Tunable non-interacting free-energy functionals: Development and applications to low-density aluminum

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http://www.qtp.ufl.edu/ofdft

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Publications, preprints, local pseudopotentials, and codes at
http://www.qtp.ufl.edu/ofdft

Warm Dense Matter (WDM)

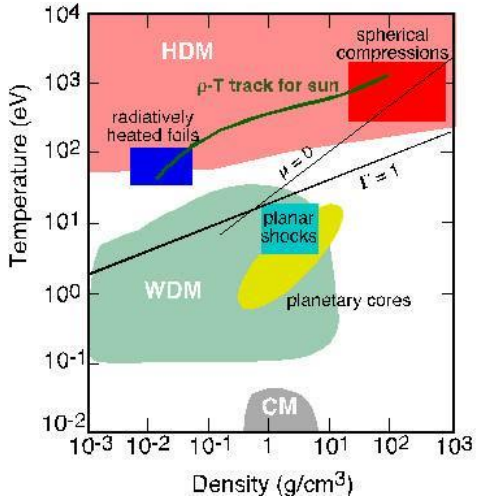
- **Challenging region *between* normal condensed matter and plasmas:**
  T < 100eV (≈1,100,000 K)
  Densities: from gas to ≈100 × equilibrium density
  (*i.e.* $P \rightarrow$ thousands of GPa).
- **Inertial confinement fusion pathway; interiors of giant planets & exo-planets, shock compression experiments**

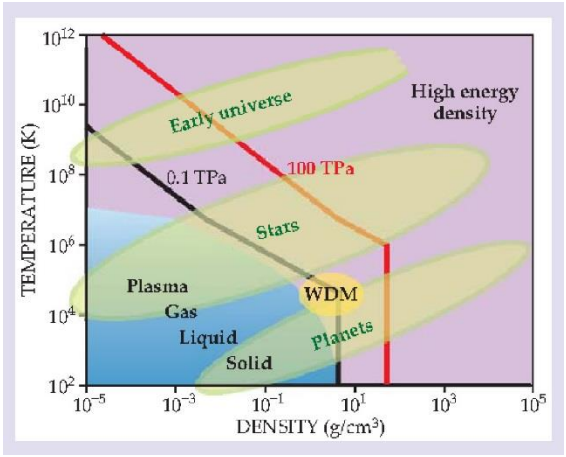
- **Both the Coulomb coupling constant** $\Gamma = e^2 / r_s k_B \mathrm{T}$
  and the Fermi-degeneracy parameter $t = \theta := k_B \mathrm{T} / E_F$
  are in the intermediate region ⇒
  no perturbation expansion.

- **Methods developed for WDM regime also work well for high-energy density physics and dense plasmas.**

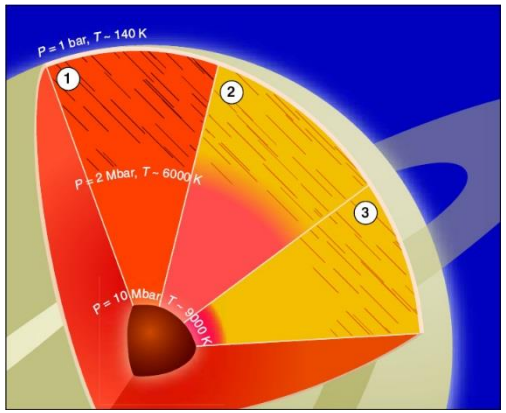
Motivation, Physical problem

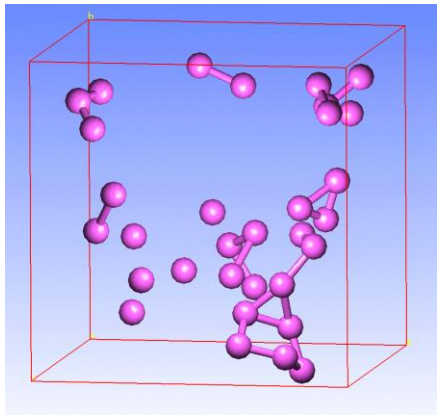
Warm Dense Matter (WDM)





Schematic temperature-density diagrams - Left: Hydrogen [from R. Lee, LLNL**] Right: Aluminum [**Phys. Today 63(6), 28 (2010)**]**





Left: **Interior of Saturn [**J.J. Fortney, Science 305, 1414 (2004)**]:**

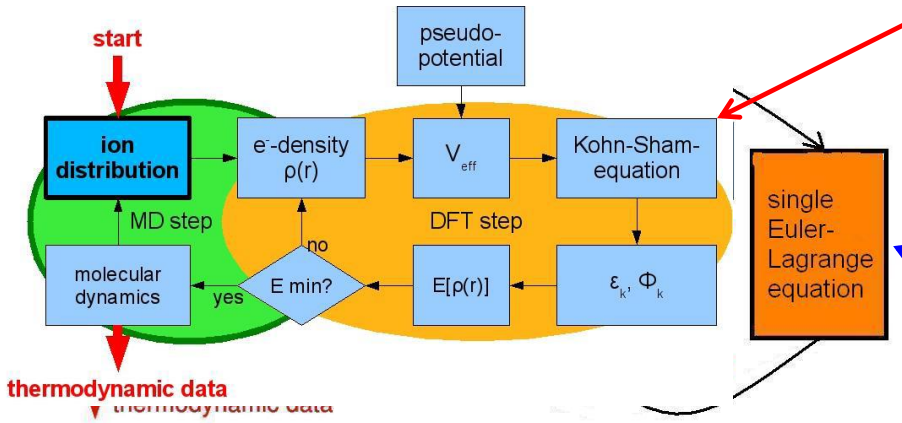
(1) At an age of ≈ 1.5 billion years

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

(3) The current Saturn according to new evolutionary models

Right: **MD snapshot of Al (0.20 g/cm^3) at T=5 kK. Shows complexity of WDM regime, formation of ions, molecules, and clusters.**

Computational Challenge



KS computational cost scales as cube of the number of occupied levels. Scaling worsens with increasing T (non-integer occupation).

Orbital-free Free Energy DFT – *No* explicit KS orbitals . Scales with system size.

Mermin, Hohenberg-Kohn DFT

$$\Omega[n] = F[n] + \int d\mathbf{r}\,(v_{\text{ext}}(\mathbf{r}) - \mu)\, n(\mathbf{r}) \qquad \text{Grand potential}$$

$$F[n] = F_{\text{s}}[n] + F_{\text{H}}[n] + F_{\text{xc}}[n] \qquad \text{Universal free energy functional}$$

$F_{\text{H}}[n]$ = Hartree free energy , $F_{\text{s}}[n]$ = Non-interacting (KS) free energy,

$F_{\text{xc}}[n]$ = eXchange-Correlation (XC) free energy

KS equation

$$\left\{-\tfrac{1}{2}\nabla_{r_1}^2 + v_{\text{H}}\left(\mathbf{r}_1;\{\mathbf{R}\}\right) + v_{\text{xc}}\left(\mathbf{r}_1;\{\mathbf{R}\}\right) + v_{\text{ext}}\left(\mathbf{r}_1;\{\mathbf{R}\}\right)\right\}\varphi_j\left(\mathbf{r}_1;\{\mathbf{R}\}\right) = \varepsilon_j\,\varphi_j\left(\mathbf{r}_1;\{\mathbf{R}\}\right)$$

$$n\left(\mathbf{r}_1;\{\mathbf{R}\}\right) = \sum_j f(\varepsilon_j)\left|\varphi_j\left(\mathbf{r}_1;\{\mathbf{R}\}\right)\right|^2 \quad ; \quad v_{\text{xc}}[n] = \frac{\delta F_{\text{xc}}}{\delta n}$$

Electrons Nuclei

Original Image: W. Lorenzen

Finite-Temperature OF-DFT Basics

OFDFT requirements: reliable, orbital-free approximations for

$$F_s[\{\varphi\}] = T_s[\{\varphi\}] - \mathrm{T}S_s[\{\varphi\}]$$

← **Non-interacting (Kohn-Sham) free energy**

$$F_{xc}[n] = (T[n] - T_s[n]) - \mathrm{T}(S[n] - S_s[n]) + (U_{ee}[n] - F_H[n])$$

← **Exchange-Correlation free energy**

$$\frac{\delta F_s[n]}{\delta n(r)} + v_s([n];r) = \mu, \quad \text{where} \quad v_s = v_{ext} + v_H + v_{xc}$$

← **Single Euler equation to solve**

Partial history of finite-*T* functional development:

- **(1949) Feynman, Metropolis: finite-T Thomas-Fermi:** $F_s^{TF}[n]$
- **(1979) Perrot: Gradient corrections to TF:** $F_s^{SGA}[n]$
- **(2012) Karasiev, Sjostrom, Trickey: Finite-T GGA formalism:** $F_s^{GGA}[n]$ Phys. Rev. B **86**, 115101 (2012)
- **(2013) Karasiev, Chakraborty, et al.: Non-empirical GGA:** $F_s^{GGA}[n]$ Phys.Rev. B **88**, 161108(R) (2013)

- **(1979-2000) finite-*T* XC based on different models:** $F_{xc}[n]$
- **(2014) Karasiev, Sjostrom, Dufty, Trickey: finite-T LDA XC** $F_{xc}^{LDA}[n]$ Phys. Rev. Lett. **112**, 076403 (2014)
- **(2017) Karasiev, Dufty, Trickey: finite-T GGA XC** $F_{xc}^{GGA}[n]$ Phys. Rev. Lett. (submitted) (2017)

PROFESS@Quantum-Espresso package

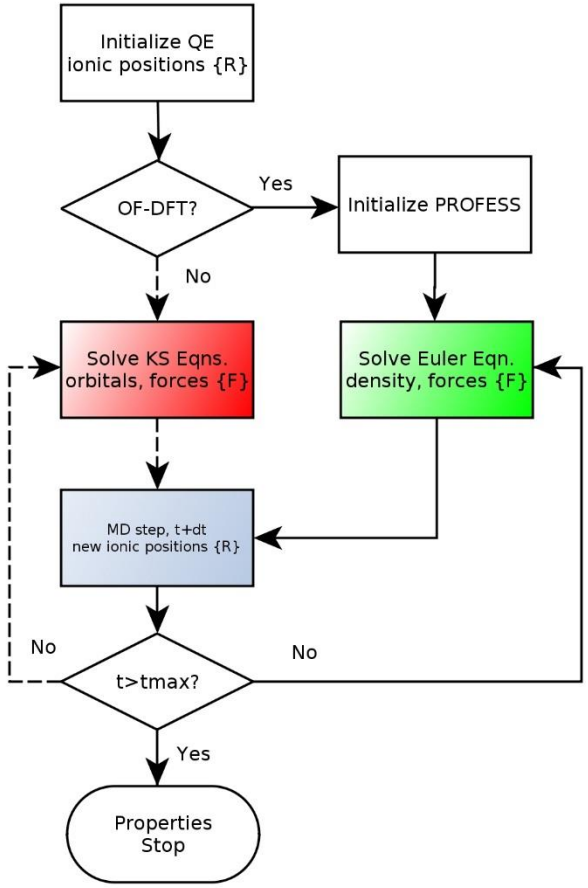
- **Finite-T OF-DFT functionals are implemented in the PROFESS code.**

- **T-dependent XC implemented in PROFESS and Q-Espresso**

- **Our analytical representations of Fermi-Dirac integral combinations are implemented**

- **PROFESS@Q-Espresso interface gives Quantum-Espresso MD driven by OF-DFT forces**

- **Vers. 2.0 was released recently – go to http://www.qtp.ufl.edu/ofdft**



Flow chart for MD simulation with PROFESS@Q-Espresso

Karasiev, Sjostrom, Trickey, Comput. Phys. Commun. 185, 3240 (2014)

Optical Conductivity & XC thermal effects

OF-DFT MD and subsequent Kohn-Sham and Kubo-Greenwood conductivity calculations -

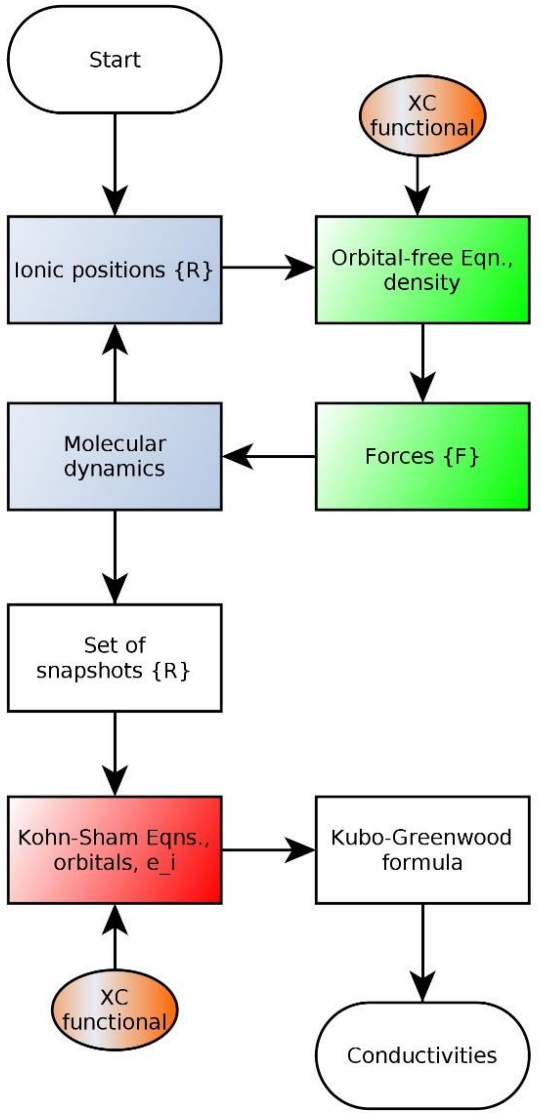
- **Non-interacting free-energy functional is a critical input to OF-DFT MD**
- **2 to 10 "snapshots"; explicit KS to get orbitals and eigenvalues**
- **XC free-energy functional is a critical input for both OF-DFT MD and snapshot KS**

Kubo-Greenwood Electron Conductivity Expression and Implementation for Projector Augmented Wave Datasets

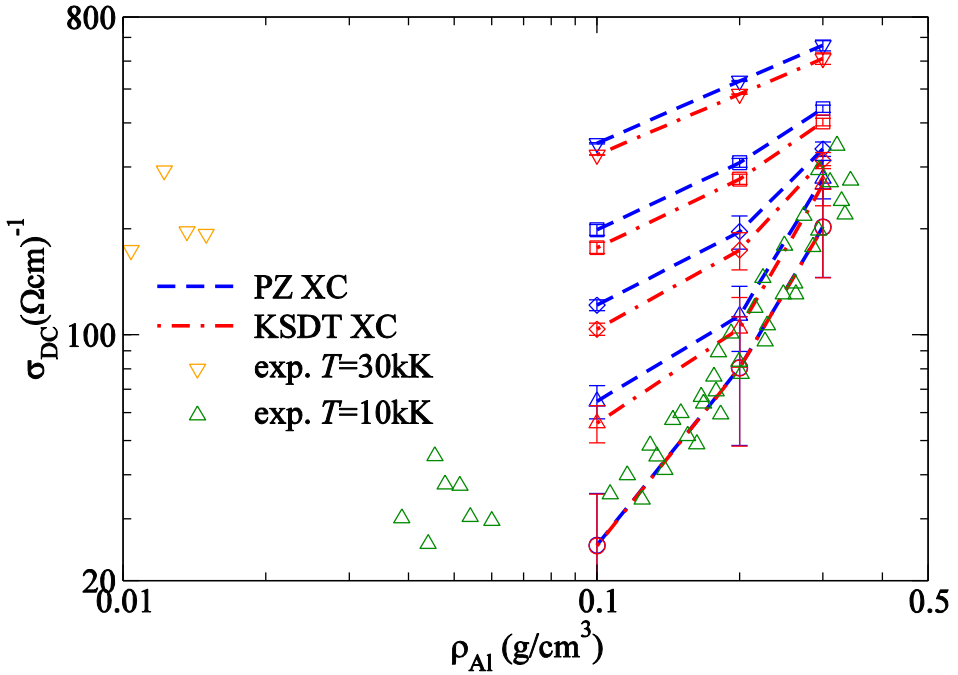
L. Calderín, V. Karasiev, S.B. Trickey; QTP, Physics and Chemistry, Univ. Florida

2 Mar 2017; version 3; not for circulation outside UF WDM/OFDFT group

Paper & code in preparation for GPL release.



Optical Conductivity & XC thermal effects

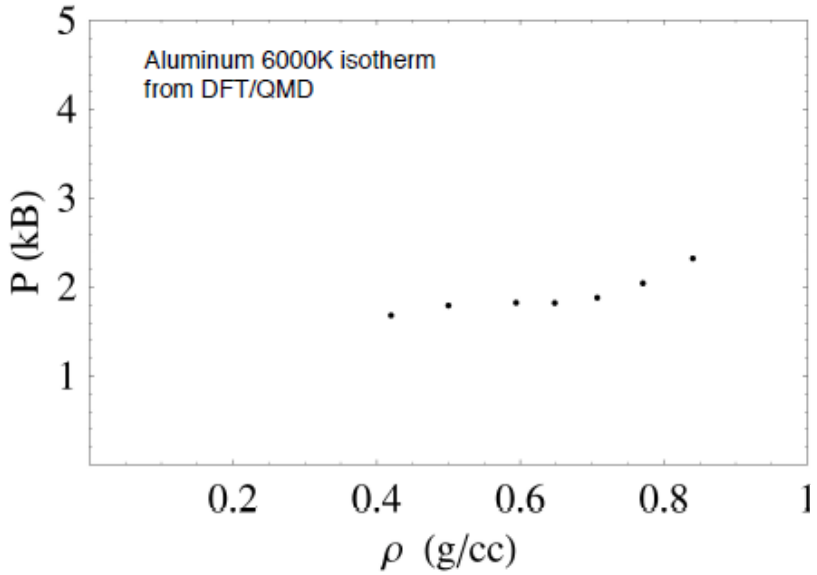


Aluminum DC conductivity as a function of material density from calculations with T-dependent KSDT (dot-dashed) and ground state PZ (dashed) XC functionals for five isotherms: 5, 10, 15, 20, and 30 kK (bottom to top).

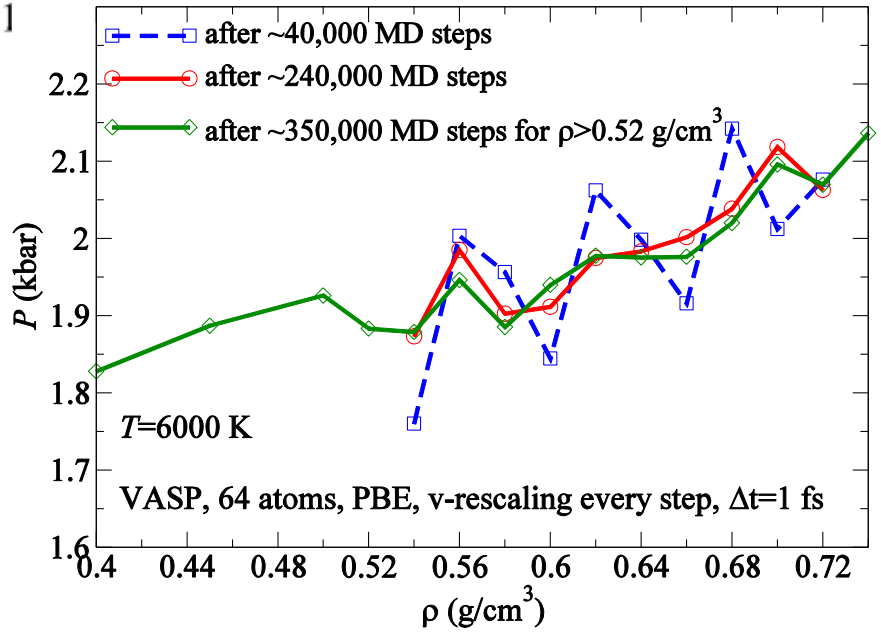
Use of explicitly T-dependent XC lowers the DC conductivity of low-density Al, yielding improved agreement with experiment.

[Karasiev, Calderín, Trickey, Phys. Rev. E 93, 063201 (2016)]

Low-density System Challenge: Liquid-vapor transition in Al



M.P. Desjarlais [Atom. Proc. Plasmas CP-1161, 32 (2009)] "**very tedious**" **KS-MD calculations**



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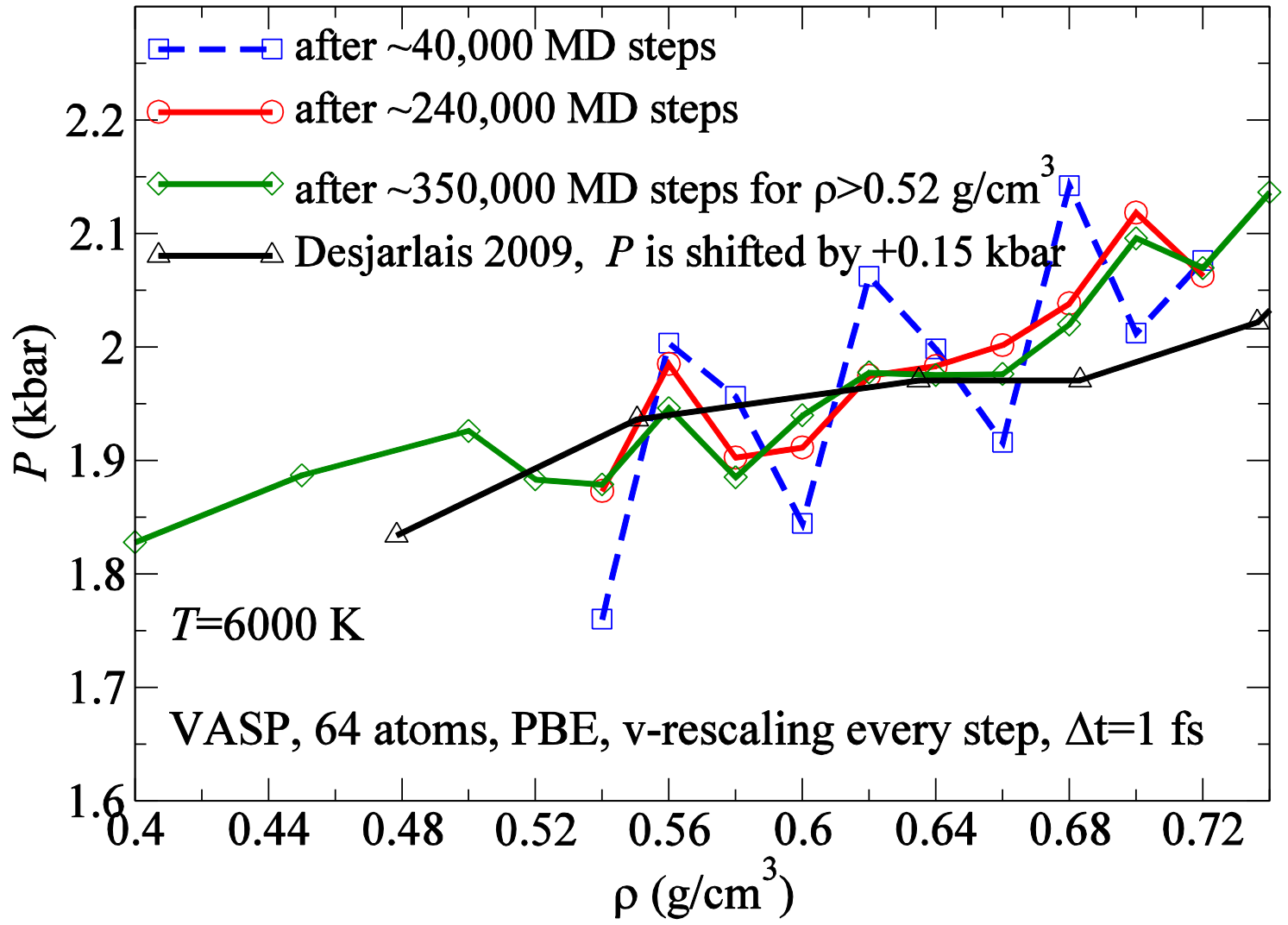


Low-density System Challenge

Challenge to OF-DFT removal of Kohn-Sham bottleneck: all known orbital-free non-interacting functionals (including ours) are grossly inaccurate for low density Al.

Pragmatic response: Develop tunable functionals to work with particular system at relevant thermodynamic conditions.

Tuning: Adopt a functional form with parameters, set most of them to match exact conditions, set the rest to match reference Kohn-Sham calculations at some matching temperatures T_m ***and material densities*** ρ_m **.**

Build transferability to higher $T > T_m$ ***by incorporating exact high-T limit by construction.***

Orbital-free tunable non-interacting functional

1) *Zero-T kinetic energy GGA enhancement factor*

$$F_t(s) = \frac{1 + a_2 s^2 + a_4 s^4 + a_5 s^5 + a_6 s^6}{1 + b_2 s^2 + b_4 s^4} \qquad s(n, \nabla n) = \frac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}}$$

2) *Apply the finite-T GGA framework* [*Karasiev, Sjostrom, Trickey, PRB 86, 115101 (2012)*] **:**

$$F_\tau(s_\tau) = F_t(s_\tau); \quad F_\sigma(s_\sigma) = 2 - F_t(s_\sigma)$$

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

$$s_\tau(n, \nabla n, \mathrm{T}) := s(n, \nabla n) \sqrt{\frac{\tilde{h}(t) - t(\mathrm{d}\tilde{h}/\mathrm{d}t)}{\xi(t)}} \qquad s_\sigma(n, \nabla n, \mathrm{T}) := s(n, \nabla n) \sqrt{\frac{t(\mathrm{d}\tilde{h}/\mathrm{d}t)}{\zeta(t)}} \qquad t = T / T_F$$

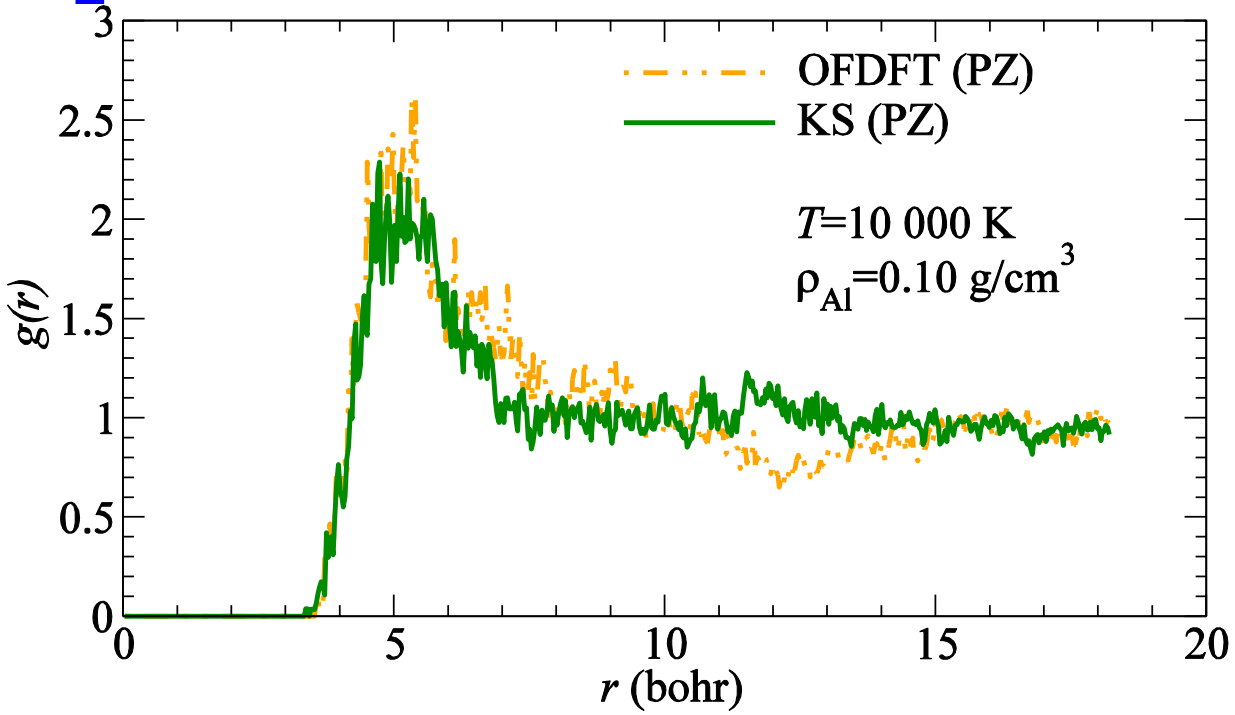
3) *Most parameters determined from constraints; leave a few free.*

4) *Tune free parameters to match the KS static lattice hot curve (pressure vs. volume), not KS AIMD, at T=T$_m$ and relevant bulk density regime.*

Orbital-free tunable non-interacting functional

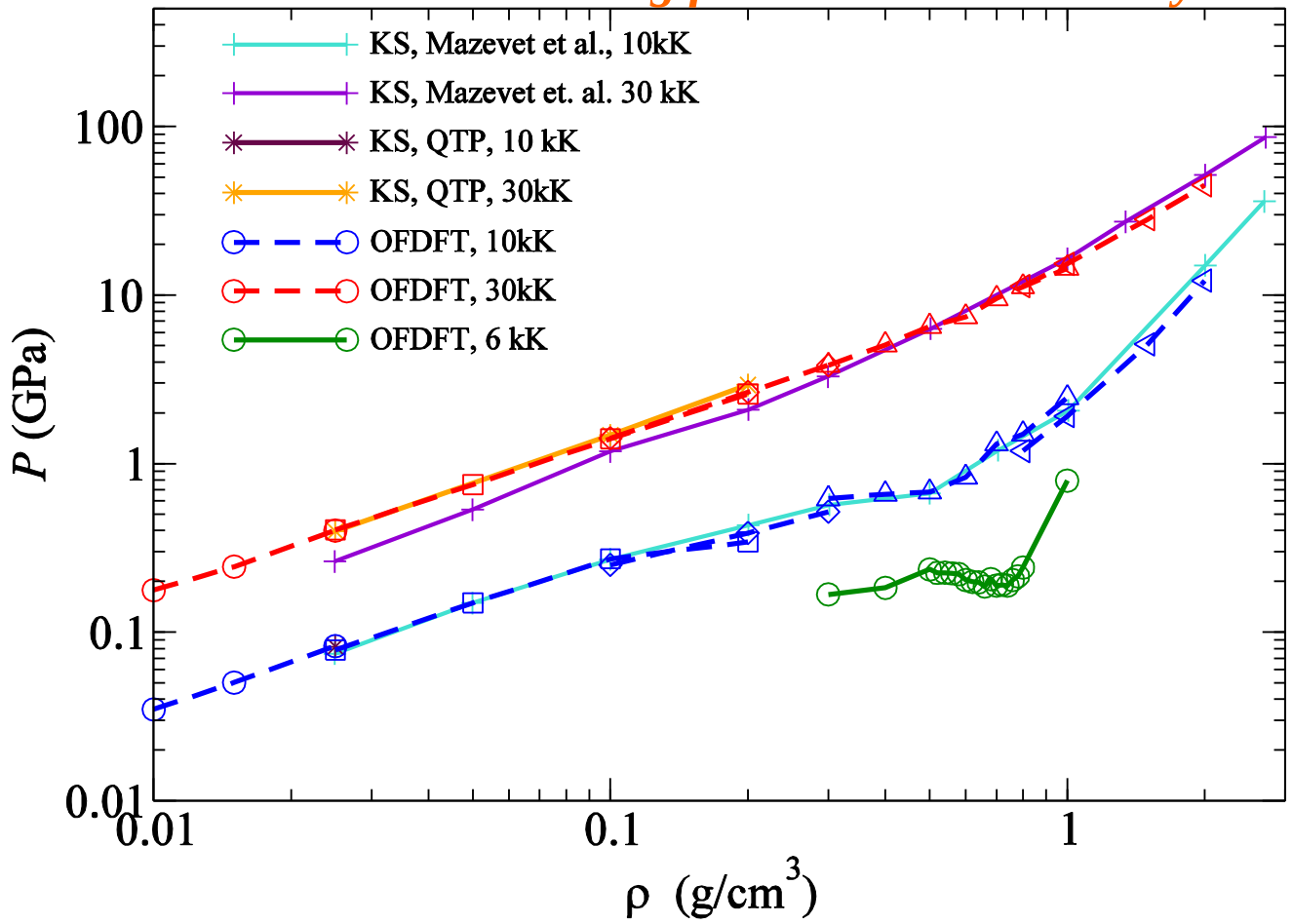
Functional tuned at one T_m= 8kK is usefully accurate for T ≥ 10 kK.

Conservative approach: Run KS-MD for T ≤ 10 kK, and use tunable in OF-DFT MD for T ≥ 10 kK.



OF-DFT and KS ion pair-correlation functions for Al at ρ_{Al}=0.10 g/cm^3 & T=10 kK.

Tunable OF Non-interacting functional: Low density Al



Low-density Al EOS at T=10 kK and 30 kK; tunable OF-DFT functional compared to KS. Tuned at T_m = 8kK & three ρ_m (1.0, 1.5, 2.0 g/cm^3)

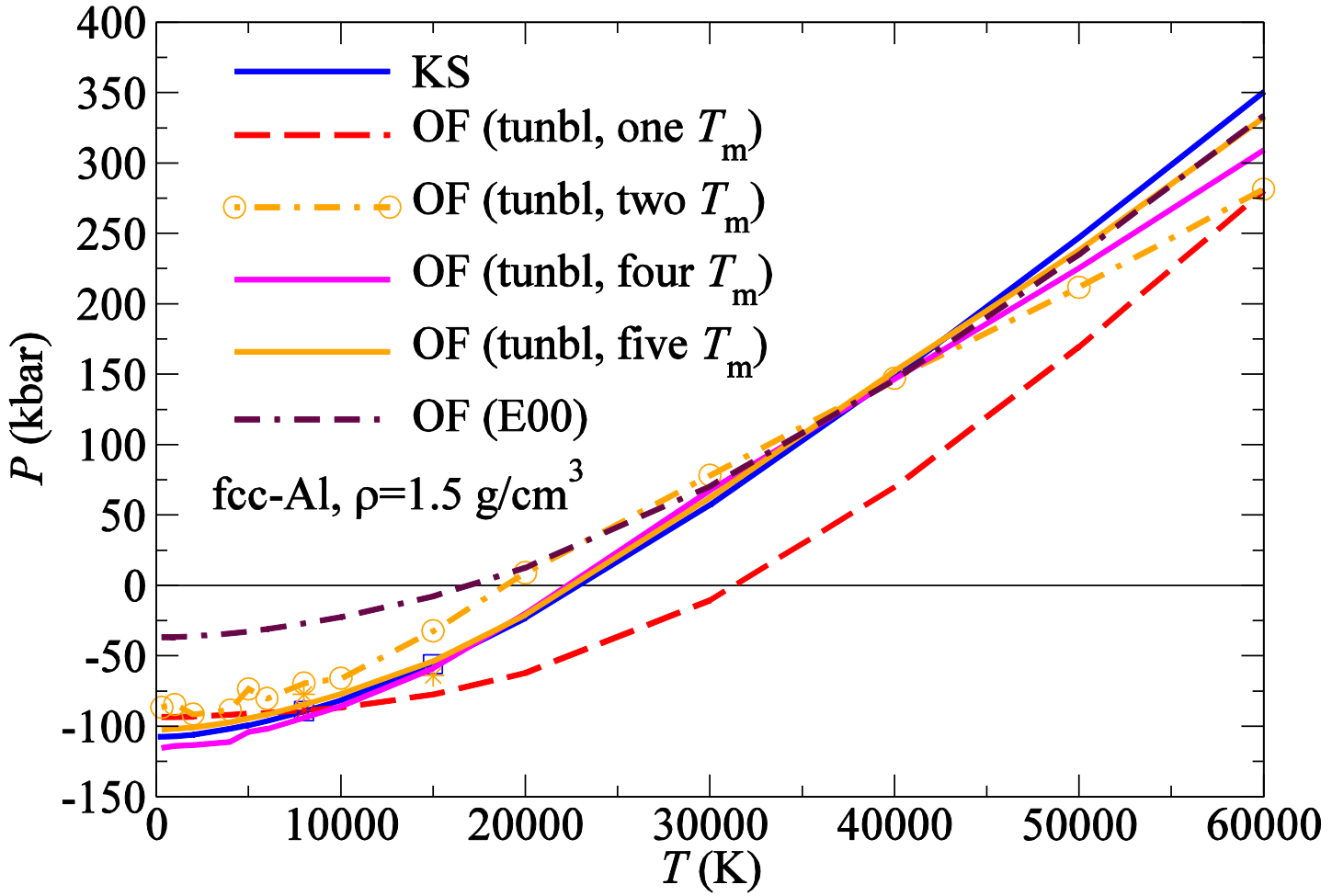
Number of atoms in simulation cell: 8 → 108.

10 kK. 30 kK OF-DFT ≈ 12,000 steps
6 kK ≈ 6,000 steps

Liquid-vapor critical point -

- **Does not model two phases (phase separation or co-existence)**
- **Searches for the diverging isothermal compressibility** $\kappa = \left(n \frac{\partial P}{\partial n}\Big|_T \right)^{-1}$
- **Requires very long MD due to slow convergence of averages over MD steps.**

Tuning – At how many Temperatures?



T_m sets = {8 kK}; {8, 15 kK}; {8, 15, 30, 60 kK}; {8, 15, 30, 40, 60 kK}

ρ_m set = {1.0, 1.5, 2.0} g/cm^3

Summary

- **Real progress on orbital-free DFT (both T = 0 K and T > 0 K):**
  - *** Finite-T GGA formalism (for the non-interacting free-energy)**
  - *** First non-empirical GGAs for non-interacting free-energies**
  - *** Tunable non-interacting functional enables far-reaching extension of static KS calculations into OF-DFT MD**

- **Real progress on finite-T XC:**
  - *** "KSDT" LSDA XC based on parametrization of quantum Monte-Carlo data**
  - **Non-empirical "KDT16" GGA XC free-energy (submitted)**
  - **TODAY: Room 289; 11:51 am – 12:03 pm; L26.00004, V.V. Karasiev**

- **Software:**
  - *** Profess@Q-Espresso orbital-free package**
  - *** Kubo-Greenwood post-pocessing transport properties package for QE (soon)**
  - **www.qtp.ufl.edu/ofdft**