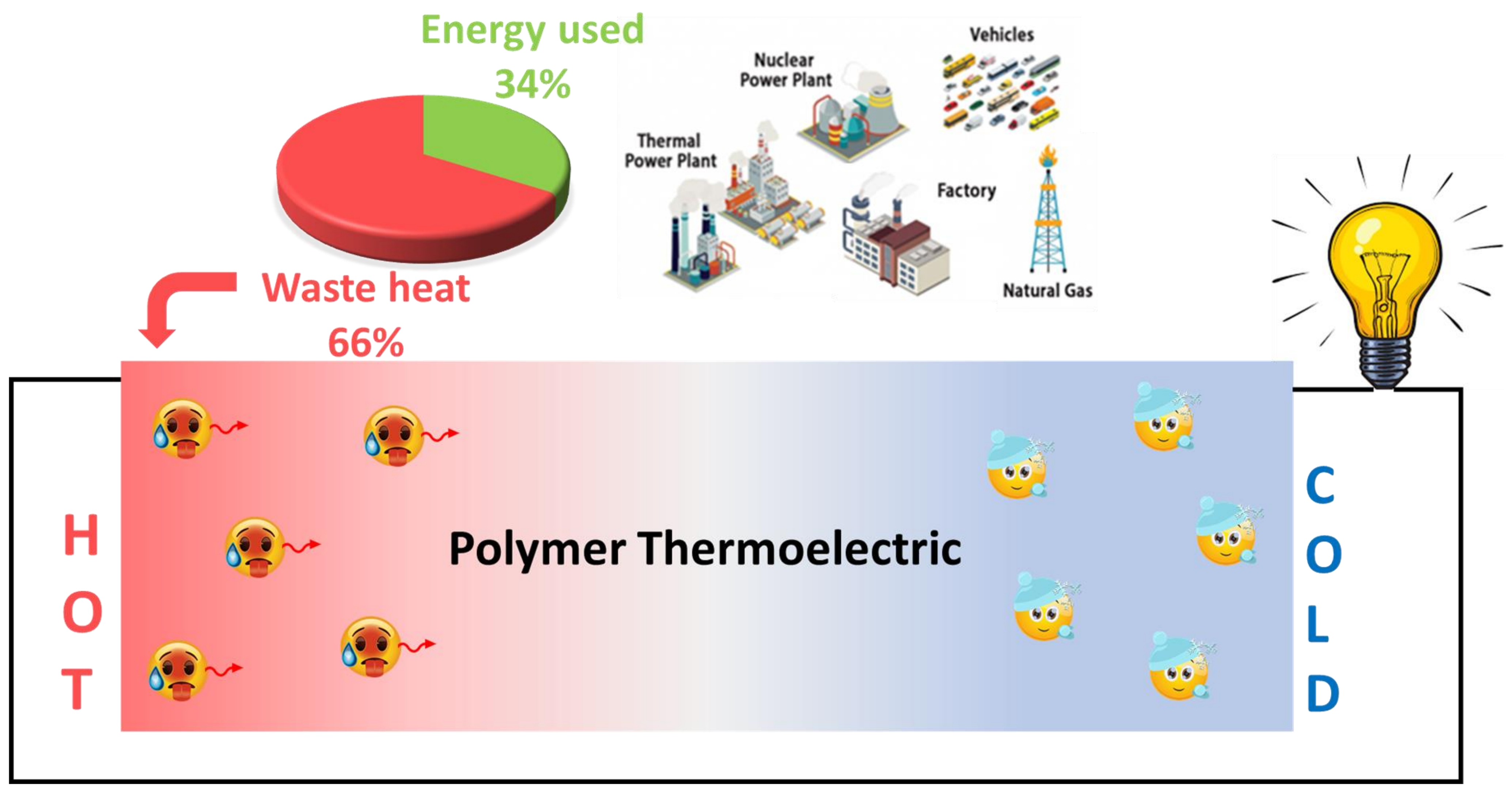
ABSTRACT

- Organic materials have attracted interest as thermoelectric (TE) converters due to their low cost and ease of fabrication.
- We examine the effect of disorder, morphology, dopant-polymer Coulombic interactions and charge transport dynamics on the TE properties of semiconducting polymers based on a modified Gaussian Disorder Model for site energies while employing Pauli's master equation approach to model hopping between localized sites.

KEY RESULTS

- The long-range coulombic interaction between the ionized dopant molecules and the localized carriers further increases the width and broadens the deep tail of the electronic density-of-states (DOS), termed energetic disorder.
- Energetic disorder leads to increased energy gap between sites, hindering transport, and adversely affects both conductivity and Seebeck.
- A heterogenous distribution of dopant molecules within the sample with dopant clustering increases the energetic disorder, whereas homogenous doping maintains a narrow Gaussian DOS.
- This change in width and shape of the DOS results in a qualitative change of the Seebeck vs. conductivity curve, showing that thermoelectric performance is affected by not just *how much* but *how* the semiconductor has been doped across all carrier concentrations.

BACKGROUND

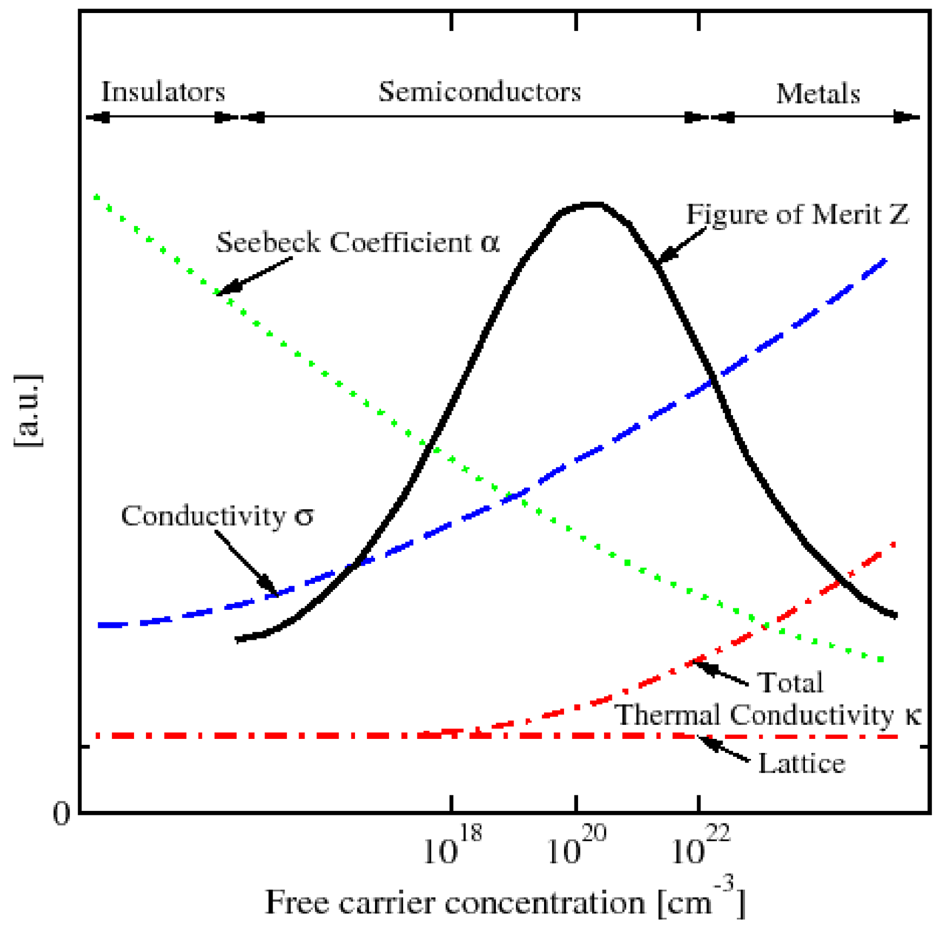


- Carnot efficiency for heat conversion,

$$\eta = \frac{T_h - T_c}{T_h}\frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_h}{T_c}} \times 100, \quad zT = \frac{\alpha^2 \sigma T}{\kappa}$$

Why polymers?

- Inherently low thermal conductivity
- Low cost and easy synthesis
- Biodegradable
- Mechanical flexibility



Z.H. Dughaish, Physica B: Condensed Matter 322, 205-223 (2002)

NUMERICAL IMPLEMENTATION

- Hopping rate:

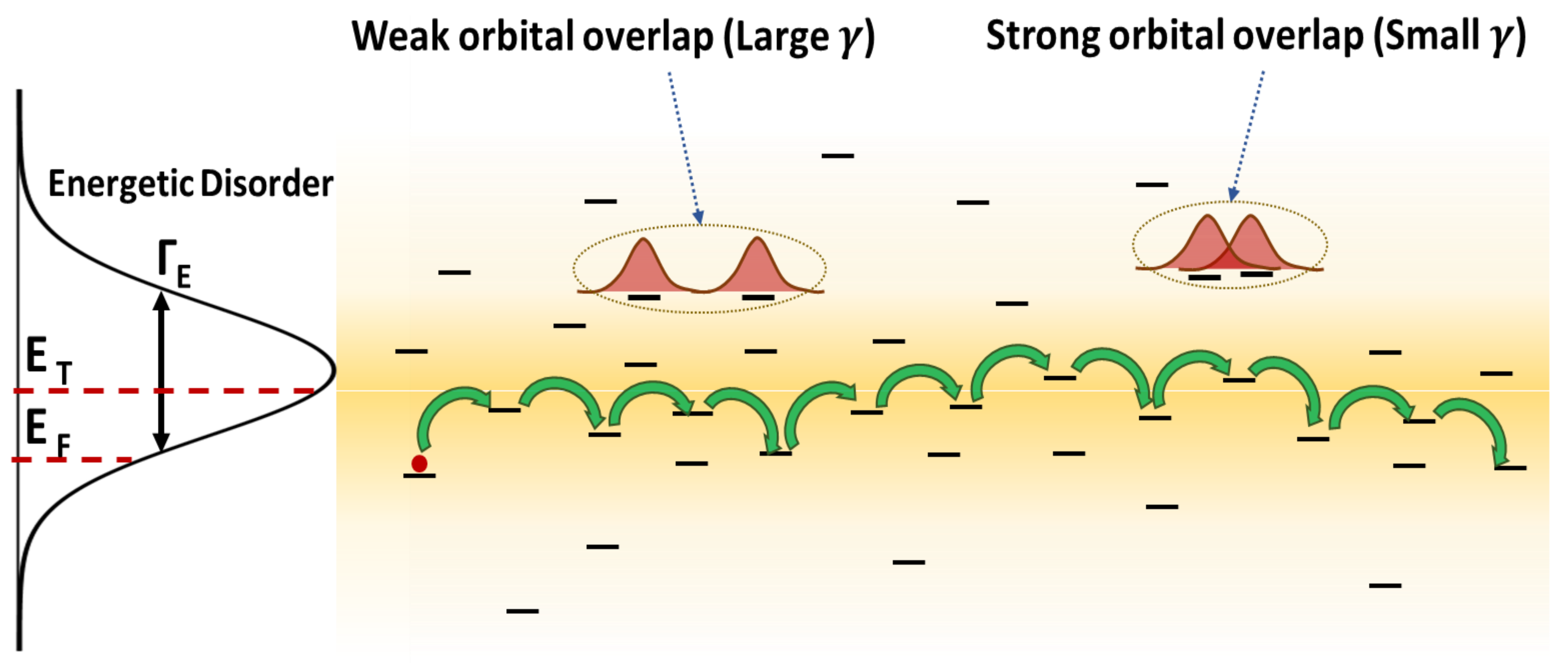
$$W_{ij} = \nu_0 exp(-2\gamma_{ij}\Delta R_{ij})\left[\left(exp\left(\frac{\Delta E_{ij}}{K_b T}\right)-1\right)^{-1} + \frac{1}{2} \mp \frac{1}{2}\right]$$

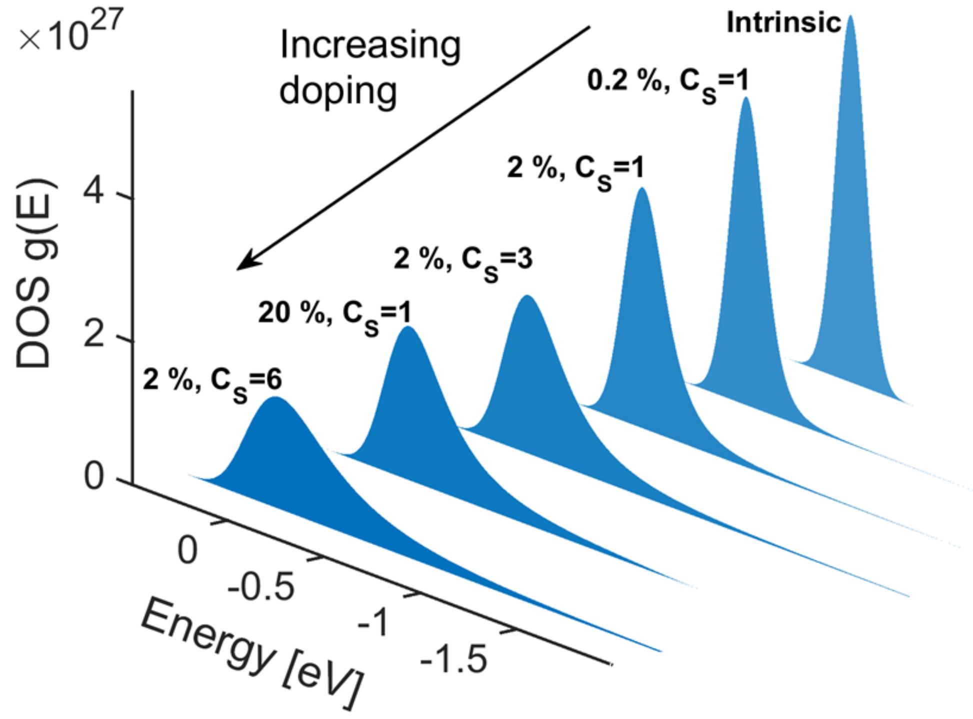
- Non-linear Master Equation in steady state:

$$\frac{dp_i}{dt} = \sum_j [W_{ji}p_j(1-p_i) - W_{ij}p_i(1-p_j)] = 0$$

- Electrical conductivity and Seebeck coefficient:

$$\sigma = \frac{e}{a^3 NF}\sum_{i,j} W_{ij}p_i(1-p_j)R_{ij,x}, \ \alpha = \frac{E_f - E_T}{eT}$$





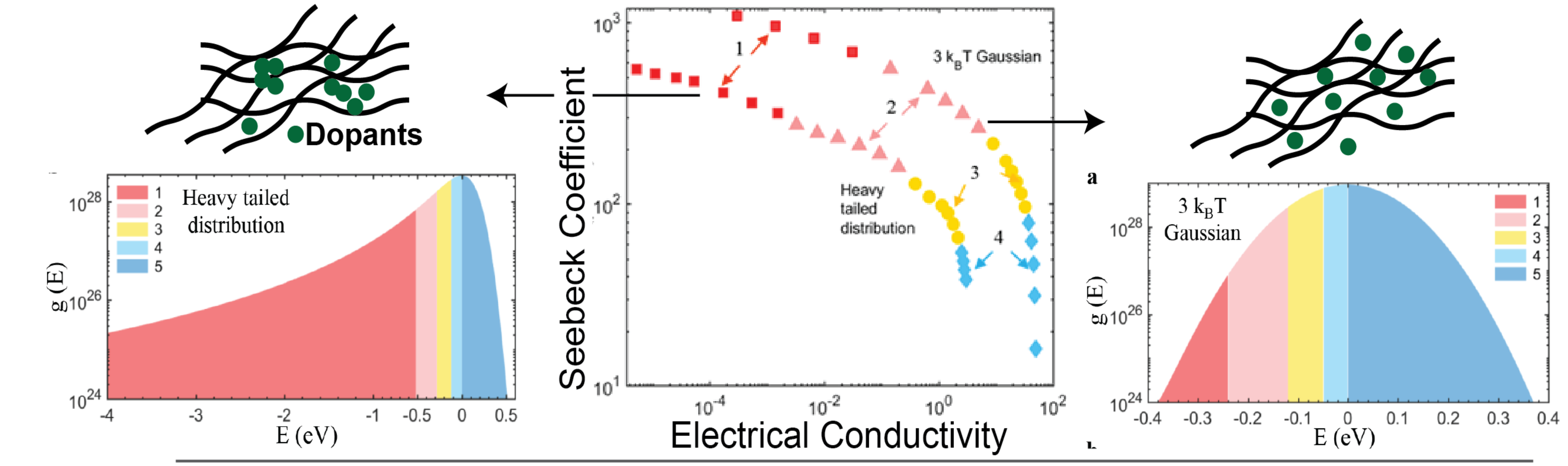
RESULTS

Doped at low T

Doped at high T

Heterogenous Distribution

Homogenous Distribution



Boyle, Upadhyaya, et al., Tuning charge transport dynamics via clustering of doping in organic semiconductor thin films, Nature Communications 10, 2827 (2019)

Upadhyaya, Boyle, et al., Effects of Disorder on Thermoelectric Properties of Semiconducting Polymers, Scientific Reports 9, 5820 (2019)

Email: mupadhyaya@umass.edu