Temperature and the strong-interaction limit of density functional theory

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Optimal Transport Methods in Density Functional Theory
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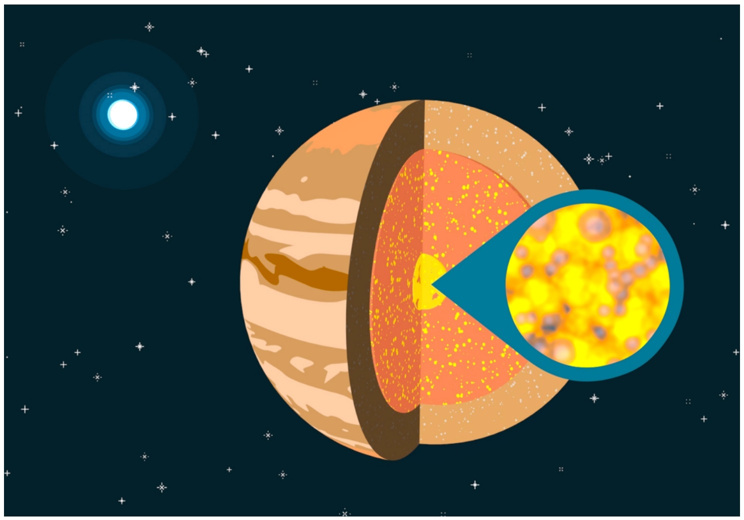
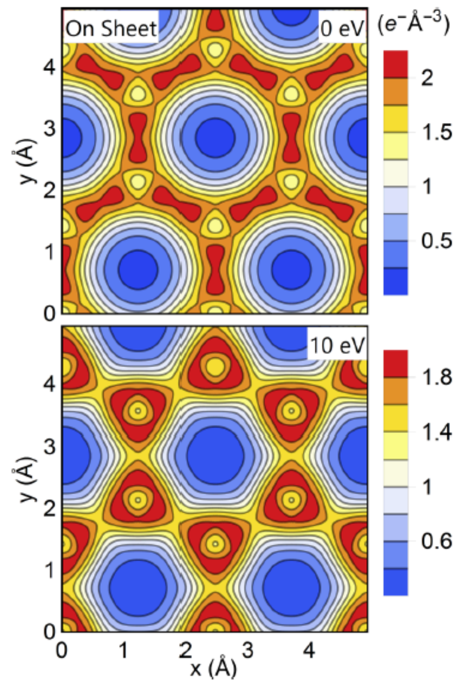
Warm Dense Matter

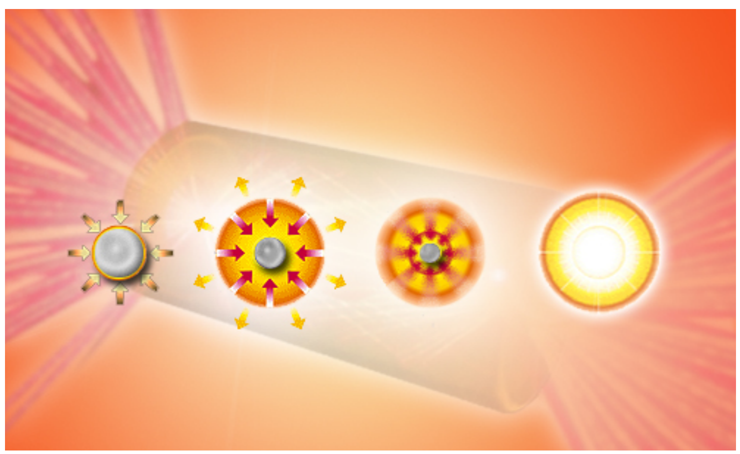


Planetary cores

Materials under extreme conditions

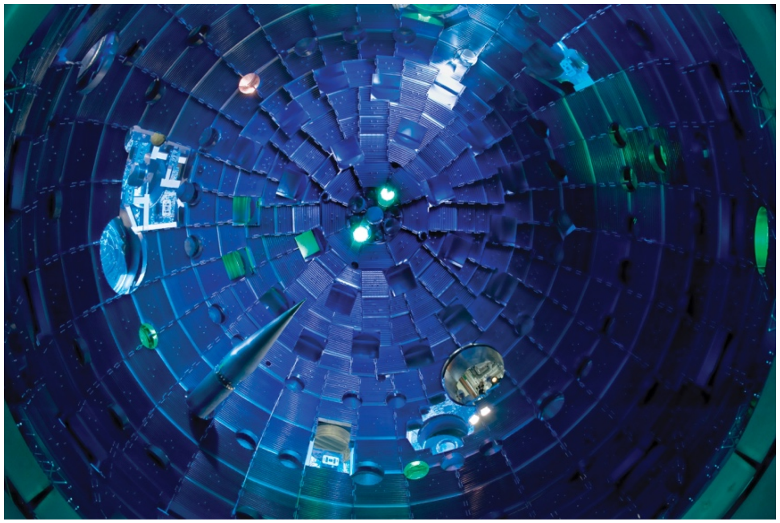


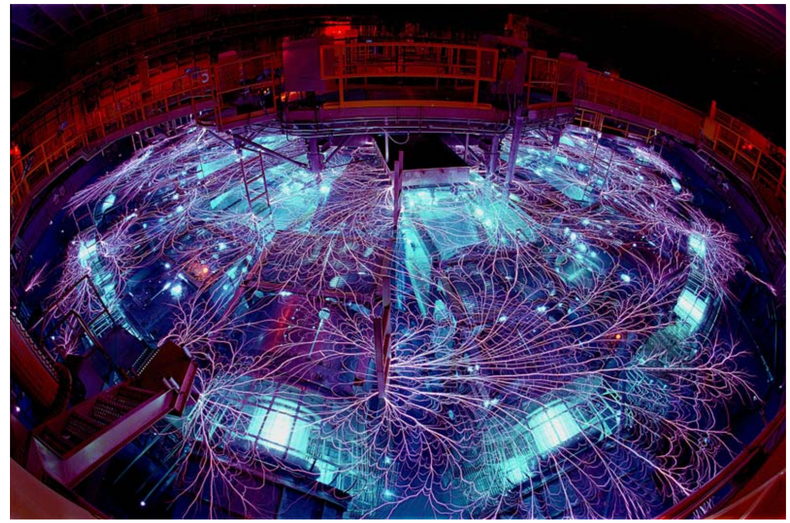
Fusion capsules



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

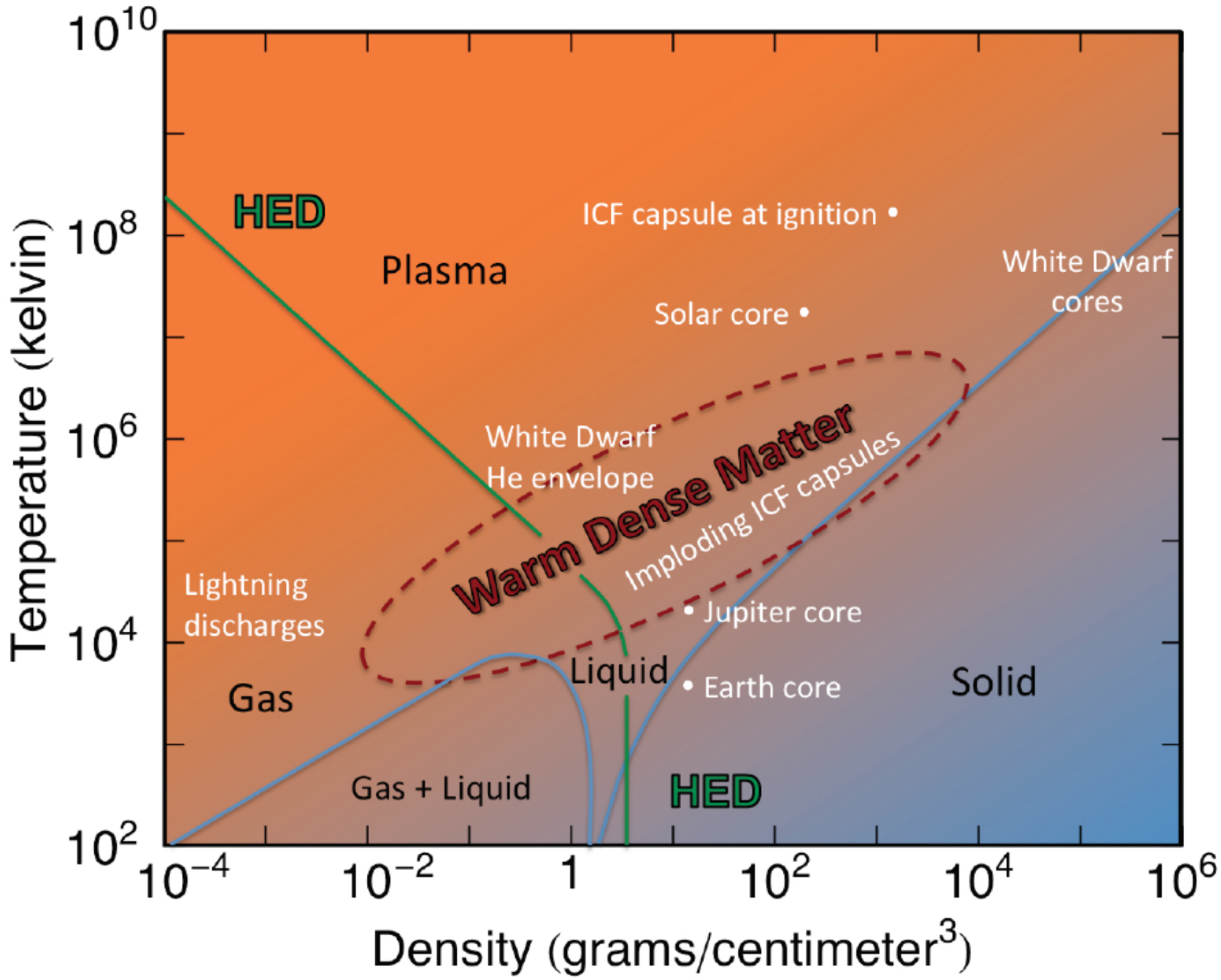
Flagship Facilities





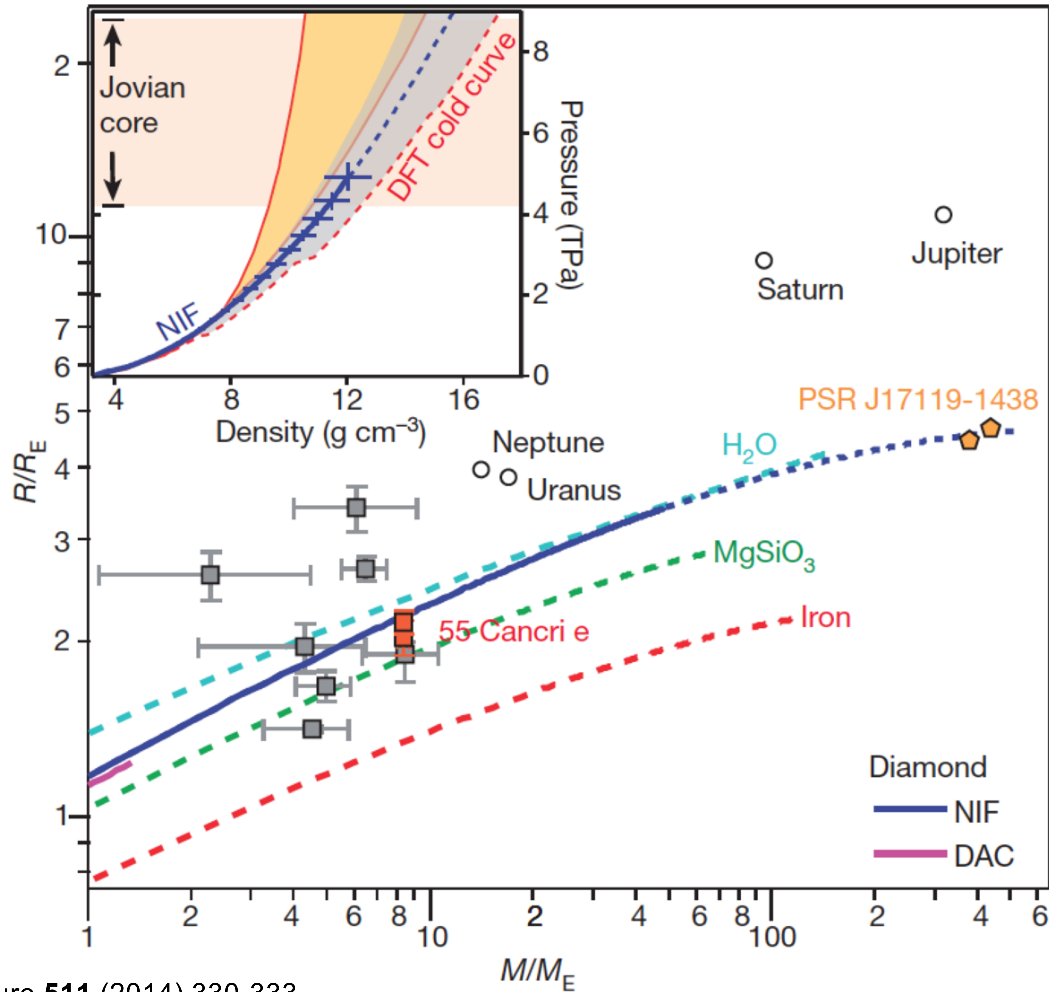
LLNL, SNL, LBL websites

The Malfunction Junction



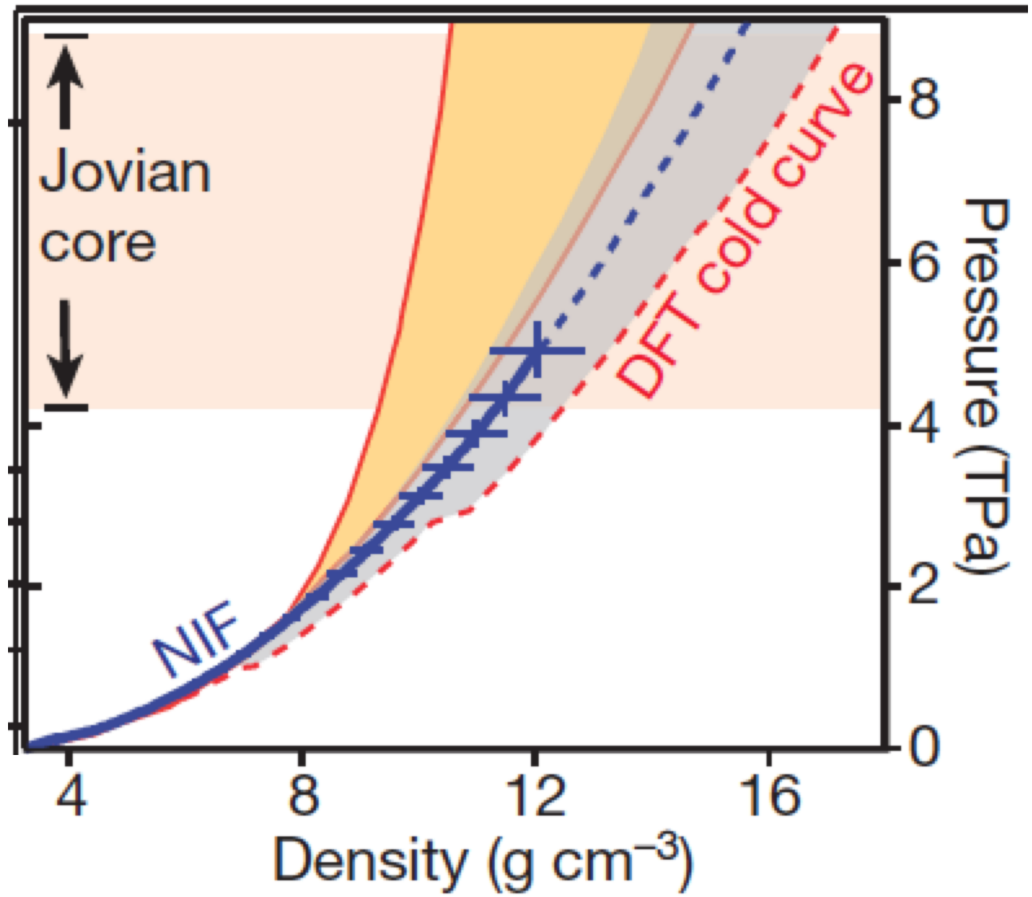
Basic Research Needs for HEDLP: Report of the Workshop on HEDLP Research, DOE (2009)

Probing Planetary Conditions



R.F. Smith et al., Nature **511** (2014) 330-333

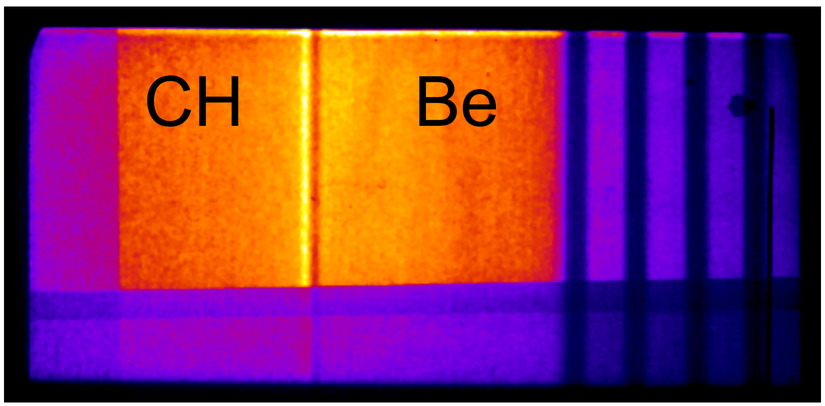
Probing Planetary Conditions



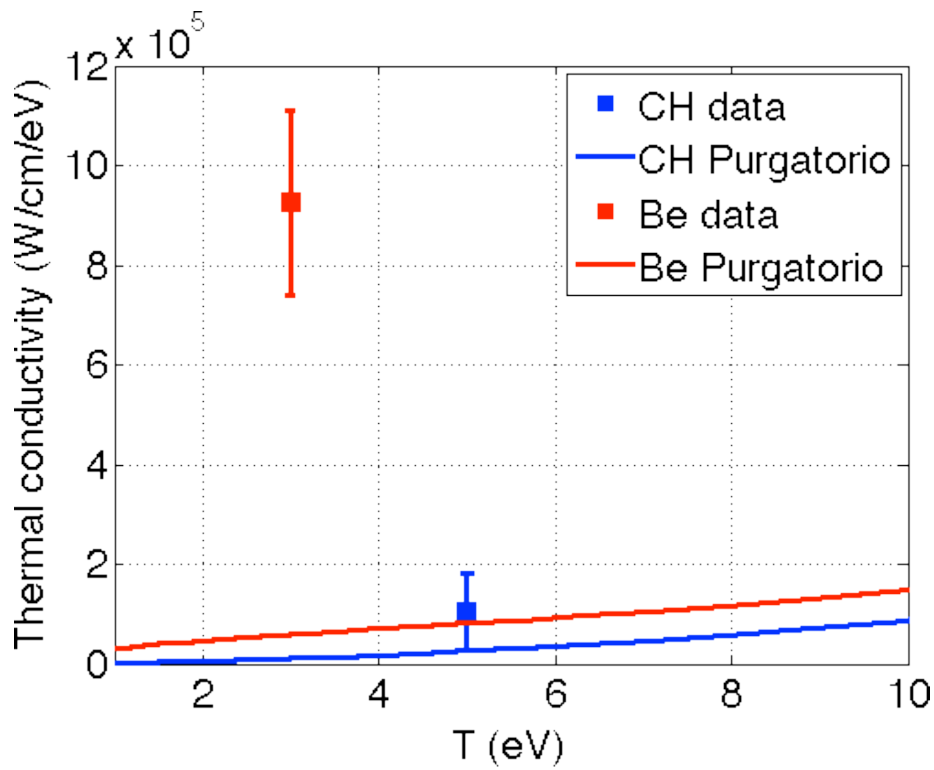
R.F. Smith et al., Nature **511** (2014) 330-333

Inaccurate Transport Properties

***Challenge:** discrepancy between theoretical and measured electronic heat conductivities.*



Yuan Ping, preliminary results (2016).



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).

Entropy and Statistics

Entropy operator:

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

Statistical operator:

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

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

Map interacting system to non-interacting system with same density.

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

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

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

Kohn and Sham, 1965.

Free Energies: Helmholtz and XC

Temperature-dependent free energy:

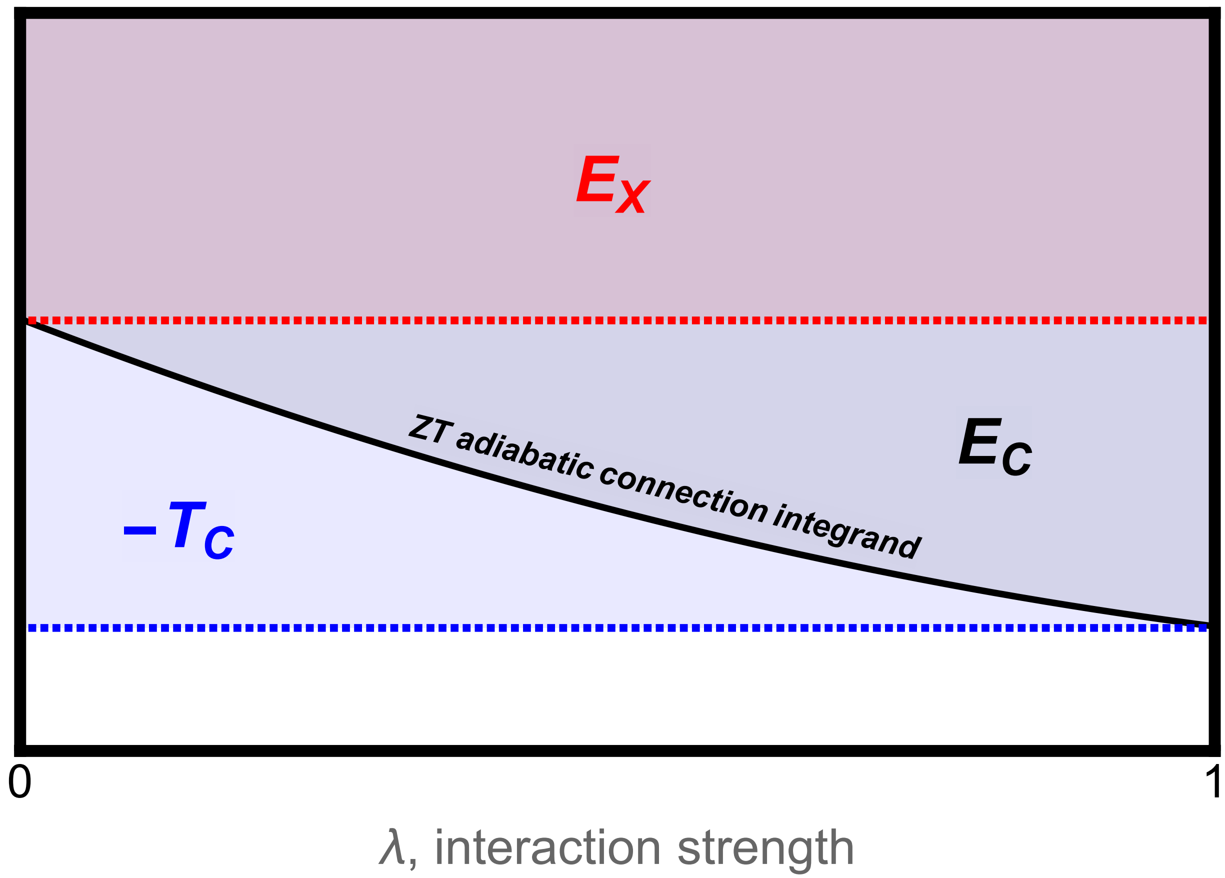
$$A^\tau[n] = T[n] + V_{\rm ee}[n] + V[n] - \tau S[n]$$
$$= T_{\rm S}[n] + U[n] + V[n] - \tau S_{\rm S}[n] + A_{\rm XC}[n]$$

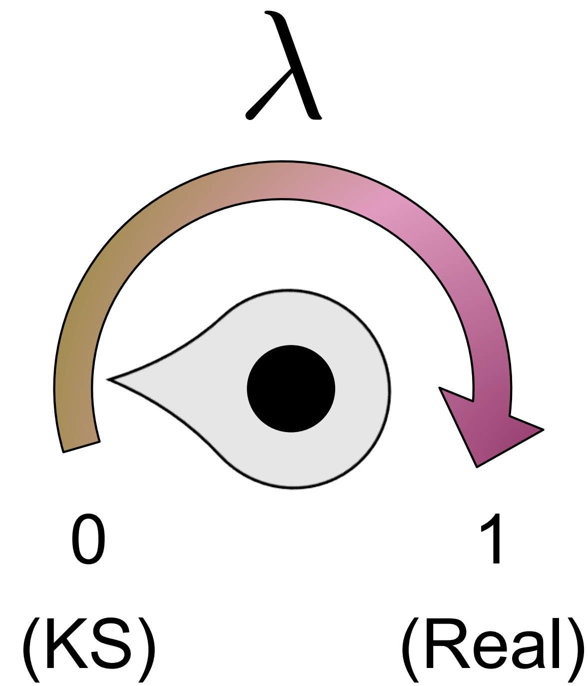
Kinetic, potential, entropic exchange-correlation:

$$A^\tau_{\rm XC}[n] = T_{\rm XC}[n] + U_{\rm XC}[n] - \tau S_{\rm XC}[n]$$

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.

Adiabatic Connection

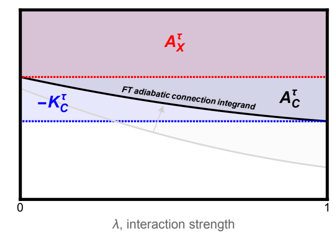




Exact Conditions for Thermal DFT

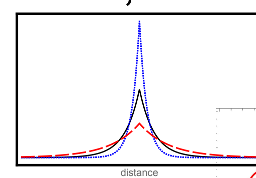
Combine finite-temperature ACF (Pittalis, et al., 2011)

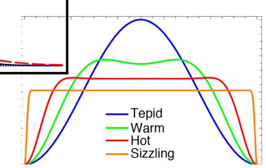
$$A_{\mathrm{C}}^{\tau}[n] = \int_0^1 \frac{d\lambda}{\lambda}\, U_{\mathrm{C}}^{\tau,\lambda}[n]$$



with coupling constant-coordinate-temperature scaling (Pittalis, et al., 2011)

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



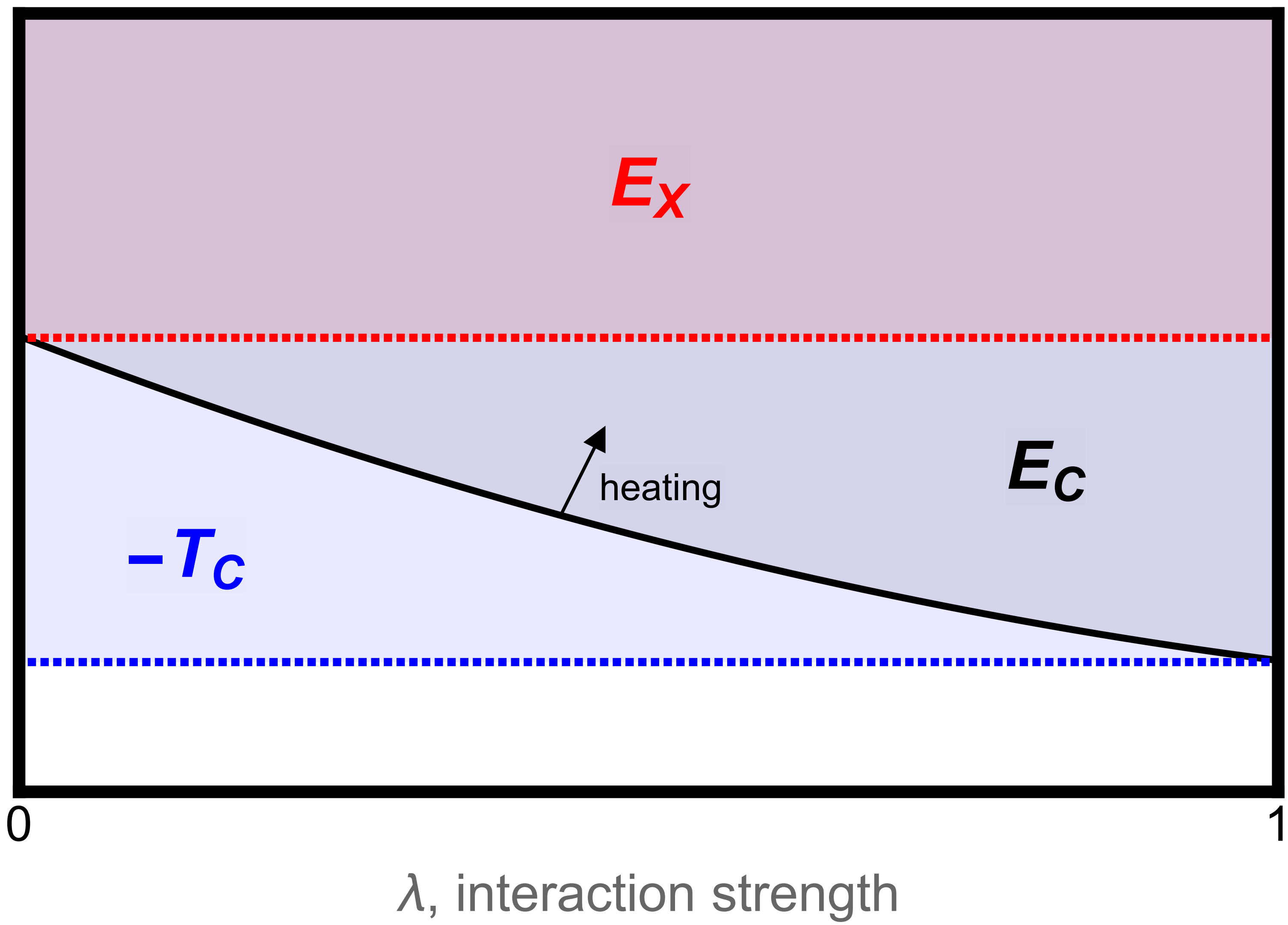


Change of variables yields thermal connection formula:

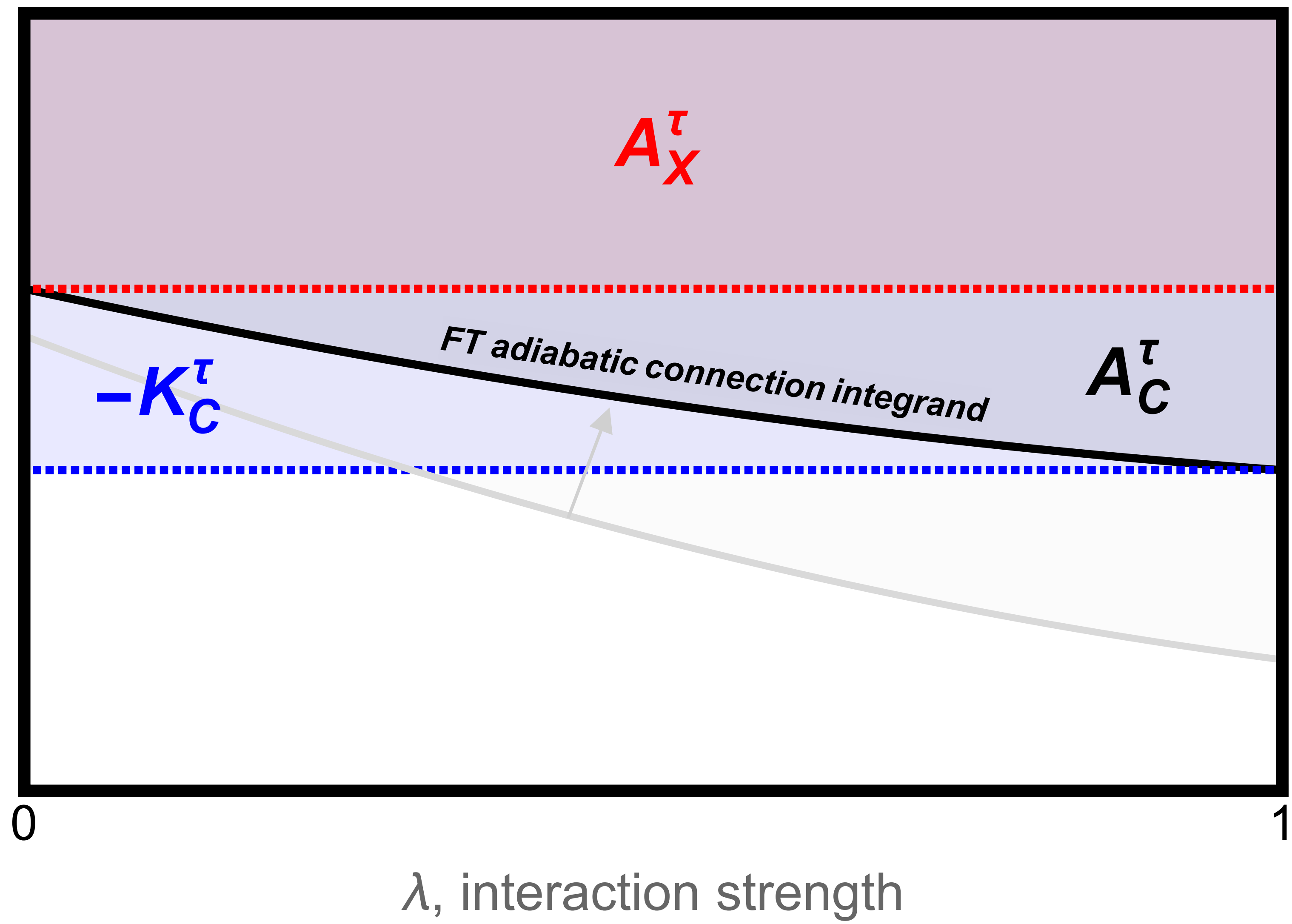
$$A_{\mathrm{XC}}^{\tau}[n] = \frac{\tau}{2} \lim_{\tau''\to\infty} \int_{\tau}^{\tau''} \frac{d\tau'}{\tau'^2}\, U_{\mathrm{XC}}^{\tau'}[n_{\sqrt{\tau'/\tau}}]$$

APJ and K. Burke, Phys. Rev. B **93**, 205140 (2016)

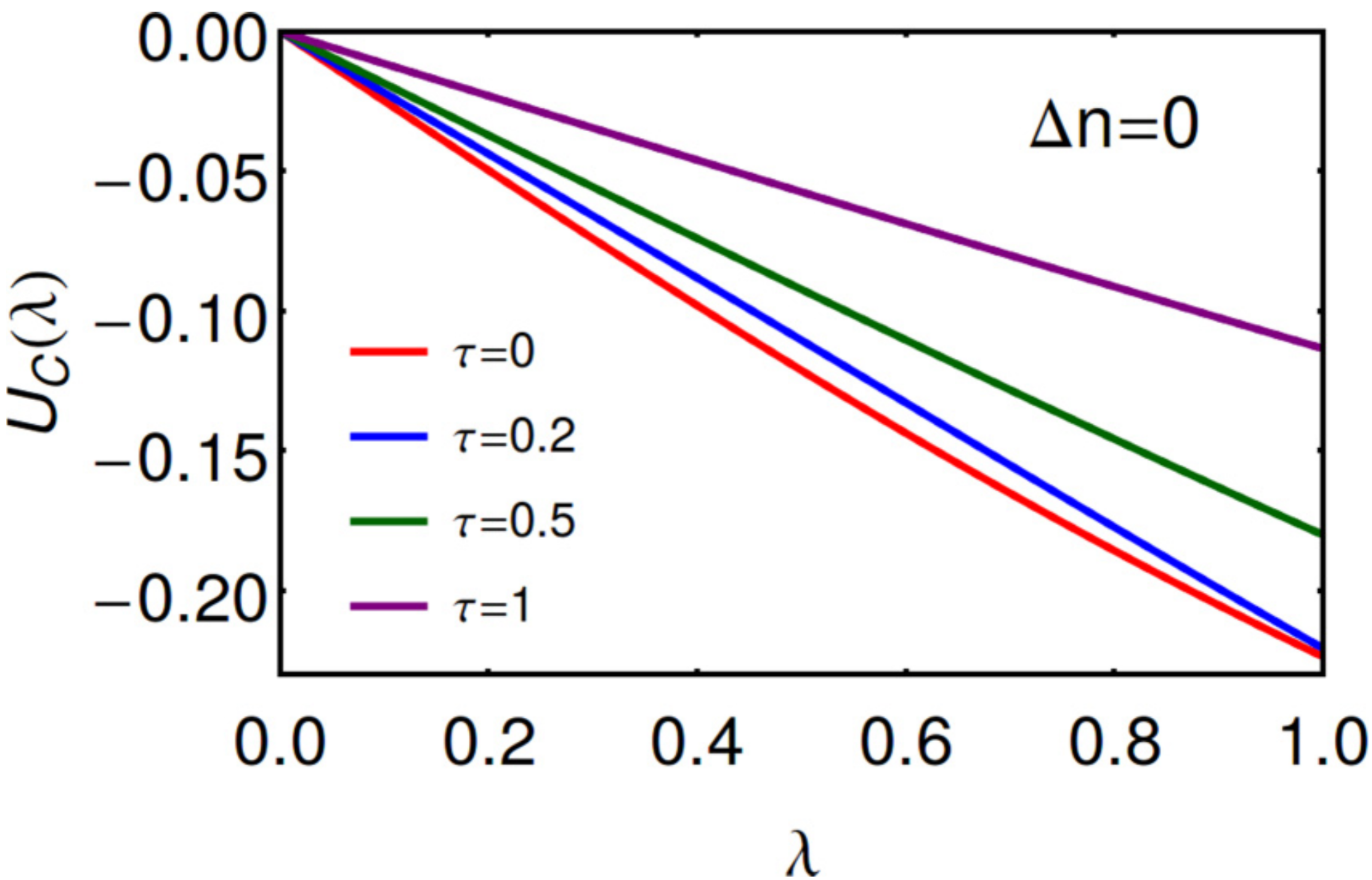
Adiabatic Connection: Heating



Adiabatic Connection: Shifted

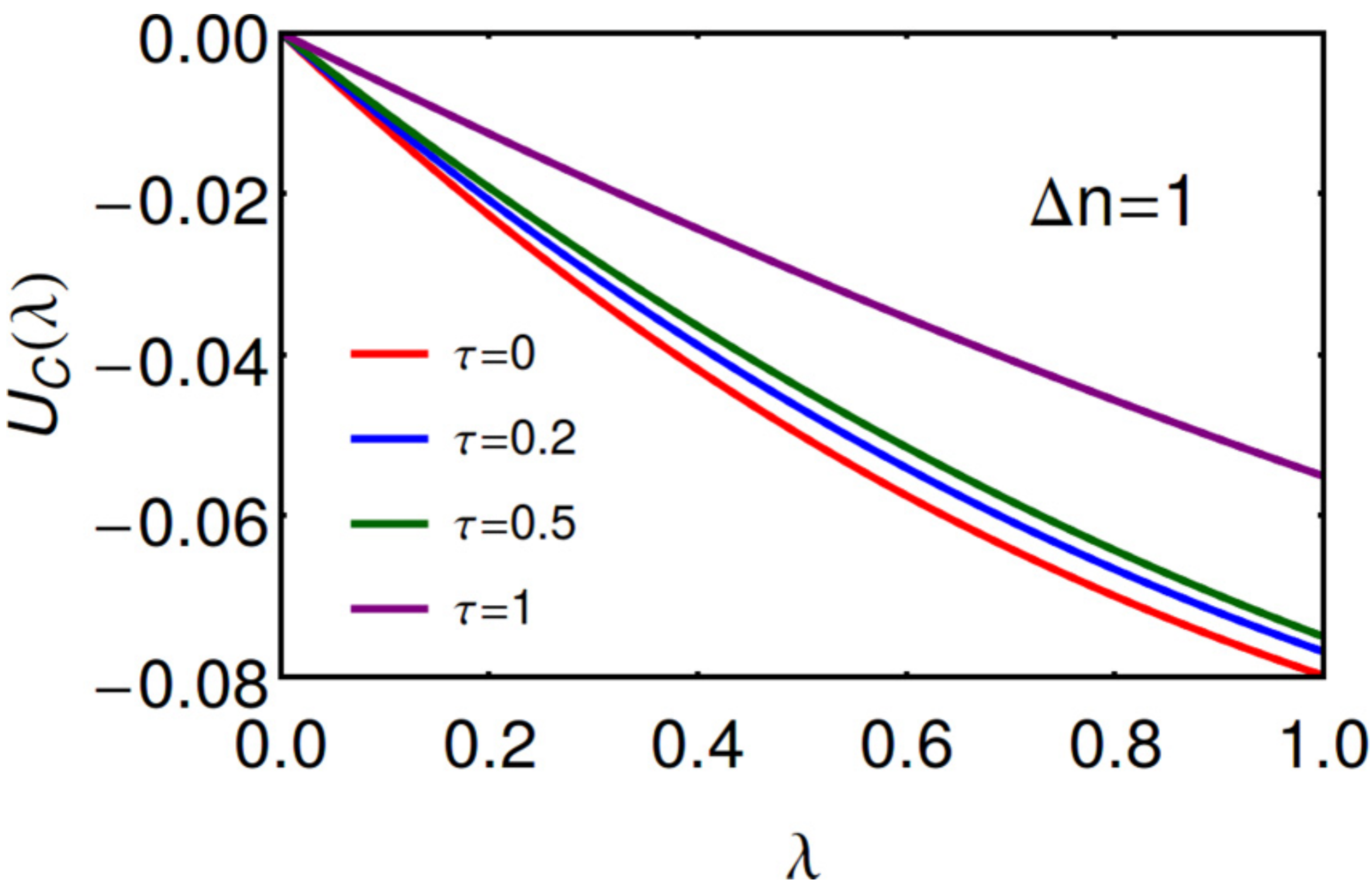


Evidence: Hubbard Dimer



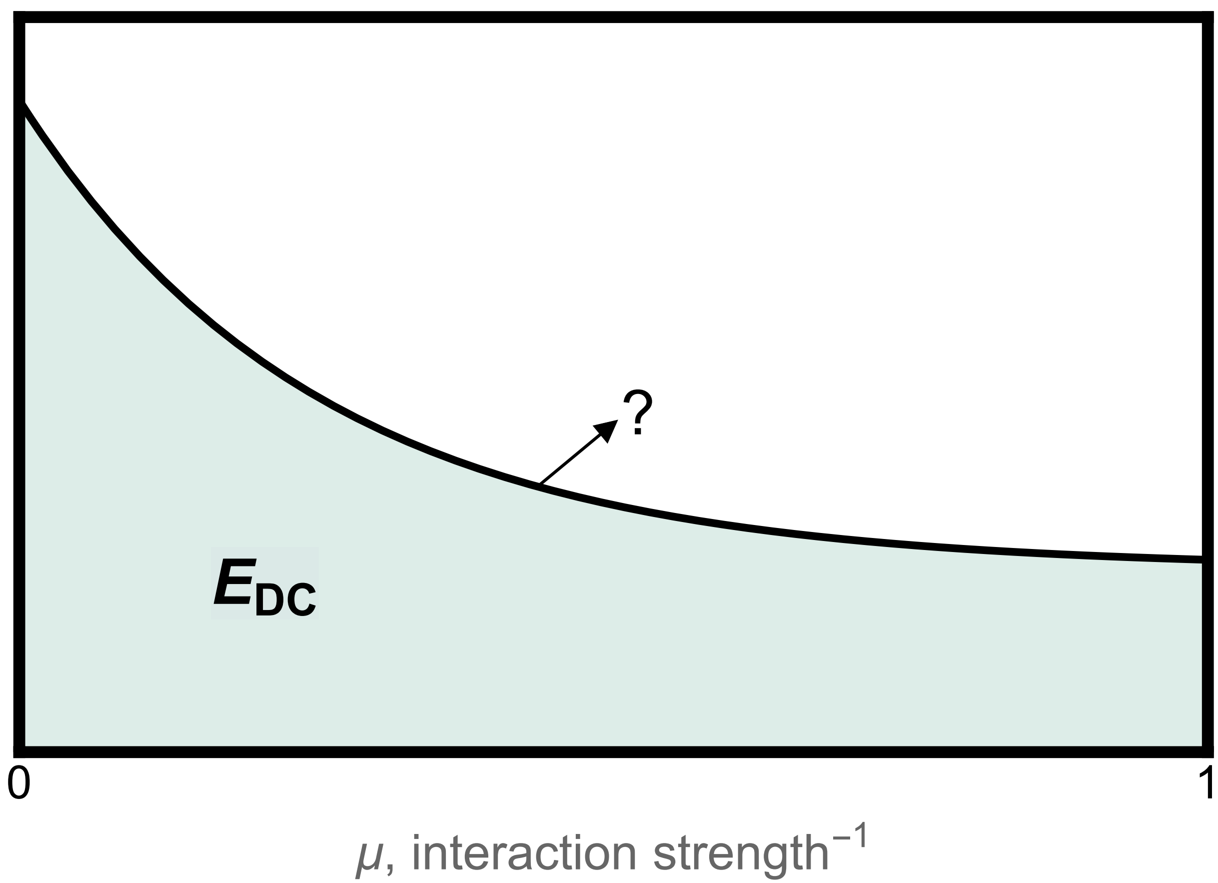
Smith, J.C., APJ, Burke, K. Phys. Rev. B, **93**, 245131 (2016).

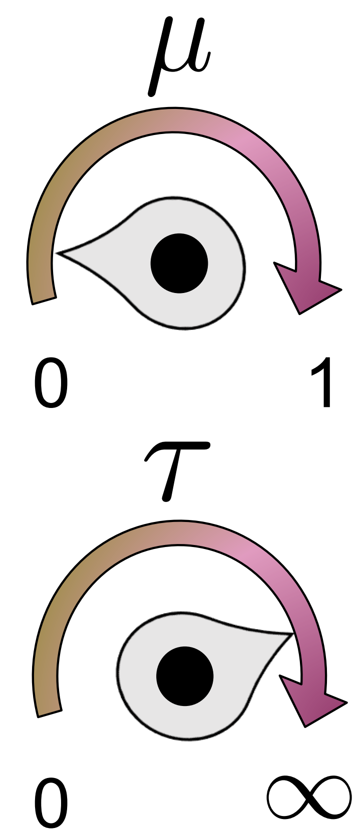
Evidence: Hubbard Dimer



Smith, J.C., APJ, Burke, K. Phys. Rev. B, **93**, 245131 (2016).

The Upside Down with heating





Reference system

Map interacting system to strictly correlated system with same density.

$$A^{\tau}[n] = U_{SC}[n] + \int d^3r \; v_{\text{ext}}(\vec{r})n(\vec{r}) + K_S^{\tau}[n] + A_{DC}^{\tau}[n]$$

where

$$\begin{aligned}
K_S^{\tau}[n] &= T_S^{\tau}[n] - \tau S_S[n] \\
U_{SC}^{\tau}[n] &= \sum_i \mathtt{w}_i^{\tau} \langle \Psi_i^{\infty} | \hat{V}_{ee} | \Psi_i^{\infty} \rangle \\
A_{DC}^{\tau}[n] &= E_{DC}^{\tau}[n] - \tau S_{DC}^{\tau}[n] \\
&= K_{DC}^{\tau}[n] + U_{DC}^{\tau}[n].
\end{aligned}$$

Upside-down thermal ACF

Traditional adiabatic connection formula at finite temperature (Pittalis, 2011):

$$A_C^\tau[n] = \int_0^1 \frac{d\lambda}{\lambda} U_C^{\tau,\lambda}[n]$$

Upside-down adiabatic connection formula at finite temperature:

$$A_{DC}^\tau[n] = \int_0^1 d\mu \; 2\mu \; K_C^{\frac{\tau}{\mu^2},\mu}[n]$$

Different integrand temperature due to quadratic kentropic scaling.

Exact Conditions for SCE

Can use tied coordinate-temperature-interaction scaling to show:

$$\mathtt{M}_{\mu}^{\frac{\tau}{\mu^2}}[n] = 2\mu\ K_C^{\frac{\tau}{\mu^2},\mu}[n]$$
$$= \frac{2}{\mu^3}\ K_C^{\mu^2\tau,\mu^3}[n_{\mu^2}]$$

Can use scaled expression to examine limits:

$$\text{As } \mu \to \infty,$$
$$\mathtt{M}_{\mu}^{\frac{\tau}{\mu^2}}[n] \to 0$$
$$\text{As } \mu \to 0,$$
$$\mathtt{M}_{\mu}^{\frac{\tau}{\mu^2}}[n] \to \text{ZT SC system}$$

Connecting SCE to KS ACF

Since we can write the correlation kentropy in terms of the ACF integrand,

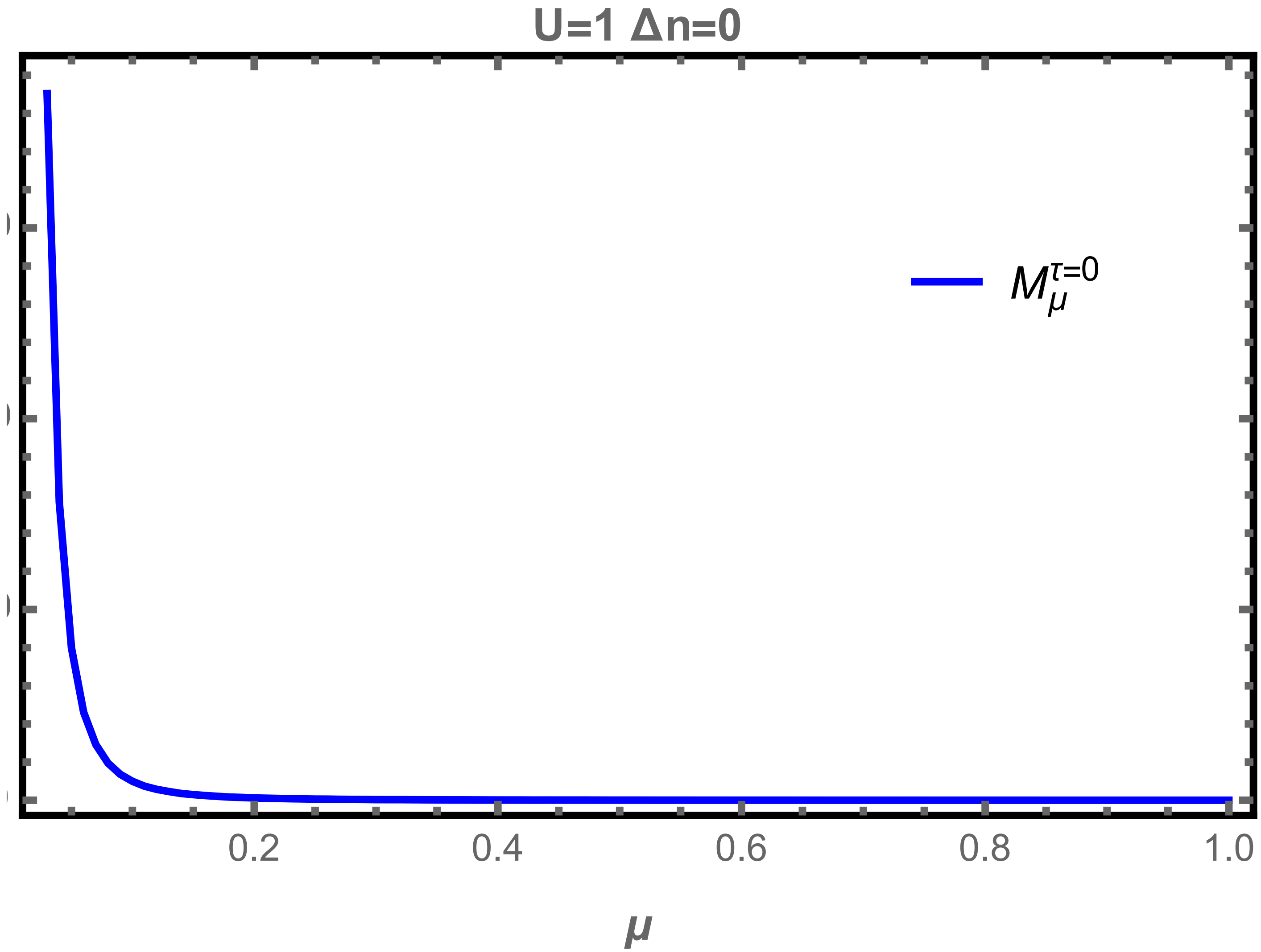
$$K_c^{\tau,\mu}[n] = \int_0^{1/\mu^2} W_\lambda^\tau[n] d\lambda - \frac{1}{\mu^2} W_{1/\mu^2}^\tau[n]$$

we can also write the upside-down ACF integrand in terms of original:

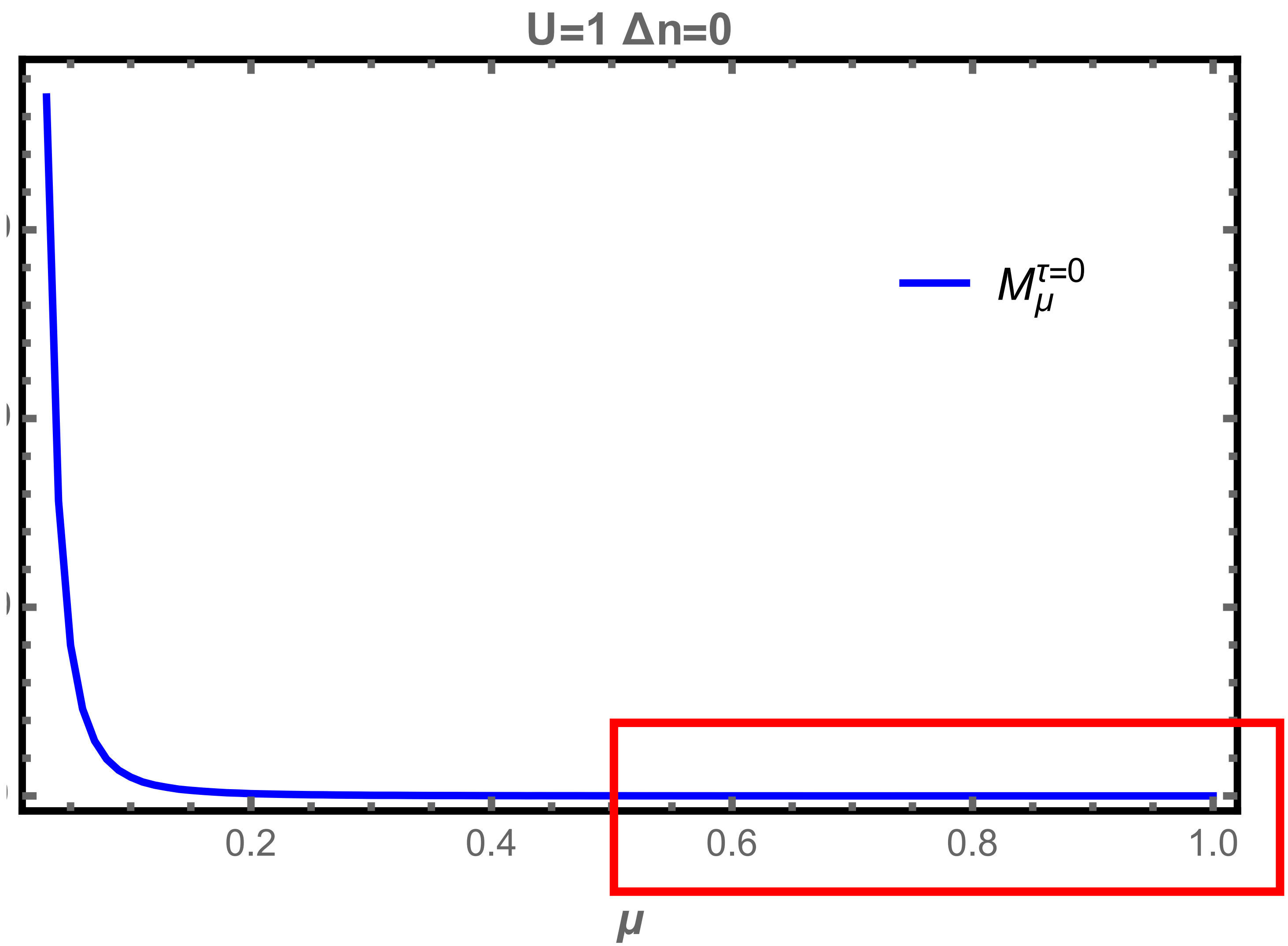
$$M_\mu^\tau[n] = 2\mu \int_0^{1/\mu^2} W_\lambda^\tau[n] - W_{1/\mu^2}^\tau[n] \; d\lambda$$

Now we can use Hubbard adiabatic connection (or any other exact or approximate one) to plot upside-down connection.

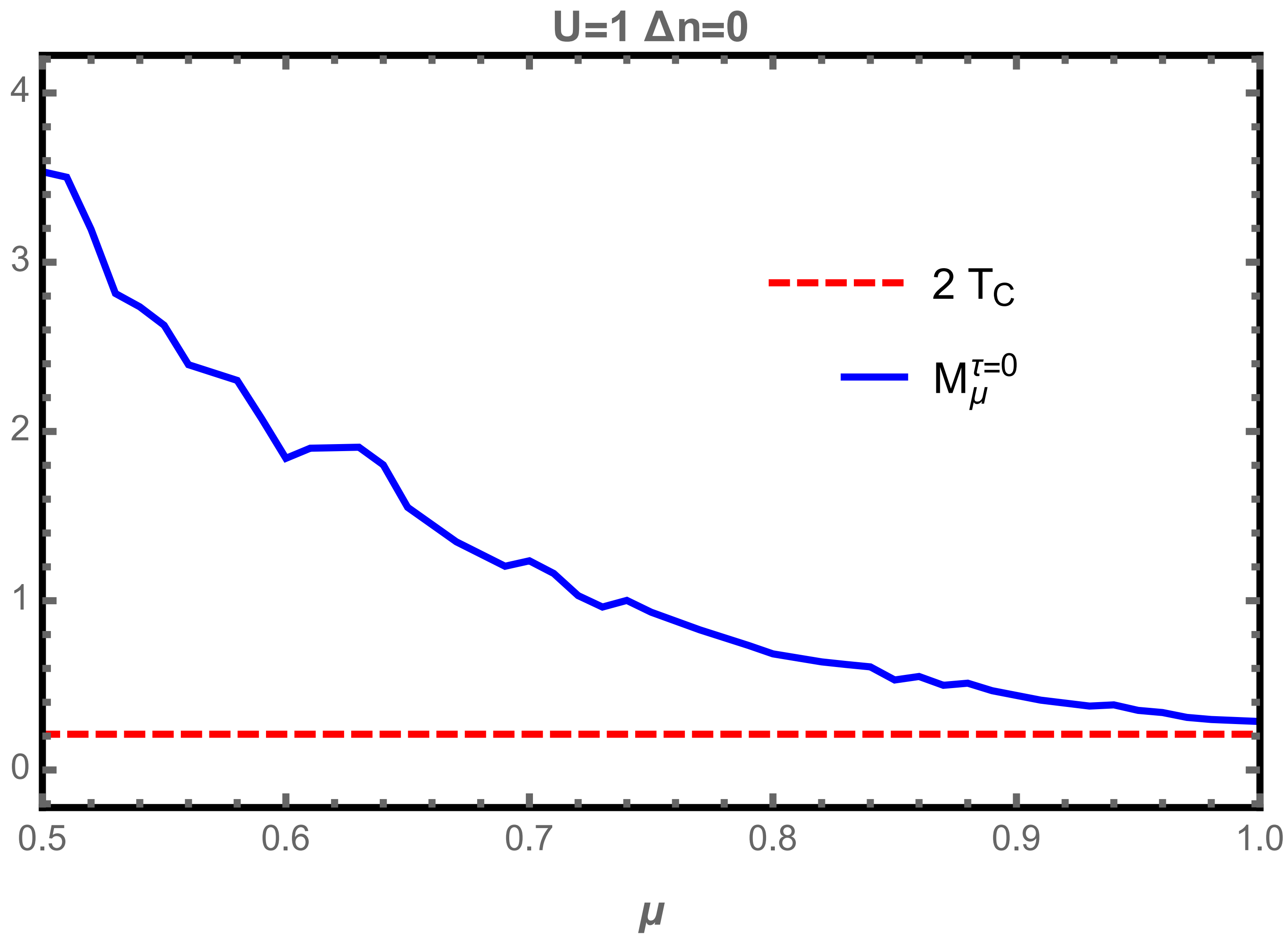
Odd Preliminary Results, check ZT



Preliminary Results



Something's off… zoom in



Future Work & Open Questions

- Numerical demonstrations: asymmetric Hubbard model, various uniform electron gas parametrizations, more exact conditions

- Zero-point oscillations with temperature effects: what is the effect of quadratic temperature scaling, kentropy expansion

- Interpolated approach for WDM? Helpful with WDM ionization processes? Should we interpolate between low-temperature/strong-interaction and high-temperature/weak-interaction regimes? Or another scheme?

- FT KS SCE: SCE as functional for FT KS DFT
  - What is the effect of choice of Hartree definition?
  - Will FT be more or less accurate for intermediate interaction strengths/densities?
  - Will ZTA be more accurate for FT KS SCE than MKS?

Acknowledgments

Collaborators and Students

Liam Stanton (SJSU), Brittany Harding (UCM), Zachary Mauri (UCM), Justin Smith (US Census), Kieron Burke (UCI)

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1. **Thermal DFT:** collaborations with national laboratories and academic partners, professional development through CfHEDS
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3. **Nonlinear Conductivities of WDM**: collaboration with Alfredo Correa and Xavier Andrade (LLNL)

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