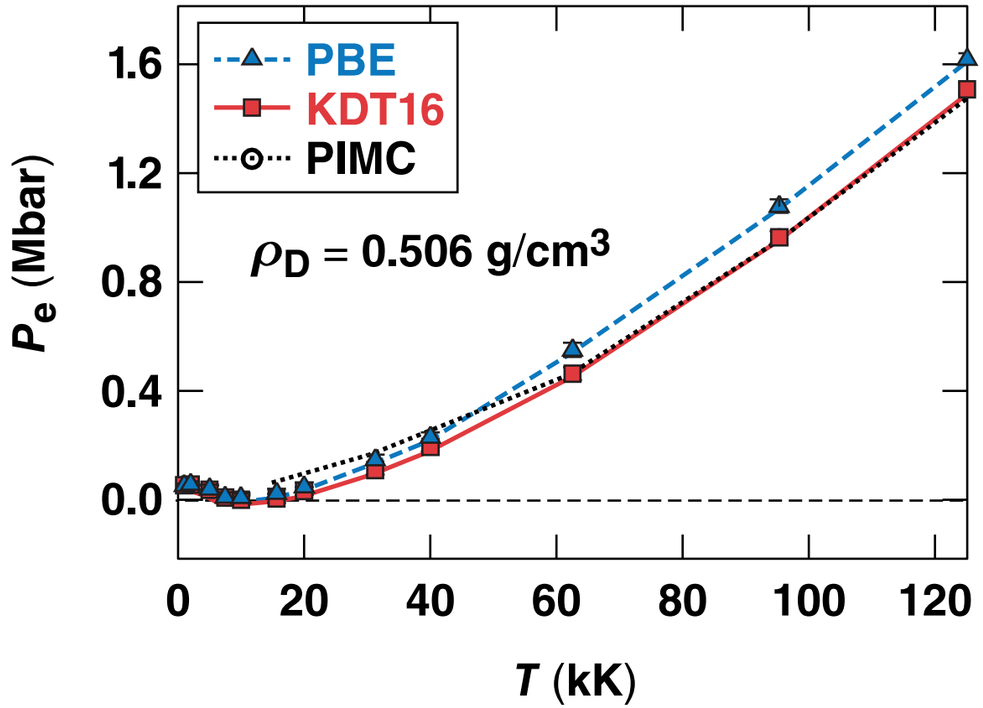
Development of Fast and Reliable Free-Energy Density Functional Methods for Simulations of Dense Plasmas from Cold- to Hot-Temperature Regimes



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Summary

Thermal effects on exchange correlation (XC) (especially at $T \approx 0.5\ T_F$) must be taken into account to accurately predict the properties of warm dense matter (WDM)

- A framework for temperature-dependent XC functionals for WDM simulations was developed
- Orbital-free generalized gradient approximation (GGA) noninteracting free-energy functionals are accurate at elevated temperatures
- A practical approach makes it possible to extend the range of temperatures accessible for simulations
  - use Kohn–Sham density function theory (DFT) at low temperatures (when it is computationally affordable)
  - use orbital-free DFT with accurate GGA functionals at intermediate and high temperatures

Collaborators

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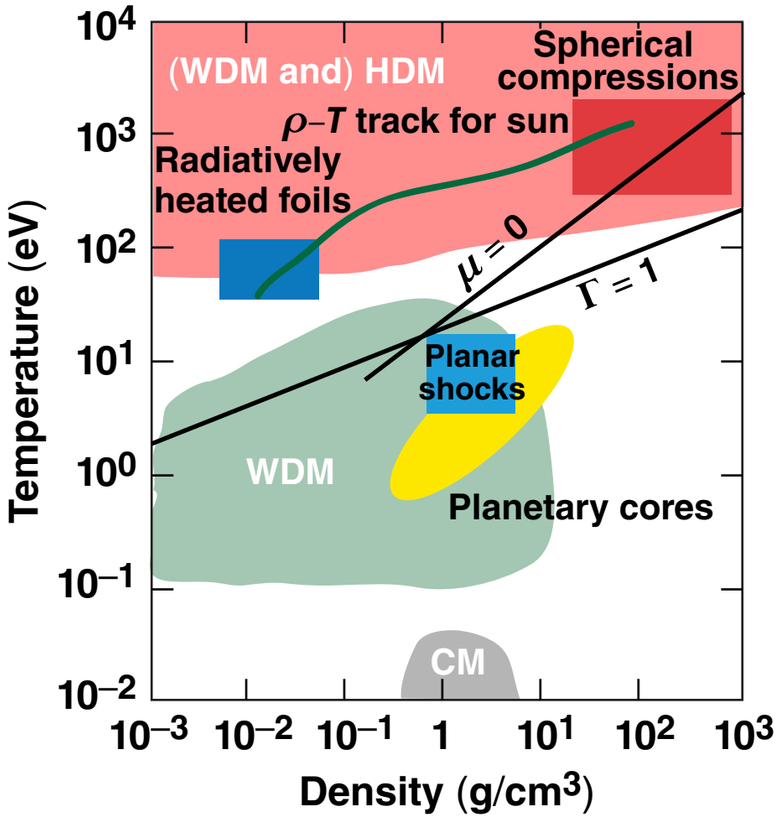
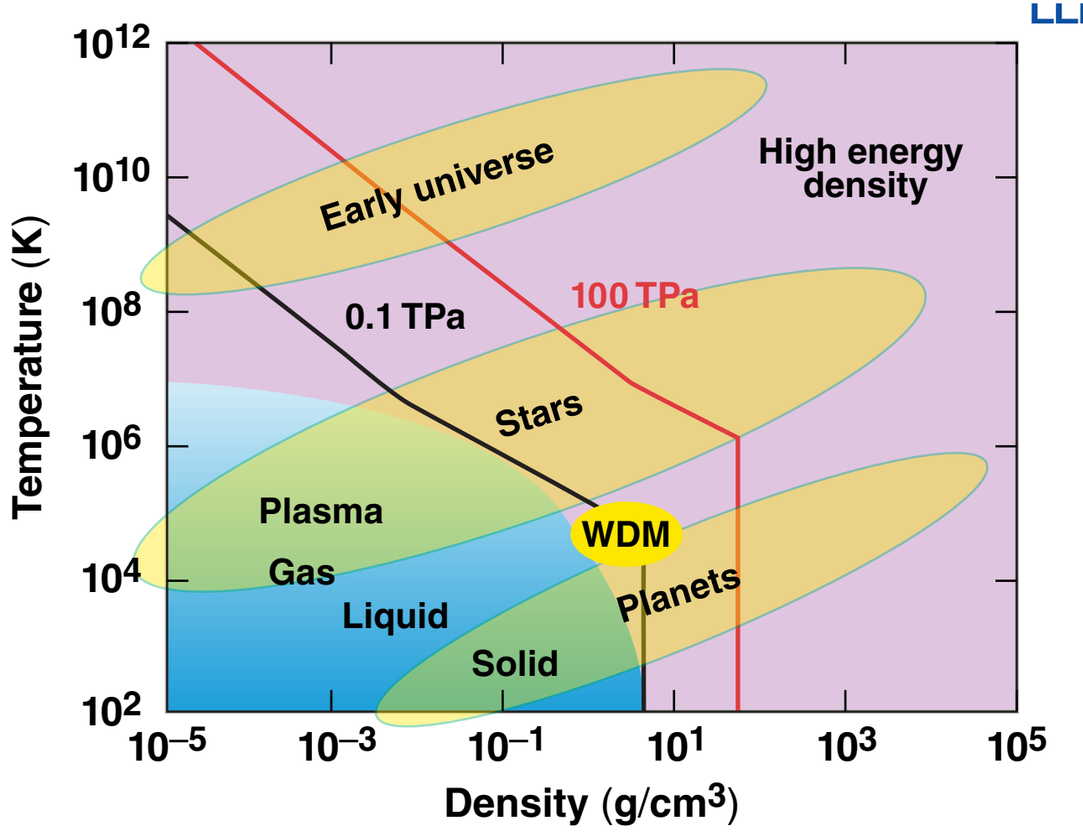
Warm and hot dense matter (HDM) is of interest in geo/astrophysics and in inertial confinement fusion (ICF)



Temperature-density diagram for hydrogen

R. Lee, LLNL.
CM: condensed matter



Temperature-density diagram for aluminum

R. P. Drake, Phys. Today 63, 28 (2010).

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HEDP* requires development of new methods and functionals to accurately predict the properties of matter

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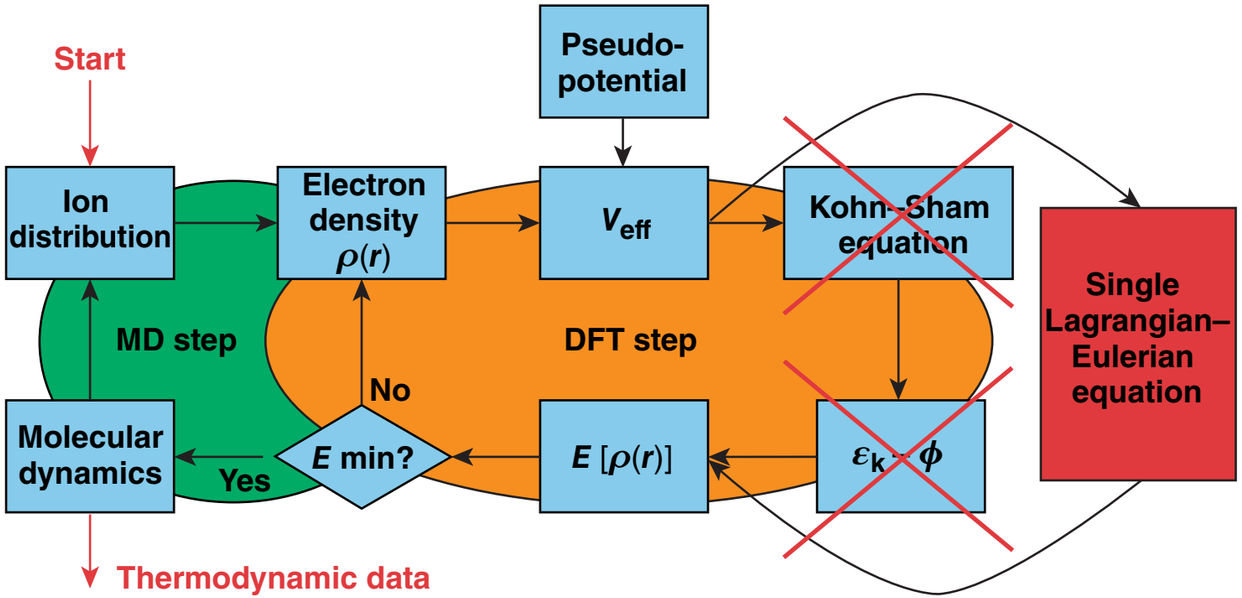
Standard computational approach

- Classical molecular dynamics (MD) for ions
- Quantum Kohn–Sham (KS) or orbital-free density functional theory (OF-DFT) for electrons



Computational methods often cease to work at high pressures and temperatures

- Most quantum MD simulations use XC functionals developed for $T = 0$
- The XC thermal effects in the WDM regime are not taken into account
- There is a drastic increase of computational cost as the temperature increases

  cost ~ $(N_{band})^3$
- Strong quantum effects at intermediate temperatures
- Limited transferability of pseudopotentials and PAW's** developed for near-ambient thermodynamic conditions

*HEDP: high-energy-density physics
**PAW: projector augmented wave

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We developed a framework for temperature-dependent XC functionals to address the issue of thermal effects

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Generalized gradient approximation

Exchange

$$F_x^{GGA}[n,T] = \int n\, f_x^{LDA}(n,T) F_x[s_{2x}(T)]\mathrm{d}\vec{r}$$

$$F_x(s_{2x}) = 1 + \frac{v_x s_{2x}}{1 + \alpha |s_{2x}|}$$

$$s_{2x}(n,\nabla n,T) \equiv s^2(n,\nabla n)\tilde{B}_x(t);$$

$$f_x^{LDA}(n,T) = \varepsilon_x^{LDA}(n)\tilde{A}_x(t); t = T/T_F$$

Correlation

$$F_c^{GGA}[n,T] = \int n\, f_c^{GGA}(n,\nabla n,T)\mathrm{d}\vec{r}$$

GGA correlation energy per particle:

$$f_c^{GGA}(n,\nabla n,T) = f_c^{LDA}(n,T) + H\left[f_c^{LDA}, q_c(T)\right]$$

$$q_c(n,\nabla n,T) \equiv q(n,\nabla n)\sqrt{\tilde{B}_c(n,t)}$$

Constraints

- Reproduce finite-temperature gradient expansion
- Satisfy Lieb–Oxford bound at zero-temperature
- Reduce to correct zero-temperature limit
- Reduce to correct high-temperature limit

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- Reduce to correct high-temperature limit

*V. V. Karasiev, J. W. Dufty, and S. B. Trickey, "Non-Empirical Semi-Local Free-Energy Density Functional for Matter Under Extreme Conditions," submitted to Physical Review Letters; see also arXiv: 1612.06266v1.

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Orbital-free noninteracting free-energy functionals were developed to address the issue of computational cost at elevated temperature

Noninteracting GGA free energy

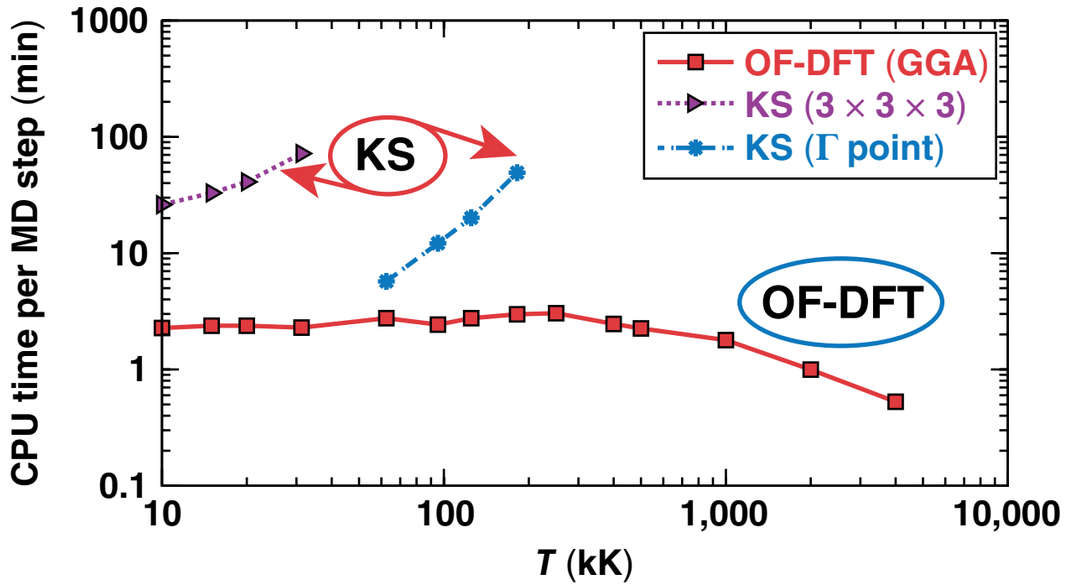
$$F_s^{GGA}[n,T] = \int d^3 r \tau_0^{TF}(n)\xi(T)F_\tau[s_\tau(T)] - \int d^3 r \tau_0^{TF}(n)\varsigma(T)F_\sigma[s_\sigma(T)]$$

$$F_\sigma^{GGA}(s_\sigma) := 2 - F_\sigma^{GGA}(s_\sigma)$$

Orbital-free DFT: single Euler equation to solve

$$\frac{\delta F_s(n)}{\delta n(r)} + v_s[(n);r] = \mu,$$

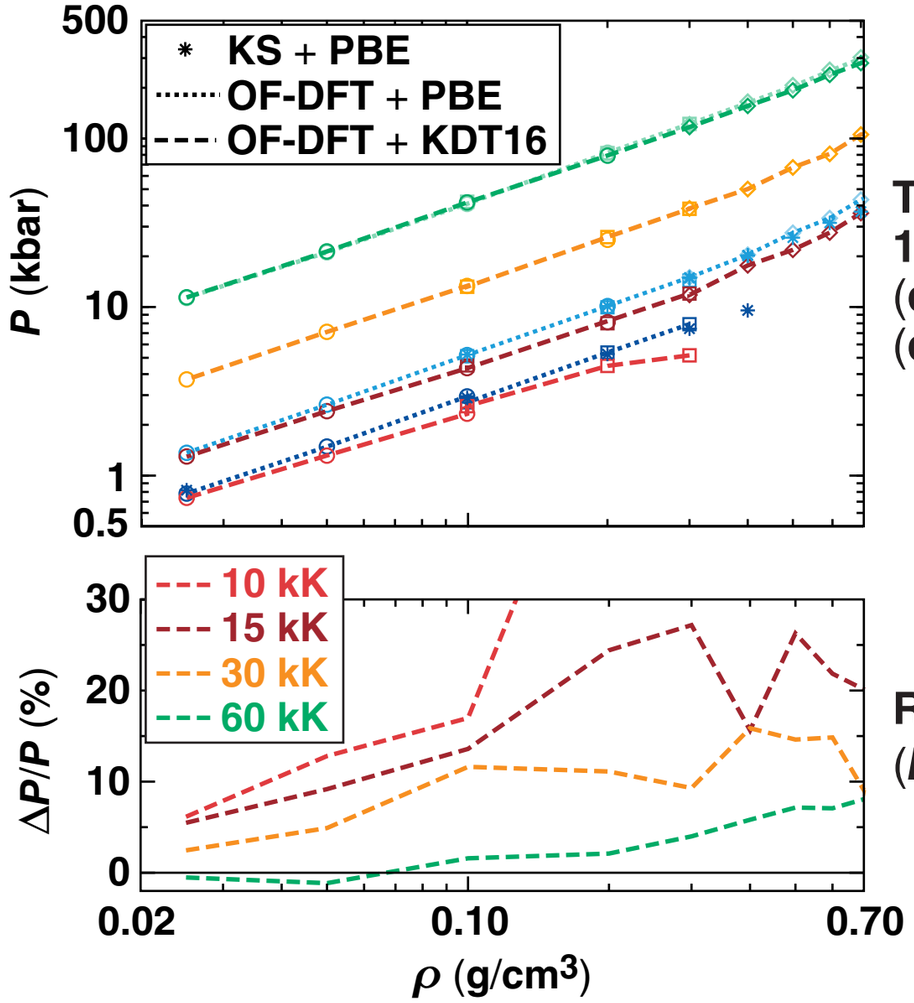
where $v_s = v_{ext} + v_H + v_{XC}$



- CPU time per MD step as a function of temperature
- The KS results terminate because of run-time limitations
- System: 128 D atoms, 1.964 g/cm^3

V. V. Karasiev, T. Sjostrom, and S. B. Trickey, Phys. Rev. B 86, 115101 (2012); V. V. Karasiev *et al.*, Phys. Rev. B 88, 161108(R) (2013).

The most-accurate EOS* of aluminum plasmas (material density in 0.02- to 0.70-g/cm^3 range) were calculated with XC thermal effects taken into account



Total pressure along four isotherms (T = 10, 15, 30, and 60 kK) for the ground-state PBE** (dotted curves) and finite-temperature KDT16† (dashed curves) XC functionals

Relative magnitude of XC thermal effects for pressure: $(P^{PBE} - P^{KDT16})/P^{PBE} \times 100\%$

*EOS: equation of state
**PBE: Perdew–Burke–Ernzerhof
†KDT16: Karasiev–Dufty–Trickey, 2016

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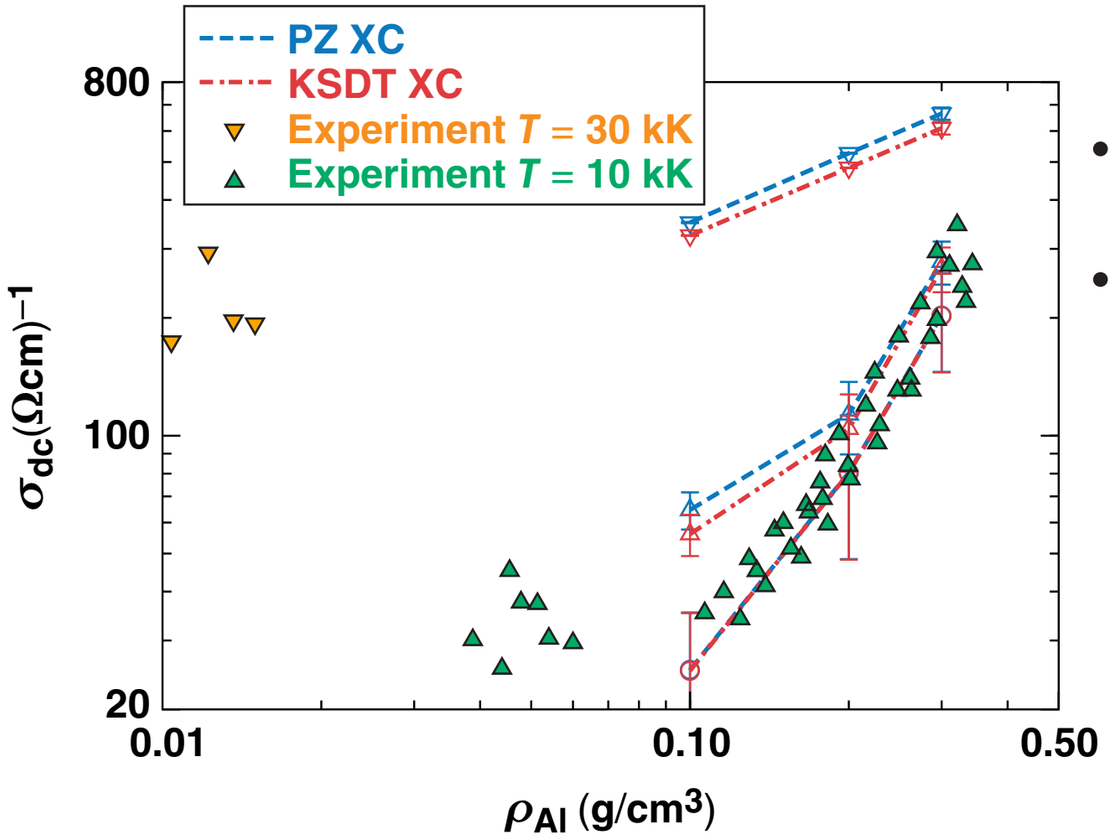
Comparisons between our simulations and experiments indicate that the thermal XC effects are important for electrical dc conductivity



- Aluminum dc conductivity as a function of density for T = 10 and 30 kK
- Perdew–Zunger (PZ) ground-state XC versus finite-temperature Karasiev–Sjostrom–Dufty–Trickey (KSDT)

Calculations: V. V. Karasiev, L. Calderín, and S. B. Trickey, Phys. Rev. E 93, 063207 (2016).
Experiment: A. W. DeSilva and J. D. Katsouros, Phys. Rev. E 57, 5945 (1998); 59, 3774(E) (1999).

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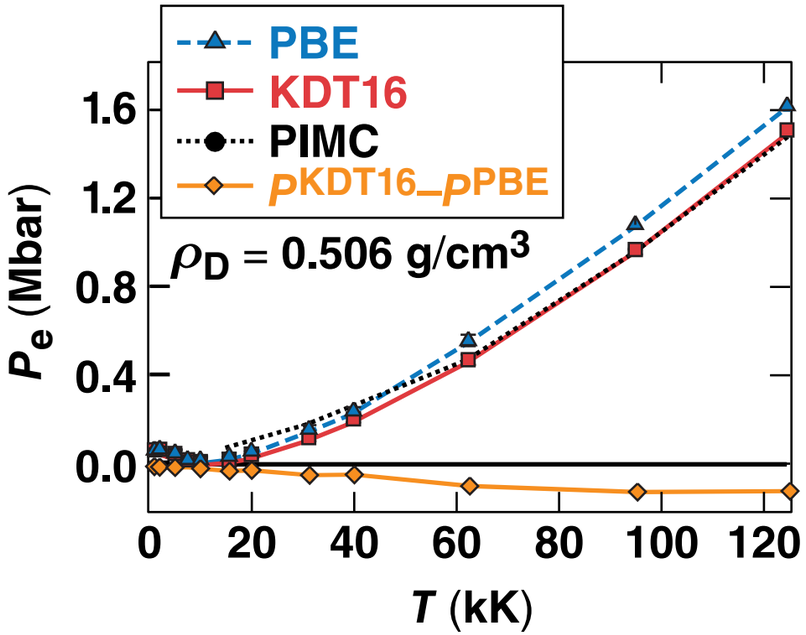
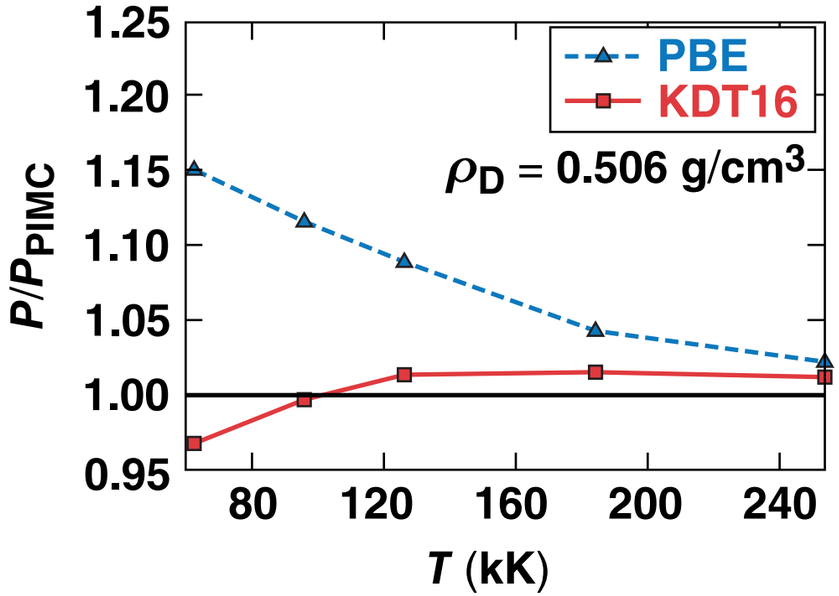
Our temperature-dependent XC calculations of deuterium EOS are in perfect agreement with reference PIMC* results, while the standard zero-temperature PBE calculations overestimate pressure by up to 15%

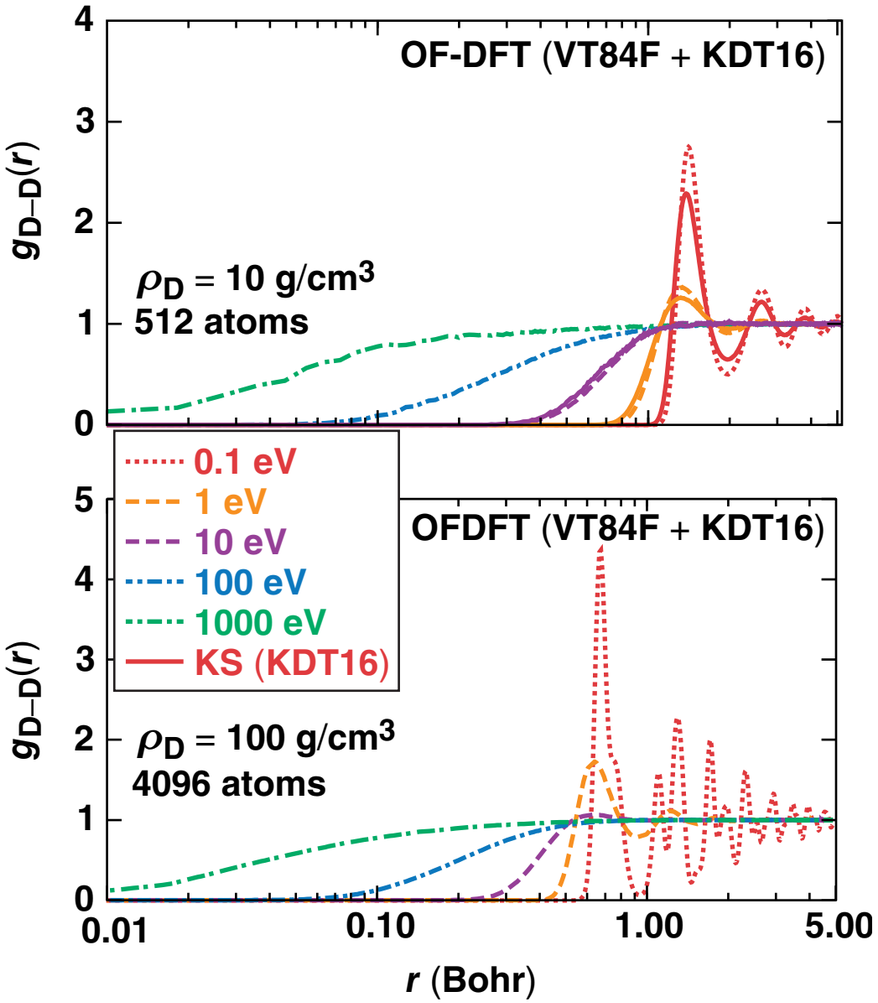




- Deuterium electron pressure versus temperature for the finite-temperature GGA ("KDT16") and ground-state PBE XC functionals, as well as PIMC reference results
- MD supercell simulations, Γ point only, for 128 atoms (8500 steps, $T \leq 40$ kK) or for 64 atoms (4500 steps, $T \geq 62$ kK)

S. X. Hu *et al.*, Phys. Rev. B 84, 224109 (2011).
*PIMC: path-integral Monte Carlo

With our orbital-free functionals we are able to treat very large systems (thousands of ions) up to very high temperatures (1000 eV or higher)



Ion–ion pair-correlation function ρ_D = 10 g/cm^3, T = 0.1 to 1000 eV from KS and orbital-free MD with 512 atoms

Ion–ion pair-correlation function ρ_D = 100 g/cm^3, T = 0.1 to 1000 eV from orbital-free MD with 4096 atoms

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