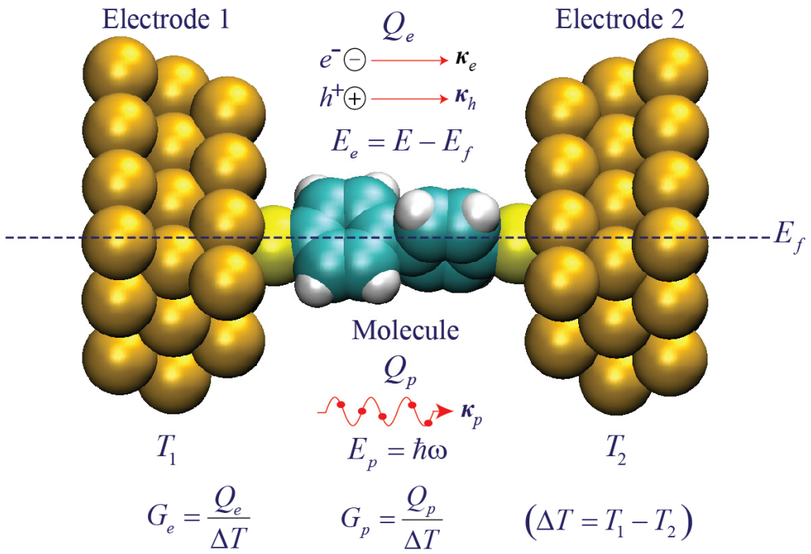
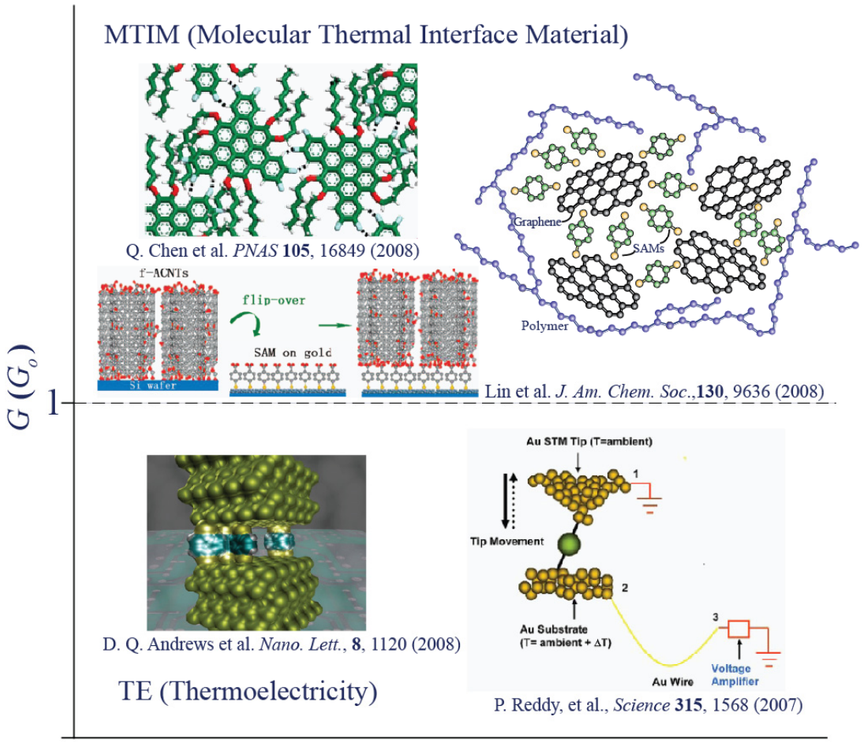
Molecular Junction Thermal Conductance

Heat flow across molecular junctions is of interest in thermoelectricity and in thermal interface materials. The heat flow is by charged particles (electron) and vibration-rotation (phonon). Depending on the bond formed with the leads and the structure of the junction, the junction thermal conductance varies. The presence of junction atoms causes restructuring of the leads surface atoms. The quantum features of the thermal transport become more pronounced because of the junction size.



Schematic of molecular junction. Thermal energy is transported by phonons and electrons. The energy of each phonon is $\hbar\omega$ and for each electron is E-E_f , where E_f is the Fermi energy of the system. Phonon and electron thermal transport is characterized by conductance G_p and G_e, which are defined by dividing the thermal current (Q_p and Q_e) by the temperature difference between the two electrodes.



Diverse applications of molecular junctions. For thermoelectricity, low thermal conductance is desirable as explained by the figure of merit (*ZT*), which represents the efficiency of thermoelectric device : $ZT = \alpha_S^2 \sigma_e T/(k_p + k_e)$, where α_S is the Seebeck coefficient, σ_e is the electrical conductivity, k_p is the phonon thermal conductivity and k_e is the electrical thermal conductivity. In contrast, high thermal conductance is necessary for the fast heat dissipation in molecular electronic components or TIMs. Thermal conductance (G) can be normalized by the quantum thermal conductance ($G_o = \pi k_B^2 T/6\hbar$).

Phonon Thermal Transport ($G_p = Q_p/\Delta T$)

Approaches

Molecular Dynamics Simulation (MD)

- Classical Newtonian mechanics with empirical or semi-empirical potential models
- Nonequilibrium setting with thermostat algorithms
  [by calculation of the heat flow (Q_p) in thermostats]

Nonequilibrium Green Function (NEGF)

- Transmission $\tau_p^{12}(\omega)$ in Landauer formula calculated by Green function theory

(Landauer formula for phonon transport $Q_p = \int_0^\infty \frac{d\omega}{2\pi} \hbar\omega \tau_p^{12}(\omega)\left[f_{p,1}^o(\omega,T) - f_{p,2}^o(\omega,T) \right]$)

- Phonon Green functions are calculated from the dynamic matrix from DFT

	NEGF	MD
Harmonicity	Harmonic Approximation	Able to Include Anharmonicity
Temperature	Low Temperature	High Temperature
Force Field	Density Functional Theory	Approximate Interatomic potential
System Size	Small	Large

Charge Thermal Transport ($G_e = Q_e/\Delta T$)

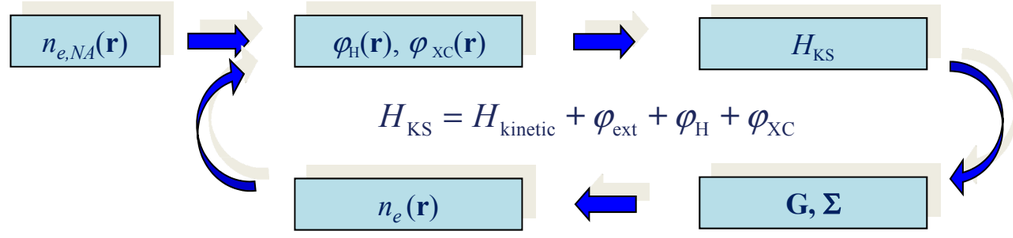
Nonequilibrium Green Function for Charge Transport

- Transmission $\tau_e^{12}(E)$ in Landauer formula by electron Green function theory

(Landauer formula for electron thermal transport $Q_e = \int \frac{dE}{2\pi\hbar}(E - E_f)\tau_e^{12}(E)\left[f_{e,1}^o(E,T) - f_{e,2}^o(E,T) \right]$)

- Electron Green functions from the Kohn-Sham Hamiltonian (H_{KS}) from DFT

Self-Consistent Process with DFT and Green functions



(n_e – electron density, **G** – electron Green function, **Σ** – self-energy, φ_{ext} - external potential, φ_{XC} – exchange-correlation potential, φ_H - Hartree energy)