Generalized Gradient Approximation for Exchange-Correlation Free Energy

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APS March Meeting 2017, New Orleans, LA

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Funding Acknowledgments:
U.S. DoE DE-SC0002139

NERSC National Energy Research Scientific Computing Center

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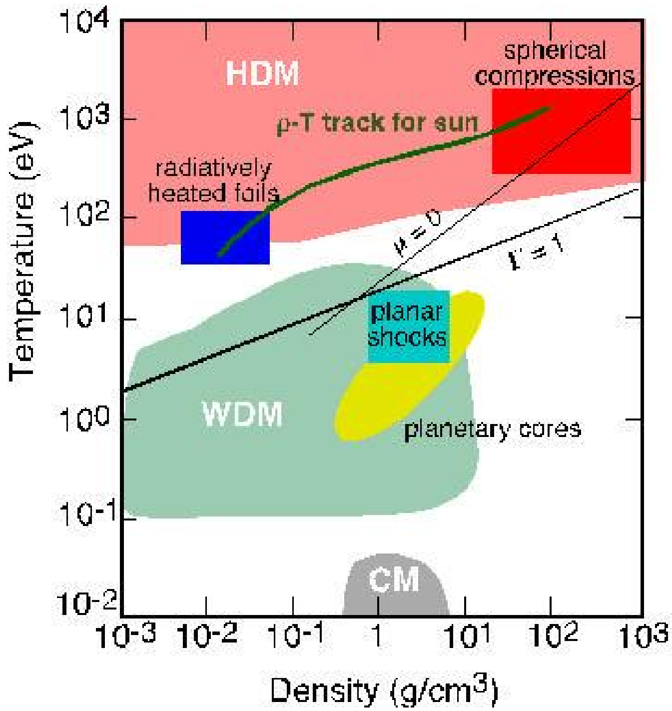
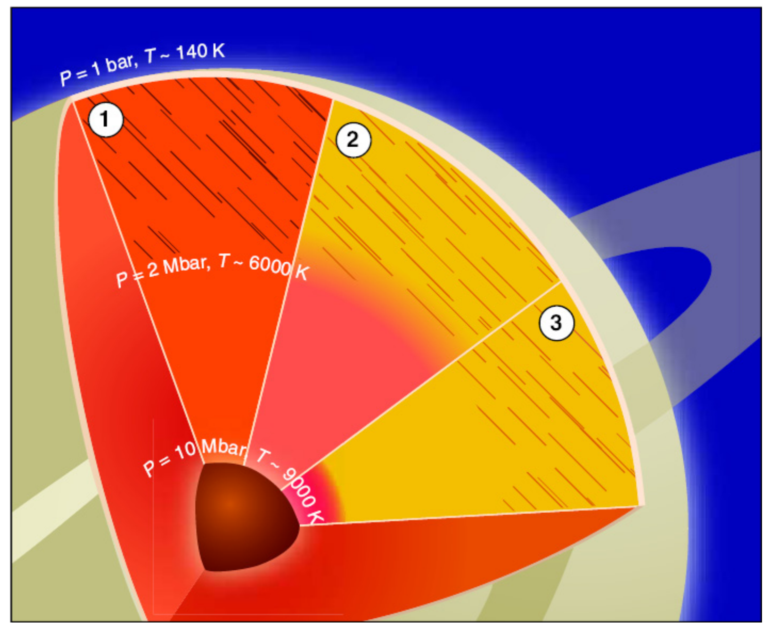
Motivation, Physical problem



<u>Warm Dense Matter</u>

← Schematic temperature-density diagram for Hydrogen (from R. Lee, LLNL).

Interior of Saturn →



(taken from: Fortney J. J., Science <u>305</u>, 1414 (2004):

(1) At an age of ~1.5 billion years

(2) The current Saturn according to previous H-He phase diagram

(3) The current Saturn according to new evolutionary models

Motivation, challenges to Developers

Why does the WDM regime require development of new methods & functionals?

Standard computational methods often cease to work at extreme compressions (high *P*) and temperatures (high *T*) –

- **Limited transferability of pseudopotentials and PAWs developed for near-ambient thermodynamic conditions.**

- **Drastic increase of computational cost as *T* increases:**

  cost ~ $(N_{band})^3$

- **Strong quantum effects => Usually not possible to go down in *T* to WDM regime from the hot plasma regime; classical approaches fail at lower *T***

- **Exchange-correlation effects at finite *T* are not taken into account by use of ground-state (zero-*T*) XC functionals**

Motivation, challenges to Developers

Need for thermal DFT functionals –

- **Thermal DFT is a part of standard treatment (of WDM)**
- **Choice of the XC free energy $\mathcal{F}_{xc}$ [*n*] may affect reliability of results**
- **Common practice is to use a *T*=0 XC functional:** $\mathcal{F}_{\mathrm{xc}}[n,T] \approx \mathcal{E}_{\mathrm{xc}}[n(T)]$
- **First rung XC free-energy functional (VVK, Sjostrom, Dufty, & Trickey, Phys. Rev. Lett. 112, 076403 (2014)) takes into account XC thermal effects in the local density approximation (LDA)**
- **Next rung GGA XC free-energy is required to take into account XC thermal and non-homogeneity effects which include *T*-dependent density gradients**

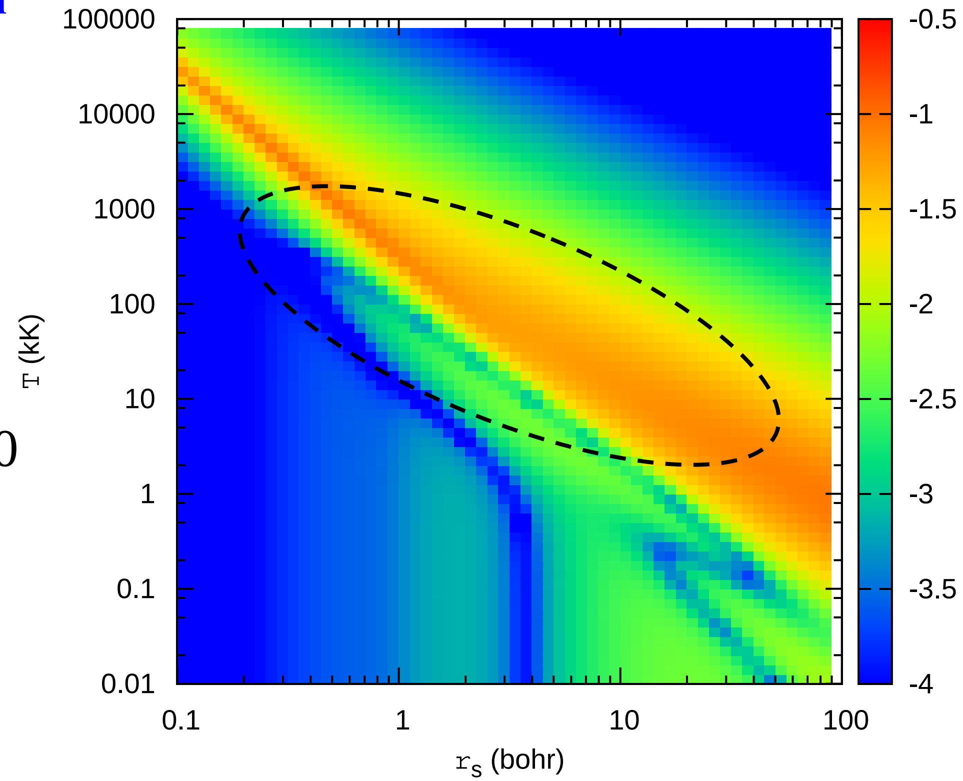
XC thermal effects for the homogeneous electron gas (HEG)

XC thermal effects are significant in WDM regime:

$$\log_{10} \frac{\left| f_{xc}(r_s,T) - \varepsilon_{xc}(r_s) \right|}{\left| f_s(r_s,T) \right| + \left| \varepsilon_{xc}(r_s) \right|}$$

f_{xc} = XC free energy per particle
ε_{xc} = XC energy per particle at T=0
f_s = non-interacting free energy

Rough WDM region in ellipse.



Common practice is to use a *T*=0 XC functional:

$$\mathcal{F}_{xc}[n,T] \approx \mathcal{E}_{xc}[n(T)]$$

May not be accurate in WDM regime

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Framework for GGA XC free-energy functional development

Climbing Jacob's Ladder in the Warm Dense Environment: Generalized Gradient Approximation Exchange-Correlation Free-Energy Functional

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(Dated: 19 Dec. 2016)

The potential for density functional theory (DFT) calculations to address, reliably, the extreme conditions of warm dense matter (WDM) is predicated upon having an accurate representation for the exchange-correlation (XC) free energy functional. To that end, we give a systematic, constraint-based construction of a non-empirical finite-temperature (T) generalized gradient approximation (GGA), based on the XC free energy gradient expansion. The new functional provides the correct

- **Identify *T*-dependent gradient variables for X and C free-energies**
- **Identify relevant finite-*T* constraints**
- **Use our finite-*T* LDA XC as an ingredient**
- **Propose appropriate analytical forms, incorporate constraints**
- **Implementation, tests, applications**

VVK, Dufty, Trickey, Phys. Rev. Lett. (submitted, 2017)
see also arXiv: 1612.06266v1

T-dependent density gradient for X

Start with finite-*T* gradient expansion for X:

$$f_{\mathrm{x}}^{\mathrm{LDA}}(n,T) = \varepsilon_{\mathrm{x}}^{\mathrm{LDA}}(n)\tilde{A}_{\mathrm{x}}(t) \quad ; \quad t = T/T_F$$

$$\tilde{A}_{\mathrm{x}}(t) = \frac{t^2}{2}\int_{-\infty}^{(\beta\mu)} I_{-1/2}^2(\eta)d\eta$$

$$f_{\mathrm{x}}^{(2)}(n,\nabla n,T) = f_{\mathrm{x}}^{\mathrm{LDA}}(n,T)\left[1+\frac{8}{81}s^2(n,\nabla n)\tilde{B}_{\mathrm{x}}(t)\right]$$

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

Finite-*T* GGA X functional: $F_{\mathrm{x}}^{\mathrm{GGA}}[n,T] = \int n\, f_{\mathrm{x}}^{\mathrm{LDA}}(n,T)\, \mathrm{F}_{\mathrm{x}}(s_{2\mathrm{x}})d\mathbf{r}$

Enhancement factor is defined from several ground-state and finite-*T* constraints:

$$\mathrm{F}_{\mathrm{x}}(s_{2\mathrm{x}}) = 1 + \frac{\nu_{\mathrm{x}} s_{2\mathrm{x}}}{1+\alpha|s_{2\mathrm{x}}|}$$

Constraints:

- **Reproduce finite-*T* small-s grad. expansion**
- **Satisfy Lieb-Oxford bound at *T*=0**
- **Reduce to correct *T*=0 limit**
- **Reduce to correct high-*T* limit**

T-dependent density gradient for C

Finite-*T* gradient expansion for XC:

$$f_{\mathrm{xc}}^{(2)}(n,\nabla n,T)=\frac{1}{2}g_{\mathrm{xc}}^{(2)}(n,T)\,|\nabla n|^2$$

$$=C_{\mathrm{x}}^{(2)}\varepsilon_{\mathrm{x}}^{\mathrm{LDA}}(n)s^2(n,\nabla n)\tilde{B}_{\mathrm{x}}(t)+C_{\mathrm{c}}^{(2)}n^{1/3}s^2(n,\nabla n)\tilde{B}_{\mathrm{c}}(n,t)$$

$C_{\mathrm{x}}^{(2)}=8/81$; $C_{\mathrm{c}}^{(2)}=0.162125$;

$$\tilde{B}_{\mathrm{x}}(t)=\left(\frac{3}{2}\right)^{4/3}I_{1/2}^{4/3}(\beta\mu)\left[\frac{I'_{-1/2}(\beta\mu)}{I_{-1/2}(\beta\mu)}-3\frac{I''_{-1/2}(\beta\mu)}{I_{-1/2}(\beta\mu)}\right]$$

$\tilde{B}_{\mathrm{c}}(n,t)$ is defined from equation for $f_{\mathrm{xc}}^{(2)}$ (above)

with use of numerical RPIMC-based data for $g_{\mathrm{xc}}^{(2)}(n)$

T-dependent density gradient for C (Contd.)

From finite-*T* gradient expansion for C we identify new *T*-dependent gradient variable:

$$n^{1/3}s^2(n,\nabla n)\tilde{B}_{\rm c}(n,t) \propto q^2\tilde{B}_{\rm c}(n,t)$$

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

where q is a ground-state reduced density gradient for correlation.

GGA correlation energy per particle:

$$f_{\rm c}^{\rm GGA}(n,\nabla n,T) = f_{\rm c}^{\rm LDA}(n,T) + H(f_{\rm c}^{\rm LDA},q_c)$$

where the function $H(f_c^{\rm LDA},q_c)$ is defined by the ground-state PBE functional to guarantee a widely used zero-*T* limit.

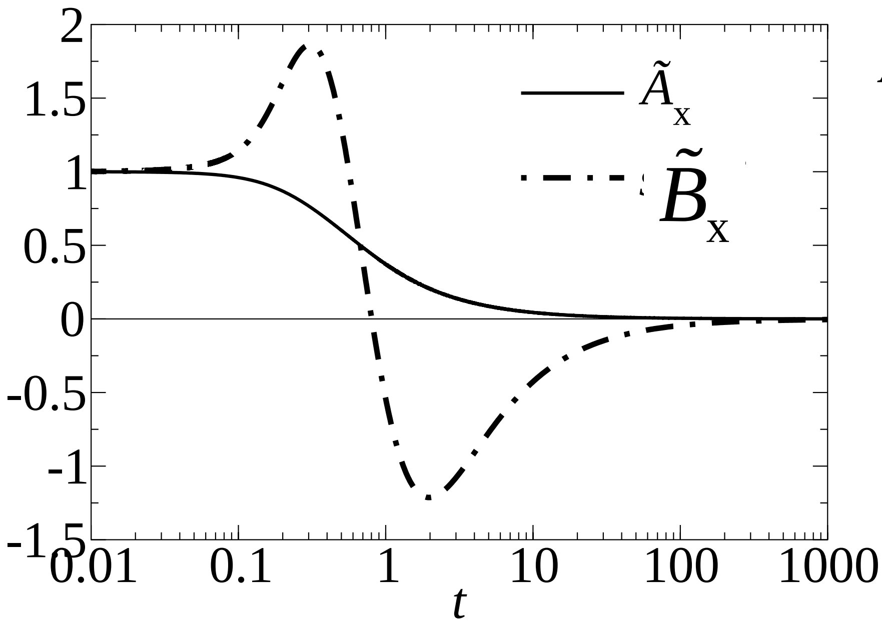
Finite-*T* GGA C functional:

$$F_{\rm c}^{\rm GGA}[n,T] = \int n\, f_{\rm c}^{\rm GGA}(n,\nabla n,T)d\mathbf{r}$$

Constraints:

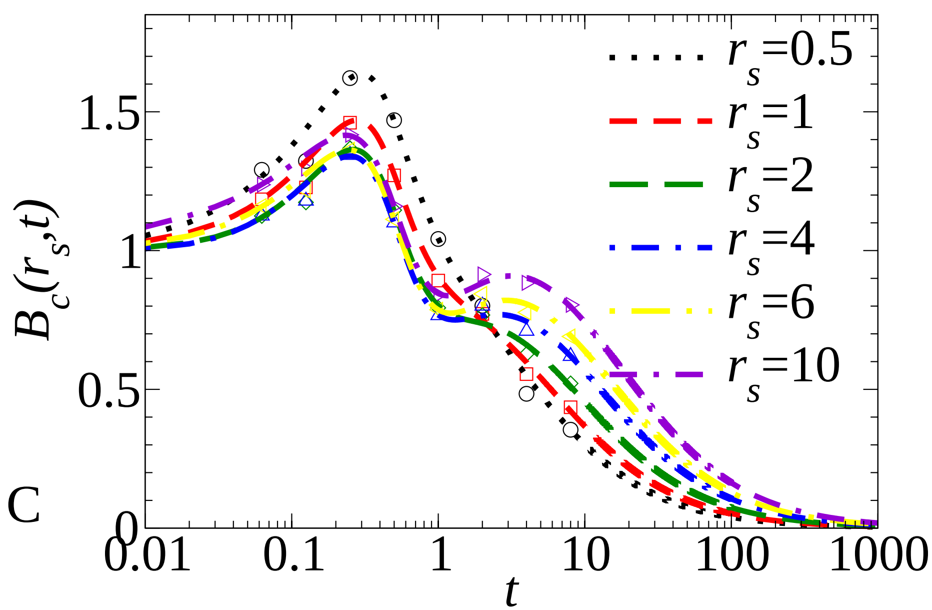
- **Reproduce finite-*T* small-s grad. expansion**
- **Reduce to correct *T*=0 limit**
- **Reduce to correct high-*T* limit**

X and C T-dependences



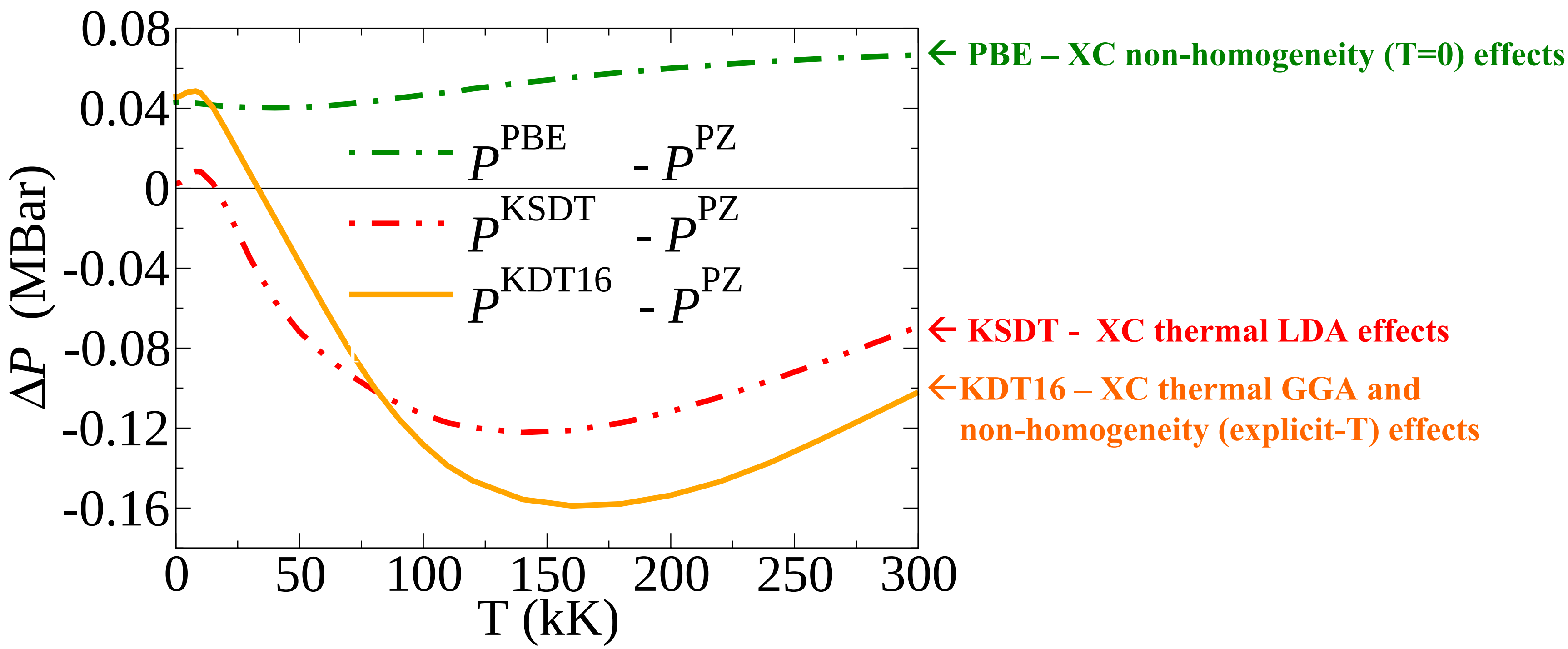
$\tilde{A}_x(t)$ - shows T-dependence of the LDA-X

$\tilde{B}_x(t)$ - shows T-dependence of the GGA reduced gradient for X



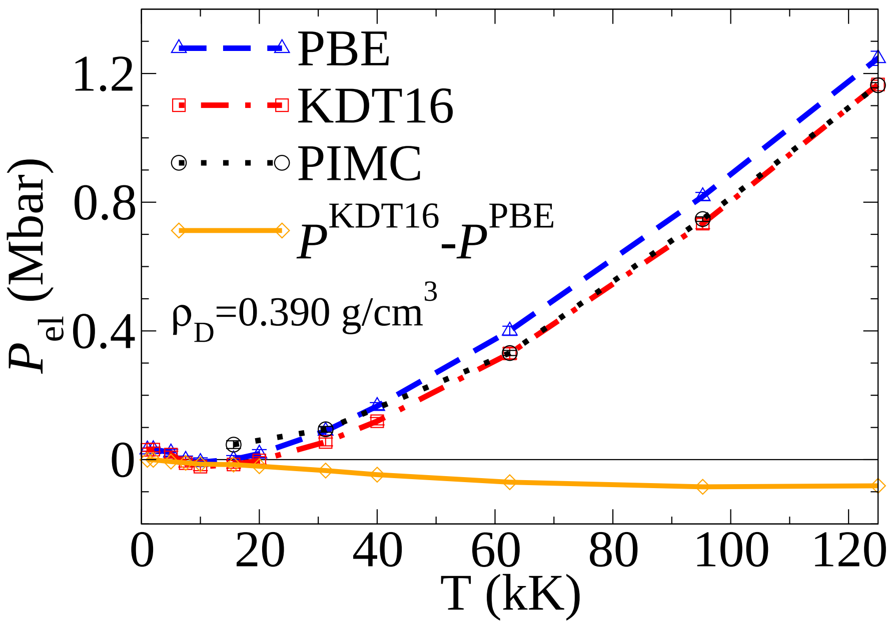
T-dependence of the GGA variable for C

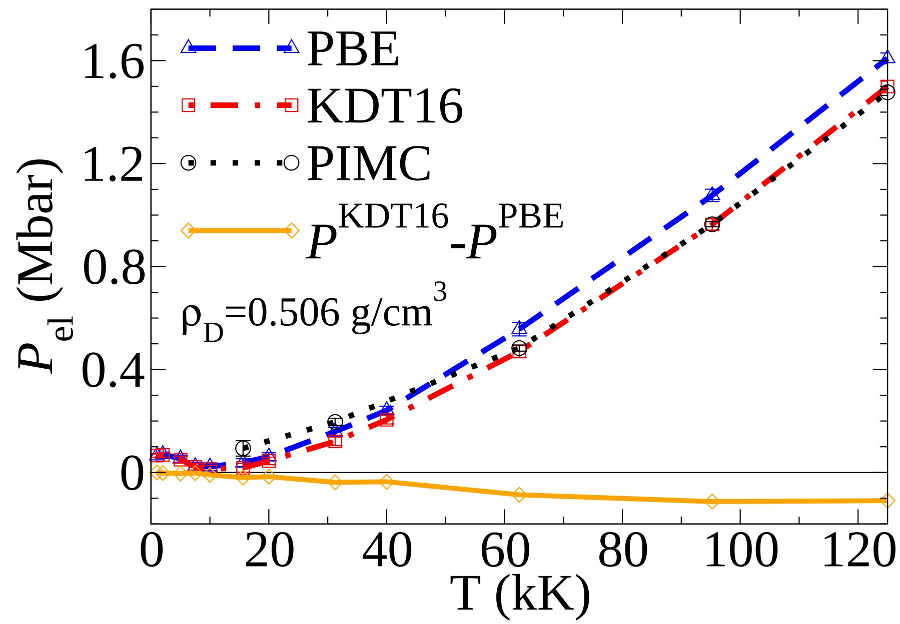
Thermal GGA XC results on fcc-Al model system



Electronic pressure differences vs. *T* for the new finite-*T* GGA ("KSDT16"), KSDT LDA, and ground-state PBE XC functionals, all referenced to PZ ground-state LDA values. Static lattice fcc Aluminum at 3.0 g/cm^3.

Thermal GGA XC results on Deuterium EOS





Deuterium electronic pressure vs. *T* for the finite-*T* GGA ("KDT16") and ground-state PBE XC functionals, as well as PIMC reference results.

AIMD super-cell simulations, Γ-point only, for 128 atoms (8500 steps, $T \leq 40$ kK) or for 64 atoms (4500 steps, $T \geq 62$ kK

PIMC results: S.X. Hu, B. Militzer, V.N. Goncharov, and S. Skupsky, Phys. Rev. B <u>84</u> 224109 (2011).

Summary

• **Framework for GGA XC free-energy functional development is presented**

⇒ virtually any ground-state XC can be extended systematically into an XC free energy

• **First GGA XC free-energy ("KDT16") functional constructed**

• **Test cases show that KDT16 provides improved accuracy in the description of XC thermal effects**

VVK, Dufty, Trickey, Phys. Rev. Lett. (submitted, 2017)
see also arXiv: 1612.06266v1