Thermal DFT

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August 7, 2019

Thermal DFT (and TDDFT)

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Reasons to Ignore Temperature

Low energy states are enough

- Occupy electronic ground state at “normal” temps

Implicit temperature dependence in XC “works”

- Using thermal densities as inputs into ZTA captures large segment of the free energy

For TDDFT, formal issues unclear

- Non-equilibrium systems don’t have defined temperatures; time-dependent weights?

Reasons to Include Temperature

Higher energy states become accessible

- High temperatures or low-lying excited states

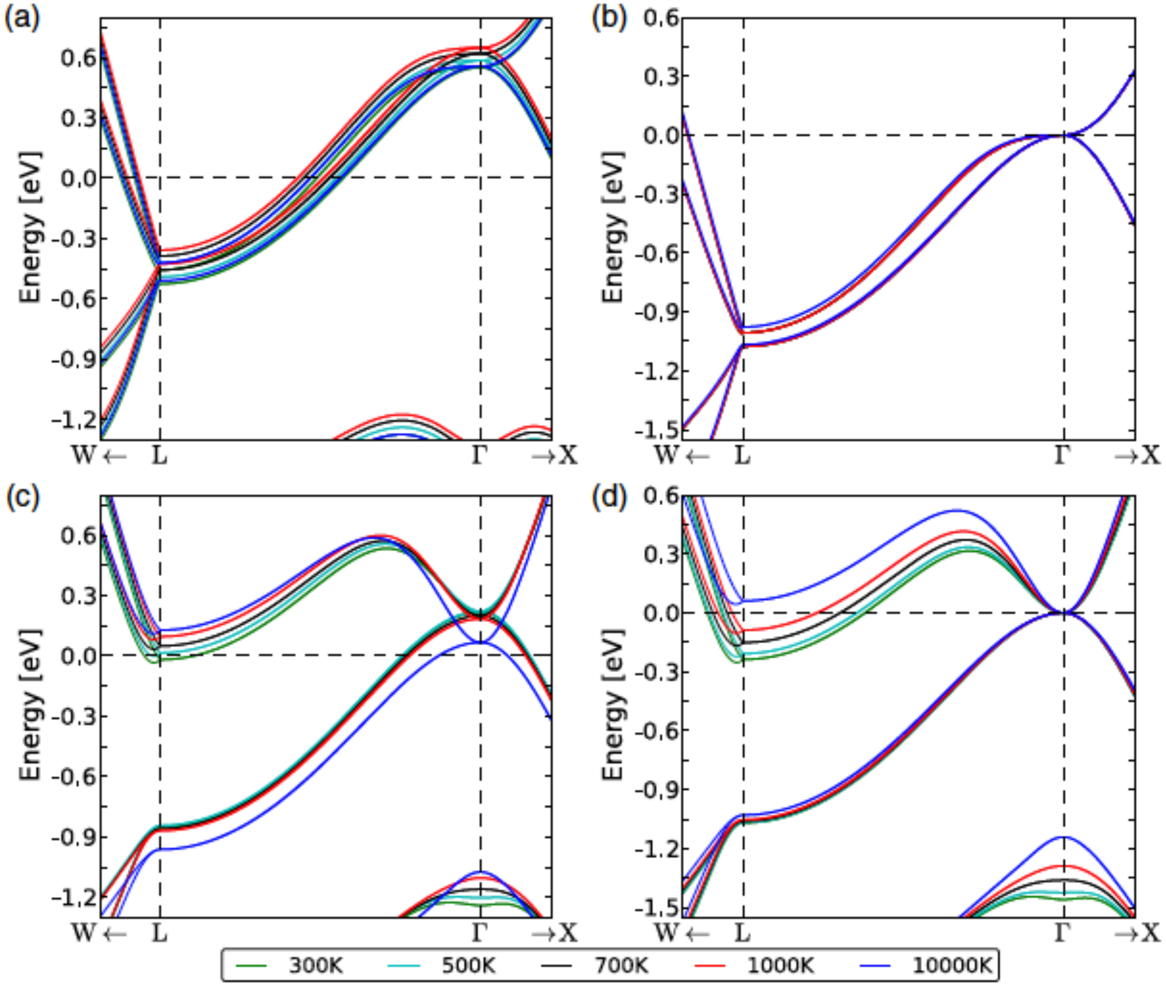
Properties needed seem sensitive to FT XC

- Optical, electronic, response, or spin properties incorrect or clearly temperature-dependent

We know it must be included formally!

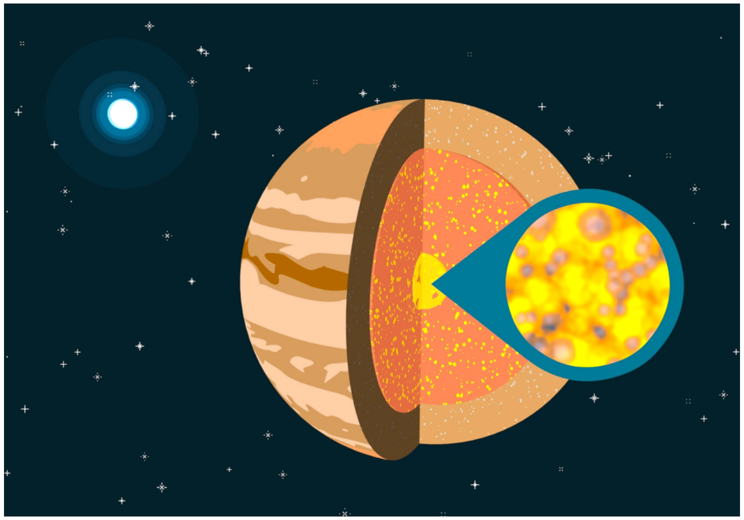
- As temperatures rise, XC is known to be temperature-dependent

Topological Phase Transitions



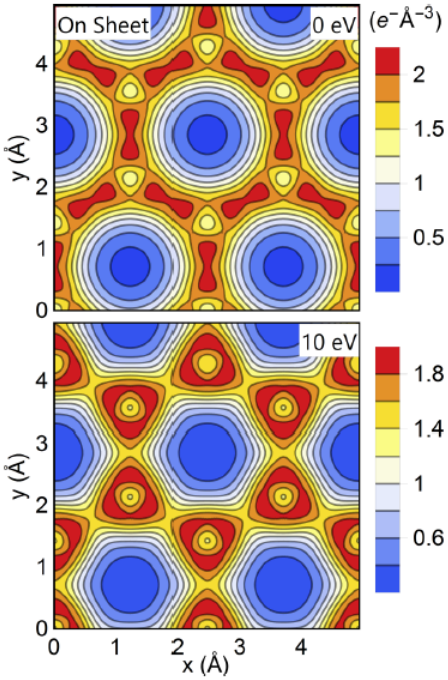
Trushin and Görling, PRL, 120, 146401 (2018)

Warm Dense Matter

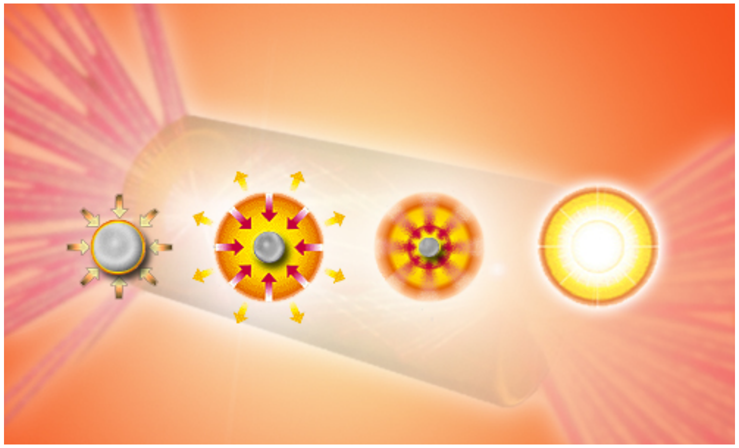


Planetary cores

Materials under extreme conditions

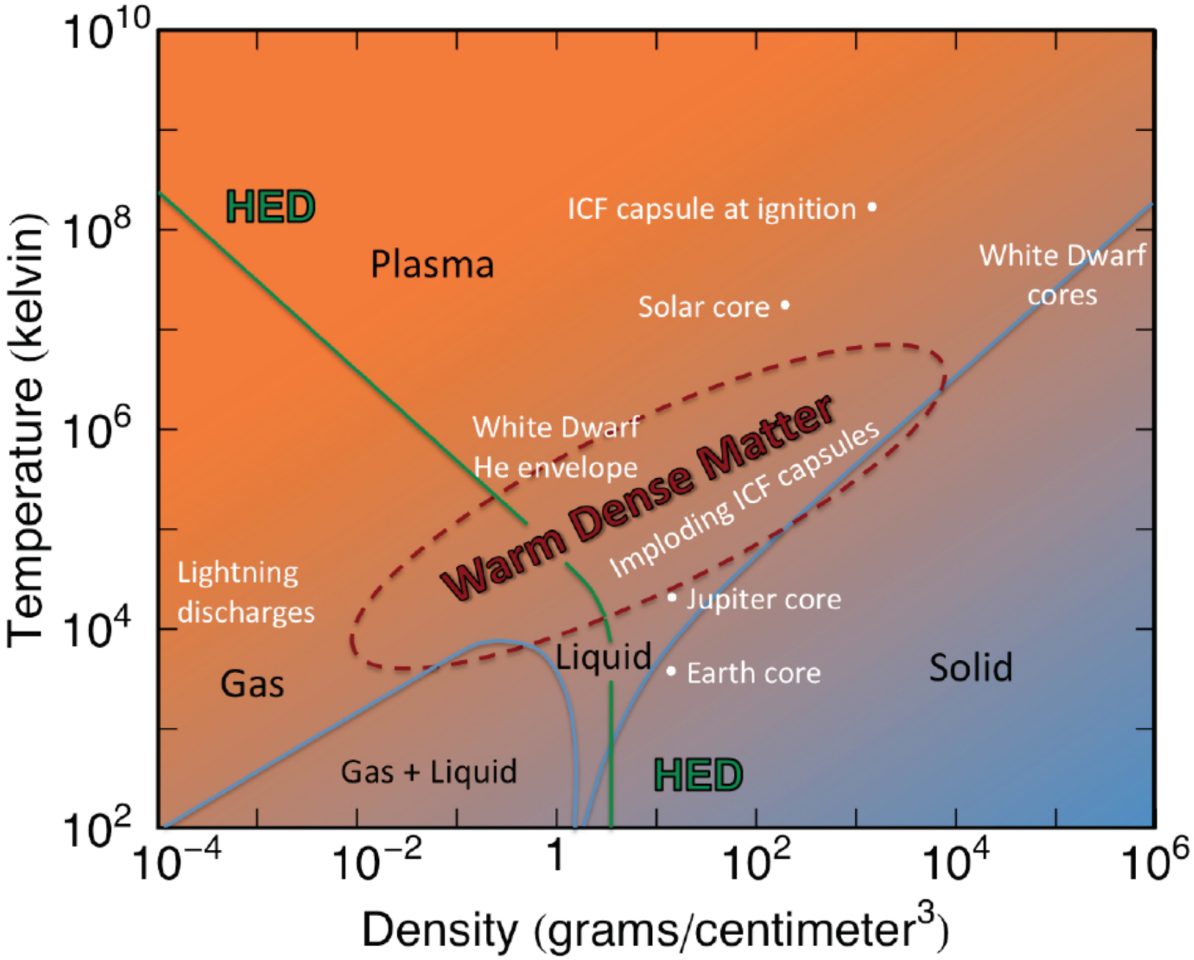


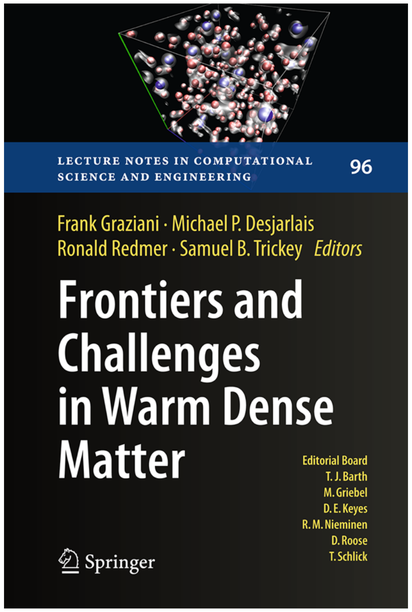
Fusion capsules



R.A. Valenza et al., Phys. Rev. B **93,** 115135 (2016); Promotional materials, SLAC, Stanford University (2015); LBL website.

Malfunction Junction





LECTURE NOTES IN COMPUTATIONAL SCIENCE AND ENGINEERING 96

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Frontiers and Challenges in Warm Dense Matter

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Basic Research Needs for HEDLP: Report of the Workshop on HEDLP Research, DOE (2009)

Heating Things Up

Grand canonical potential operator

$$\hat{\Omega} = \hat{H} - \tau \hat{S} - \mu \hat{N}$$

Electronic Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{\mathrm{ee}} + \hat{V}$$

Mermin, N.D. *Phys. Rev. A,* 137: 1441 (1965).
Pittalis, S. et al. *Phys. Rev. Lett.*, 107: 163001 (2011).

State Description and Entropy

Statistical operator:

$$\hat{\Gamma} = \sum_{N,i} w_{N,i} |\Psi_{N,i}\rangle\langle\Psi_{N,i}|$$

Weights:

$$w^0_{N,i} = \frac{e^{-\beta(E^0_{N,i} - \mu N)}}{\sum_{N,i} e^{-\beta(E^0_{N,i} - \mu N)}}$$

Entropy operator:

$$\hat{S} = - \ k_B \ln \hat{\Gamma}$$

Observables:

$$O[\hat{\Gamma}] = \mathrm{Tr}\ \{\hat{\Gamma}\hat{O}\} = \sum_N \sum_i w_{N,i} \langle\Psi_{N,i}|\hat{O}|\Psi_{N,i}\rangle$$

Pittalis, S. et al. *Phys. Rev. Lett.,* 107: 163001 (2011).
APJ et al., “Thermal DFT in Context,” *Frontiers and Challenges in Warm Dense Matter*, Springer Publishing (2014), p 25-60.

Finite-Temperature Kohn-Sham

Finite-temperature Kohn-Sham equations: temperature-dependent eigenstates and eigenvalues:

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{S}}^{\tau}(\mathbf{r})\right]\phi_i^{\tau}(\mathbf{r}) = \epsilon_i^{\tau}\phi_i^{\tau}(\mathbf{r})$$

KS system defined to have same density and same temperature as interacting system:

$$n^{\tau}(\mathbf{r}) = \sum_i f_i^{\tau}\left|\phi_i(\mathbf{r})\right|^2$$

$$f_i^{\tau} = \left(1 + e^{(\epsilon_i^{\tau}-\mu)/\tau}\right)^{-1}$$

Kohn and Sham, 1965.

Free Energies

Temperature-dependent free energy, interacting and KS versions:

$$\begin{aligned} A^{\tau}[n] &= T^{\tau}[n] - \tau S^{\tau}[n] + V_{\mathrm{ee}}^{\tau}[n] + V_{\mathrm{ext}}[n] \\ &= T_{\mathrm{s}}^{\tau}[n] - \tau S_{\mathrm{s}}^{\tau}[n] + U[n] + A_{\mathrm{xc}}^{\tau}[n] + V_{\mathrm{ext}}[n] \end{aligned}$$

Non-interacting kentropy is minimized in FT KS:

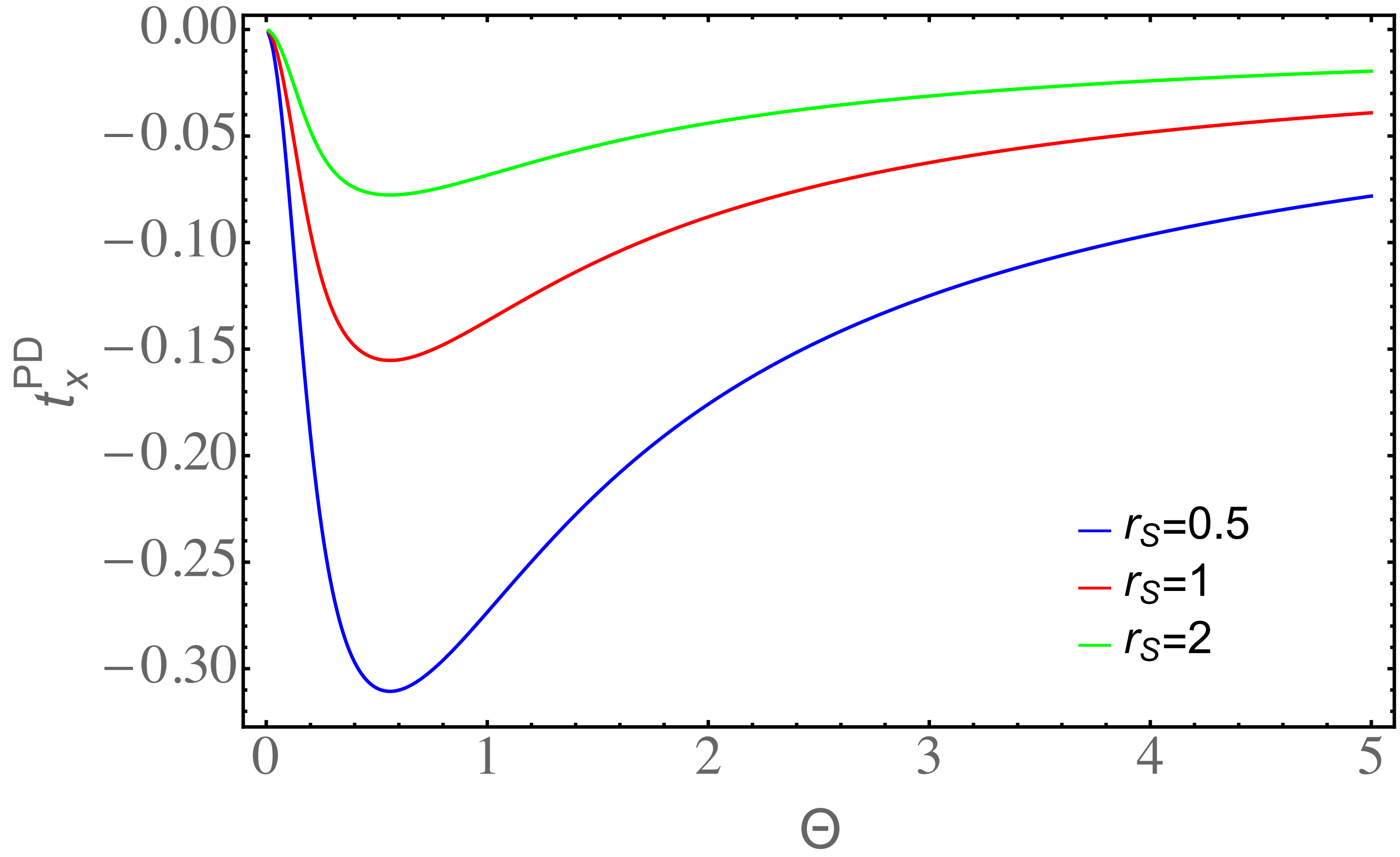
$$K_{\mathrm{s}}^{\tau}[n] = T_{\mathrm{s}}^{\tau}[n] - \tau S_{\mathrm{s}}^{\tau}[n]$$

Kinetic, potential, entropic exchange-correlation:

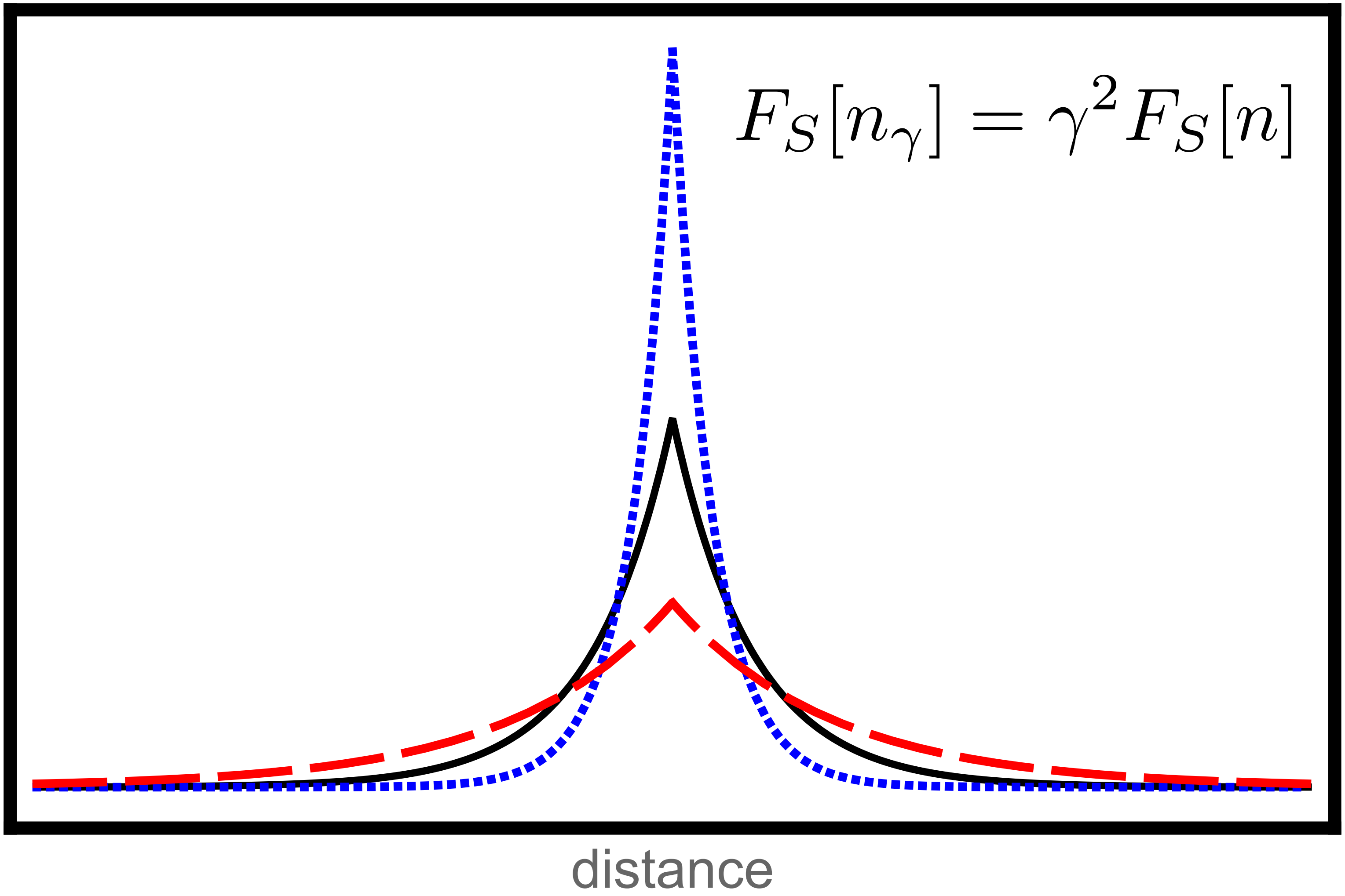
$$A_{\mathrm{xc}}^{\tau}[n] = T_{\mathrm{xc}}^{\tau}[n] - \tau S_{\mathrm{xc}}^{\tau}[n] + U_{\mathrm{xc}}^{\tau}[n]$$

Pittalis, S. et al. *Phys. Rev. Lett.,* 107: 163001 (2011).
APJ et al., “Thermal DFT in Context,” *Frontiers and Challenges in Warm Dense Matter*, Springer Publishing (2014), p 25-60.

Kinetic Exchange?

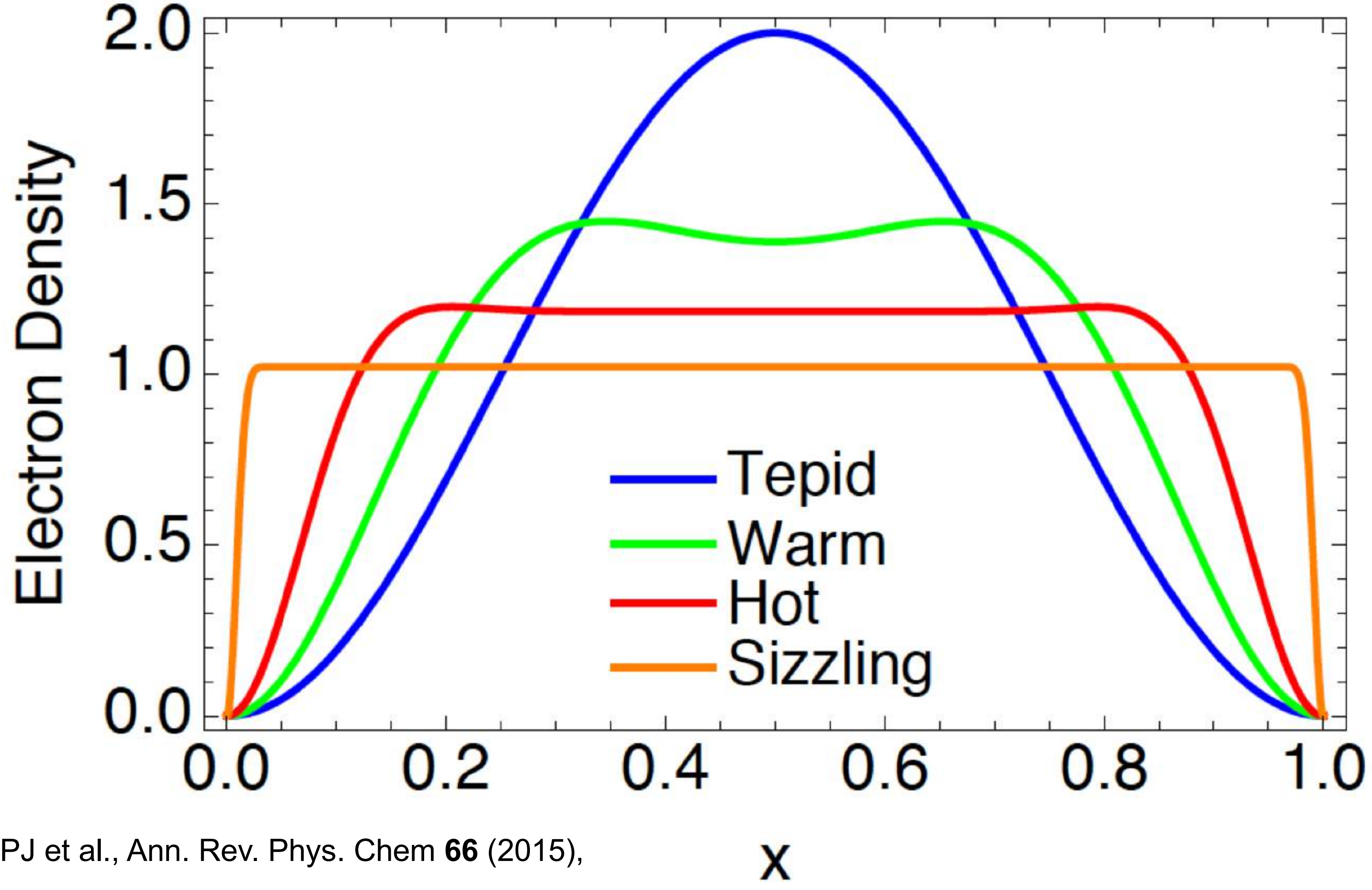


Coordinate Scaling...



…Tied to Temperature Scaling…

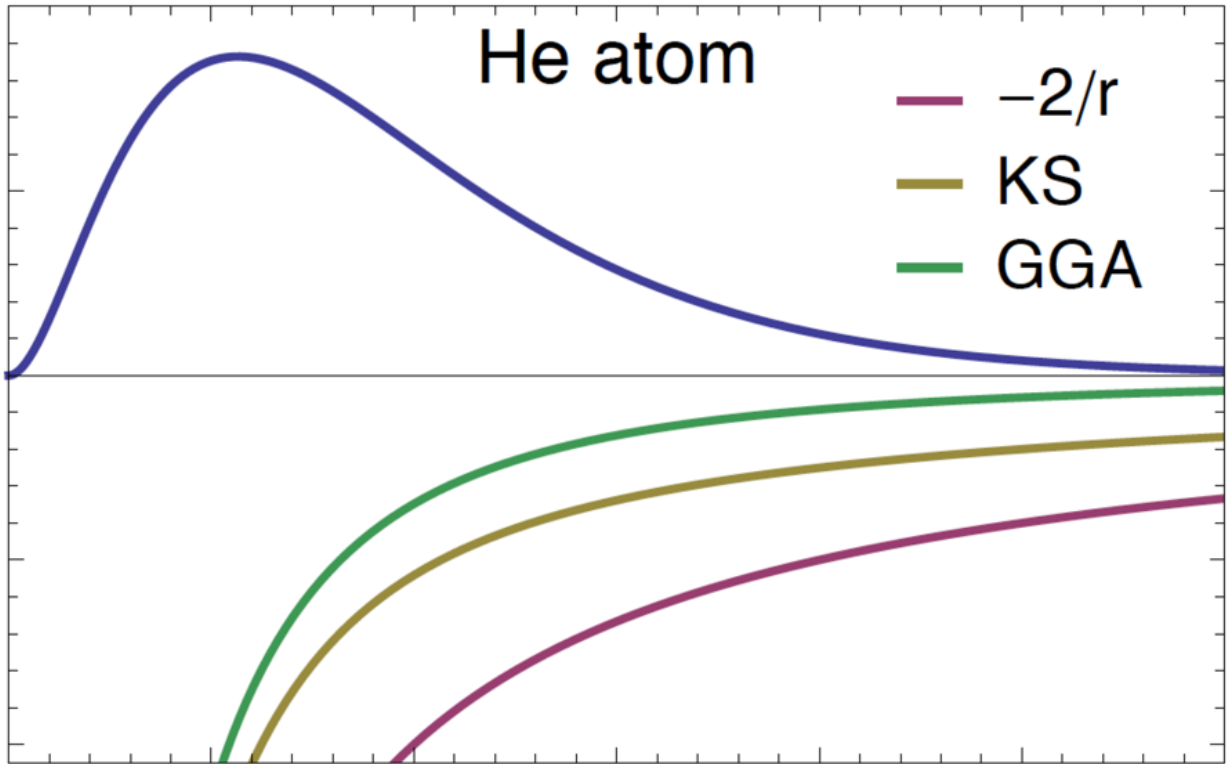
$$F_S^{\tau}[n_\gamma] = \gamma^2 F_S^{\tau/\gamma^2}[n]$$

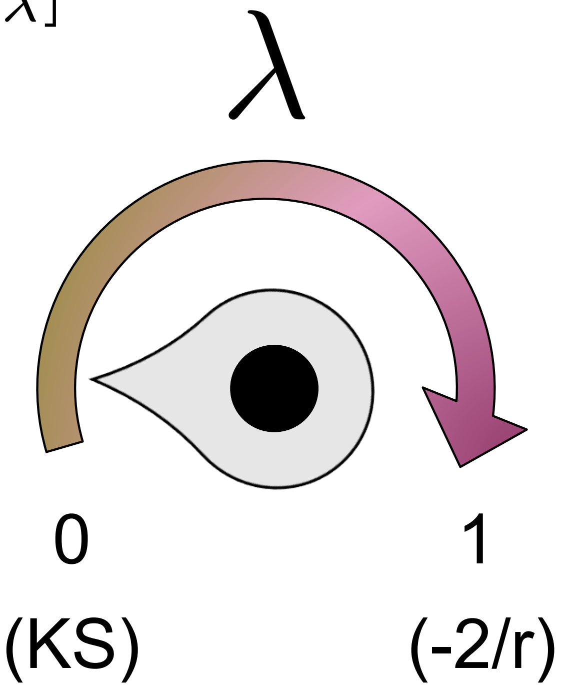


APJ et al., Ann. Rev. Phys. Chem **66** (2015),

…Tied to Interaction Scaling

$$F^{\tau,\lambda}[n] = \lambda^2 F^{\tau/\lambda^2}[n_{1/\lambda}]$$





APJ et al., Ann. Rev. Phys. Chem **66** (2015),

Your Turn

For discussion with your neighbors:

1. *Describe what happens to the density as gamma increases. Is it the same or different as what happens as temperature increases?*
2. *Can we make a high density spread out by scaling to larger or smaller temperatures?*
3. *What about interaction strength? Does it squeeze or spread density as it increases?*