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Electron-Ion Energy Transfer and Time-Dependent Density Functional Theory – Successes and Failures

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What Do I Mean By Time-Dependent Density Functional Theory (TDDFT)?

- **Integrate time-dependent Kohn-Sham equation**

$$i\hbar\frac{\partial\psi_i(t)}{\partial t} = H_{KS}\left(n(t), R_\alpha(t), t\right)\psi_i(t)$$

- **TDDFT density matches many-body density**

$$n(t) = \sum_{i=1}^{N}\left|\psi_i(t)\right|^2 = \left\langle\Psi\right|\hat{n}(t)\left|\Psi\right\rangle$$

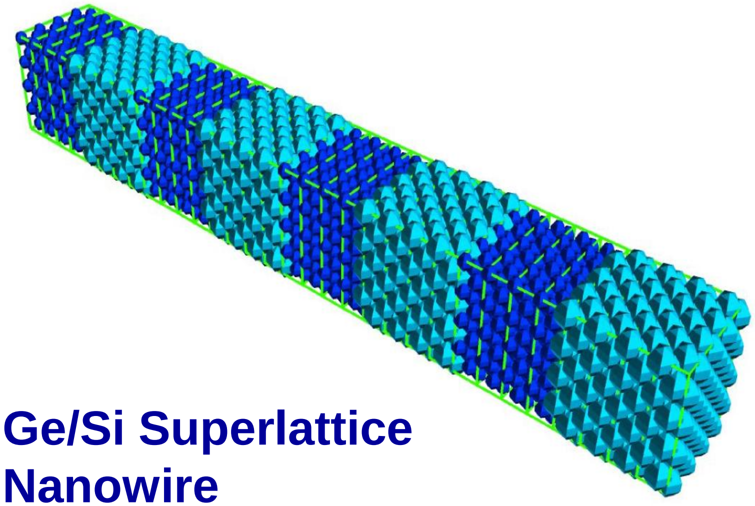
- **Integrate Newton's equations for ions**

$$m_\alpha\frac{\partial^2 R_\alpha(t)}{\partial t^2} = F\left(\psi_i(t), R_\alpha(t), t\right)$$

Application A: Electronic Contribution to Thermal Transport

Material	Thermal Conductivity [w/K-m]			Heat Capacity [J/K-kg]			Debye T [K]	e-p coupling [W/K-m^3]
Cu	401	11.2	244	385	394	10.8	345	2.6 X 10^{17}
Si	148	120	0.02	705	888	0.0002	645	1.0 X 10^{11}

- **Both phonons and electrons contribute to thermal properties**
- **At macroscale, electron-phonon equilibrium gives aggregate thermal properties**
- **What about at nanoscale?**



Ge/Si Superlattice Nanowire

Two Temperature Model (TTM)

- **Second moment of Boltzmann equation**
- **Two temperatures: phonon θ_p and electron θ_e**
- **Two coupled, diffusive systems**

$$c_p \frac{\partial \theta_p}{\partial t} = \nabla \cdot \left(k_p \nabla \theta_p\right) - g\left(\theta_p - \theta_e\right) + r_p\left(\vec{x}, t\right)$$

$$c_e \frac{\partial \theta_e}{\partial t} = \nabla \cdot \left(k_e \nabla \theta_e\right) - g\left(\theta_e - \theta_p\right) + r_e\left(\vec{x}, t\right)$$

- **Where c is heat capacity, k is conductivity, r is a heat source, and g is electron-phonon exchange**

When Can We Assume Electron-Phonon Equilibrium?

- **The uniform solution gives a time scale**

$$\tau_{ep} = \frac{c_e c_p}{g(c_e + c_p)} \qquad \theta_e - \theta_p = (\theta_e - \theta_p)_{t=0} \exp\left(-\frac{t}{\tau_{ep}}\right)$$

- **The static solution gives a length scale**

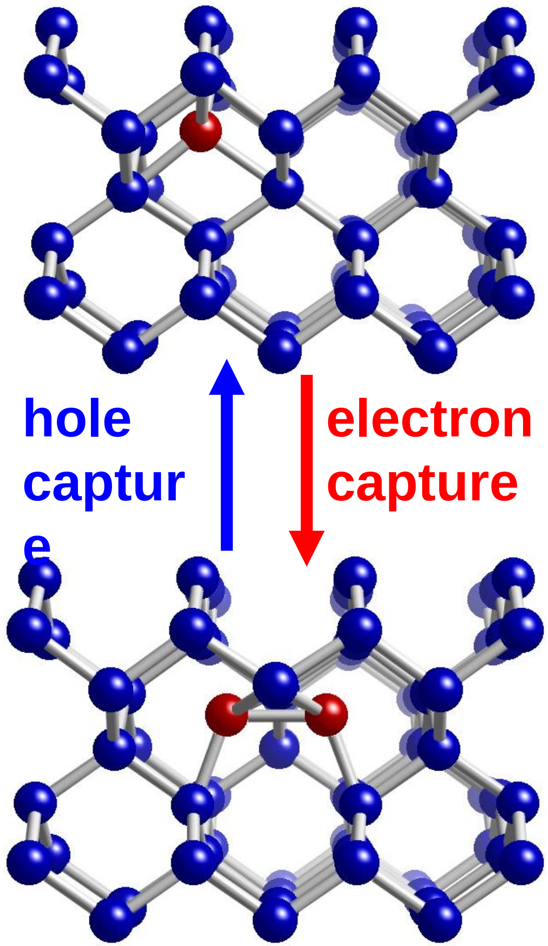
$$\lambda_{ep} = \sqrt{\frac{k_e k_p}{g(k_e + k_p)}} \qquad \theta_e - \theta_p = (\theta_e - \theta_p)_{x=0} \exp\left(-\frac{x}{\lambda_{ep}}\right)$$

Material	τ_{ep}	λ_{ep}
Cu	0.36 ps	6.41 nm
Si	5.8 ps	494 nm

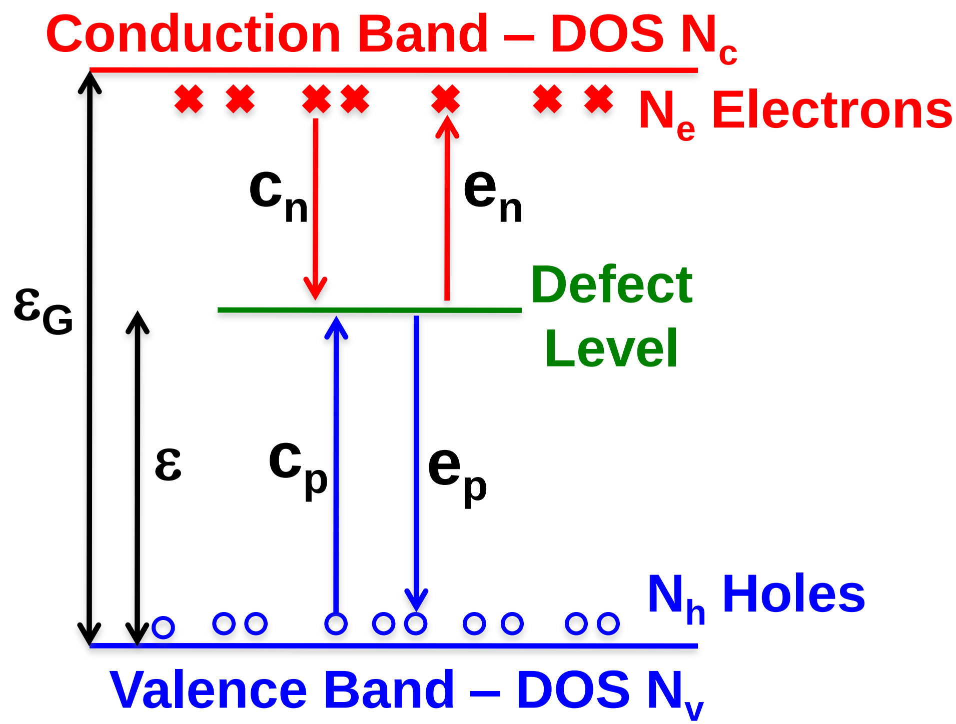
Below these time and length scales, it is not safe to assume that phonons and electrons are in equilibrium!

Application #B: Carrier Capture at Defects

+1 Si Interstitial



Neutral Si Interstitial



$$c_n = \sigma_n \langle v \rangle N_e$$

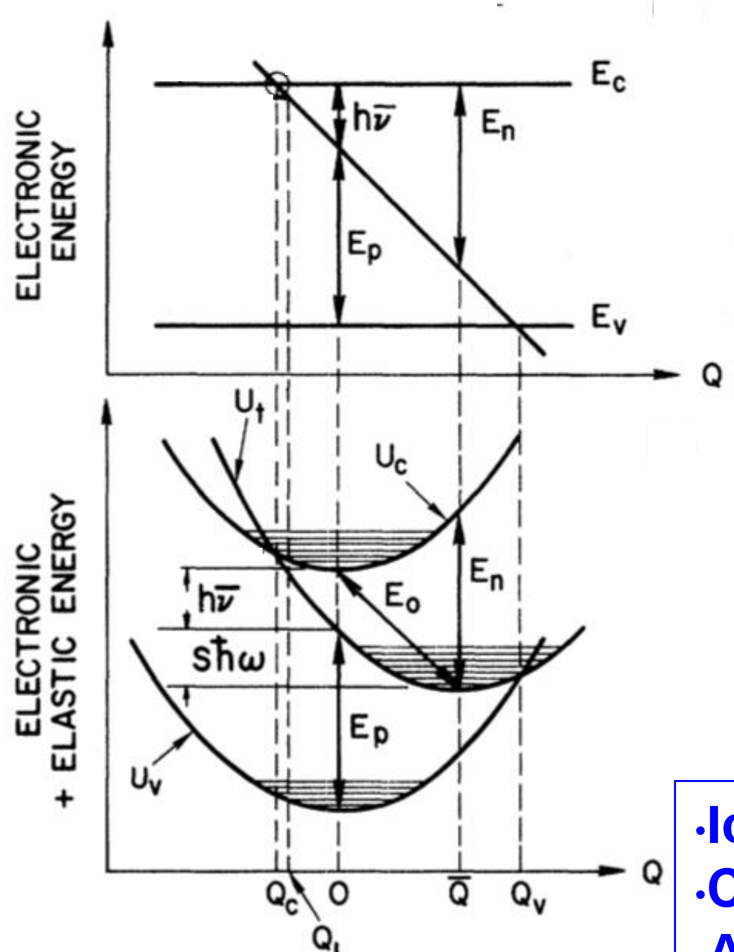
$$c_p = \sigma_p \langle v \rangle N_h$$

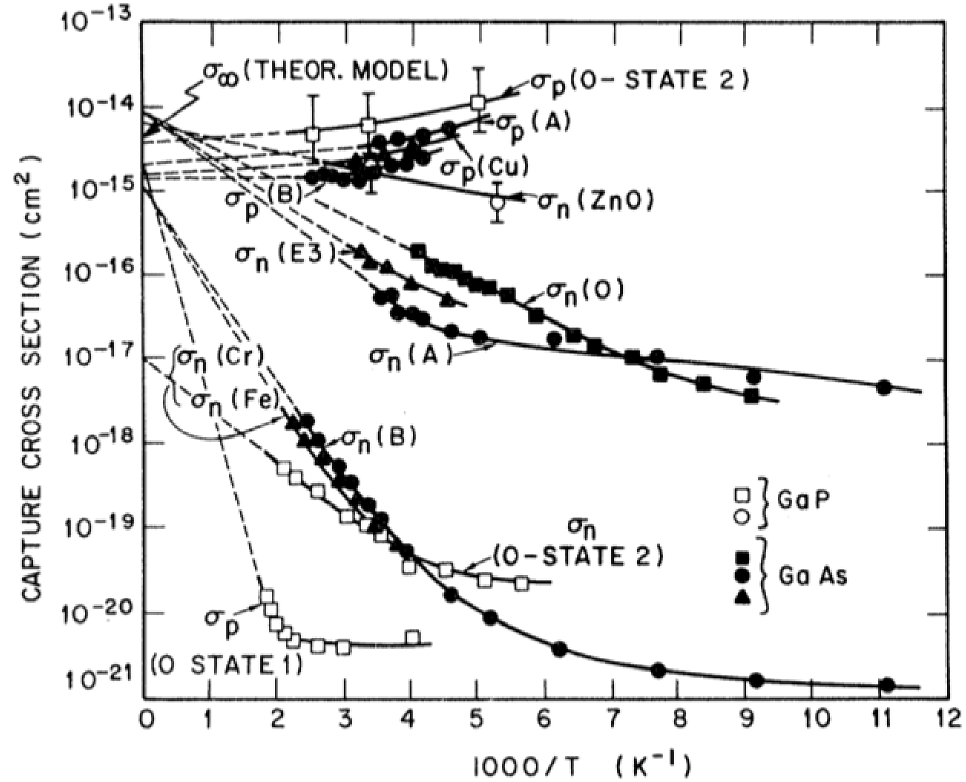
$$e_e = \sigma_e \langle v \rangle N_c \exp(-(\varepsilon_G - \varepsilon)/kT)$$

$$e_p = \sigma_p \langle v \rangle N_v \exp(-\varepsilon/kT)$$

Physics of Carrier Capture

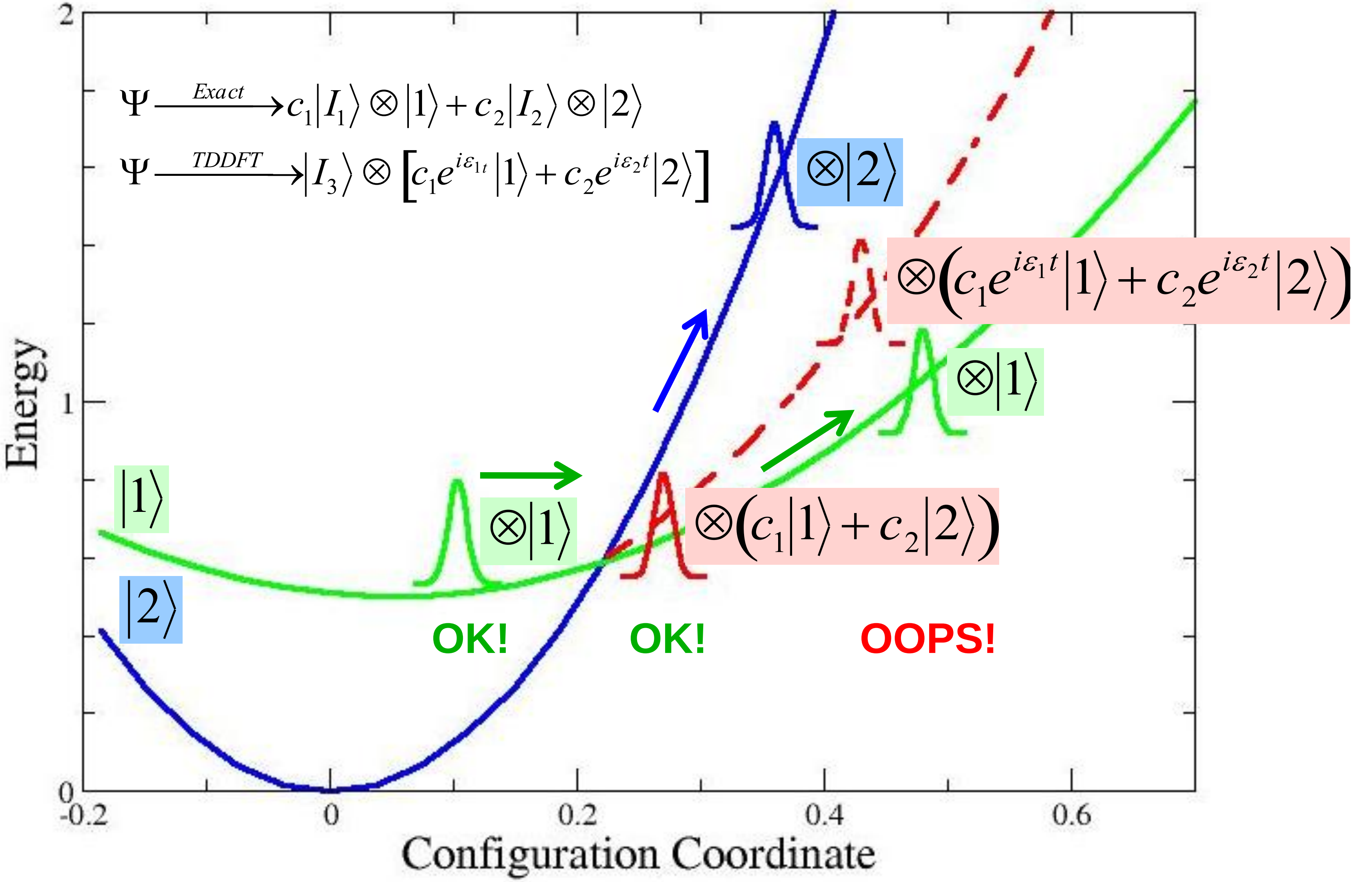
From Henry and Lang, PRB 1977



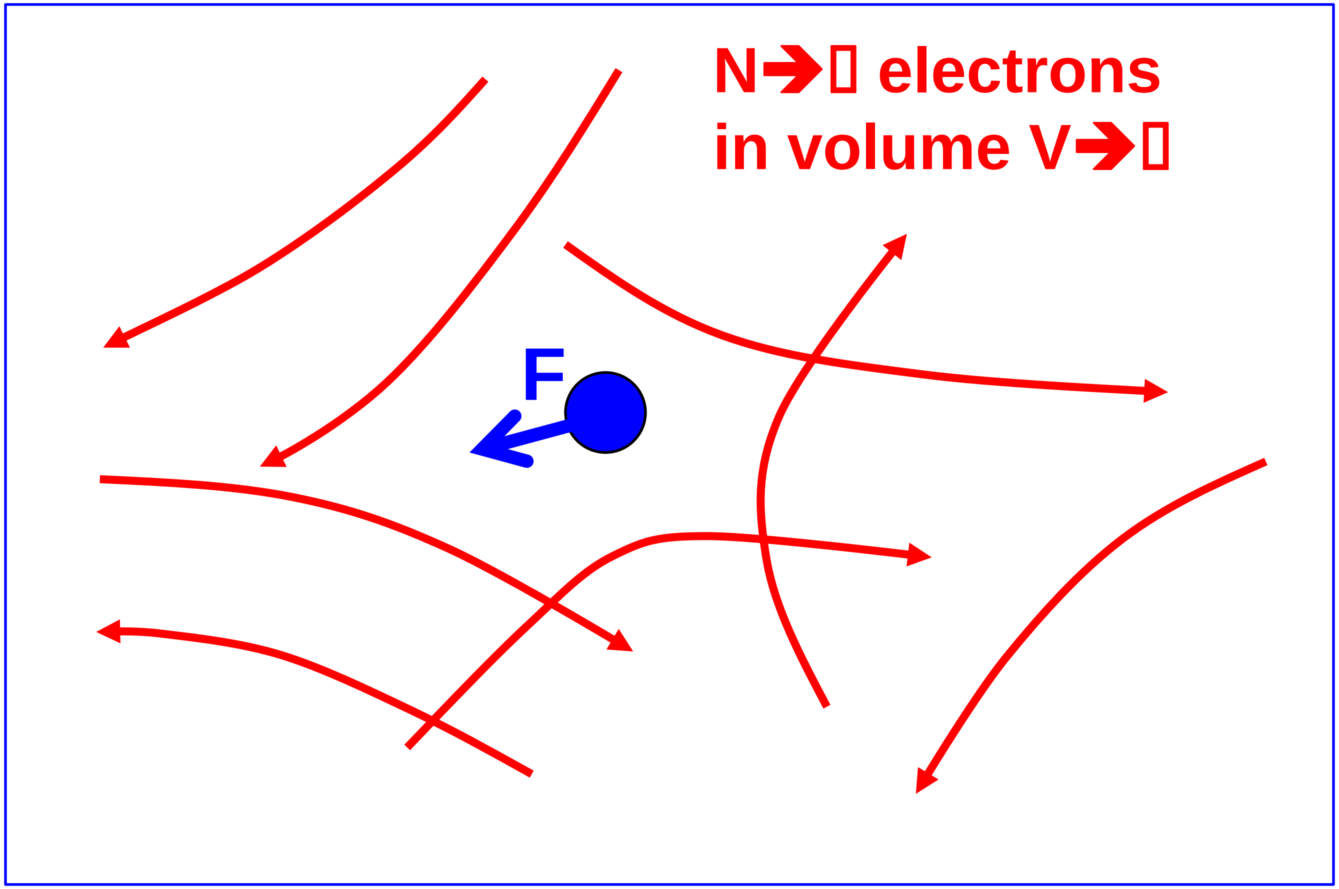


- **Ionic motion along a coordinate**
- **Capture can occur at "level crossings"**
- **Activation energy to reach crossing**

Issue #1: Electron-Ion Correlation



Is There Hope for Bulk Systems?



Effect of any given electron on the ionic force should be small, so electron-ion correlations may be small

Our Approach to "Thermodynamics" with TDDFT

- Analogous to microcanonical molecular dynamics

- Propagate electronic pure state and time average

- Given many-body eigenstates $|\Phi_\alpha\rangle$, consider

$$|\Psi\rangle = Z^{-1/2} \sum_\alpha e^{-E_\alpha/2kT} e^{i\theta_\alpha} |\Phi_\alpha\rangle$$

- State is normalized, $\langle\Psi|\hat{H}|\Psi\rangle = Tr\left(\hat{\rho}\hat{H}\right)$, and for any $\hat{A}$

$$\left\langle\langle\Psi|\hat{A}|\Psi\rangle\right\rangle_{\theta \text{ or } t} = \left\langle Z^{-1} \sum_{\alpha,\beta} e^{-\left(E_\alpha+E_\beta\right)/2kT} e^{i\left(\theta_\beta-\theta_\alpha\right)} \langle\Phi_\alpha|\hat{A}|\Phi_\beta\rangle \right\rangle_\theta$$

$$= Z^{-1} \sum_\alpha e^{-E_\alpha/kT} \langle\Phi_\alpha|\hat{A}|\Phi_\alpha\rangle = Tr\left(\hat{\rho}\hat{A}\right)$$

Some More Issues:

- **Symmetry breaking**

$$\sum_S S\left[\left|\Psi_I\right\rangle \otimes \left|\Psi_E\right\rangle\right] \quad \textbf{vs.} \quad \sum_S S\left[\left|\Psi_I\right\rangle\right] \otimes \sum_S S\left[\left|\Psi_E\right\rangle\right]$$

- **Small systems, DOS sampling, & conservation laws**

- **TDDFT gives** $n(t) = \left\langle \Psi \middle| \hat{n}(t) \middle| \Psi \right\rangle$

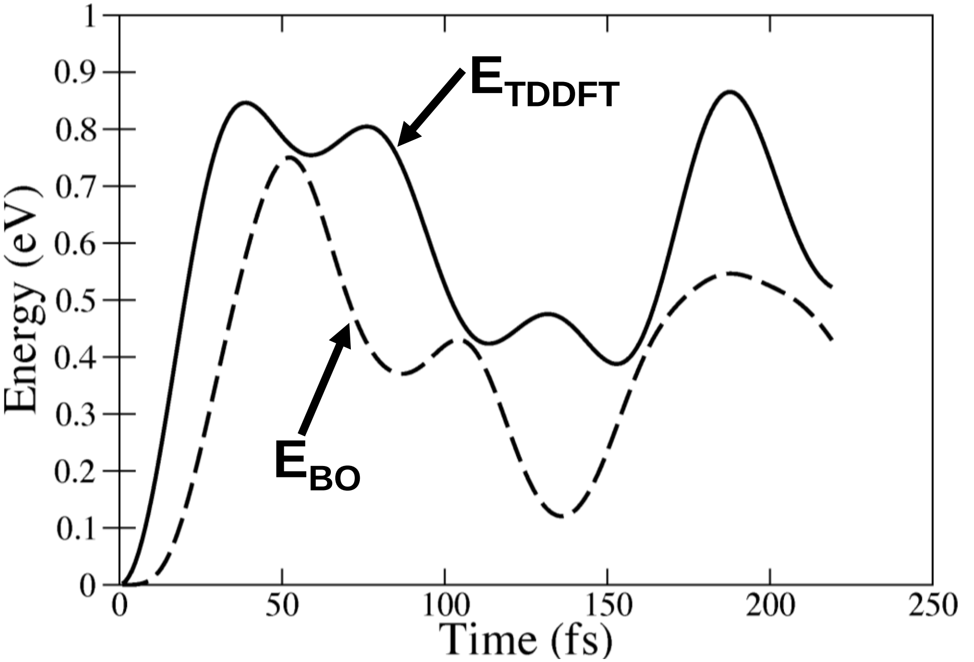
$$\left\langle \left\langle \Psi \middle| \hat{n}(0) \middle| \Psi \right\rangle \left\langle \Psi \middle| \hat{n}(t) \middle| \Psi \right\rangle \right\rangle_{\Theta} \quad \textbf{vs.} \quad \left\langle \left\langle \Psi \middle| \hat{n}(0)\hat{n}(t) \middle| \Psi \right\rangle \right\rangle_{\Theta}$$

- **How do we initialize TDDFT?**

Energy Transfer with Hot Ions and Cold Electrons

- Initially, ions in thermal motion and electrons in ground state
- TDDFT energy E_{TDDFT} rises above Born-Oppenheimer (ground state) energy E_{BO}
- $E_{TDDFT} – E_{BO}$ is instantaneous thermal energy of electrons

TDDFT Run for 32 Atoms of Al



TDDFT Calculation of Electron-Phonon Thermal Equilibration Time in Al

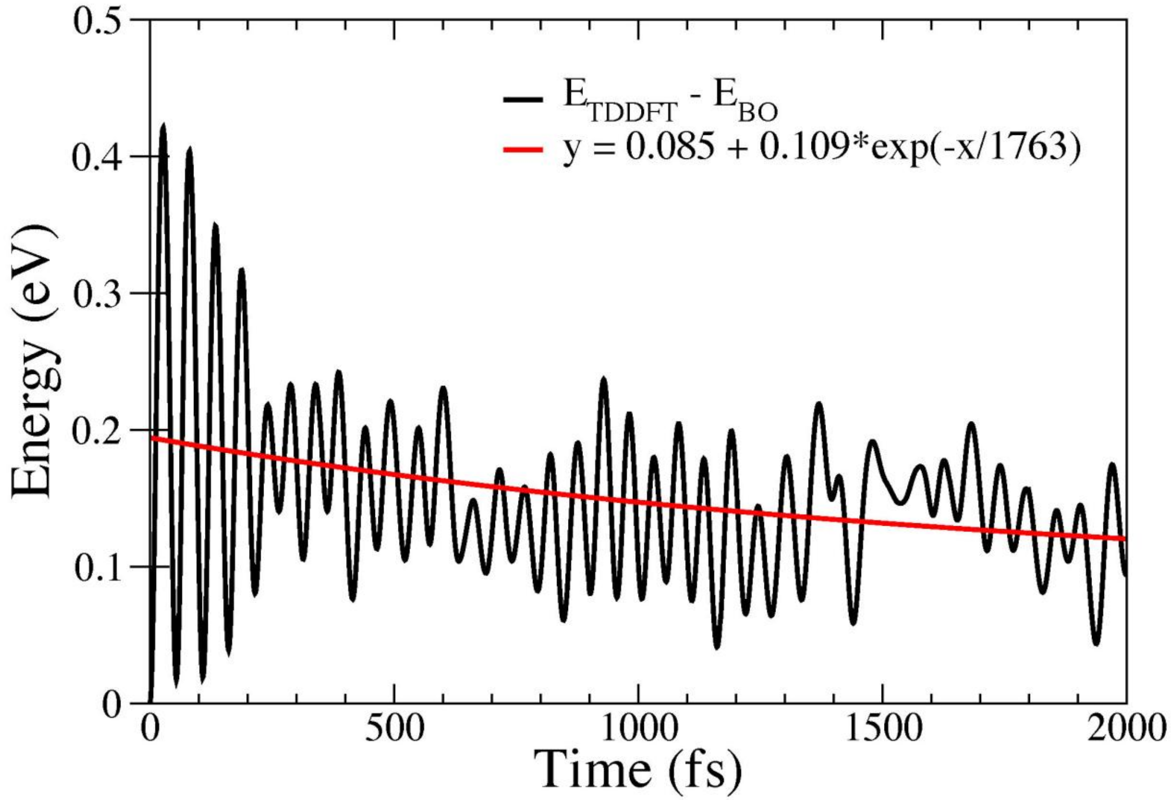
- Very rapid initial energy transfer to electrons due to impulsive initial conditions

- Then, electrons transfer energy back to ions with time constant τ_{ep}= 1.8 ps

$$\tau_{ep} = \frac{c_e c_p}{g\left(c_e + c_p\right)}$$

- Good agreement with 1.5-2.0 ps equilibration time from experiment (Kandyla, Shih, and Mazur, 2007)

Electronic Thermal Energy vs. Time



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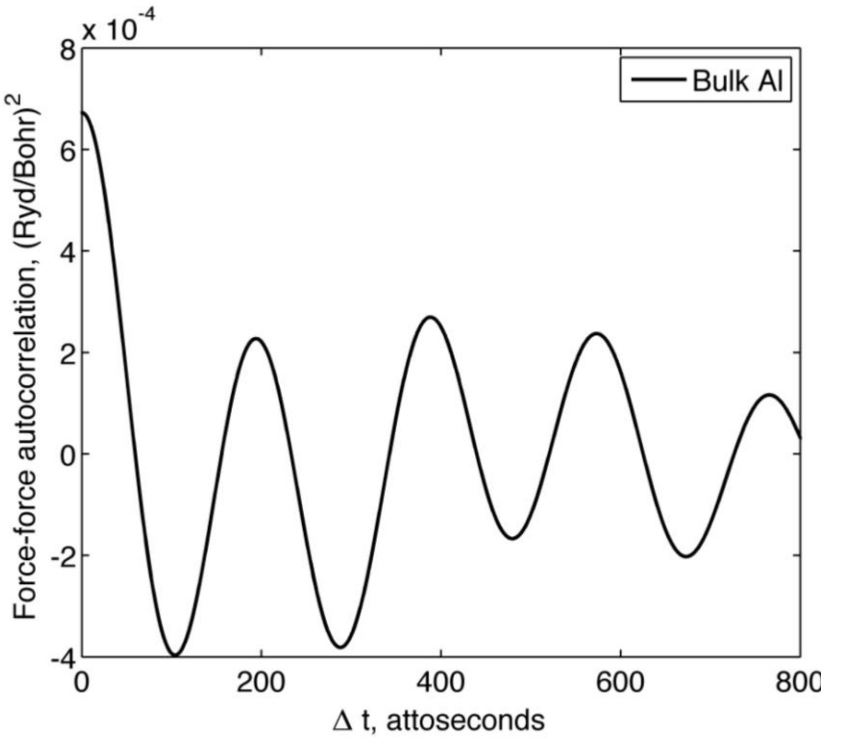
Working on TDDFT-Based Green-Kubo Approach to Improve Efficiency

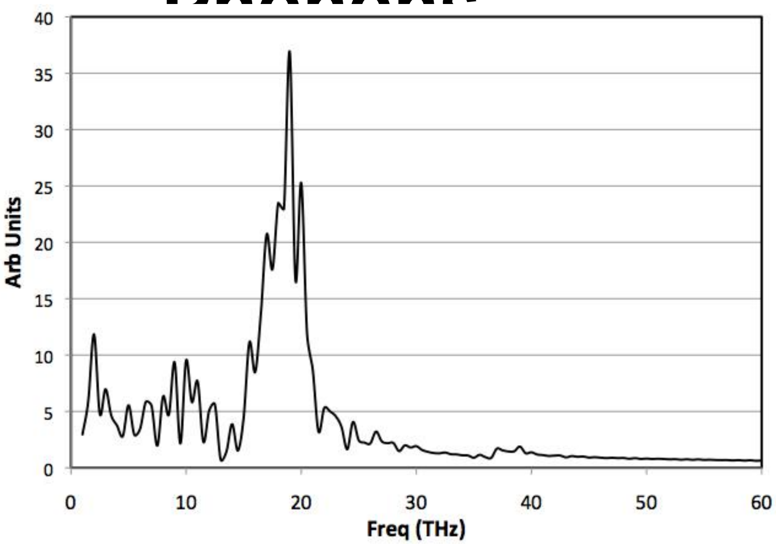
- Explicit energy flow is computationally expensive
- Green-Kubo approach gives same quantities from steady state fluctuations
- Electron-Phonon coupling obtained from fluctuations in the ionic force
- Can calculate a wide variety of quantities with same approach



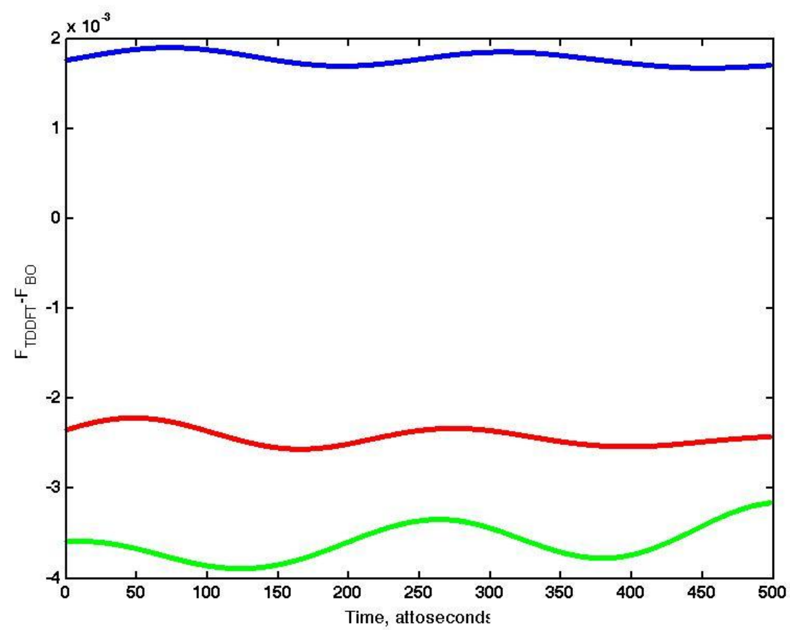
Problem: Autocorrelation functions oscillate strongly!

What are the fluctuations in TDDFT?

Low energies: Phonons



High energies: Plasmons



How do we isolate the electron-hole excitations?

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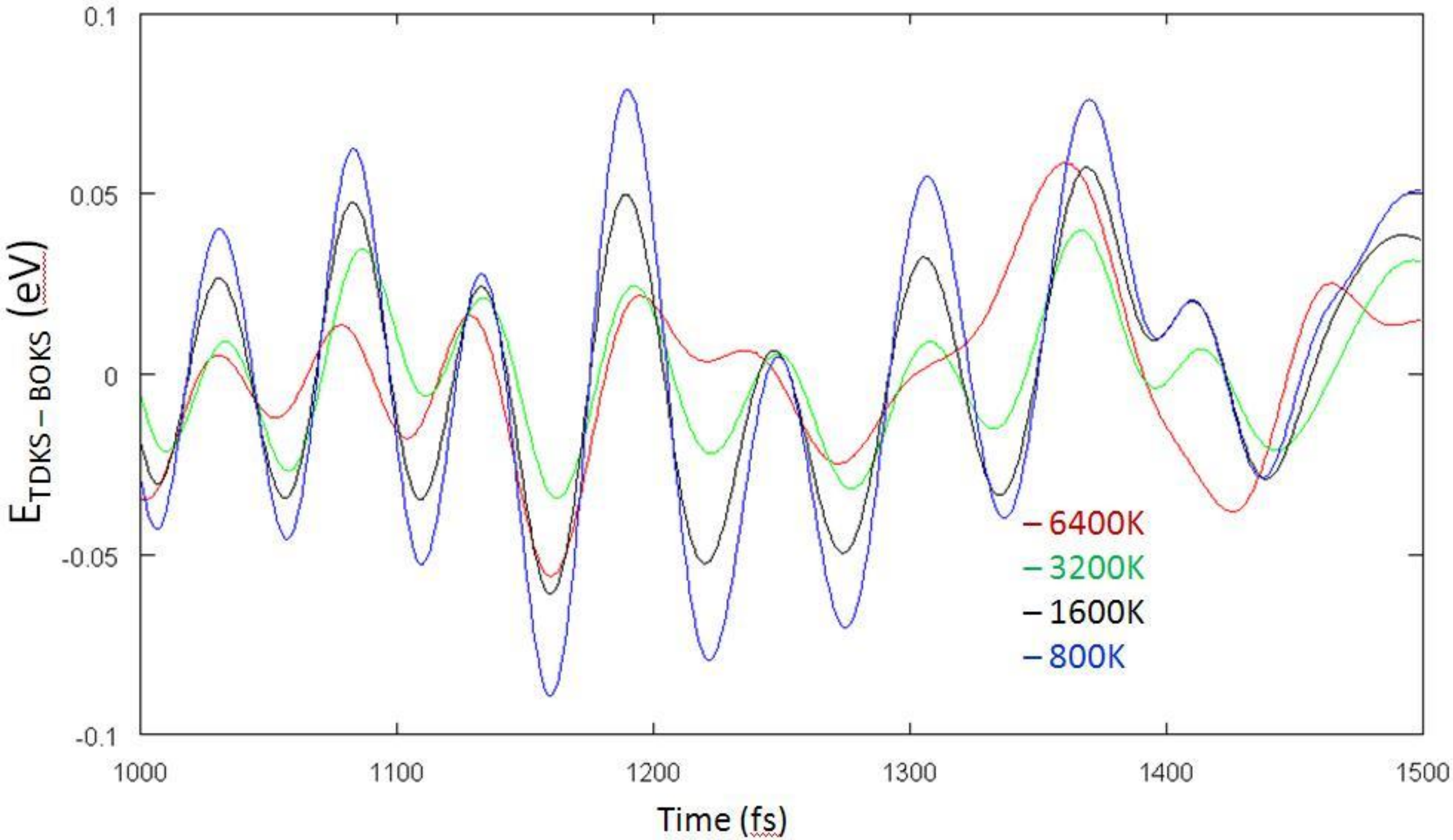
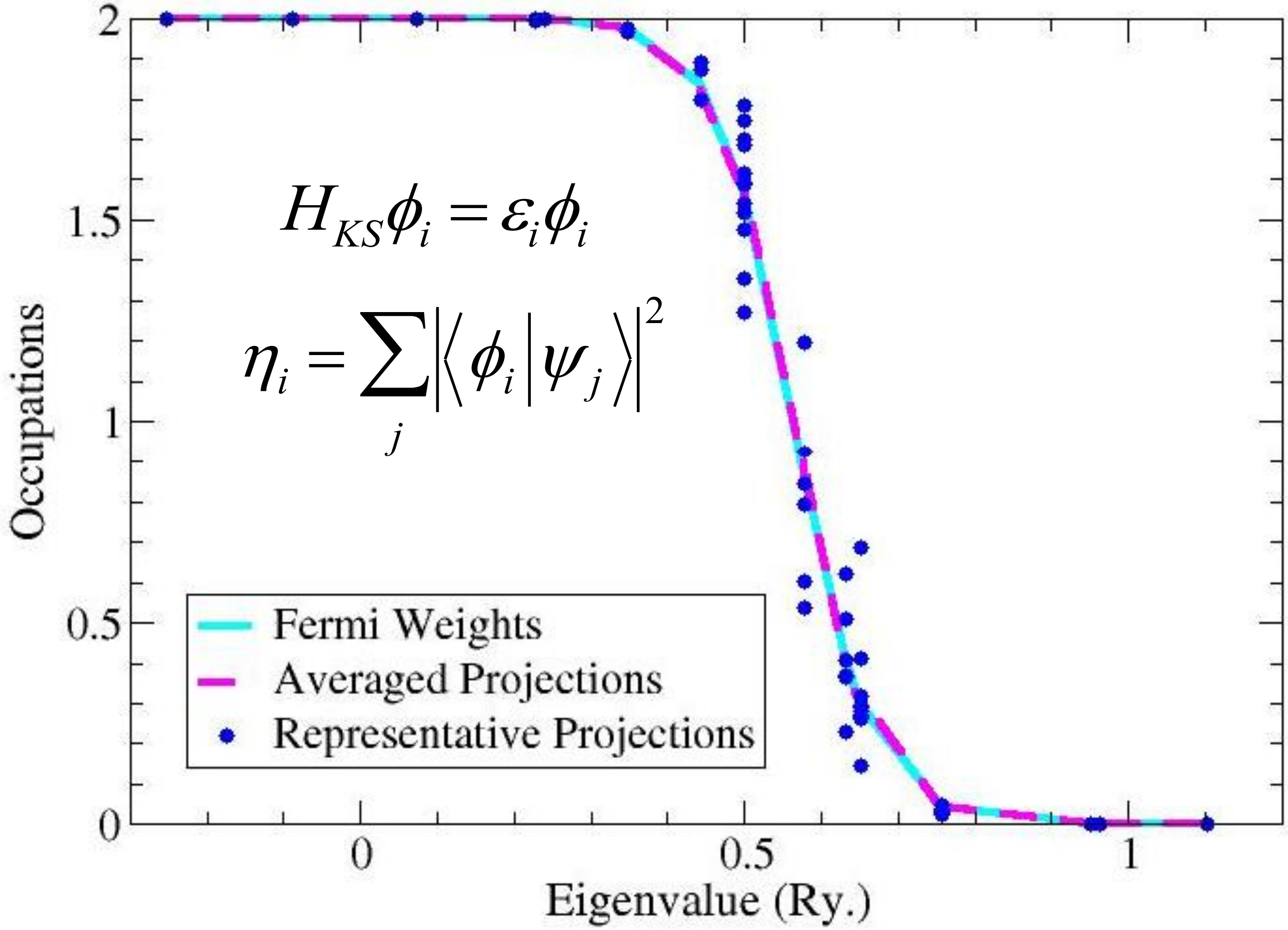
Why does $E_{TDDFT} - E_{BO}$ fluctuate with the phonons?



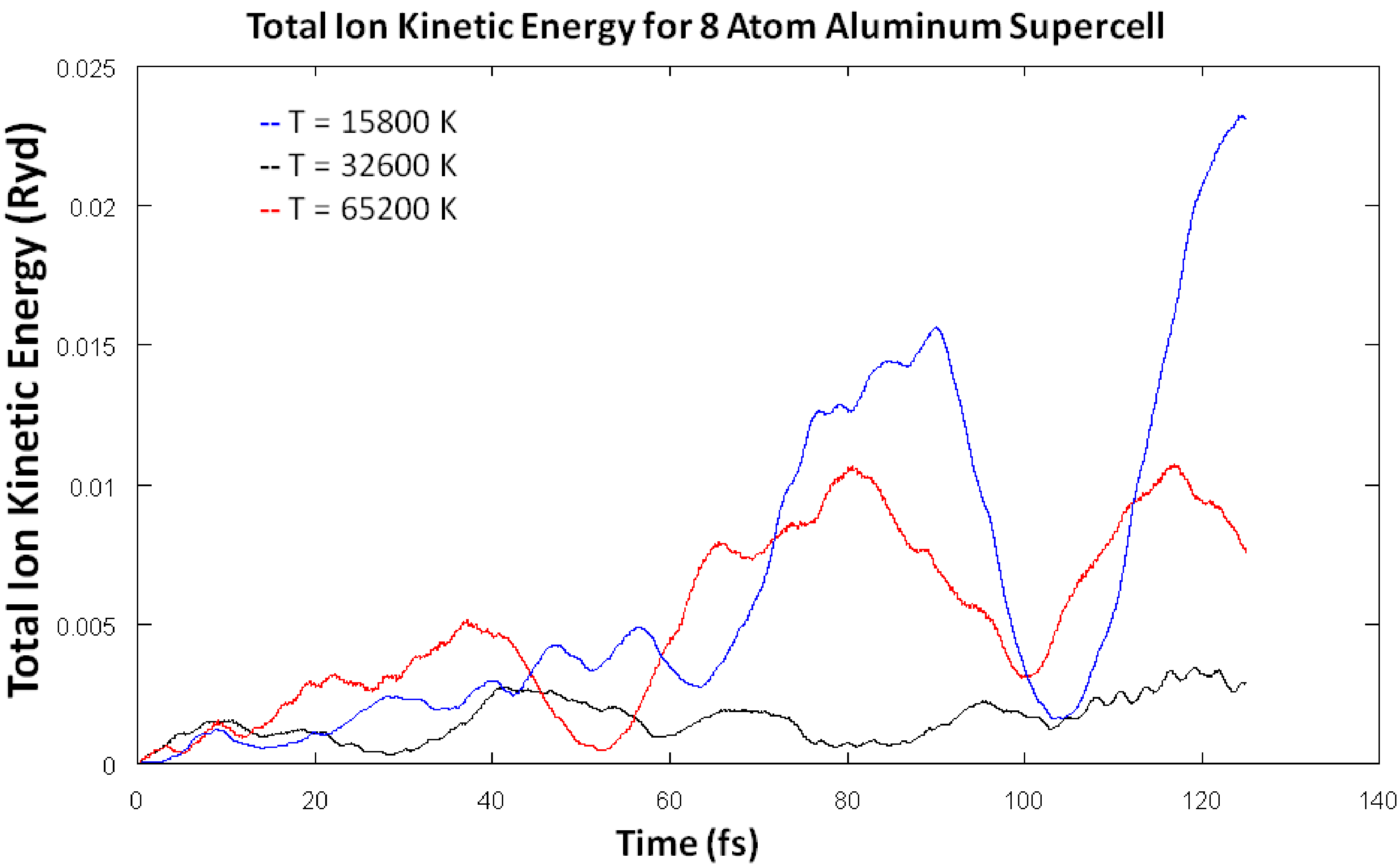
Electronic excitations change the potential surface for ionic motion

Can We Create Hot Electrons?



Construct initial states ψ_j with "occupations" that fluctuate around the Fermi occupations

Energy Transfer with Hot Electrons and Cold Ions



Results are promising, but need multiple runs to average out the fluctuations

Conclusions

- **Real-time TDDFT with ionic motion is a promising tool to study electron-ion energy transfer**
- **We are investigating a "microcanonical" dynamics approach to finite-temperature electronic systems**
- **Fundamental issues with electron-ion correlation limit direct application of TDDFT to some problems**
- **Careful handling of several issues is required to get meaningful results from TDDFT**

Current TDDFT Work

- Understand, model, and remove phonon effects

- <u>OR</u> work with non-moving ions (but what about equilibration?)

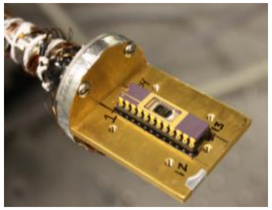
- Develop better initialization to start closer to equilibrium
  - Eliminate plasmons and accentuate electron-hole pairs

- Can we get hot ions and cold electrons?

Novel Experimental Work at CINT – Thermal Transport at the Nanoscale

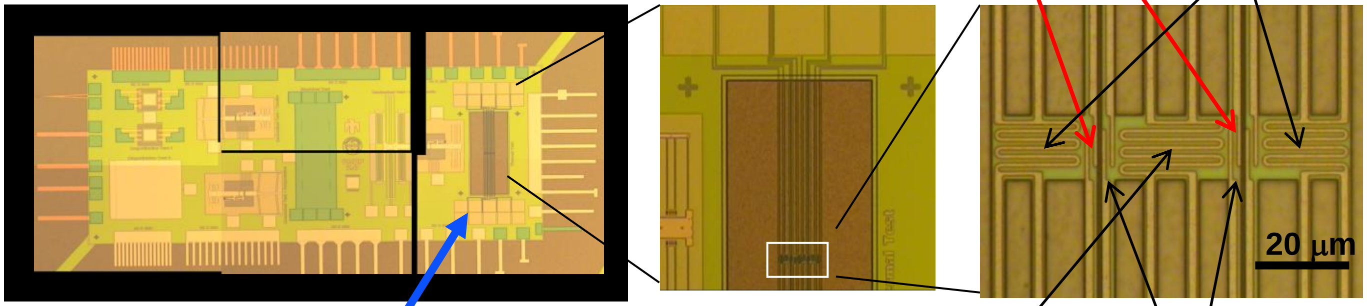
Critical experimental requirement: Methods to sensitively measure thermal, electrical & Seebeck coefficient simultaneously for single nanostructures

In situ TEM to probe structure



J. Huang

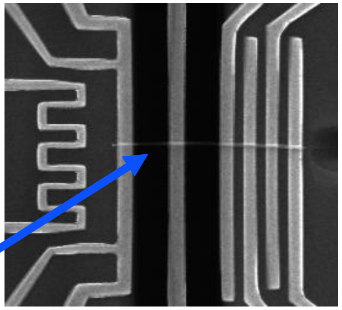
Cantilever Array Discovery Platform 2.0



J. Sullivan

NW transport structure

Test structure



T. Harris, J. Huang

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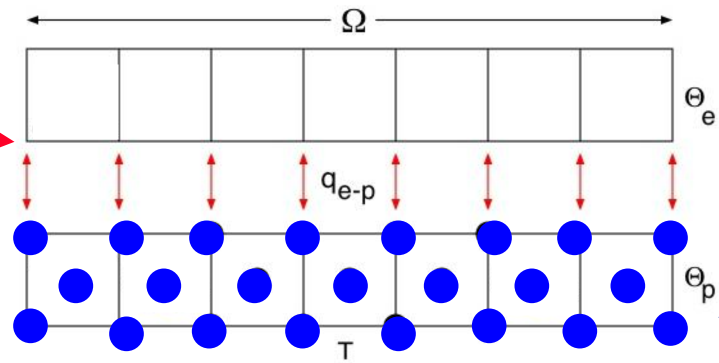
Issues in Modeling Heat Transport at the Nanoscale

- Time-dependent electronic structure (e.g., TDDFT)
  - Captures full electron and ion dynamics, BUT
  - Not feasible for most nanoscale systems
- Partial Differential Equation (PDE) based methods
  - Works well at macroscale, BUT
  - Misses effects of nanoscale structure on phonons (e.g., phonon confinement, ballistic transport, etc.)
- Molecular Dynamics (MD)
  - Explicitly represents phonons and their effects, BUT
  - Physics of electronic transport is absent

Our Modeling Approach: MD for Phonons, PDE for Electrons

PDE Model of Electrons

(Electrical and Thermal Conduction, Thermoelectric Coupling, Joule Heating)

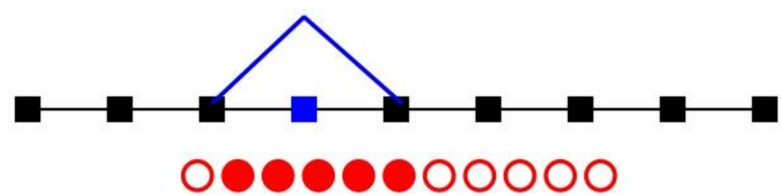


MD Model of Phonons

(Phonon Confinement, Ballistic Transport, Scattering Mechanisms)

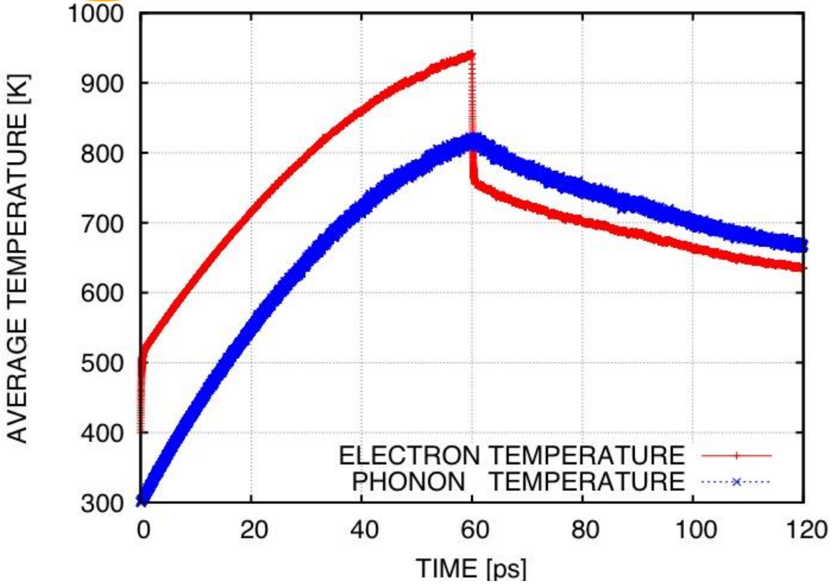
- Use finite elements to solve PDE for electronic temperature θ_e
- Obtain local ionic temperature θ_p from MD velocities

$$\theta_p \equiv \sum_{I,\alpha} \frac{m_\alpha}{3k_B} \tilde{N}_{I\alpha} \langle v_\alpha \cdot v_\alpha \rangle$$

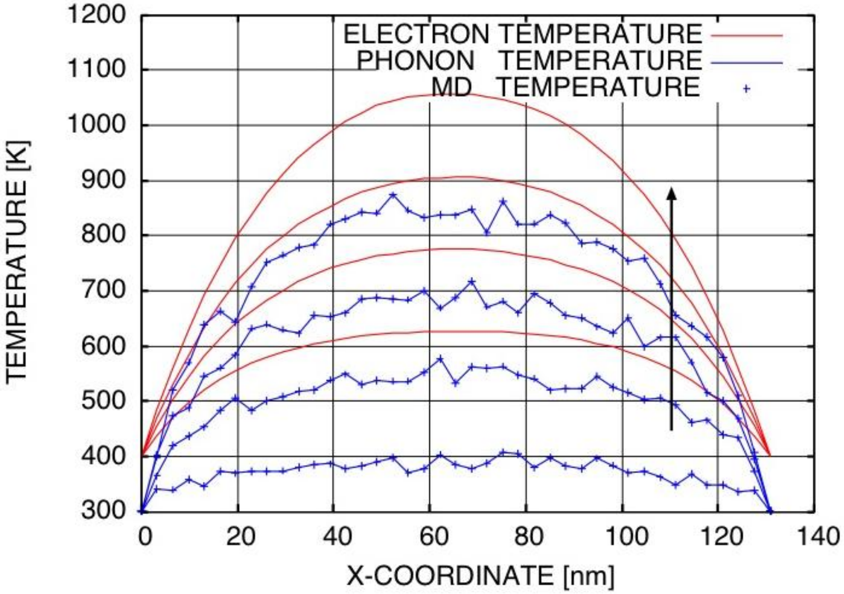


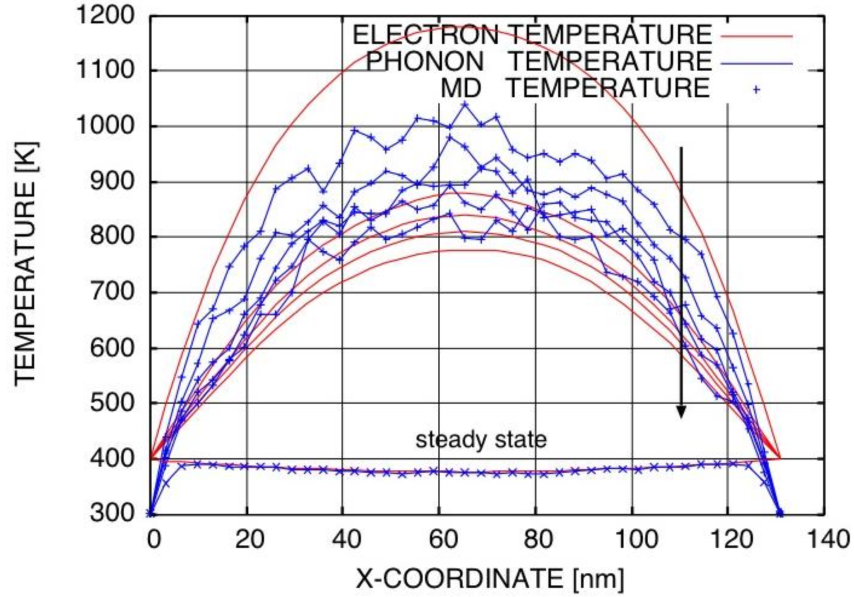
- Ionic thermostats enforce Two Temperature Model coupling

Example 1: Cu Nanowire with Electrons Uniformly Heated by 60 ps Pulse



- **Small electron heat capacity - Rapid electron response**
- **Large phonon heat capacity - Slower phonon response**
- **Different profiles for electron and phonon temperatures**

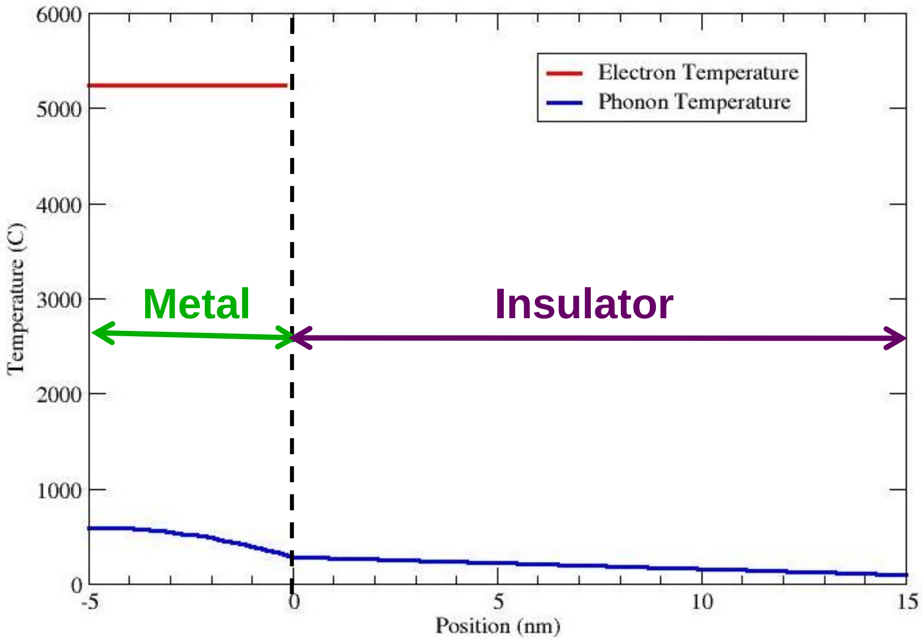




Large Electron-Phonon Temperature Differences in Steady State Systems

Example 2: A Thin Metal Film on an Insulator

Uniform Heating in Electrons of Metal



Uniform Heating in Phonons of Metal