The Uniform Electron Gas
at Warm Dense Matter Conditions

Tobias Dornheim, Simon Groth, and Michael Bonitz, *Physics Reports* **744**, 1-86 (2018)

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Introduction: warm dense matter

Warm dense matter (WDM):

- Nearly classical ions
- Degenerate non-ideal electrons
- Coupling parameter:

$$r_s = \frac{\bar{r}}{a_B} \sim 0.1 \ldots 10$$

- Degeneracy parameter:

$$\theta = k_B T / E_F \sim 0.1 \ldots 10$$

- Temperature, degeneracy and coupling effects equally important
  → No small parameters
  → Perturbation theory and ground-state approaches (DFT etc.) fail

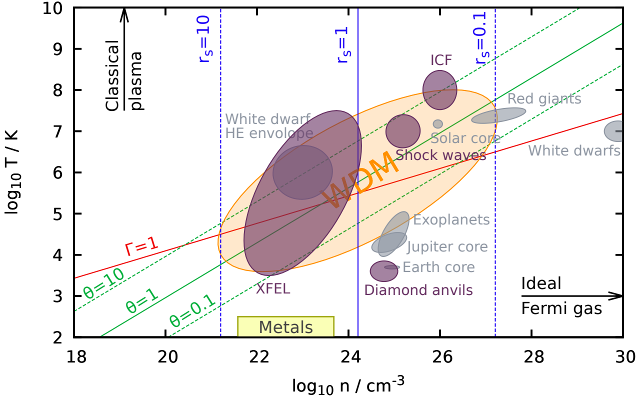


Figure: T. Dornheim, S. Groth, and M. Bonitz, *Phys. Rep.* **744**, 1 (2018) (https://doi.org/10.1016/j.physrep.2018.04.001)

Improved *ab initio* simulations needed to capture all effects in WDM

The uniform electron gas - Coulomb interacting electrons in a uniform positive background

Ground state:

- Model description of metals
- **Input for density functional theory (DFT)**
- Accurate parametrization of XC-energy[1] for all r_s from ground state Monte Carlo data[2]
  $\rightarrow$ DFT simulations of real materials

Warm dense matter:

- Ground state DFT not sufficient[3]
  $\rightarrow$ **Thermal DFT**[4]
  $\rightarrow$ **Requires finite-T XC-functional**[3]
  (XC free energy f_{xc})
- Finite-T XC-functional directly incorporated into
  - **EOS models** of astrophysical objects[5]
  - **approximations in QHD**[6]

Reliability of these approaches crucially depends on accurate parametrization of $f_{xc}(r_s, \theta)$

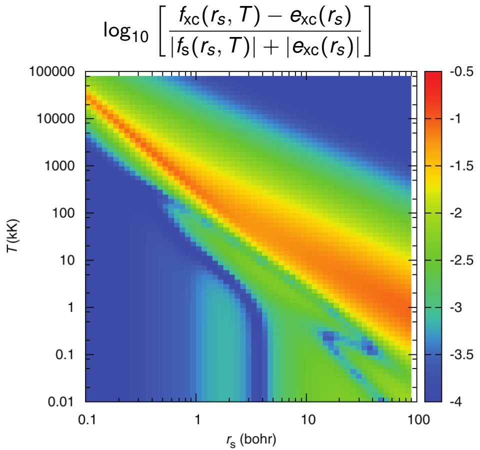


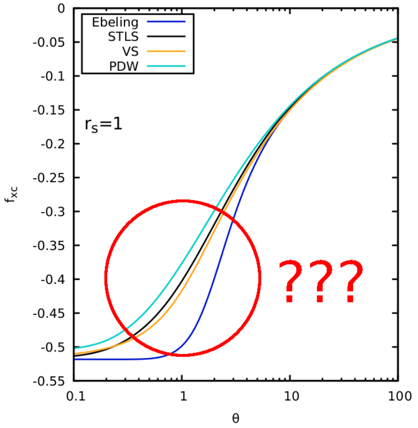
Figure: Relative importance of finite-T XC-functional[3] (diagonal corresponds to $\theta \sim 0.5$)

[1] J.P. Perdew and A. Zunger, PRB **23**, 5048 (1981) [2] D.M. Ceperley and B. Alder, PRL **45**, 566 (1980) [3] V. Karasiev *et al.*, PRE **93**, 063207 (2016) [4] N.D. Mermin, Phys. Rev **137**, A1441 (1965)
[5] A.Y. Potekhin and G. Chabrier, *A&A* ***550**, A43* (2013) [6] D. Michta *et al.*, Contrib. Plasma Phys. **55** (2015)

Many parametrizations for f_{xc} based on different approximate approaches:

- Semi-analytical approaches by **Ebeling**[1]
- Dielectric methods, e.g. Singwi-Tosi-Land-Sjölander[2] (**STLS**) and Vashista-Singwi[3] (**VS**)
- Quantum-classical mappings, e.g. Perrot and Dharma-wardana[4] (**PDW**)
- **Most recent:** Fit by Karasiev[5] *et al.* (**KSDT**) to Restricted Path Integral Monte Carlo (**RPIMC**) data[6]

  But: RPIMC invokes *fixed node approximation*
  $\rightarrow$ induces **uncontrolled systematic errors**[7]



Accuracy of existing parametrizations for $f_{xc}(r_s, \theta)$ unclear

***Ab initio* description of the warm dense UEG highly needed**

[1] W. Ebeling and H. Lehmann, Ann. Phys. **45**, (1988) [2] S. Ichimaru, H. Iyetomi, and S. Tanaka, Phys. Rep. **149**, (1987) [3] T. Sjostrom and J. Dufty, PRB **88**, (2013)
[4] F. Perrot and MWC Dharma-wardana, PRB **62**, (2000) [5] V.V. Karasiev *et al.*, PRL **112**, (2014) [6] E.W. Brown *et al.*, PRL **110**, (2013) [7] T. Schoof *et al.*, PRL **115**, (2015)

Path integral Monte Carlo (PIMC) simulation of the warm dense UEG

- Standard PIMC in warm dense regime severely hampered by ***fermion sign problem***:
  - First results[1] by E. Brown, D. Ceperley *et al.* (2013) based on ***fixed node approximation*** (**RPIMC**)
  - Induces **systematic errors** of unknown magnitude
  - **RPIMC** limited to $r_s \gtrsim 1$

Our approach:

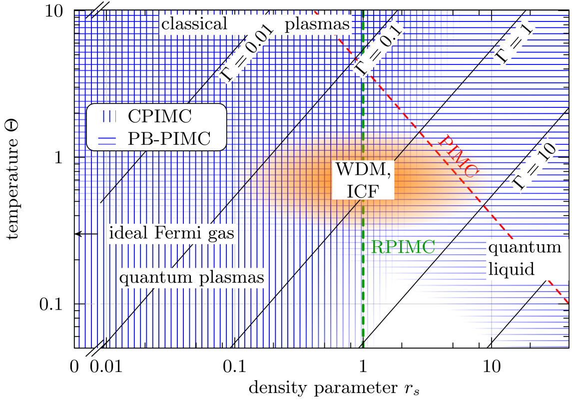
Avoid fermion sign problem by combining two novel exact and complementary QMC methods:

1. **Configuration PIMC (CPIMC)**[2,3]

   → Excels at high density $r_s \lesssim 1$ and strong degeneracy

2. **Permutation blocking PIMC (PB-PIMC)**[4,5]

   → Extends standard PIMC towards stronger degeneracy



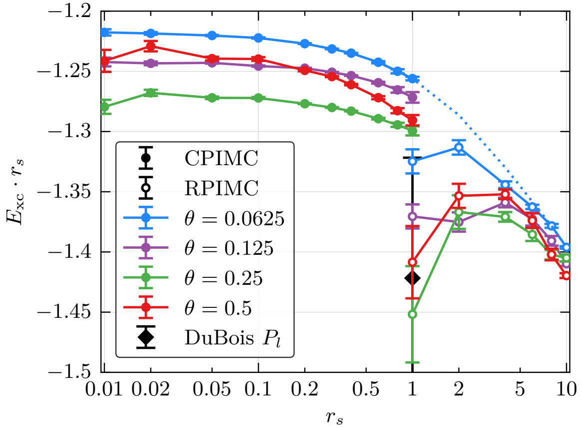
Exact *ab initio* simulations over broad range of parameters

[1] E.W. Brown *et al.*, PRL **110**, 146405 (2013)   [2] S. Groth *et al.*, Phys. Rev. B **93**, 085102 (2016)   [3] T. Schoof *et al.*, Contrib. Plasma Phys. **55**, 136 (2015)
[4] T. Dornheim *et al.*, New J. Phys. **17**, 073017 (2015)   [5] T. Dornheim *et al.*, J. Chem. Phys. **143**, 204101 (2015)

Results I: CPIMC for $N = 33$ spin-polarized electrons

Exchange-correlation energy $E_{xc} = E - E_0$ (E_0 : ideal energy)

T. Schoof, S. Groth, J. Vorberger, and M. Bonitz, PRL **115**, 130402 (2015)



RPIMC carries systematic errors exceeding 10%

RPIMC: E.W. Brown *et al.*, PRL **110**, 146405 (2013) **DuBois:** ($\theta = 0.0625$) J.L. DuBois *et al.*, arXiv:1409.3262 (2014)

Results II: Combination of CPIMC and PB-PIMC

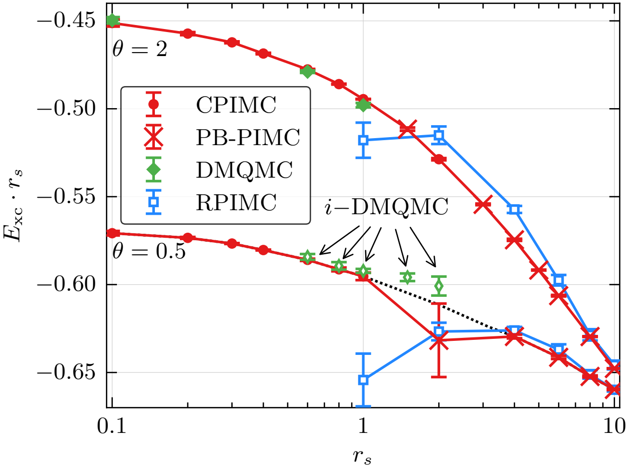
- **RPIMC** limited to $r_s \geq 1$
- **CPIMC** excels at high density
- **PB-PIMC** applicable at $\theta \gtrsim 0.5$

Combination[1] yields exact results over entire density range down to $\theta \sim 0.5$

- Also applies to the **unpolarized** UEG[2]
- Our results confirmed by recent **DMQMC** simulations[3]

UEG well understood[4] for finite N

How to extend the simulations to the thermodynamic limit ($N \to \infty$) ???



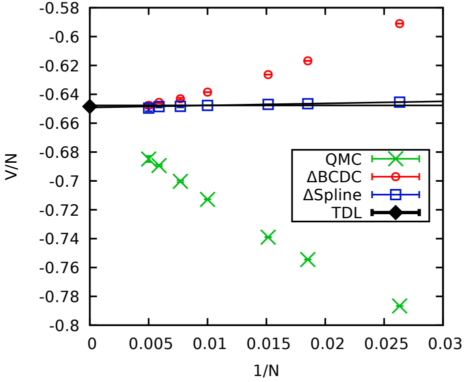
[1] S. Groth *et al.*, Phys. Rev. B **93**, 085102 (2016)
[2] T. Dornheim *et al.*, Phys. Rev. B **93**, 205134 (2016)
[3] F.D. Malone *et al.*, Phys. Rev. Lett. **117**, 115701 (2016)
[4] T. Dornheim *et al.*, Phys. Plasmas **24**, 056303 (2017)

Results III: Extension to thermodynamic limit[1]

- QMC results are afflicted with finite-size error $\Delta V(N)$ (exceeding 20%)
- Extrapolation and previous finite-size[2] corrections are unreliable
- **Solution:** Combine QMC data for $S(k)$ with long-range behavior from RPA, STLS [exact for $S(k \to 0)$]

Improved finite-size correction for all WDM parameters!

$$\nu = \frac{V_N}{N} + \Delta V(N)$$



[1] **ΔSpline:** T. Dornheim *et al.*, PRL **117**, 156403 (2016) [2] **ΔBCDC:** E.W. Brown *et al.*, PRL **110**, (2013)

Results IV: Extension to ground state

- With our two novel quantum Monte-Carlo (QMC) methods[1-4] and improved FSC[5] we

Obtained the first unbiased QMC data[5] for the potential energy of the UEG over the entire r_s-θ-plane for $\theta \geq 0.5$ (restriction due to fermion sign problem)

- For $\theta = 0$ use exact ground state QMC data[6] v_0
- For $0 < \theta < 0.25$ add (small) STLS[7] temperature-correction to v_0

$$v(\theta) = v_0 + \left[v^{\text{STLS}}(\theta) - v^{\text{STLS}}(0) \right]$$

$\rightarrow$ Highly accurate ($\sim 0.3\%$) data set for $v(\theta, r_s)$ over entire WDM regime

- Exchange-correlation free energy f_{xc} linked to potential energy via

$$2 f_{xc}(r_s, \theta) + r_s \left. \frac{\partial f_{xc}(r_s, \theta)}{\partial r_s} \right|_\theta = v(r_s, \theta)$$

- Use suitable parametrization for f_{xc} and fit l.h.s. to r.h.s.

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[1] T. Schoof *et al.*, Contrib. Plasma Phys. **51**, 687 (2011) [2] T. Schoof *et al.*, Contrib. Plasma Phys. **55**, 136 (2015) [3] T. Dornheim *et al.*, New J. Phys. **17**, 073017 (2015)
[4] T. Dornheim *et al.*, J. Chem. Phys. **143**, 204101 (2015), [5] T. Dornheim *et al.*, PRL **117**, 156403 (2016) [6] G.G. Spink *et al.*, Phys. Rev. B **88**, 085121 (2013)
[7] S. Tanaka, S. Ichimaru, J. Phys. Soc. Jpn. **55**, 2278 (1986)

Results V: Parametrization of $f_{xc}(r_s, \theta)$

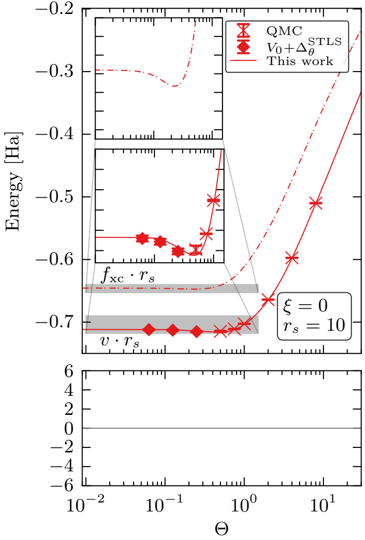
S. Groth, T. Dornheim, T. Sjostrom, F.D. Malone, W.M.C. Foulkes, and M. Bonitz, *PRL* **119**, 135001 (2017)

Construct finite-T XC-functional:

- Temperature-corrected ground state data smoothly connects to exact finite-T QMC data (over entire WDM regime)
  $\rightarrow$ Smooth fit through all data points for $v(r_s, \theta)$

$\rightarrow$ Obtain highly accurate ($\sim$ 0.3%) parametrization for f_{xc}

Comparison to other parametrizations reveals deviations of $\sim 5-12\%$ (depending on r_s and θ)



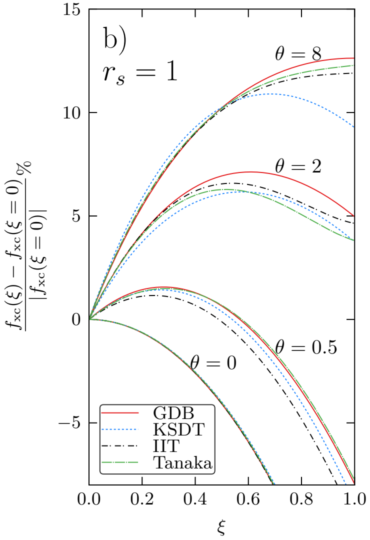
Results VI: Ab initio description of spin-polarization effects

S. Groth, T. Dornheim, T. Sjostrom, F.D. Malone, W.M.C. Foulkes, and M. Bonitz, *PRL* **119**, 135001 (2017)

- DFT in local spin-density approximation requires $f_{xc}(r_s, \theta)$ at arbitrary $\xi = (N_\uparrow - N_\downarrow)/(N_\uparrow + N_\downarrow)$
- Extend parametrization $f_{xc}(r_s, \theta) \longrightarrow f_{xc}(r_s, \theta, \xi)$
- Extensive new QMC data for $\xi = 0, 1/3, 0.6$, and 1

$\rightarrow$ **First *ab initio* ξ-dependency**

No previous parametrization captures correct spin-dependency of f_{xc}



KSDT: V.V. Karasiev *et al.*, PRL **112** (2014) **IIT:** S. Ichimaru, H. Iyetomi, and S. Tanaka J. Phys. Reports **149**, (1987) **Tanaka:** S. Tanaka, J. Chem. Phys. **145** (2016)

Summary:

- QMC at finite-T severely hampered by ***fermion sign problem*** **(FSP)**
  $\rightarrow$ **Common solution: *fixed node approximation* (RPIMC)**[1] $\rightarrow$ systematic errors exceed 10%[2]
- **Our approach:** circumvent FSP by combining **two novel exact QMC methods**[3,4]
- Presented **improved finite-size correction**[5] $\rightarrow$ Extrapolate finite-N QMC data to TD limit

First exact data of the warm dense UEG down to $\theta = 0.5$[5]

- Combined **ground state QMC data**[6] + **STLS temperature-correction** for $\theta \lesssim 0.25$

Accurate ($\sim 0.3\%$) and consistent parametrization[7] **of f_{xc} across entire r_s-θ-ξ-space for the UEG at WDM conditions ($r_s \lesssim 20, \theta \lesssim 8$)**

- **First benchmarks of previous parametrizations**[7]
  - Systematic errors of $5-12\%$ in WDM regime
  - Unsatisfactory description of spin-dependency

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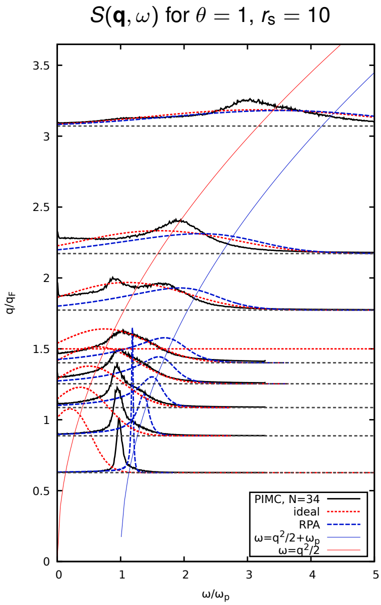
[1] E.W. Brown *et al.*, PRL **110**, 146405 (2013) [2] T. Schoof *et al.*, PRL **115**, 130402 (2015) [3] S. Groth *et al.*, PRB **93**, 085102 (2016) [4] T. Dornheim *et al.*, Phys. Plasmas **24**, 056303 (2017)
[5] T. Dornheim *et al.*, PRL **117**, 156403 (2016) [6] G.G. Spink *et al.*, PRB **88**, 085121 (2013) [7] S. Groth *et al.*, PRL **119**, 135001 (2017)

Concluding remarks:

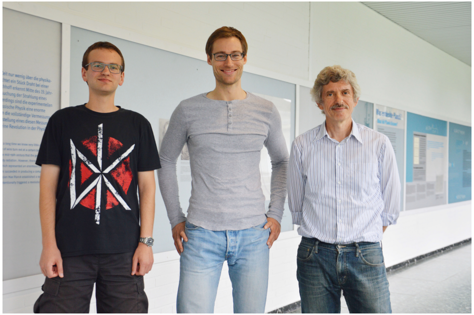
- Use our new f_{XC}-functional as input for
  - DFT calculations
  - Quantum hydrodynamics
  - Equation of state models of astrophysical objects
- Functional available online (C++, Fortran, Python) at https://github.com/agbonitz/xc_functional
- Implemented in libxc4.0.4: LDA_T_GDSMFB

Outlook:

- *inhomogeneous* UEG
  $\rightarrow$ Access to static local field correction
- *ab initio* results for imaginary-time correlation functions
  $\rightarrow$ Reconstruction of dynamic structure factor $S(\mathbf{q}, \omega)$[1]



[1] T. Dornheim, PhD thesis, Kiel University 2018



Tobias Dornheim, Simon Groth, and Michael Bonitz
(picture courtesy J. Siekmann)

Bonitz group homepage: http://www.theo-physik.uni-kiel.de/bonitz/

Acknowledgements:
We thank Matthew Foulkes, Fionne Malone, Tim Schoof, Travis Sjostrom and Jan Vorberger for fruitful collaboration on this project.