Path Integral Monte Carlo Methods for the Homogeneous Electron Gas

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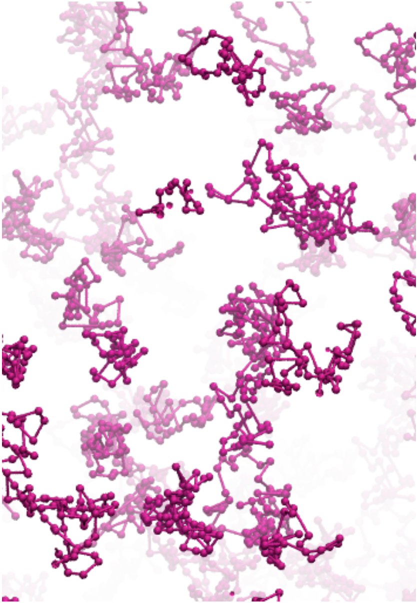
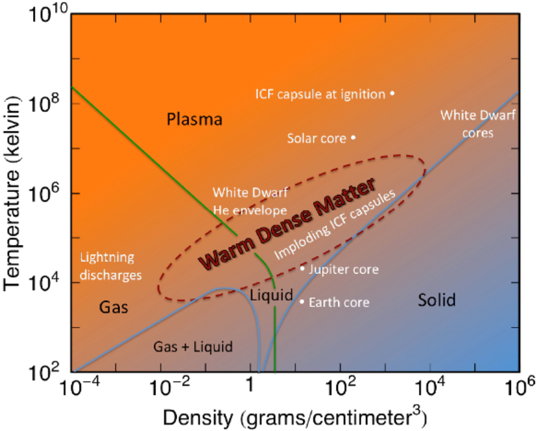
INT, Seattle, July 17, 2013



Warm Dense Matter

Somewhere between weakly coupled plasma and condensed matter physics

- Coulomb coupling: $\Gamma \equiv (q^2/a)/k_B T \sim 1$
- Degeneracy temperature: $\Theta \equiv k_B T/\epsilon_F \sim 1$
- Thermal DeBroglie Wavelength: $\lambda_T/a \equiv (\hbar/mk_B T)^{1/2}/a > 1$



(http://www.qtp.ufl.edu/ofdft/problem/wdmissue.shtml, 2012)

Density Functional Theory

Kohn-Sham DFT:

$$E_{V_{KS}}[n] = \min_{\psi \to n(r)} \langle \psi \mid \hat{T} \mid \psi \rangle + E_H[n] + E_{xc}[n] + \int V(r)n(r)dr$$
$$\text{where } n(r) = \sum_\alpha \mid \phi_\alpha \mid^2$$

Local Density Approximation:

$$E_{xc}[n] = \int d^d r n(r) e_{xc}(r) \approx \int d^d r n(r) e_{xc,0}^{hom}(n(r)) \equiv E_{xc}^{LDA}[n]$$

Mermin Formulation:

$$n(r,T) = \sum_\alpha f(\epsilon_\alpha - \mu(T)) \mid \phi_\alpha(r) \mid^2$$

Orbital-Free DFT (OFDFT):

$$E[n] = T[n] + U[n] + V[n] = T_s[n] + U_H[n] + E_{xc}[n] + V[n]$$

One Component Plasma (OCP) a.k.a. Homogeneous Electron Gas (HEG) a.k.a. Jellium

$$\begin{aligned}
\mathcal{H} &= \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{\mid r_i - r_j \mid} + \mathcal{H}_{e-b} + \mathcal{H}_{b-b} \\
&= -\frac{1}{r_s^2}\sum_i \nabla_i^2 + \frac{2}{r_s}\sum_{i\neq j}\frac{1}{\mid \vec{r}_i - \vec{r}_j \mid}
\end{aligned}$$

Wigner-Seitz radius:

$$\begin{aligned}
\frac{4\pi}{3}a^3 &\equiv \frac{1}{n} \\
r_s &\equiv a/a_B \\
\lim_{r_s\to 0} &\Longrightarrow \text{Kinetic term dominates} \\
\lim_{r_s\to\infty} &\Longrightarrow \text{Potential term dominates}
\end{aligned}$$

Coulomb Coupling Parameter,

$$\Gamma \equiv e^2/(ak_B T) \sim 1/(r_s T)$$

Degeneracy Temperature,

$$\Theta \equiv T/T_F \sim r_s^2 T$$

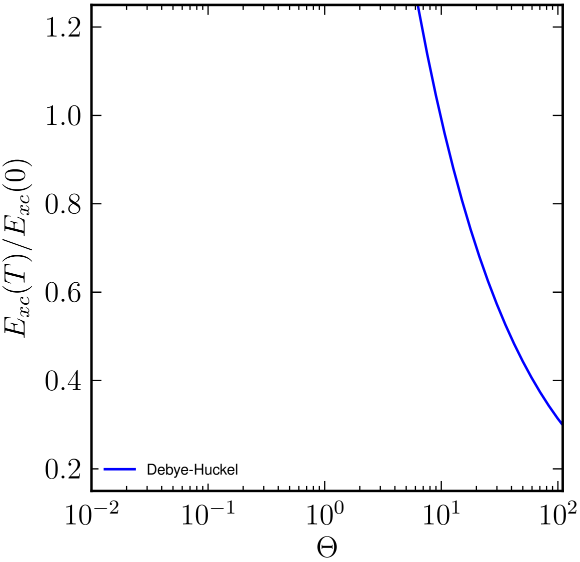
DeBroglie Wavelength,

$$\lambda_T/a \equiv (\hbar/mk_B T)^{1/2}/a \sim 1/(r_s T^{1/2})$$

Previous Semi-Classical Work

Purely Classical

- Analytics:
  Debye-Hückel Theory
  (Abe, 1959)



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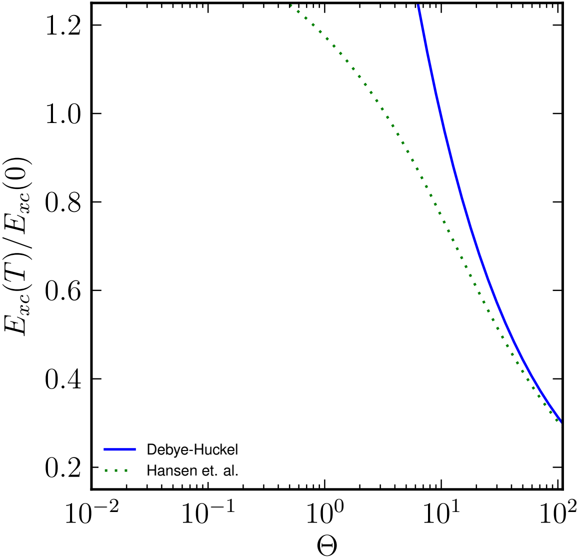

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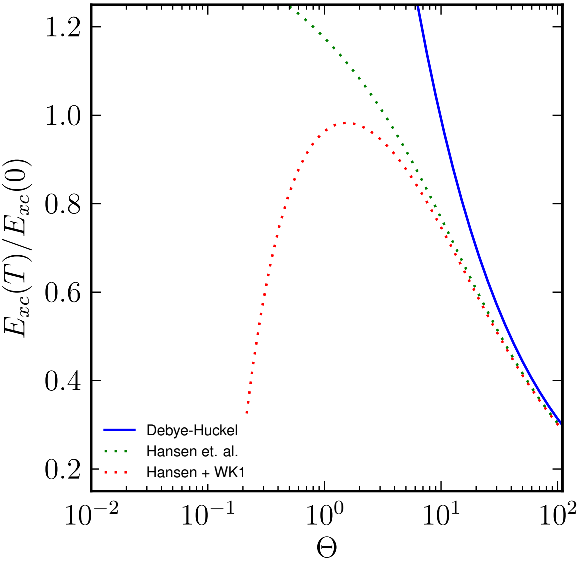
Quantum Corrections

- Wigner-Kirkwood Expansion in $\hbar$
  (Hansen and Vieillefosse, 1975)



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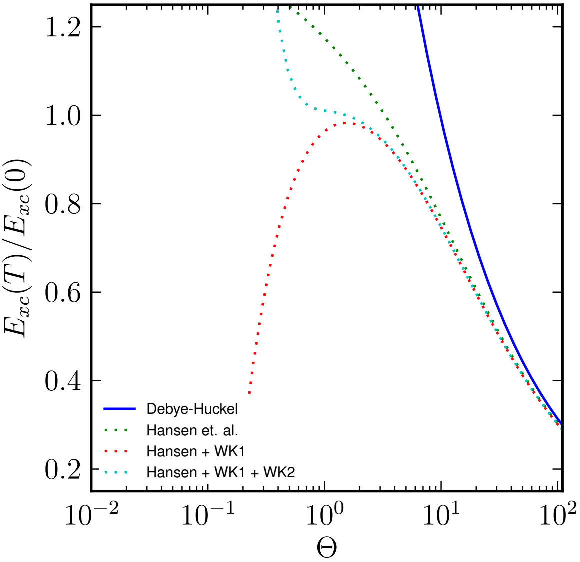

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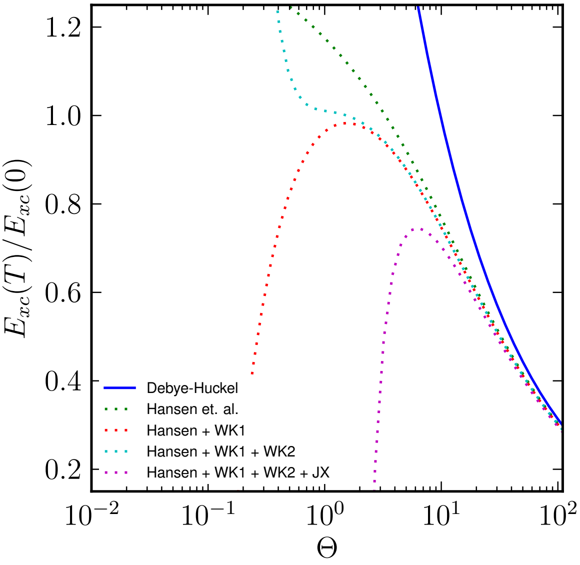
- Wigner-Kirkwood Expansion in $\hbar$ (Hansen and Vieillefosse, 1975)
- Exchange Correction to Wigner-Kirkwood expansion (Jancovici, 1978)



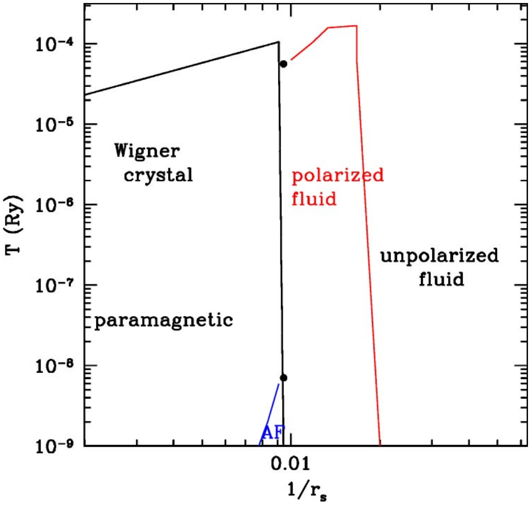
Previous Quantum Work

$T = 0$

- Variational Monte Carlo (VMC) (Ceperley, 1978)
- Diffusion Monte Carlo (DMC) (Ceperley and Alder, 1980; Ortiz, Harris, and Ballone, 1999; Zong, Lin, and Ceperley, 2002; Drummond, Radnai, Trail, Towler, and Needs, 2004)

$T \neq 0$

- Path Integral Monte Carlo (Jones and Ceperley, 1996; Cândido, Bernu, and Ceperley, 2004)
- Stoner Model



(Cândido et al., 2004)

Numerical Path Integrals

Start with many-body partition function $\mathcal{Z}$,

$$\mathcal{Z}(\beta) = Tr(e^{-\beta\mathcal{H}}) = \int dR \langle R|e^{-\beta\mathcal{H}}|R\rangle = \int dR \rho(R, R, \beta)$$

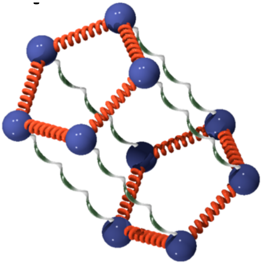
Use the convolution property of density matrices M times,

$$\rho(R_0, R_M, \beta) = \int dR_1 \dots dR_{M-1} \rho(R_0, R_1, \tau) \dots \rho(R_{M-1}, R_M, \tau)$$

where $\tau = \beta/M$.
Performing a Trotter breakup,

$$\begin{aligned} \rho(R, R', \tau) &= \lim_{J\to\infty} (e^{-\delta t V} e^{-\delta t T})^J \text{ where } \delta t \equiv \tau/J \\ &= \rho_0(R, R', \tau) \langle e^{-\int_0^\tau dt V(R(t))} \rangle_{BRW} \end{aligned}$$

where $\rho_0(R, R', \tau) = \frac{1}{(4\pi\lambda\tau)^{3N/2}} e^{-(R-R')^2/4\lambda\tau}$. Observables are sampled using Metropolis Monte Carlo as



$$\langle \hat{\mathcal{O}} \rangle = \frac{1}{\mathcal{Z}} \int dR \rho(R) \mathcal{O}(R) \approx \frac{1}{N} \sum_i^N \tilde{\mathcal{O}}(R)$$

The Pair Action

Using only pairwise interactions, straight line paths will contribute the most,

$$\begin{aligned}\langle e^{-\int_0^\tau dt V(R(t))}\rangle_{BRW} &= \langle \prod_{i<j} e^{-\int_0^\tau dt v(r_{ij}(t))}\rangle_{BRW} \\ &\approx \prod_{i<j}\langle e^{-\int_0^\tau dt v(r_{ij}(t))}\rangle_{BRW}\end{aligned}$$

Write $v(r) = v_s(r) + v_l(r)$ giving,

$$\rho(r_i, r_j, r_i', r_j', \tau) = \rho_s(r_i, r_j, r_i', r_j', \tau)\rho_l(r_i, r_j, r_i', r_j', \tau)$$

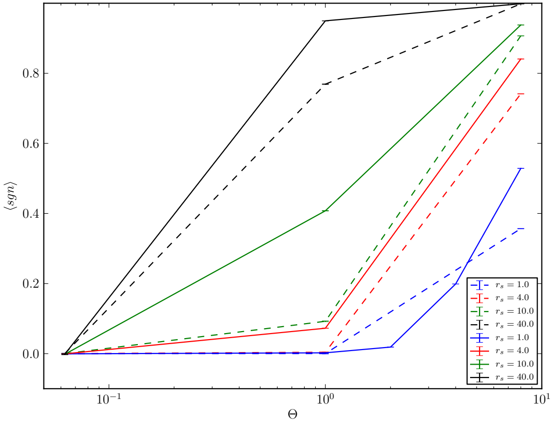
Find components using combination of coordinate transformations, Legendre polynomials, and the Random Phase Approximation. Short-ranged piece is solved for at a higher temperature, and "squared" down to the desired temperature. Long-ranged piece is solved for in Fourier space (as in Ewald summation). At the end of the day gives errors $\sim \tau^3$.

Particle Statistics

$$\rho_{B/F}(R, R', \beta) \qquad = \frac{1}{N!}\sum_{\mathcal{P}}(\pm 1)^{\mathcal{P}} \int dR_1 \dots dR_{M-1}\rho_D(R, R_1, \tau)\dots\rho_D(R_{M-1}, \mathcal{P}R', \tau)$$

For Bosons, this is not an issue since the sign of all permutations is $+1$. However, for Fermions, we run into the Sign Problem:

- Nearly identical weights of alternating sign
- Efficiency decreases as, $e^{-2\beta N(f_F - f_B)}$
- Circumvented with fixed-node (constrained path) approximation



Restricted Paths

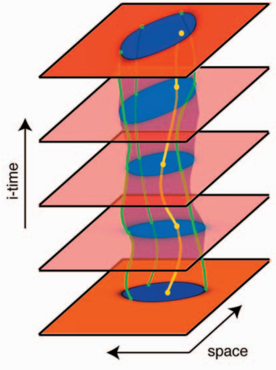
The Bloch equation for ρ_F reads,

$$\frac{\partial \rho_F(R, R_\star; t)}{\partial t} = -\mathcal{H}\rho(R, R_\star; t)$$

$$\text{where } \rho_F(R, R_\star; 0) = \mathcal{A}\delta(R - R_\star)$$

It can be shown that we may replace this initial condition with zero boundary conditions

- $R_\star$, the reference point, remains fixed for each integrated world line.
- Nodal Surface,
  $\Omega_\beta(R_\star) \equiv \{R_t \mid \rho_F(R_t, R_\star; t) = 0 \text{ and } 0 \leq t \leq \beta\}$



(Krüger and Zaanen, 2008)

Defining the Reach,

$$\Upsilon_\beta(R_\star) \equiv \{R_t \mid \exists\gamma : R_\star \to R_t \text{ where } \rho_F(R_t, R_\star; t) \neq 0 \;\forall t \;,\; 0 \leq t \leq \beta\}$$

We are left with the following expression for the density matrix,

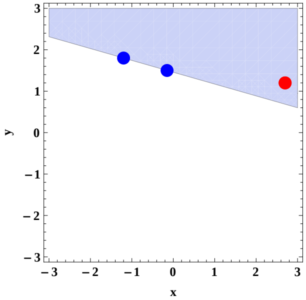
$$\rho_F(R_B, R_\star; \beta) = \int dR_0 \rho_F(R_0, R_\star; 0) \int_{\gamma:R_0 \to R_\beta}^{\gamma \subset \Upsilon_\beta(R_\star)} dR_t e^{-\mathcal{S}[R_t]}$$

Nodes

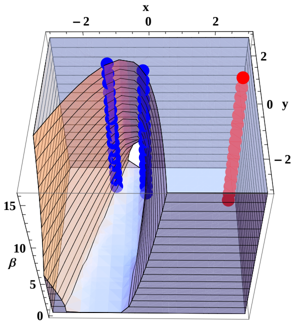
Introduce a trial density matrix ρ_T is introduced which approximates the actual nodal structure. For us, $\rho_T(R, R_\star; t) = \det \rho_{ij_{\star\uparrow}}(t) \det \rho_{ij_{\star\downarrow}}(t)$ are free particle density matrices where,

$$\rho_{ij}(t) = (4\pi\lambda t)^{-dN/2} \exp -\frac{(r_i - r_{j_\star})^2}{4\lambda t}$$

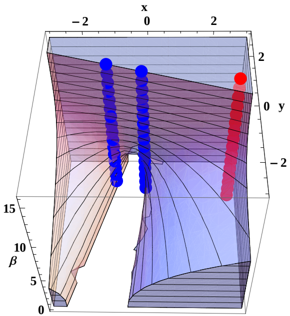
As an example consider 3 particles in $2D$ harmonic trap:



Ground State Nodes



Free Particle Nodes



Exact Nodes

Practical Considerations

Nodal Distances

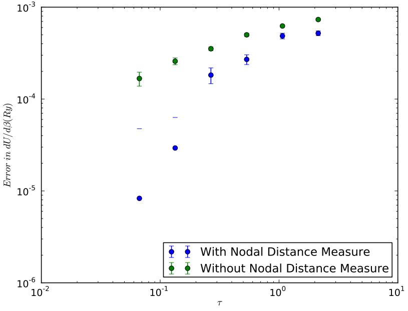
- No Measure

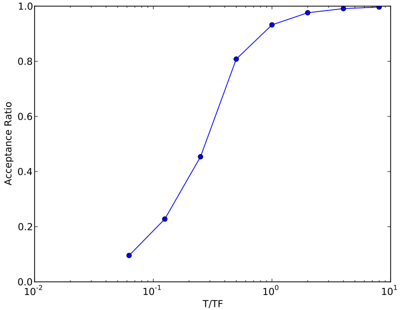
$$U_N(x_t, x_{t+\tau}) = -\log\left[1 - \exp\left(-\frac{d_t d_{t+\tau}}{\lambda\tau}\right)\right]$$

- Pauli Surface
- Hybrid Measurement (slowest step)

Reference Point Freezing

- Due to path's dependence on reference slice
- Worsens as temperature lowers
- Becomes "non-ergodic"





Possible Sources of Error

Controlled:

- Statistical (Run for longer)
- Time-step (Arises from pair action and constraint. Can extrapolate to $\tau \to 0$)
- Finite-size (correction expected to be valid provided $S(k) \sim k^2$ as $k \to 0$)

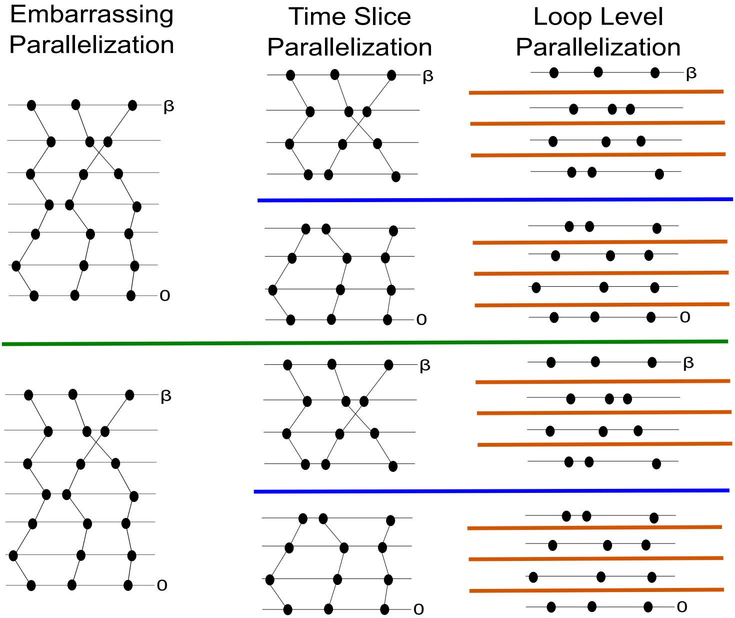
$$\begin{aligned}
\Delta V_N &= V_\infty - V_N = \frac{e^2}{4\pi^2} \int \frac{S(k)-1}{k^2} dk - \frac{2\pi e^2}{\Omega} \sum_{k \neq 0} \frac{S_N(k)-1}{k^2} \\
\Delta T_N &= T_\infty - T_N = \frac{\hbar^2}{4m(2\pi)^3} \int k^2 u(k) dk - \frac{\hbar^2}{4m\Omega} \sum_{k \neq 0} k^2 u_N(k) \\
\Delta E_{3DHEG} &= \Delta V_N + \Delta T_N = \frac{\hbar \omega_p}{2N} = \sqrt{\frac{3}{r_s^3}} \frac{1}{N}
\end{aligned}$$

(see Chiesa et. al., PRL 97, 076404 (2006))

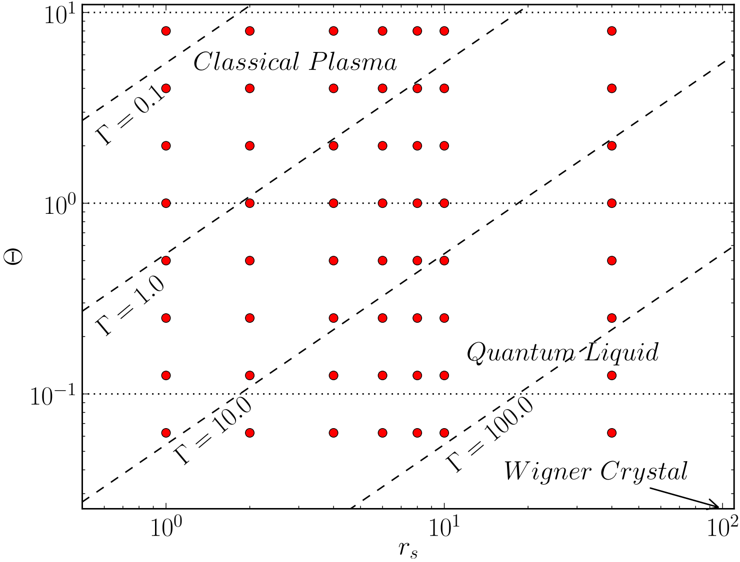
Uncontrolled: Fixed-node

- Using free-particle density matrices, $\rho_{ij}(t) = (4\pi\lambda t)^{-dN/2} \exp -\frac{(r_i - r_{j_\star})^2}{4\lambda t}$
- Believe should be good for homogeneous systems, but will confirm.
- Ergodicity problem at low temperatures, high densities

Parallelization

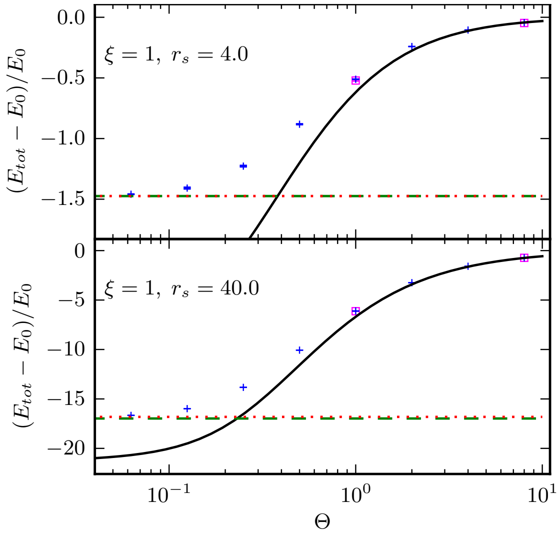


One Component Plasma in Warm-Dense Regime



Energy

$$E_{tot}(T) \equiv E_0(T) + E_{xc}(T)$$

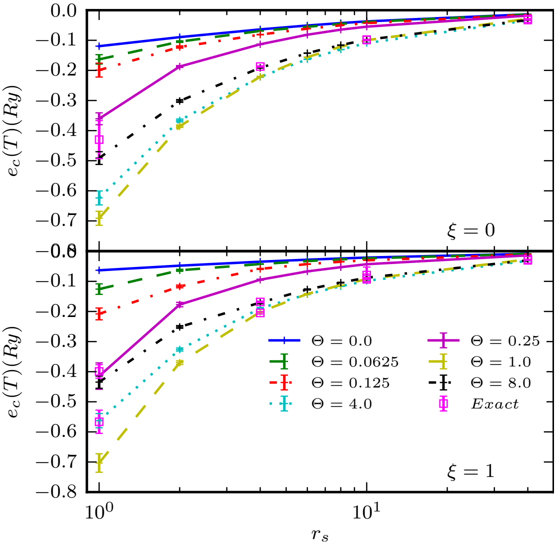


r_s	$E_{tot}(0)$	$\lim_{T\to 0} E_{tot}(T)$
1.0	$2.2903(1)^d$	2.29(1)
2.0	$0.2517(6)^a$	0.251(2)
4.0	$-0.1040(1)^d$	−0.1042(6)
6.0	$-0.1230(1)^d$	−0.1228(3)
8.0	$-0.1134(1)^d$	−0.1130(2)
10.0	$-0.1013(1)^a$	−0.1013(1)
40.0	$0.0351348(7)^c$	−0.034894(8)

(a-c) are QMC, d is the Perdew-Zunger fit to QMC.

Energy

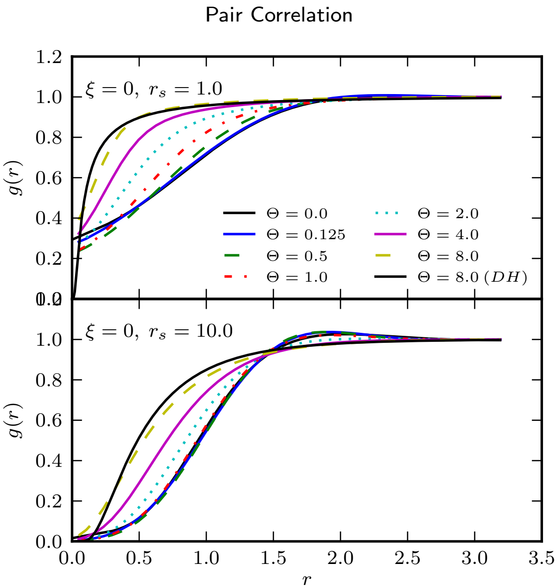
$$e_c(T) \equiv E_{xc}(T) - e_x(T)$$



r_s	$E_c(0)$	$\lim_{T\to 0} E_c(T)$
1.0	−0.1210(2)	−0.13(1)
2.0	−0.0902(4)	−0.091(2)
4.0	−0.0637(1)	−0.0632(5)
6.0	−0.0509(1)	−0.0512(2)
8.0	−0.0428(1)	−0.0428(1)
10.0	−0.03734(2)	−0.03690(8)
40.0	−0.0137104(6)	−0.013626(3)

(a-c) are QMC, d is the Perdew-Zunger fit to QMC.

Correlation



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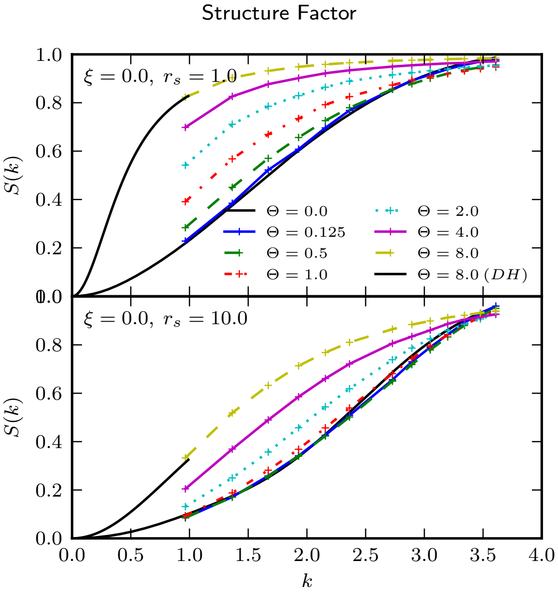


Functional Fit (The Functional)

We need a functional $E_{xc}(rs, T)$ that behaves correctly in known limits

- Analytic: High-temperature reproduces Debye-Huckel and 1st order quantum correction

$$\lim_{T\to\infty} E_{xc}(rs, T) = U_{DH} + U_Q + \mathcal{O}(T^{-3/2})$$

- Analytic: Low-temperature reproduces ground-state and Fermi liquid theory prediction

$$\lim_{T\to 0} E_{xc}(rs, T) = E_{xc}(rs, 0) - \mathcal{O}(T^2)$$

- Numeric: High-density approaches random phase approximation (RPA) limit
- Avoid complicated cancelling $T^2 \log T$ coming from e_c and e_x.

Easiest through a Padé fit.

Functional Fit (The Functional)

We need a functional

$$E_{xc}(rs, T) \equiv \frac{E_{xc}(rs, 0) - P_1}{P_2}$$

where

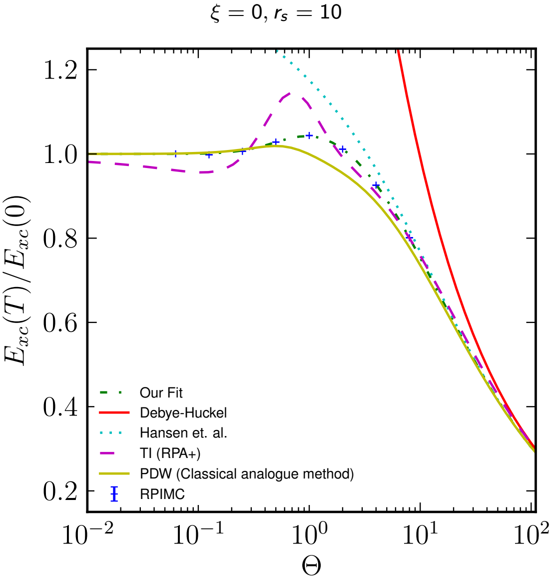
$$\begin{aligned}
P_1 &\equiv (A_2 u_1 + A_3 u_2) T^2 + A_2 u_2 T^{5/2}, \\
P_2 &\equiv 1 + A_1 T^2 + A_3 T^{5/2} + A_2 T^3, \\
A_k(rs) &\equiv \exp\left[a_k \log rs + b_k + c_k rs + d_k rs \log rs\right]
\end{aligned}$$

with u_1 and u_2 chosen such that

$$\begin{aligned}
\lim_{T\to\infty} E_{xc}(rs, T) &= U_{DH} + U_Q + \mathcal{O}(T^{-3/2}) \\
\lim_{T\to 0} E_{xc}(rs, T) &= E_{xc}(rs, 0) - \mathcal{O}(T^2)
\end{aligned}$$

avoiding cancelling $T^2 \log T$ coming from e_c and e_x. 24 parameters - 6 constraints = 18 free parameters

Functional Fit (The Fit)



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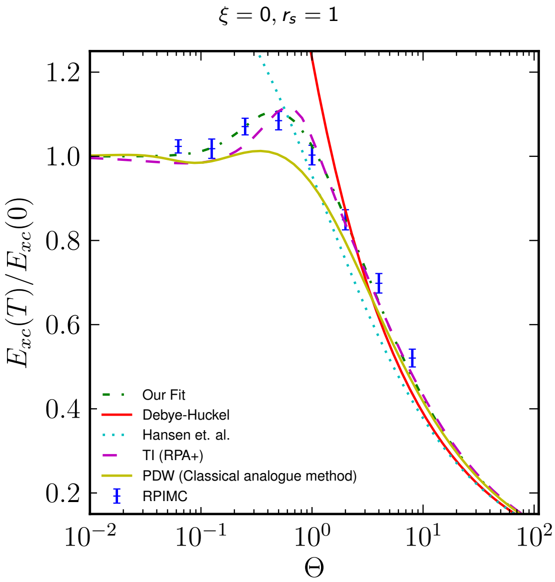
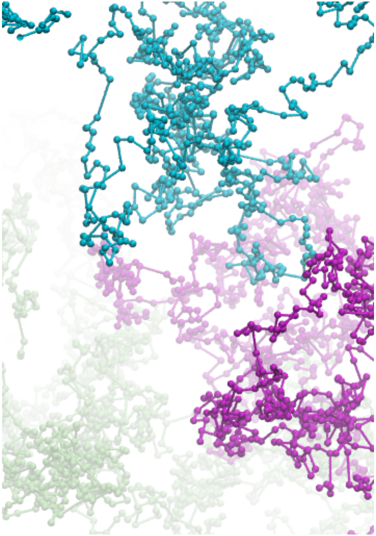


Next Steps



Direct comparison with and use in FTDFT/OFDFT for a real system

- Use Mermin equations to build up ensemble using E_0
- Test against current orbital free functionals

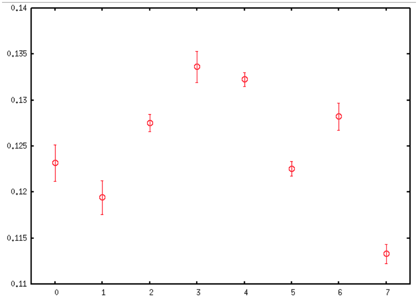
Test Other Nodal Structures

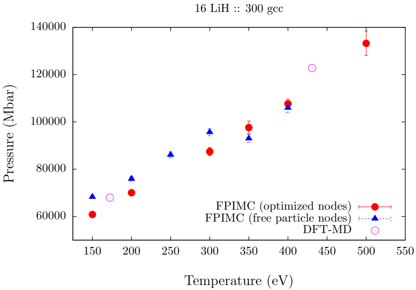
- Variational improvement through free energy
- Experiment with different nodal structures (Backflow)

Extend to higher densities / lower temperatures

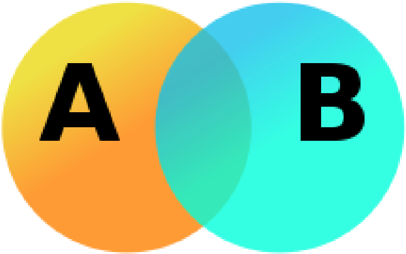
- May require algorithmic improvement (reference point freezing)
- Numerical (analytic?) RPA calculation at finite-temperature for small r_s

Free Energy Minimization





$$\exp\left[-\beta\Delta F\right] = \frac{\mathcal{Z}_A}{\mathcal{Z}_B} = \frac{\langle TimeinA \rangle_{A\bigcup B}}{\langle TimeinB \rangle_{A\bigcup B}}$$



Proof of concept

- Larges changes in observables as a result of optimization
- Seemingly no ergodic issue (at tested temperatures)
- Need for creative models

Summary

Conclusions:

- Free particle nodes effective
  - Calculations match well in classical limit
  - Smoothly approach zero-temperature calculations
  - Match exact results at temperatures with greatest deviation from ground-state results
- Precisely determined properties for the 3D-HEG in the warm-dense regime
- Functional fit to exchange-correlation energy in warm-dense regime

Future Directions:

- Direct comparison with and use in FTDFT/OFDFT
- Experiment with different nodal structures
- Determination of phase boundaries
- Measurement of other quantities (local field corrections, momentum distribution)
- 2D gas
- Application to inhomogeneous other systems

The speaker would like to thank:

- Advisor: David Ceperley
- Lab Advisor: Jonathan DuBois
- Collaborator: Bryan Clark, Markus Holzmann
- Useful Discussions: Jeremy McMinis, Miguel Morales, ChangMo Yang
- Funding Agency: DOE (DEFG5209NA29456), Lawrence Scholar Program

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Pair Product Action

$$\rho(R,R',\tau) = \lim_{J\to\infty}(e^{-\delta t V}e^{-\delta t T})^J = \rho_0(R,R',\tau)\langle e^{-\int_0^\tau dt V(R(t))}\rangle_{BRW}$$

where $\rho_0(R,R',\tau) = \frac{1}{(4\pi\lambda\tau)^{3N/2}}e^{-(R-R')^2/4\lambda\tau}$. Using only pairwise interactions, straight line paths will contribute the most,

$$\langle e^{-\int_0^\tau dt V(R(t))}\rangle_{BRW} \approx \prod_{i<j} e^{-\tau\int_0^1 dt v([1-t]r_{ij}+tr'_{ij})} \approx \prod_{i<j}\langle e^{-\int_0^\tau dt v(r_{ij}(t))}\rangle_{BRW}$$

This will be exact in the dilute limit when the correlation between any two particles is independent of other particle positions. Write,

$$v(r) = v_s(r) + v_l(r)$$

Pair Product Action (Short Range)

The short-range pair Bloch equation gives,

$$\mathcal{H}\rho_s = [-\lambda\nabla^2 + v_s(r_{ij})]\rho_s = -\dot{\rho}_s$$

Writing $\bar{r} = \frac{m_i r_i + m j r_j}{m_i + m_j}$, $r = r_i - r_j$, we have $\rho_s(r, \bar{r}, r', \bar{r}', \tau) = \rho_0(\bar{r}, \bar{r}', \tau)\rho_{s'}(r, r', \tau)$.
Expand in a Legendre series,

$$\begin{aligned} \rho_{s'}(r, r', \tau) &= \rho_0(r, r', \tau)\langle e^{-\int_0^\tau dtV(R(t))}\rangle_{BRW} = \rho_0(r, r', \tau)e^{-u_s(r,r',\tau)} \\ &= \frac{1}{4\pi rr'}\sum_{l=0}^{\infty}(2l+1)\rho_l(r, r, \tau)P_l(cos(\theta)) \end{aligned}$$

Comparing terms and using the semi-classical approximation, we have,

$$\rho_l(r, r', \tau/2^n) = \rho_{0l}(r, r', \tau/2^n)e^{-\tau/2^n \int_0^1 dtv([1-t]r_{ij}+tr'_{ij})}$$

Finally, using]he more efficient coordinates
$s \equiv| r - r' |, z \equiv| r | - | r' |, q \equiv (| r | + | r' |)/2$, we may write,

$$u_s(r, r', \tau) = \frac{1}{2}(u_s(r, r, \tau) + u_s(r', r', \tau)) + \sum_{k=1}^{k_{max}}\sum_{j=0}^{k} u_s^{kj}(q, \tau)z^{2j}s^{2(k-j)}$$

Pair Product Action (Long Range)

The full many-body Bloch equation gives,

$$\mathcal{H}\rho = [-\lambda\nabla^2 + \sum_{i<j}[v_s(r_{ij}) + v_l(r_{ij})]\rho = -\dot{\rho}$$

with local energy $E_L \equiv \frac{\dot{\rho}+\mathcal{H}\rho}{\rho} = 0$ for solution ρ. Guess the solution to be $\rho(\tau) = \rho_s(\tau)\rho_l(\tau) = \rho_s(\tau)e^{-U_l}$ by defining the long-range action to be $U_l \equiv -ln\rho_l$. Move to Fourier space, employ the random phase approximation (RPA), and numerically solve for Fourier components, e.g.,

$$\begin{aligned}
\sum_j \nabla_j U \nabla j U &= \sum_j [\sum_{k\sigma'} ike^{ikr_j}\rho_{-k}^{\sigma'}u_k^{\sigma_j\sigma'}][\sum_{q\sigma''} iqe^{iqr_j}\rho_{-q}^{\sigma''}u_q^{\sigma_j\sigma''}] \\
&= \sum_{kq} \sum_{\sigma'\sigma''\sigma'''} \rho_{-k}^{\sigma'}u_k^{\sigma'''\sigma'}\rho_{-q}^{\sigma'}u_q^{\sigma'''\sigma''}\rho_{q+k}^{\sigma'''} \\
&\approx \sum_{kq} \sum_{\sigma'\sigma''\sigma'''} \rho_{-k}^{\sigma'}u_k^{\sigma'''\sigma'}\rho_{-q}^{\sigma'}u_q^{\sigma'''\sigma''}(N_{\sigma'''}\delta_{k+q}) \\
&\approx \sum_{k} \sum_{\sigma'\sigma''\sigma'''} \rho_{-k}^{\sigma'}\rho_{k}^{\sigma'}u_{-k}^{\sigma'''\sigma'}u_k^{\sigma'''\sigma''}N_{\sigma'''}
\end{aligned}$$