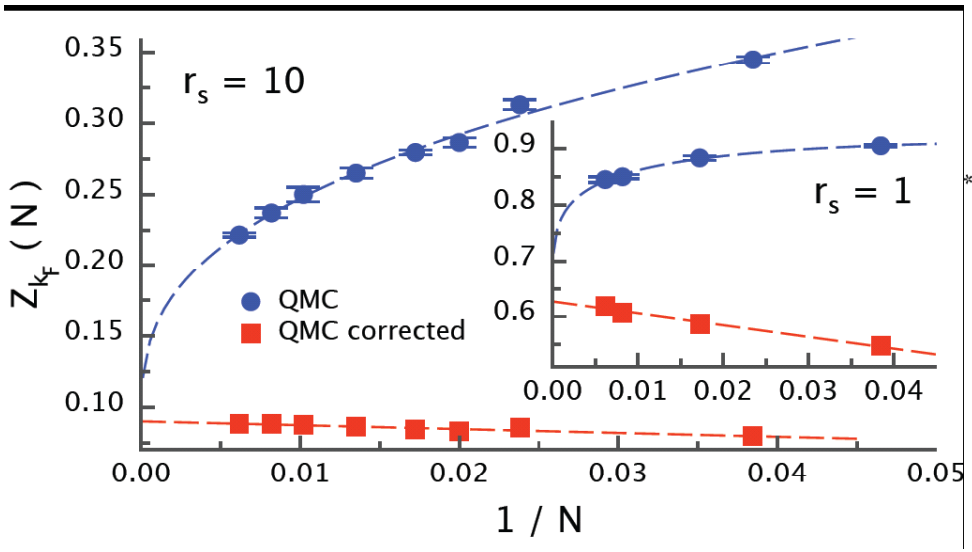


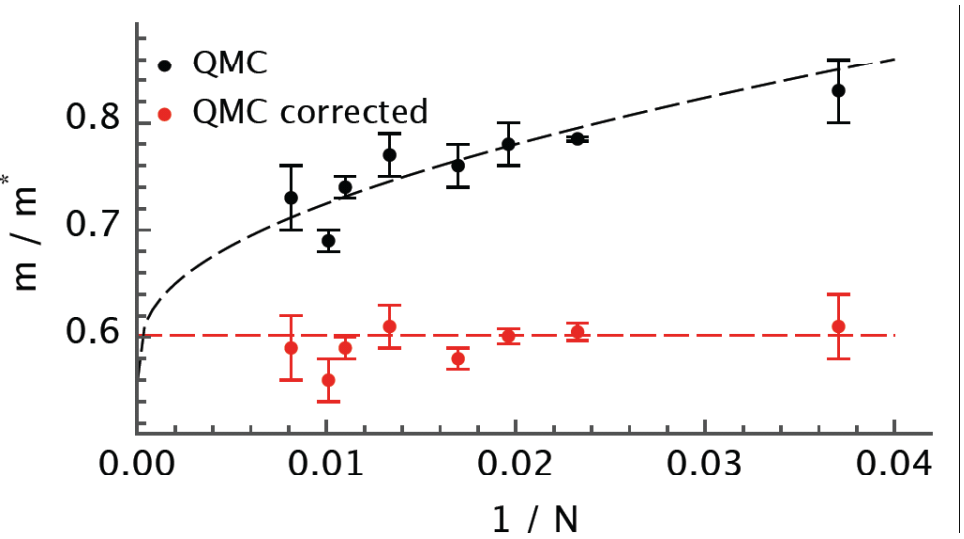
Excitations in the 2DEG

With twist averaging in the GCE we get a continuous curve with no shell effects.



But simple extrapolation gives incorrect values





Finite size theory for quasiparticle stength using long-range correlations

$$Z^{\infty}_{k_F} \simeq Z^{N}_{k_F} e^{-\Delta_N} \qquad \Delta_N \simeq \left(\frac{\pi r_s^2}{4N}\right)^{1/4}$$

Momentum distribution n(k): Size effects due to long range Jastrow

use reweighting estimator $$n_{\mathbf{k}}^N = \left\langle e^{-i\mathbf{k}\cdot\mathbf{r}-\delta U_N} \frac{D(\mathbf{R}:\mathbf{r}_j+\mathbf{r})}{D(\mathbf{R})} \right\rangle$$

with $$\delta U_N = \frac{1}{V}\sum_{\mathbf{q}\neq 0} u_q \left[e^{i\mathbf{q}\cdot\mathbf{r}_j}\rho_{-\mathbf{q}} - 1\right]\left[e^{i\mathbf{q}\cdot\mathbf{r}} - 1\right]$$

in thermodynamic limit becomes: $$\delta U_{N\to\infty} \to \int \frac{d^2\mathbf{q}}{(2\pi)^2} u_q \left[e^{i\mathbf{q}\cdot\mathbf{r}_j}\rho_{-\mathbf{q}} - 1\right]\left[e^{i\mathbf{q}\cdot\mathbf{r}} - 1\right]$$

expand estimator up to 2nd order in $$\delta U_\infty - \delta U_N \simeq \int_{-\pi/L}^{\pi/L} \frac{d^2\mathbf{q}}{(2\pi)^2} u_q \left[e^{i\mathbf{q}\cdot\mathbf{r}_j}\rho_{-\mathbf{q}} - 1\right]\left[e^{i\mathbf{q}\cdot\mathbf{r}} - 1\right]$$

use mode decoupling for k->0 and analytical behavior of u_q and struture factor S(q)

$$2nu_q \simeq -1 + \left[1 + (2nv_q/\varepsilon_q)\right]^{1/2}$$

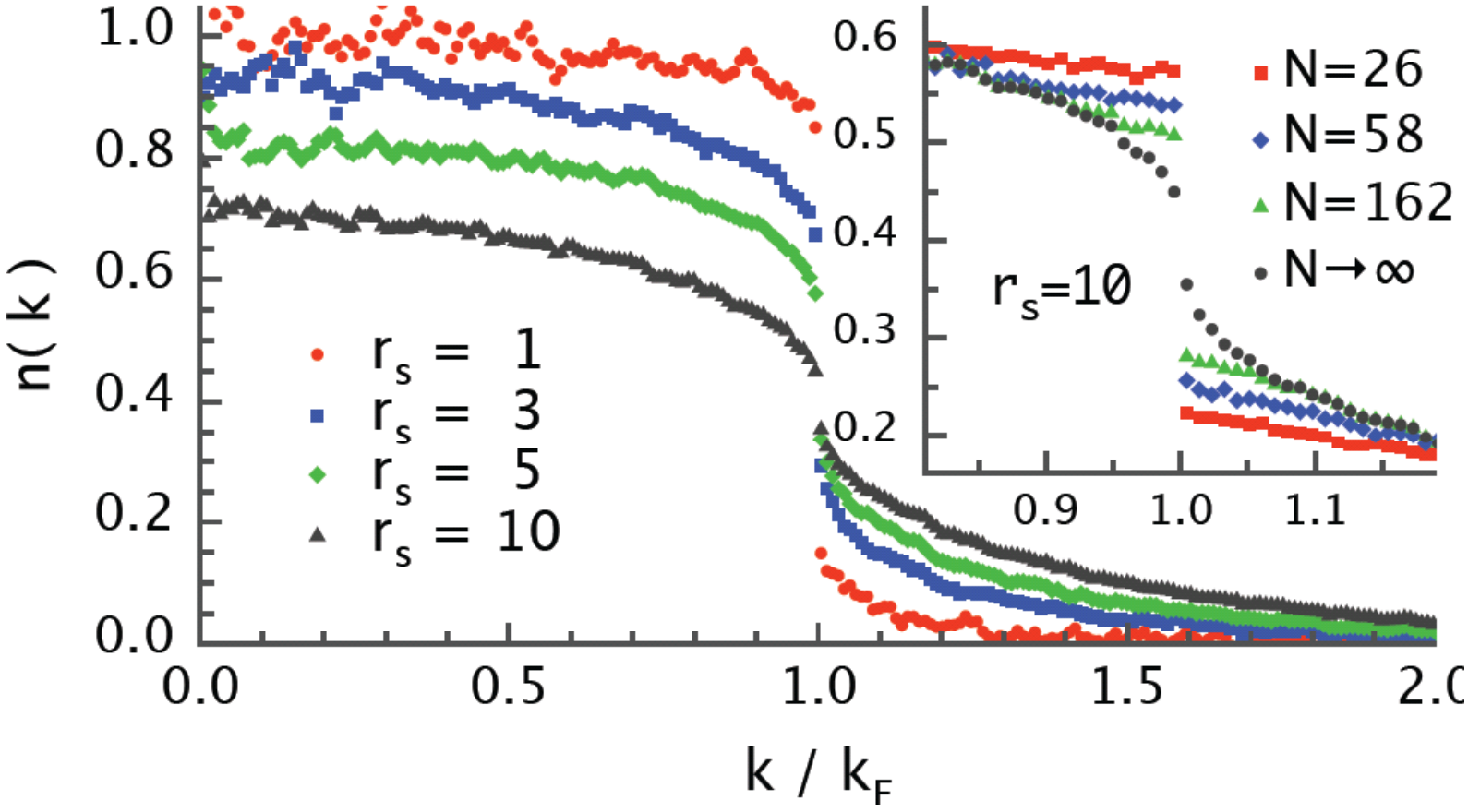
$$S(q) \simeq \left[2nu_q + 1/S_0(q)\right]^{-1}$$

analytical corrections:

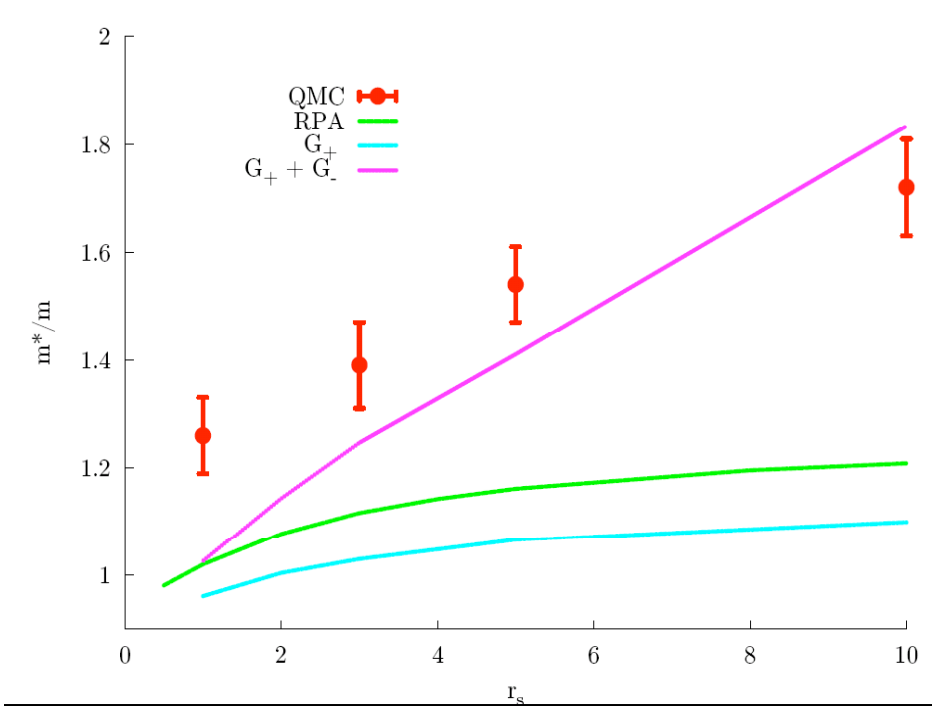
$$\delta n_{\mathbf{k}} \simeq Z_{k_F}^N \int_{-\pi/L}^{\pi/L} \frac{d^2\mathbf{q}}{(2\pi)^2}\delta(q)\left[\theta(k_F - |\mathbf{k}+\mathbf{q}|) - \theta(k_F - k)\right]$$

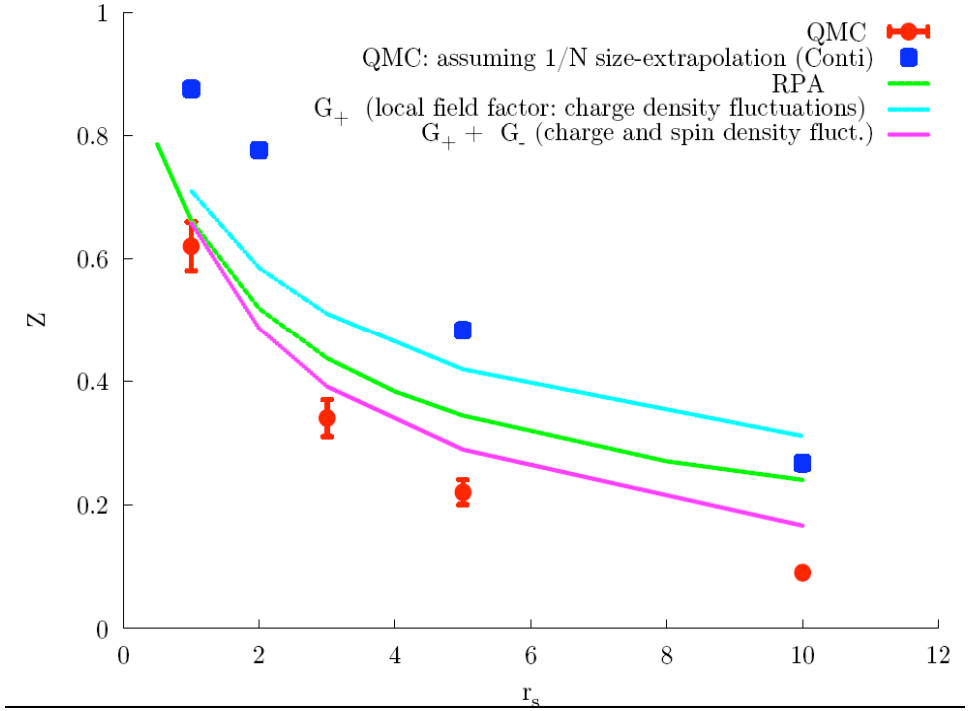
$$\delta(q) = \left[u_q\left(1 - S(q)\right) - nu_q^2 S(q)\right]$$

Corrected momentum distribution



Results are now closer to other theories



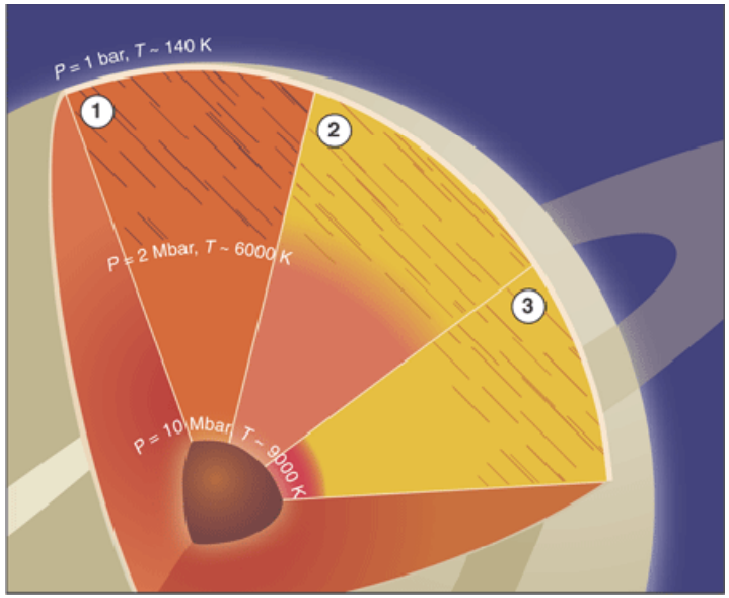


H.-J. Schulze, P. Schuck, and N. Van Giai, Phys. Rev. B **61,** 8026 2000.(RPA)

R. Asgari, B. Davoudi, M. Polini, G. F. Giuliani, M. P. Tosi, and G. Vignale, Phys. Rev. B **71, 045323 2005.**

Calculation of hydrogen and helium at high pressures

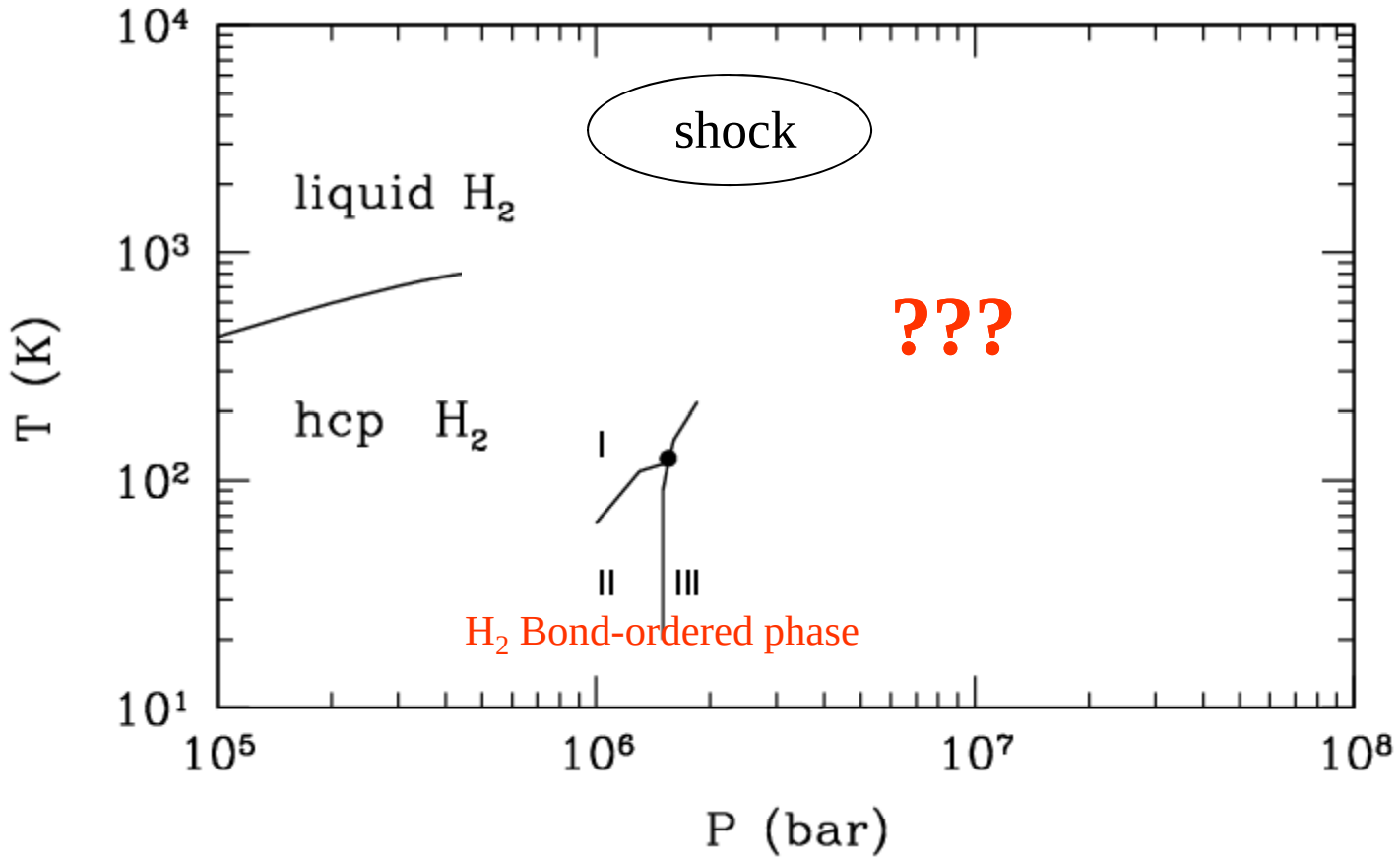
M. A. Morales, E. Schwegler,, C. Pierleoni & DMC



Taken from: Fortney J. J., *Science* **305**, 1414 (2004).

- Giant Planets
  - Primary components are H and He
  - P(ρ, T, x_i) closes set of hydrostatic equations
  - Interior models depend very sensitively on EOS and phase diagram
- Challenge from astrophysics: calculate P(ρ, T, x_i) to 1% (ab initio)

Experimentally-known High Pressure Phase Diagram of H



little experimental data available for planetary conditions

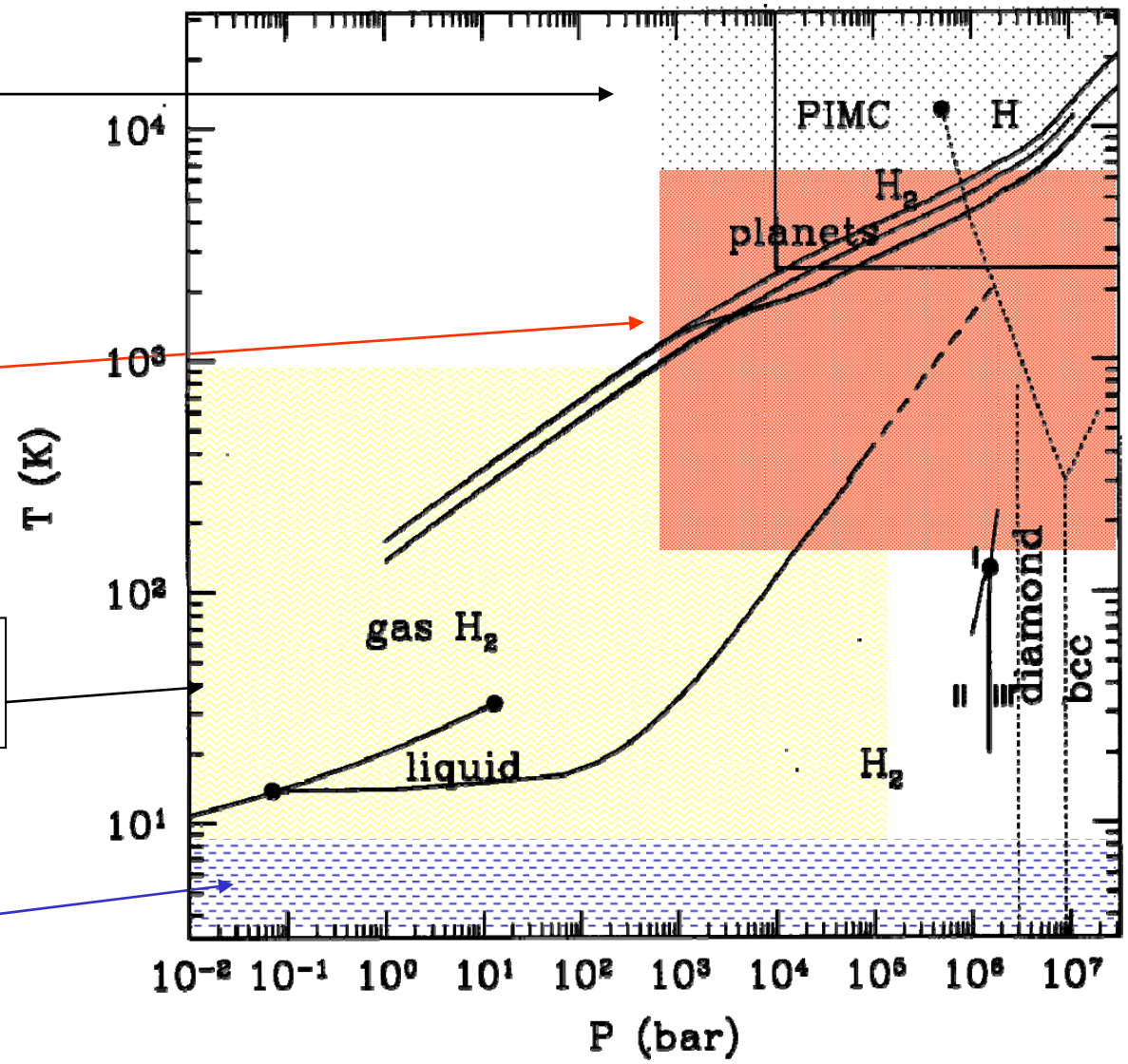
Phase diagram of Dense Hydrogen

Path Integral MC for $T > E_F/10$

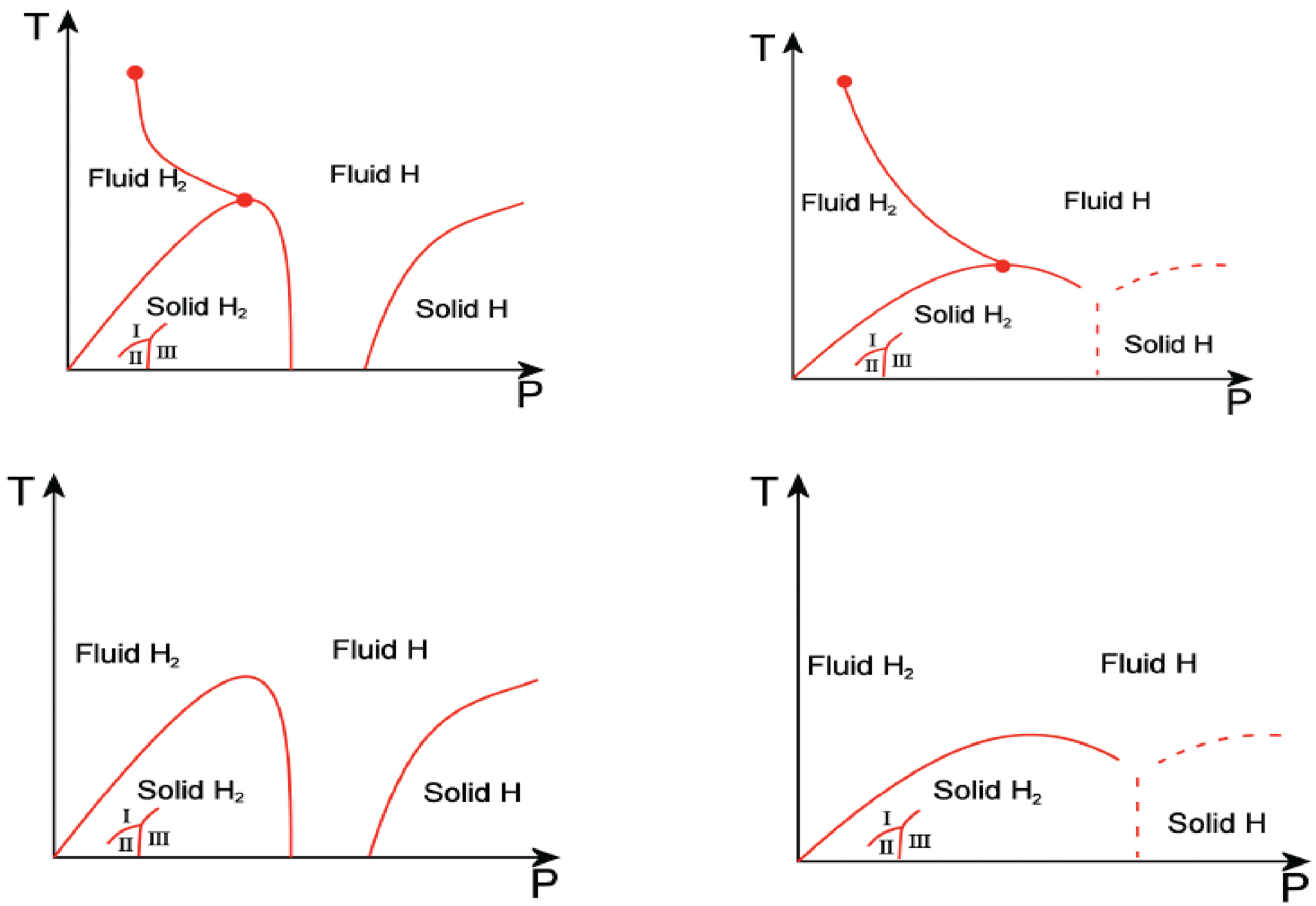
Coupled-electron Ion MC

Path Integral MC with an effective potential

Diffusion MC T=0

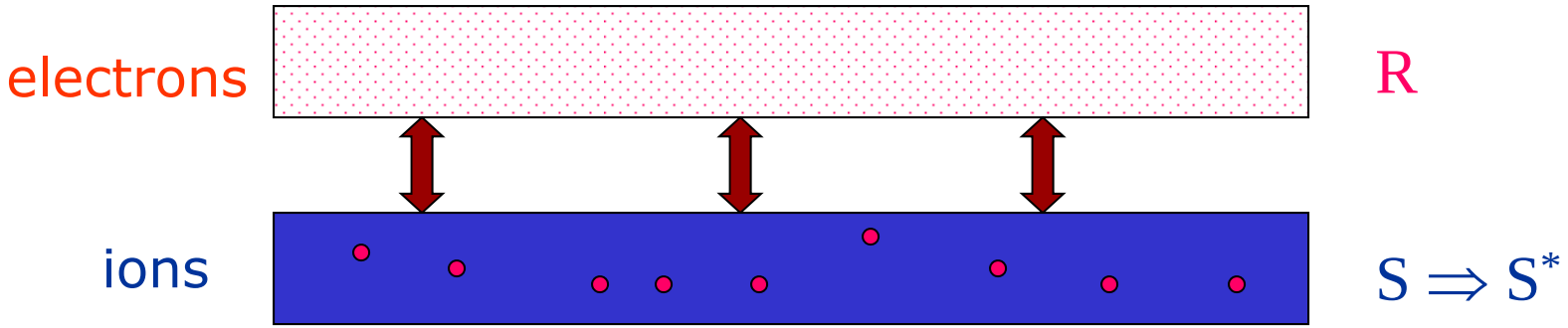


Possible Phase Diagrams for high pressure hydrogen



Coupled Electron-Ionic Monte Carlo:CEIMC

1. Do Path Integrals for the ions at T>0.
2. Let electrons be at zero temperature, a reasonable approximation for room temperature simulations.
3. Use Metropolis MC to accept/reject moves based on QMC computation of electronic energy



The "noise" coming from electronic energy can be treated without approximation using the "penalty method."

Simulation Methods

Density Functional Theory

- QBOX (LLNL) and CPMD (IBM) using PBE functional
- Born-Oppenheimer MD
- Norm-conserving pseudopotentials
- Ecut: 90-115 Ry
- Gamma-point 432 electrons

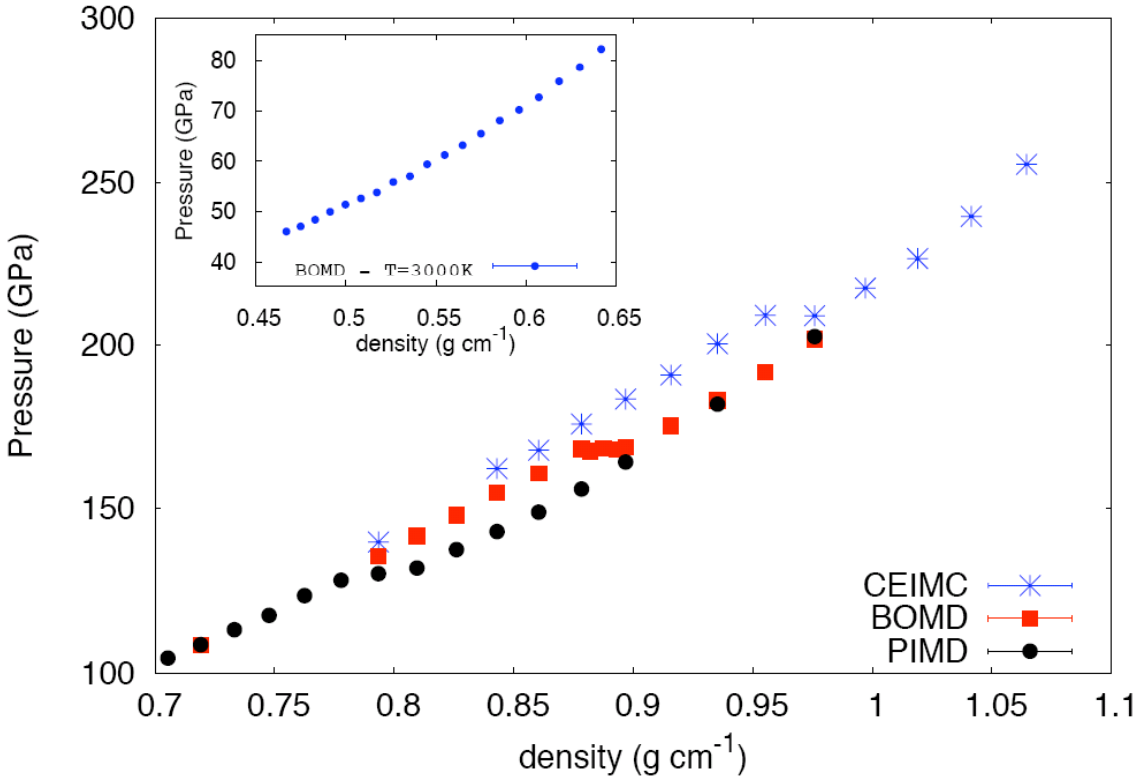
Quantum Monte Carlo

- Coupled Electron-Ion Monte Carlo
- Electrons at T=0K with Reptation Quantum Monte Carlo
- 54/108 electrons
- Slater (based on DFT) Jastrow trial wave function with backflow.

- No pseudopotential
- Twist Averaged Boundary Conditions: 4x4x4 grids
- quantum protons

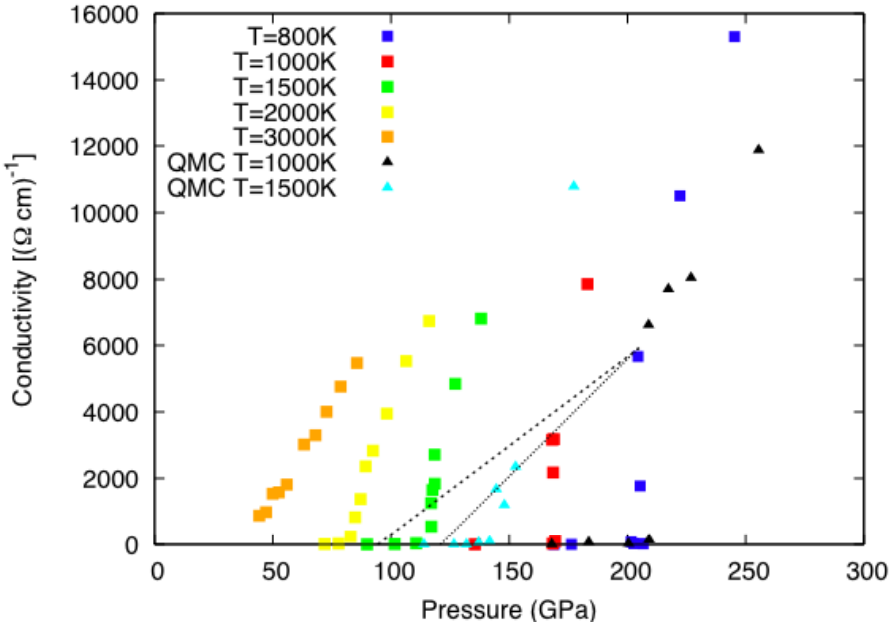
"Plasma Phase" Transition

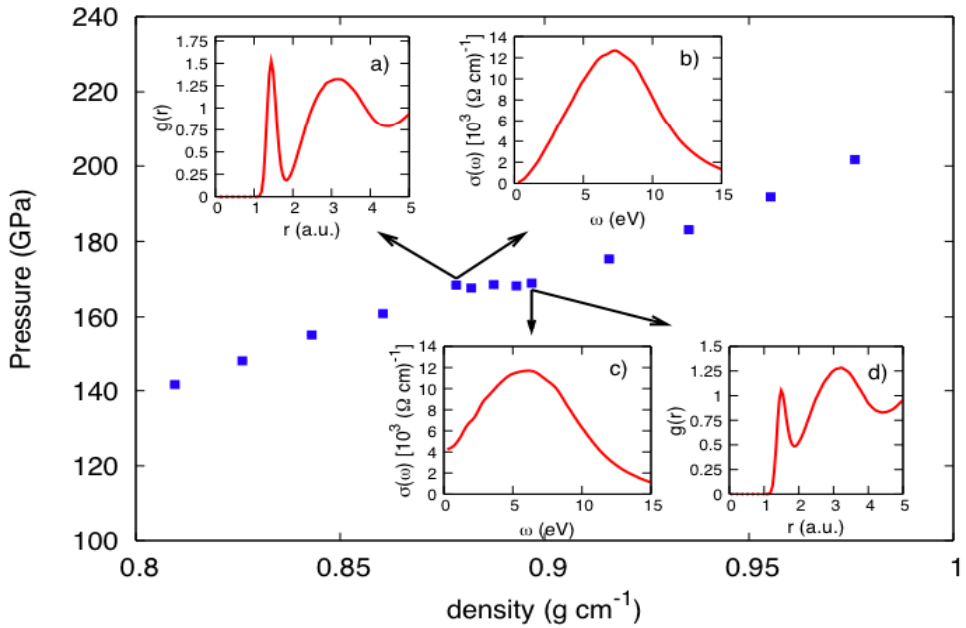
- Pressure plateau at low temperatures (T<2000K)
- signature of a 1st order phase transition
- Seen in CEIMC and BOMD at different densities
- What's new?
  - Careful convergence
  - Finite size effects
  - Narrow transition region
- Metal-insulator or atomic-molecular?



T=1000K

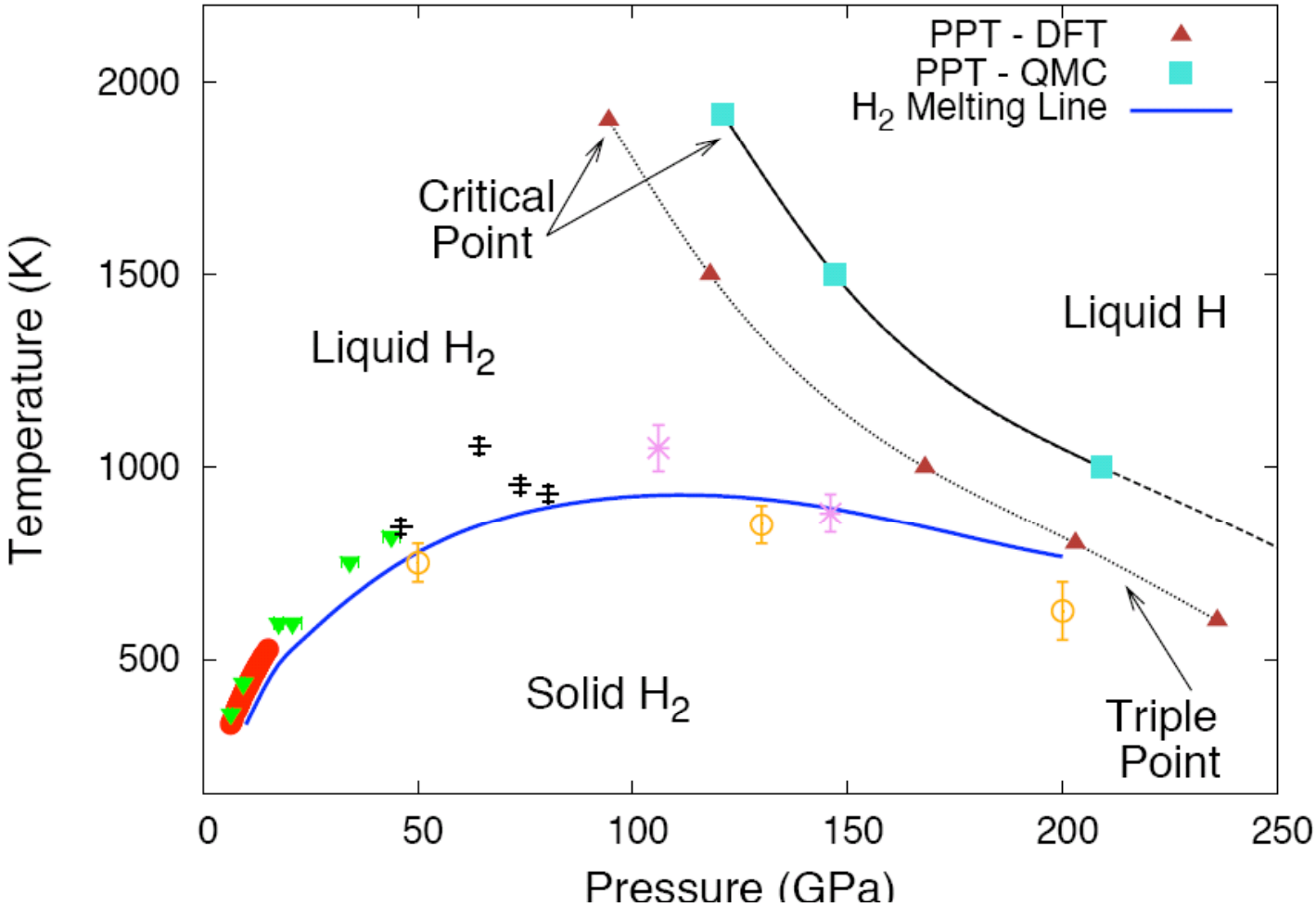
Electronic Conductivity at transition





- Sharp metallization across the transition
- Atomic-molecular transition more continuous
- Extrapolate discontinuity to find critical point

Revised Hydrogen Phase Diagram



A feature of Monte Carlo?

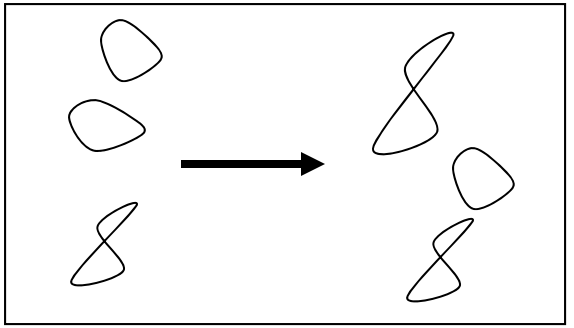
averages are almost free.

Suppose we have an extra parameter "q" to sum over.

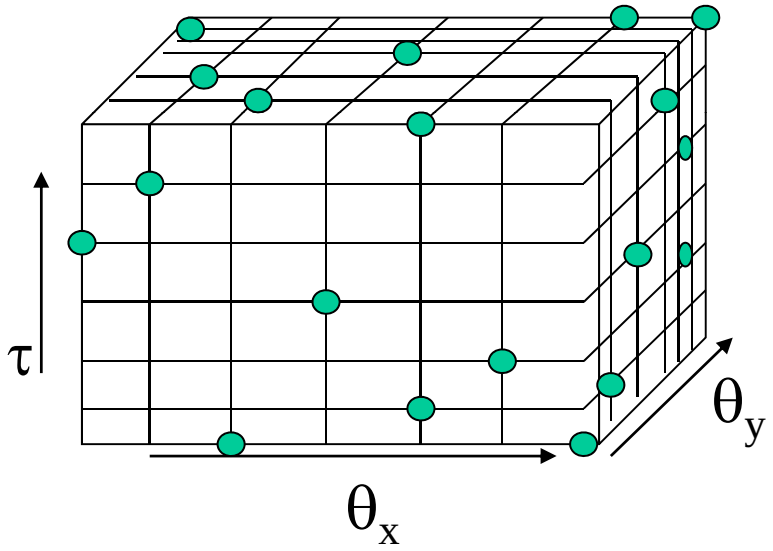
$$E(s) = \frac{1}{M}\sum_{i=1}^{M} E(s;q_i)$$

- This extra parameter will not slow down the calculation by Monte Carlo: it is just one more variable to average over.
- M calculations on M separate processors for different values of q: all serve to reduce the error bar.
  1. Path Integrals for protons(M_1 time slices)
  2. k-point sampling (M_2 k-points)
- In explicit methods such as CP-MD these extra variables will increase the CPU time by $M_1 M_2$.

- Make a move of the protonic paths
- Partition the 4D lattice of boundary conditions (θ_x θ_y θ_z) and imaginary time (τ) in such a way that each variable is uniformly sampled (stratified)
- Send them all out to M separate processes
- Do QMC to get energy differences and variances
- Combine to get global difference and variance.



$$R_\tau \rightarrow R'_\tau$$



$$\Delta E_{BO} = \frac{1}{M}\sum E_{\theta,\tau}$$

$$\sigma^2 = \frac{1}{M^2}\sum \sigma^2_{\theta,\tau}$$

The result is a code scaling well to thousands of nodes and competitive with Car-Parrinello MD.

- PPT predicted in pure hydrogen
  - Critical point at T~2000K
  - Intersects melting line below T~800K, above 200 GPa.
- QMC today is competitive with other methods for dense hydrogen and potentially much more accurate.
- Progress in these simulations in last 40 years from:
  - Computer power: this method scales with processors
  - Algorithmic power: better trial functions, QMC methods
- We are now in position to do much more accurate simulation of hydrogen, helium, mixtures…
- More work needed in algorithms to get higher accuracy, treat larger systems, and heavier elements.

First Principles Simulation of Liquid Water

John Gergely, Jeongnim Kim, Jeremy McMinis, DMC

Long autocorrelation time

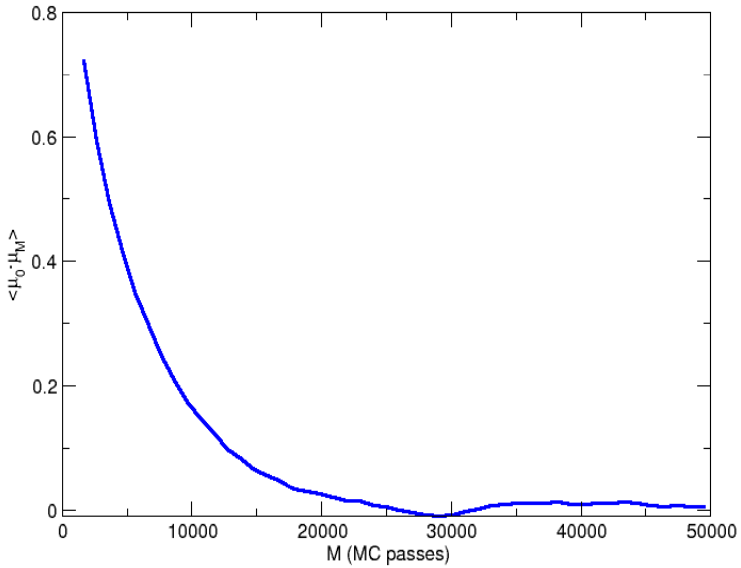
- order 1ps hydrogen bond lifetime
- May lead to unconverged simulations

Quantum Effects

- Zero point motion of protons is very important
- Standard path integral formulation increases computational cost by ~50

Electronic Structure

- How accurate is DFT-GGA?



Obtaining uncorrelated samples requires of order 10000 MC passes (equivalent to 10 ps MD trajectory)

QMC Studies of Liquid Water

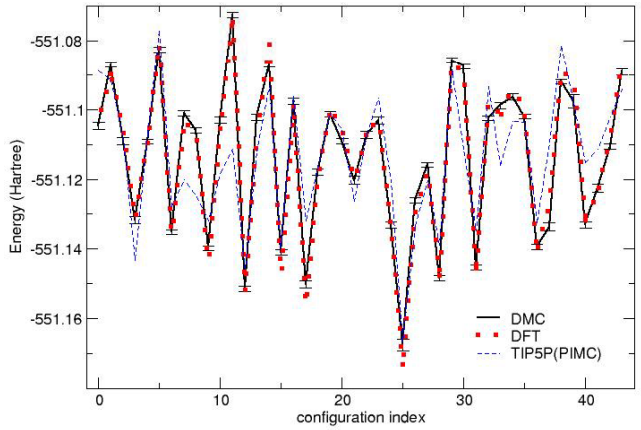
- Generated water configurations (mostly 32 molecules) using DFT and model potentials at several temperatures (T = 0, 25, 100 C, 1 atm)
- For each configuration, orbitals from self-consistent DFT-GGA (PBE) plus VMC optimization of correlated trial function.
  - 300 Ry energy cutoff
  - Trail-Needs norm-conserving pseudopotential for O.
  - DFT & VMC uses about 1% of cost
- Ran Diffusion Monte Carlo for each configuration.
- Errors on energy for 32 molecules are less than 1 mHartree (or 9K/molecule). (part per million accuracy!)
- 50K hours of run time per configuration. We have done several hundred configurations.
- Early access allocation on Jaguar-pf at Oak Ridge National Laboratory.

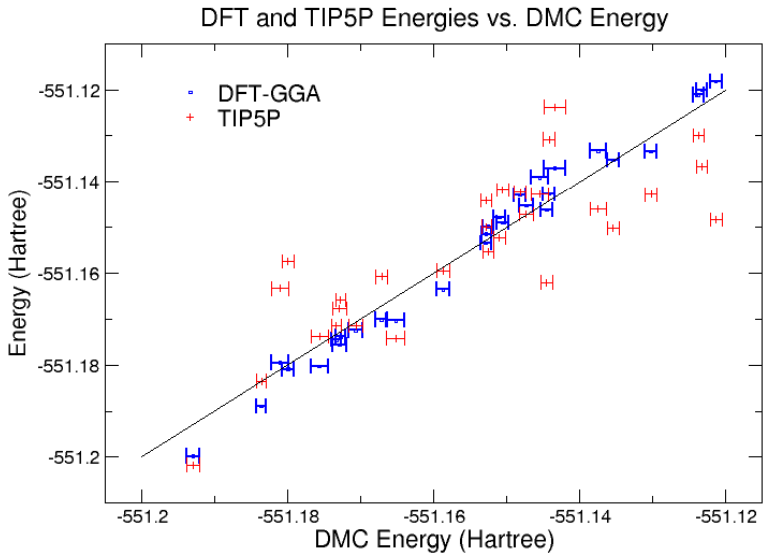
Comparing DMC with DFT-GGA &TIP5P Energies

•40 configurations from a TIP5P simulation at 300K.

•Average deviation of GGA (PBE)-DFT energies from DMC is 3.5 s or ~35K/molecule.

•Average deviation of TIP5P energies from DMC is 10 s or ~100K/molecule.





Conclusions

- Quantitative difference between DMC and DFT PES (4 σ)
- Model pairwise potentials differ from DMC by 10 σ or more
- Model and DMC PES are sufficiently correlated to make presampling viable
- VMC and DFT deviation from DMC are comparable: need to improve trial function by adding backflow, better electronic correlation,…
- Reweighting approach to structural and thermodynamic properties inconclusive due to statistical errors and algorithmic limitations

Future work

- Simulations needed for larger ice and water systems (96 molecules)
- Free energy perturbation theory of water-ice transition: can we get the melting temperature right?
- Data for new model for water. (Including forces).
- Public database for water "energy surface"
- More efficient MC sampling algorithms and new "actions" to make more efficient path integral simulations of water.
- Full *ab initio Coupled Electron - Ion MC* on water is very expensive but feasible with presampling.
- Eventual goal is speedup of order 10^3 – 10^4.
- Is CEIMC feasible on petascale computers?