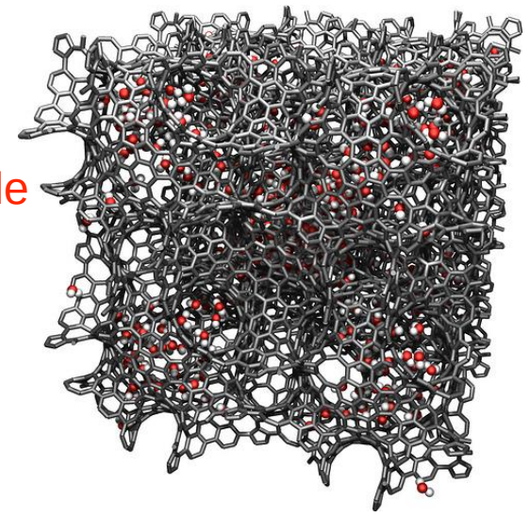
Jarod M. Younker, PhD

POLYMER PROPERTIES AND MOLECULAR MODELING

MODELING SCALES

Dynamic Properties
(Tg, miscibility, viscosity, aggregation, etc.)
< 1MM atoms
Accurate force fields available



Finite Element Method

Mesoscale
(DPD, Brownian)

Coarse-Grained MD

Monte Carlo

Atomistic Molecular Dynamics

Reactive MD

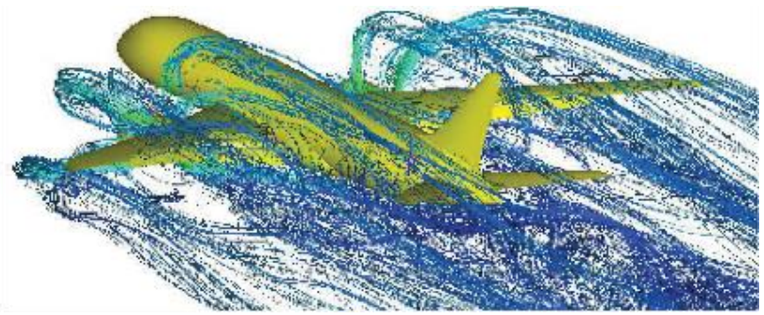
Quantum

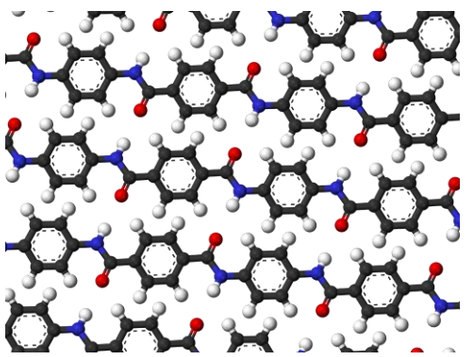
Density Functional Theory

10^{12} 10^{10} 10^{8} 10^{6} 10^{4}

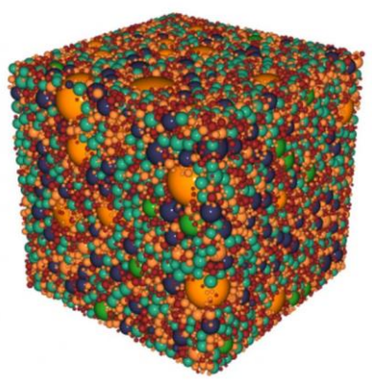
10^{-12} 10^{-11} 10^{-10} 10^{-9} 10^{-8} 10^{-7} 10^{-6}

Macroscale properties
Solution of differential equations





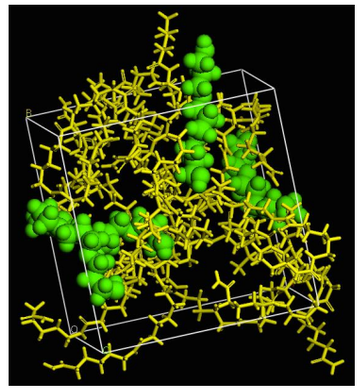
Reactions
Electronic Properties
<1000 atoms
Exact description



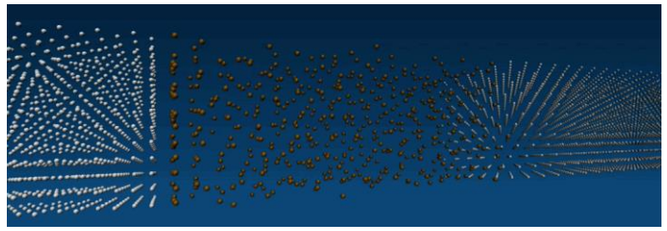
Atomic-level information replaced
< 1MM particles
General force fields unavailable, system-dependent parameterization required (e.g., iterative Boltzmann inversion)

TALK OVERVIEW

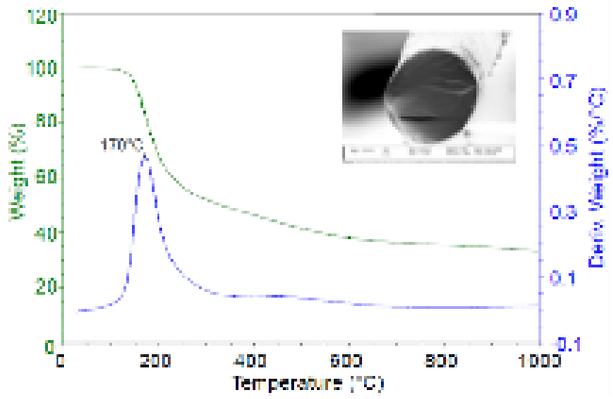
Flex Modulus/Solubility Parameters of Nylon Plasticizers



Thermal Interface Materials



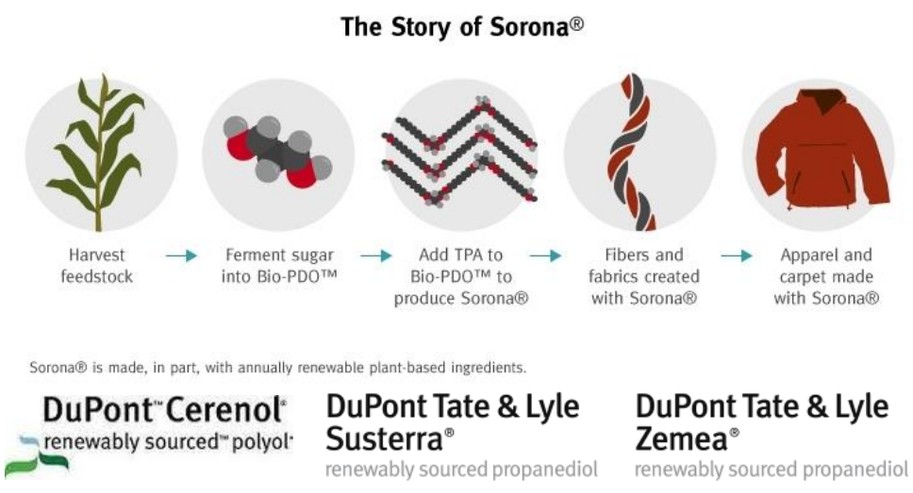
Carbon Fiber from Polyethylene



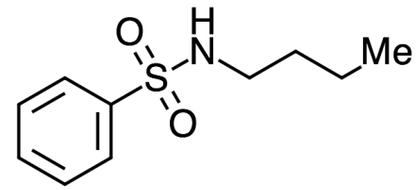
FLEX MODULUS/SOLUBILITY PARAMETERS FOR NYLON PLASTICIZERS

Current applications of 1,3-propanediol (Bio-PDO):

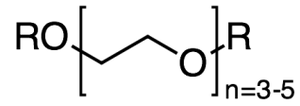
DuPont Tate & Lyle BioProducts



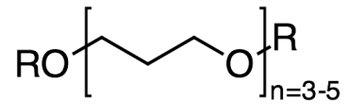
- Nylon market projected to grow by 5% annually driven by automotive industry.
- Proposed application of Bio-PDO: environmentally friendly nylon plasticizer
- Incumbent plasticizer: *n*-butylbenzenesulfonamide (NBBS)
  - Environmental contaminant
  - Probable neurotoxin



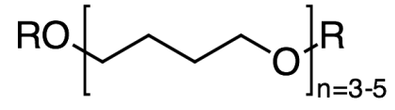
n-butylbenzenesulfonamide



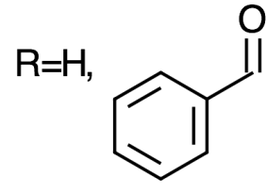
polyethylene glycol



poly(1,3-propanediol)



poly(1,4-butanediol)



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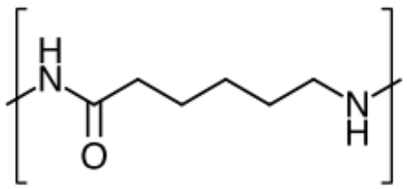
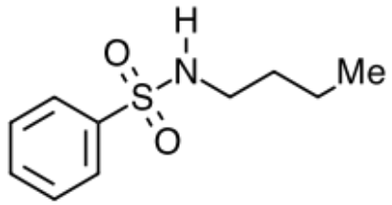
FLEX MODULUS/SOLUBILITY PARAMETERS FOR NYLON PLASTICIZERS

Hypothesis: Rigidity of polymer is a function of intermolecular hydrogen bonding.

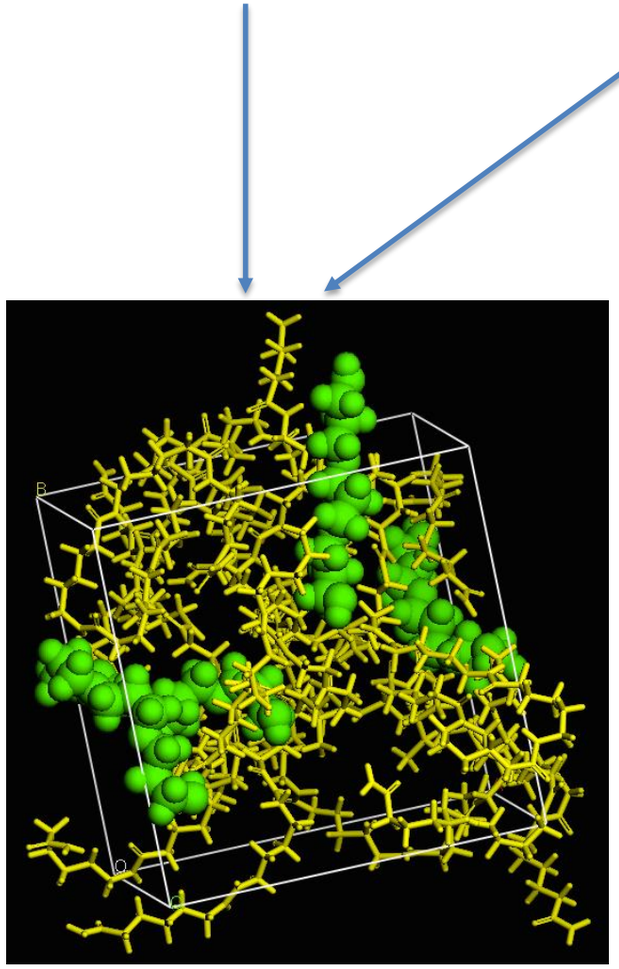
- Workflows automated using Materials Studio Perl script
- Data stored within MySQL database



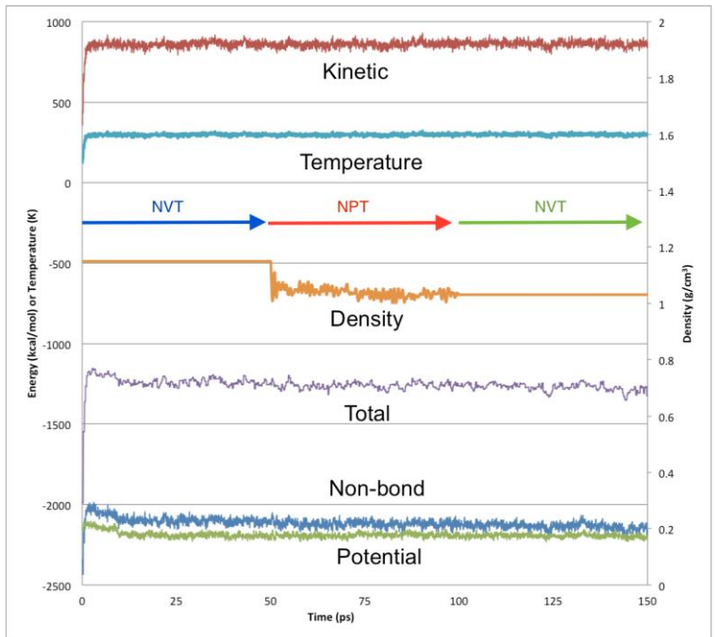
Polymer



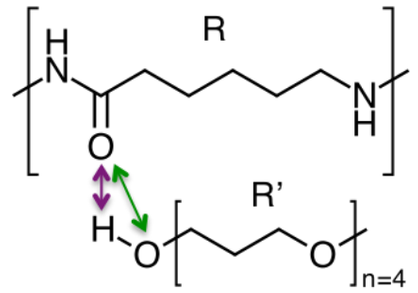
Plasticizer

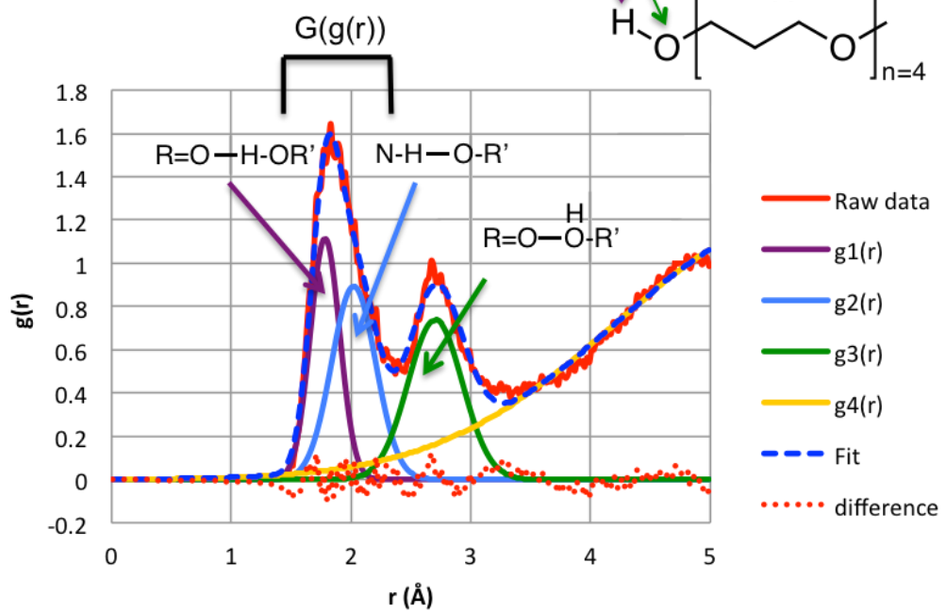


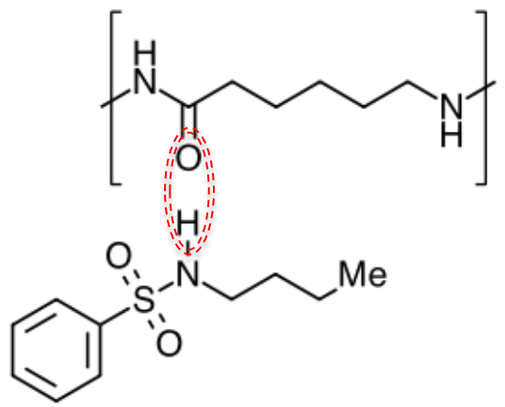
1) Screen *x* amorphous cells



2) Geometry optimization
Molecular dynamics







Probability that a donor will be within a set distance (Å) from an acceptor.

3) Pair correlation function

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FLEX MODULUS/SOLUBILITY PARAMETERS FOR NYLON PLASTICIZERS

Predicting nylon/plasticizer compatibility

$$\delta = (CED)^{1/2} = \left(\frac{\Delta E_v}{V_m}\right)^{1/2} = \left(\frac{\Delta H_v - RT}{V_m}\right)^{1/2}$$

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

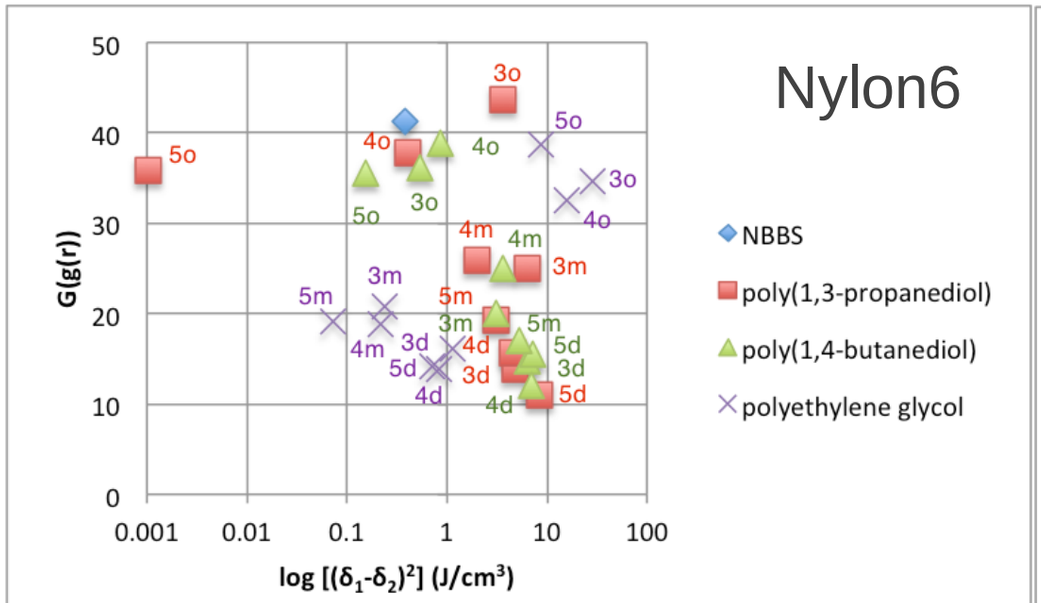
drive to zero!

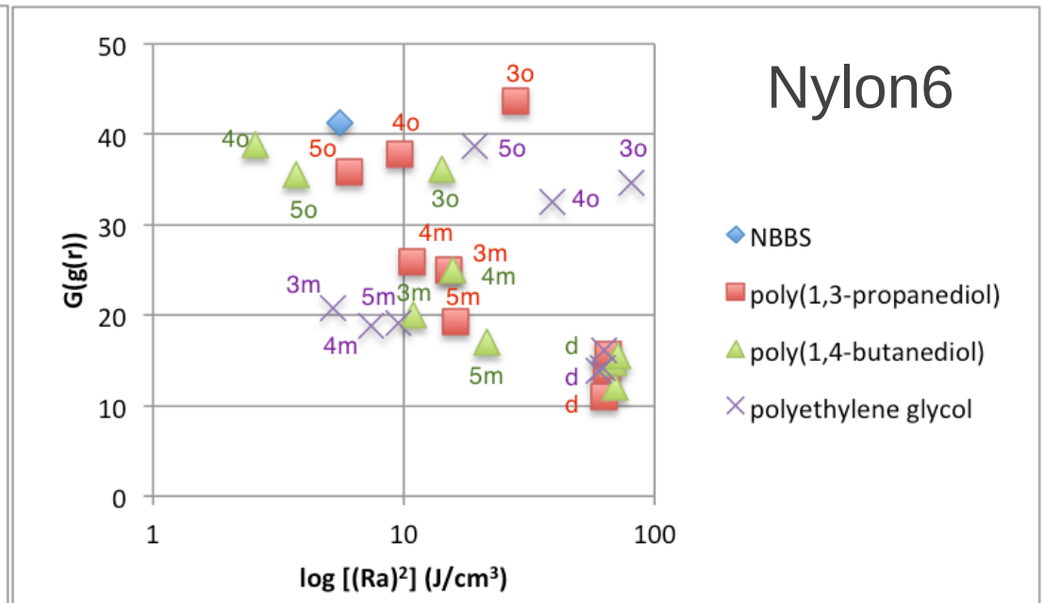
$$\Delta H_m = V'(\delta_1 - \delta_2)^2 \phi_1 \phi_2$$ Hildebrand

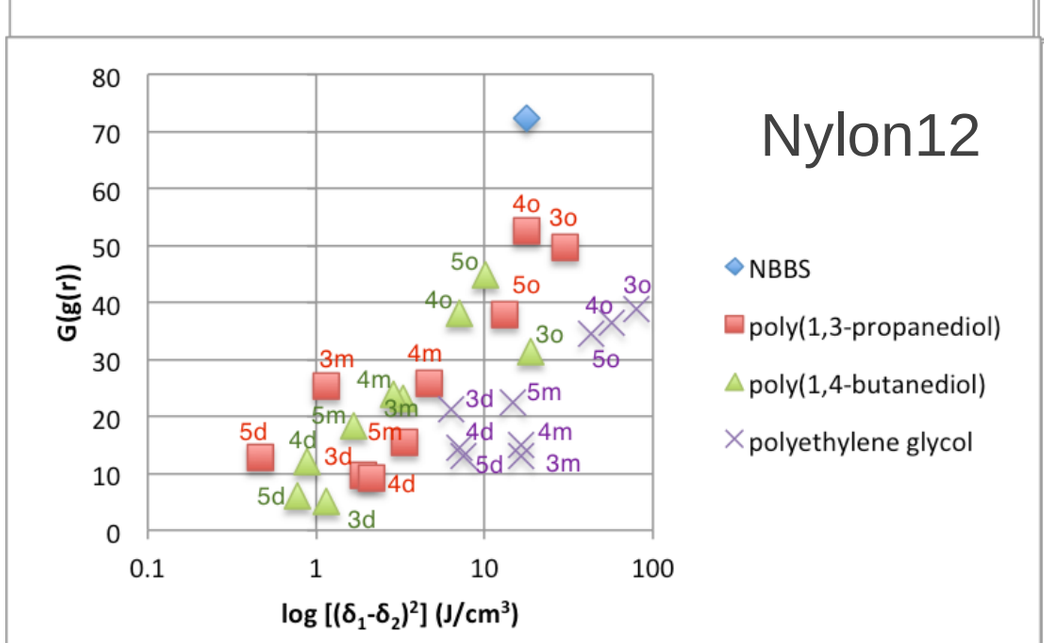
$\delta_{vdW} + \delta_{Cou}$

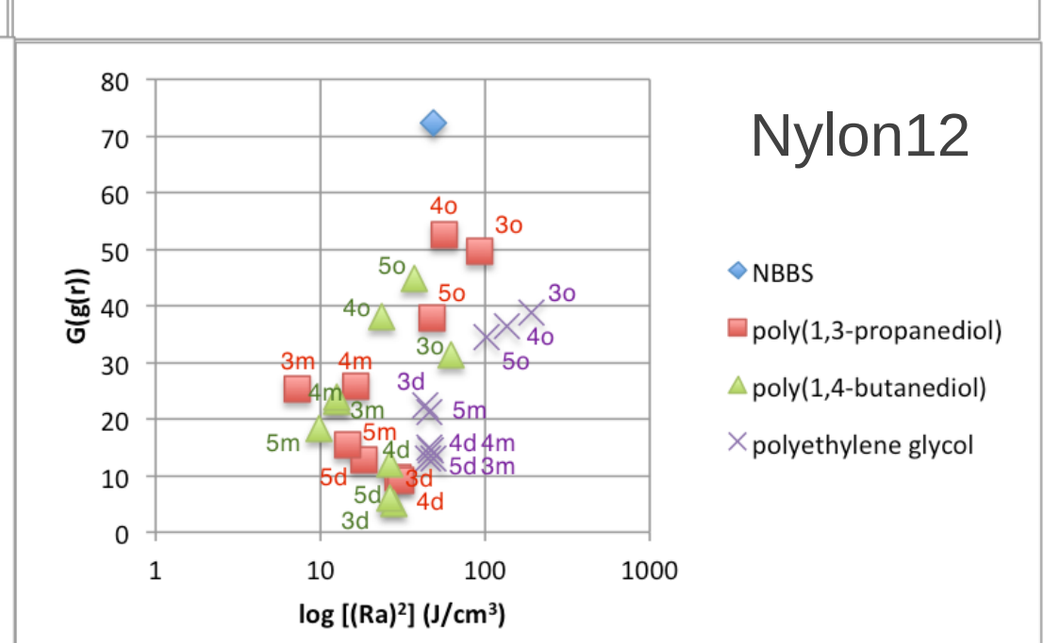
$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$ Hansen

polar hydrogen-bonding









Plasticizers are labeled as follows: nc, where n is the poly chain length (3-5) and c is the capping substituent (o=diol, m=monobenzoate, d=dibenzoate).

$$(Ra)^2 = 4(\delta_{d,1} - \delta_{d,2})^2 + (\delta_{p,1} - \delta_{p,2})^2 + (\delta_{h,1} - \delta_{h,2})^2$$

BIOVIA

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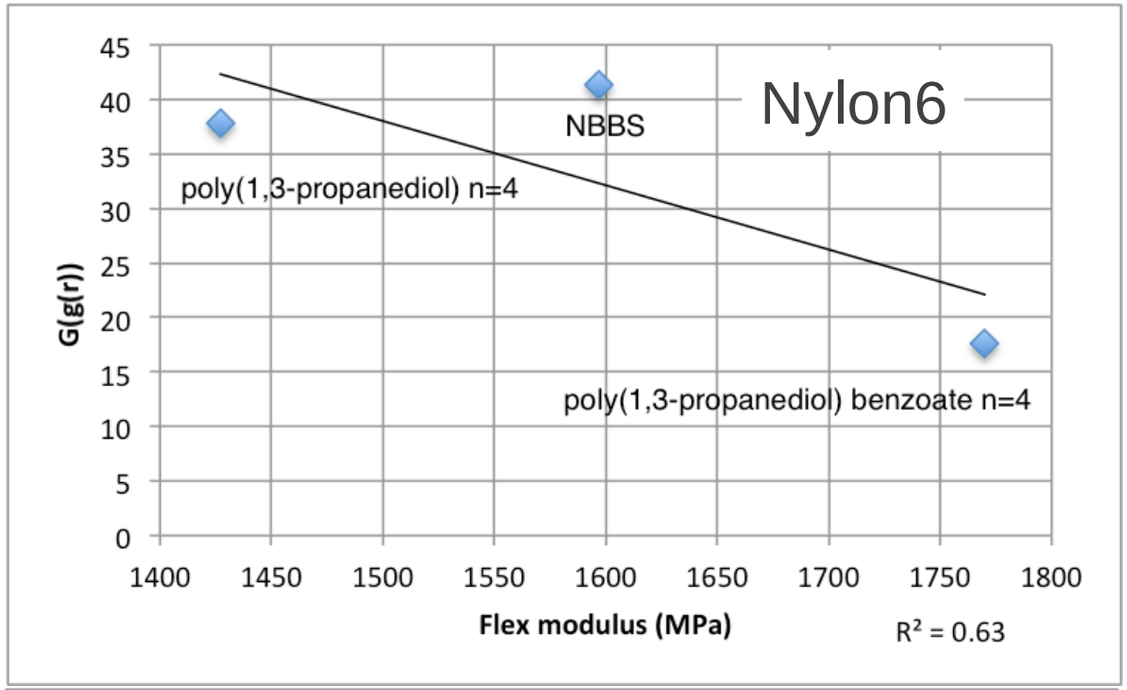
FLEX MODULUS/SOLUBILITY PARAMETERS FOR NYLON PLASTICIZERS

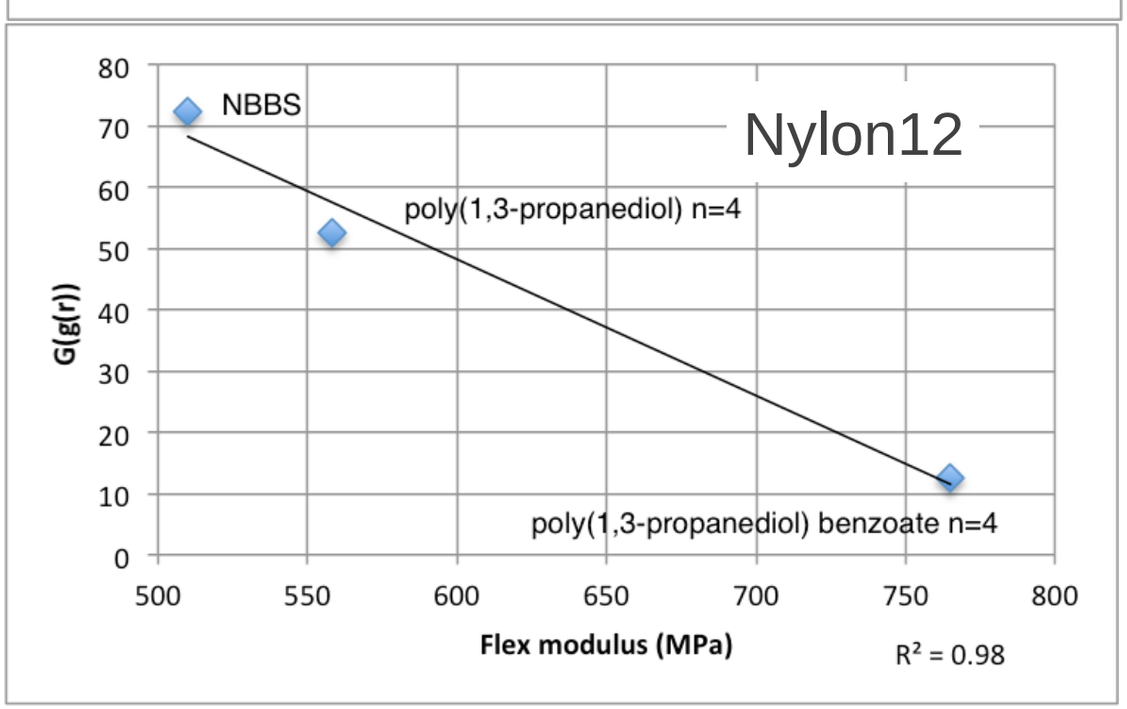
High-throughput virtual approach has been used to screen plasticizers.

Bio-PDO-based poly(1,3-propanediol) is effective at reducing the flex modulus of nylon6, but it not as effective as NBBS in nylon12.

Large difference in polar electrostatics between nylon12 and poly(1,3-propanediol) limits compatibility.

- Condensation to the benzoate ester increases compatibility, but at the expense of reduced flex modulus.





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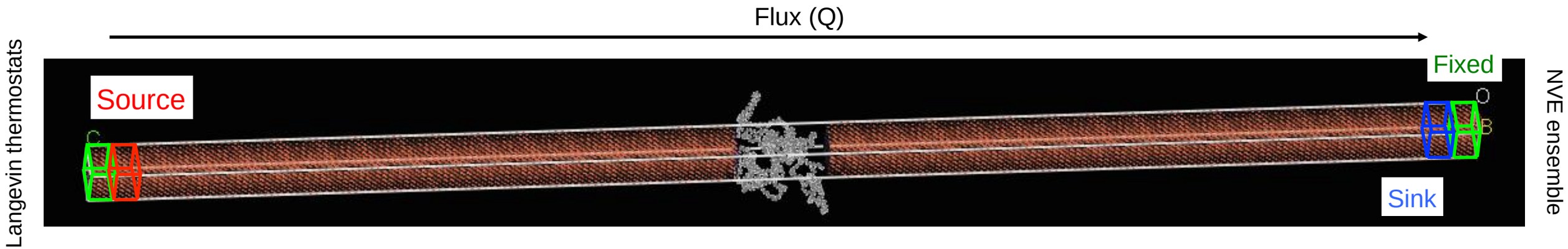
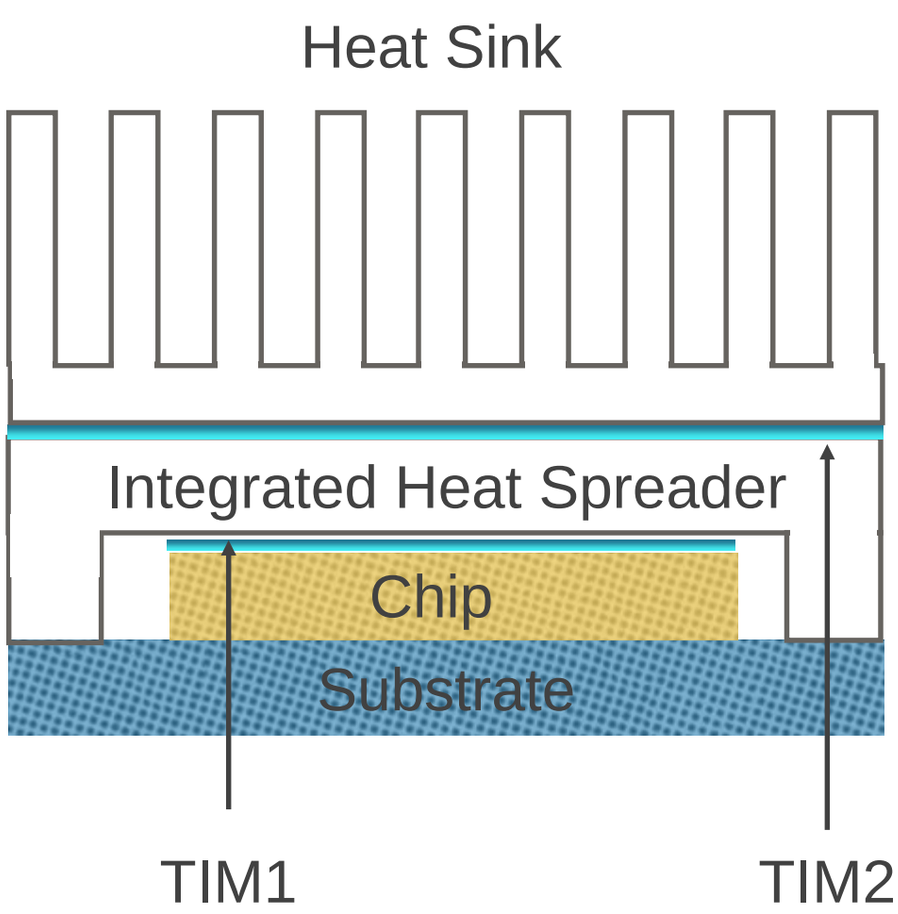
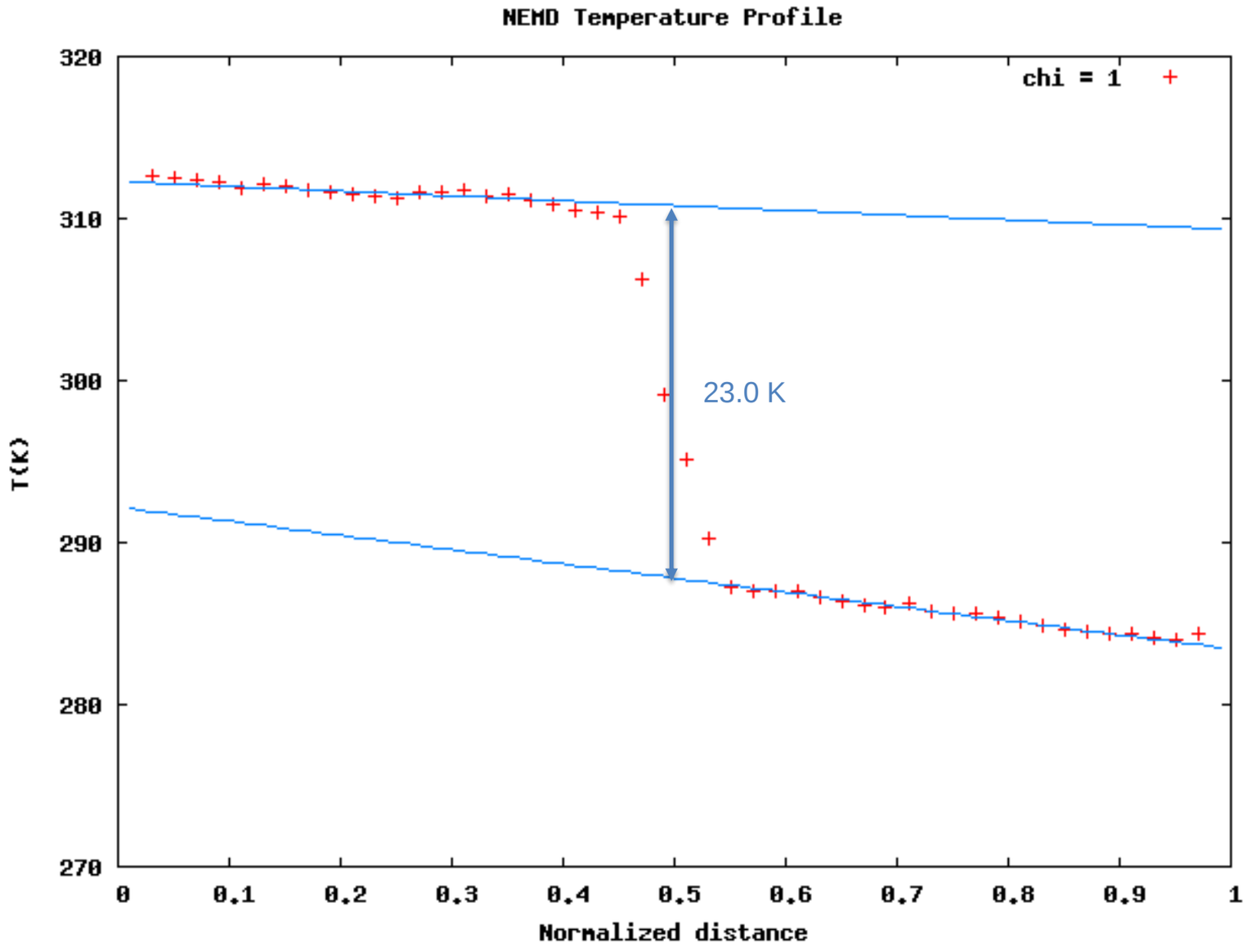
THERMAL INTERFACE MATERIALS

Objective: Screen for and engineer thin films that have high thermal conductivity.



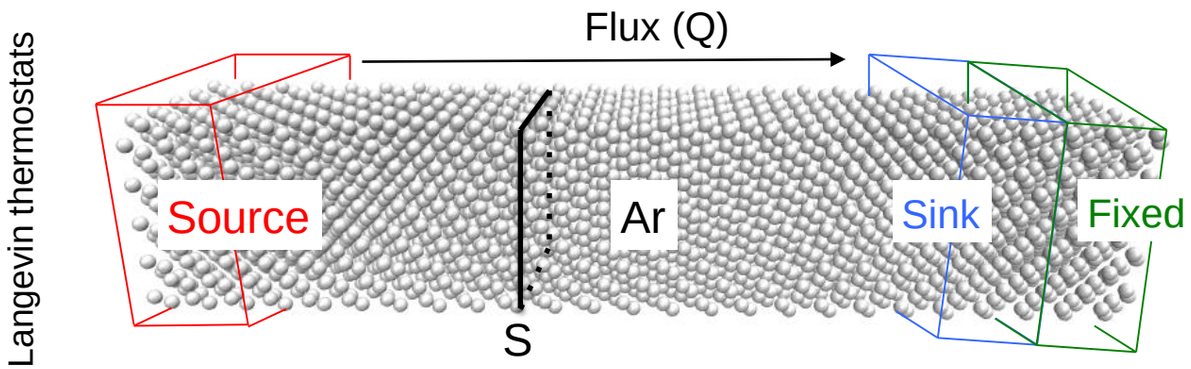




LAMMPS Younker, J. M. *in preparation*

THERMAL INTERFACE MATERIALS

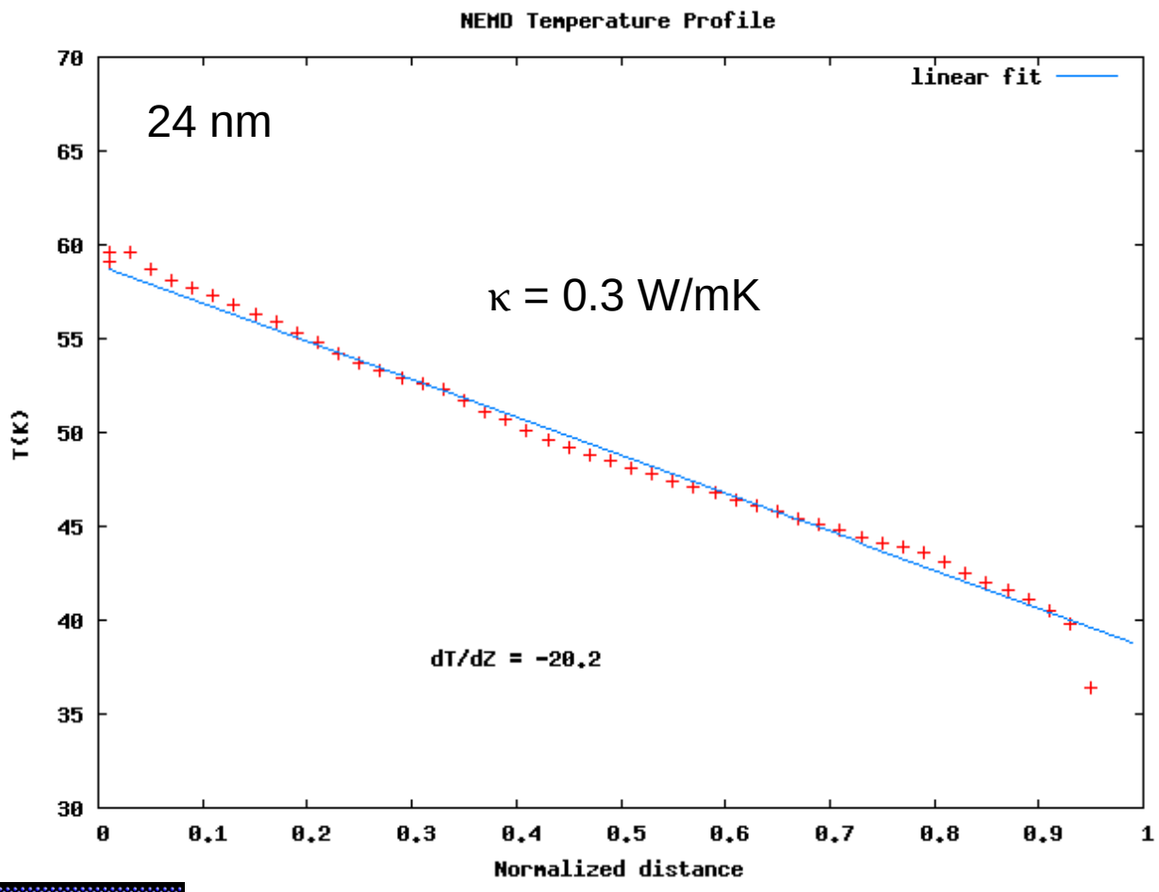
Bulk thermal conductivity

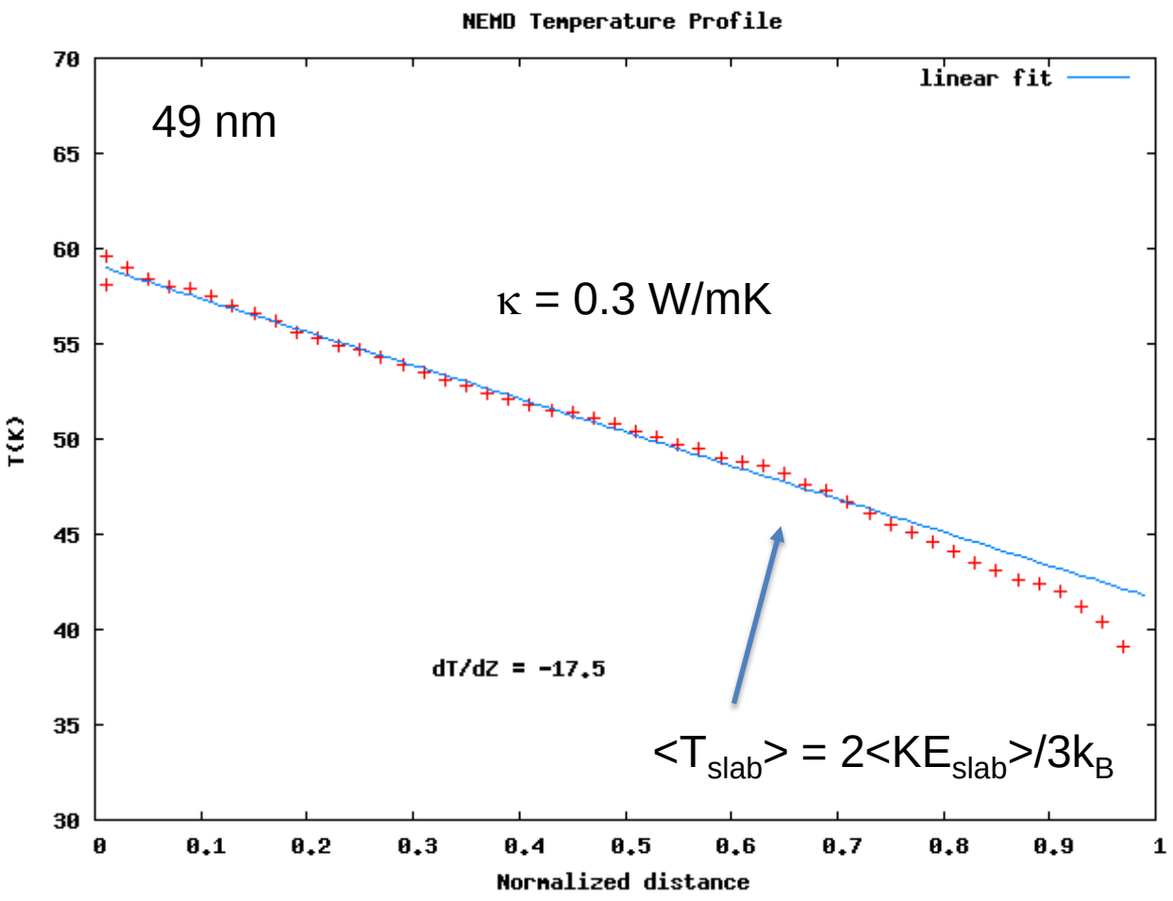


$$\kappa = \frac{Q}{dT/dZ}$$

$$\kappa = \frac{\Delta KE}{S\Delta t(dT/dZ)}$$

$\Delta KE = \Sigma$ (Source + Sink)



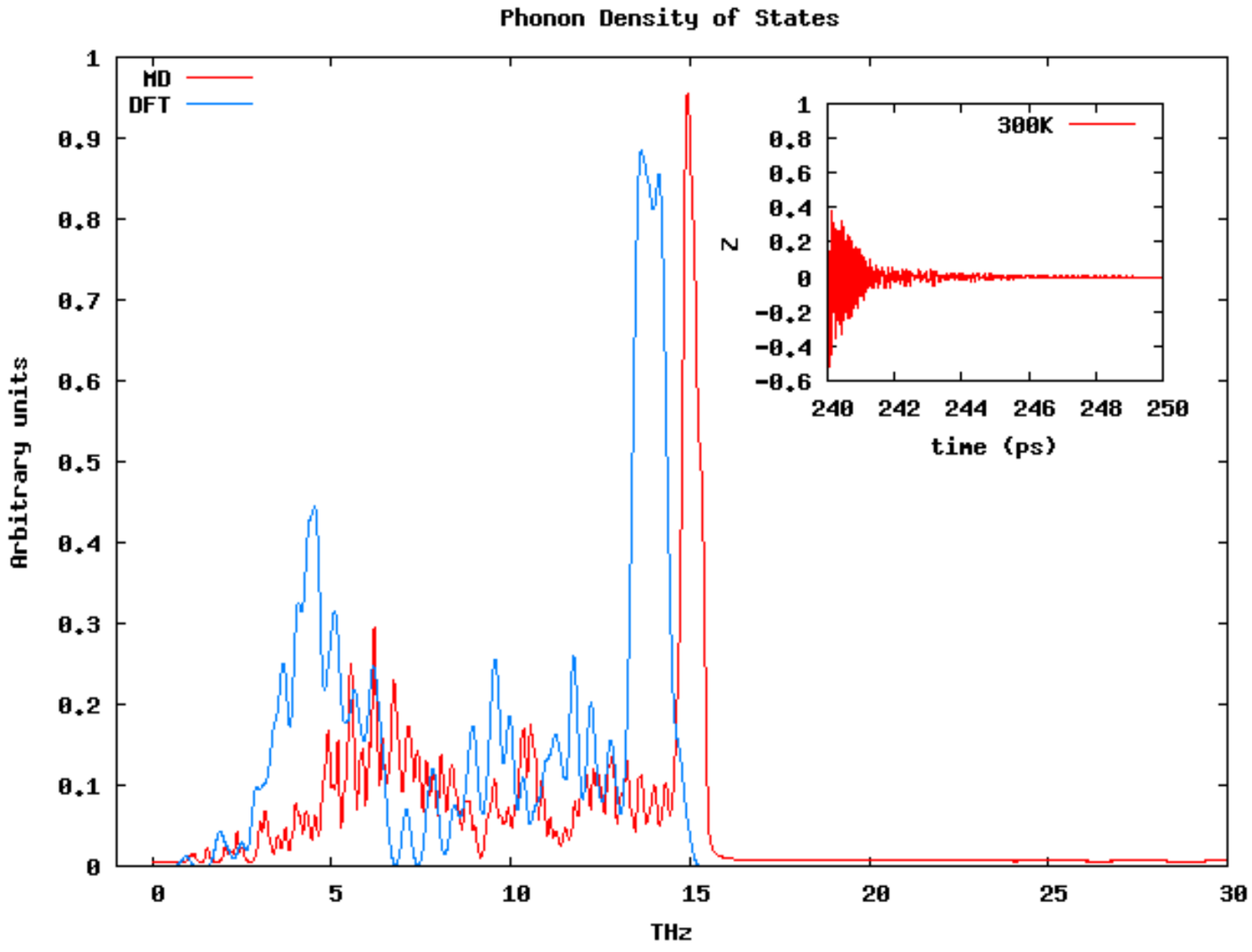


LAMMPS Younker, J. M. *in preparation*

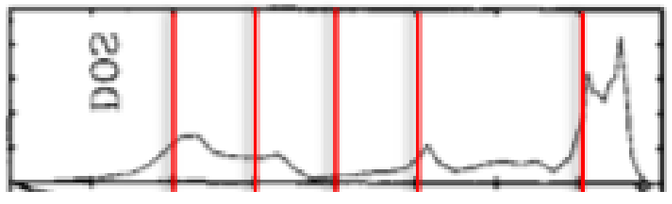
THERMAL INTERFACE MATERIALS

Bulk Silicon

Forcefield verification: Second Nearest Neighbor Modified Embedded Atom Potential (2NN-MEAM)



Experiment



0 4 6 8 10 14 16

THz

$$E = \sum_i \left[F_i(\overline{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} S_{ij} \phi_{ij}(R_{ij}) \right]$$

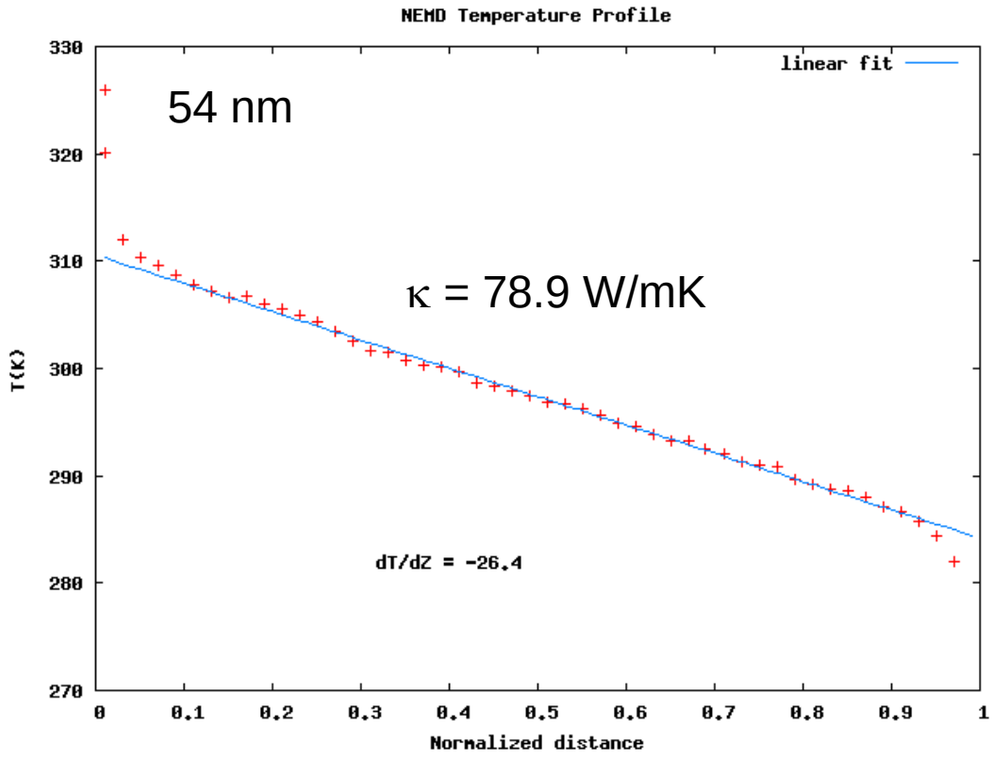
LAMMPS Younker, J. M. *in preparation*

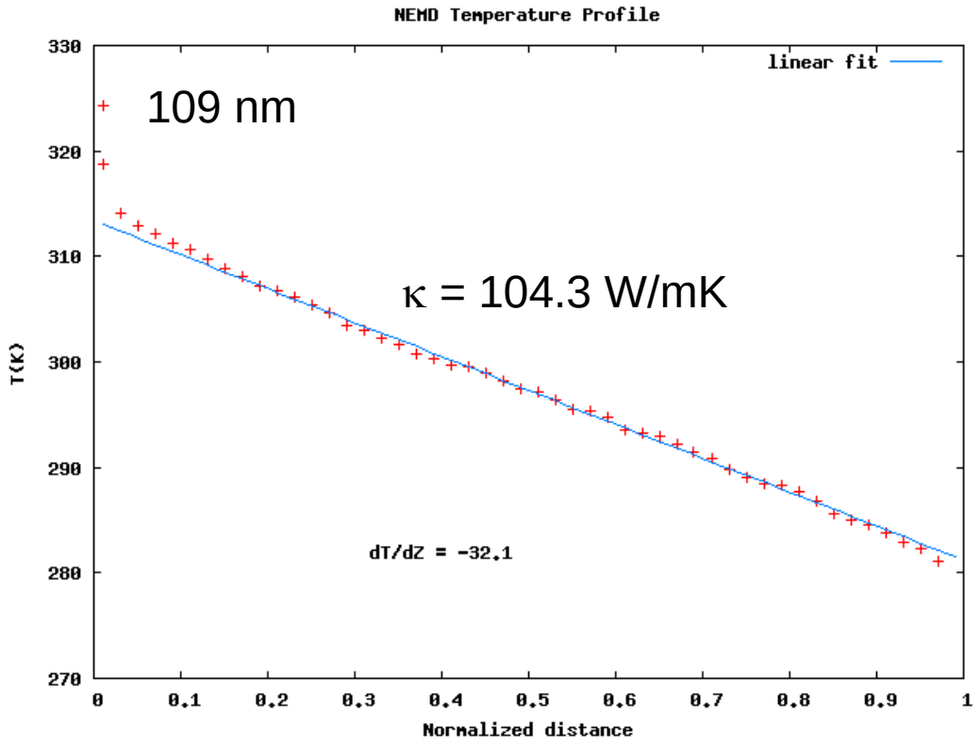
Phys. Rev. B **1994**, *50*, 2221-2226
Calphad **2007**, *31*, 95-104

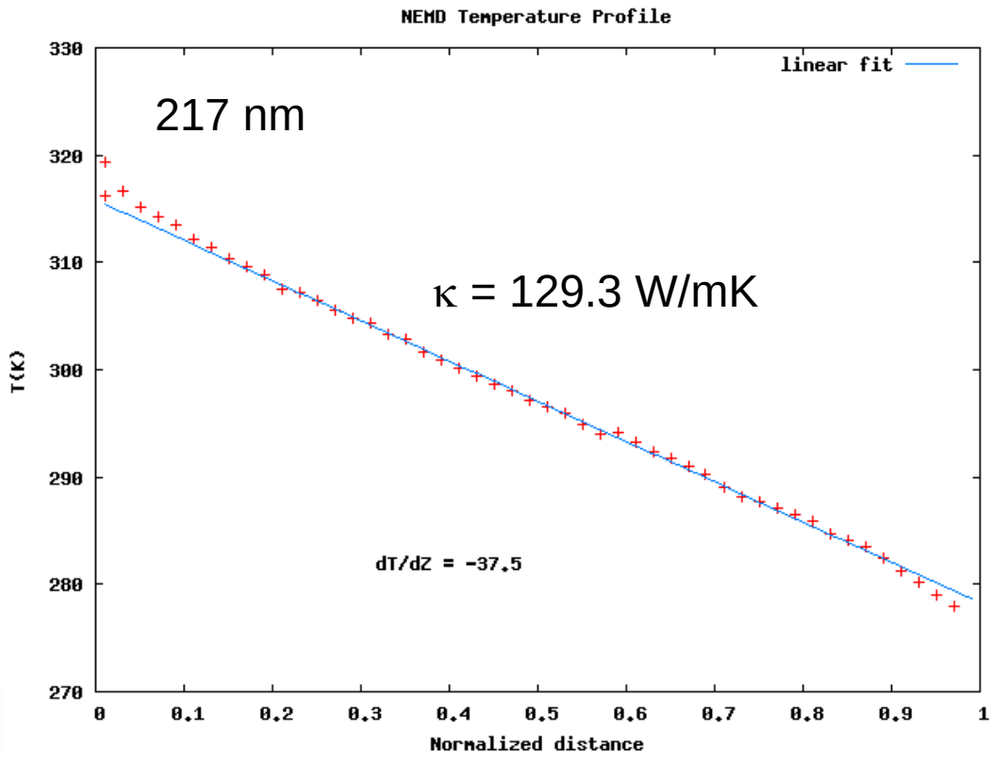
THERMAL INTERFACE MATERIALS

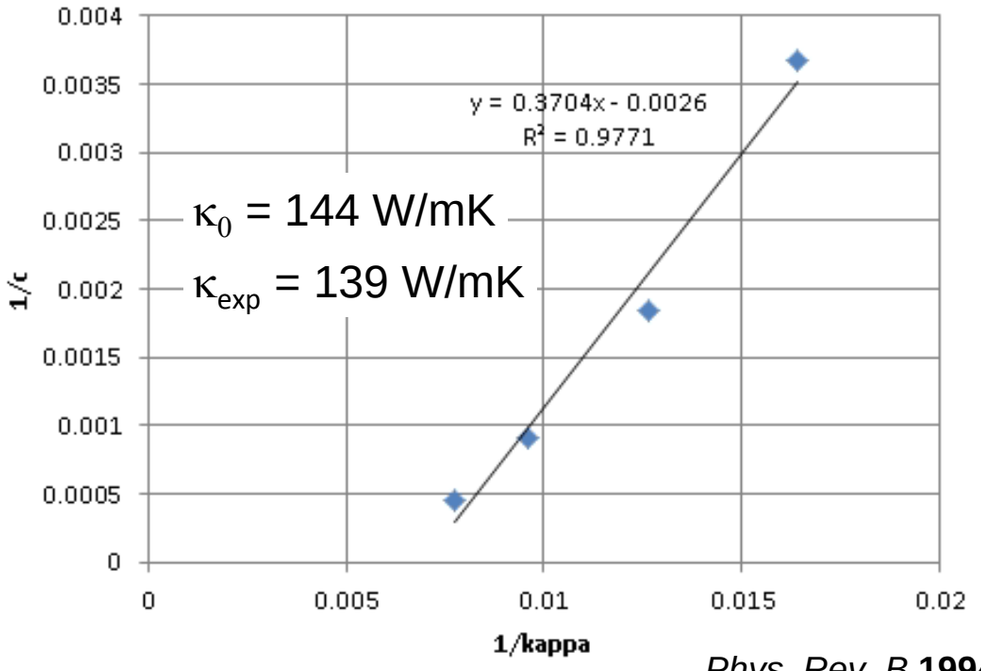
Bulk Silicon

Forcefield verification: Second Nearest Neighbor Modified Embedded Atom Potential (2NN-MEAM)







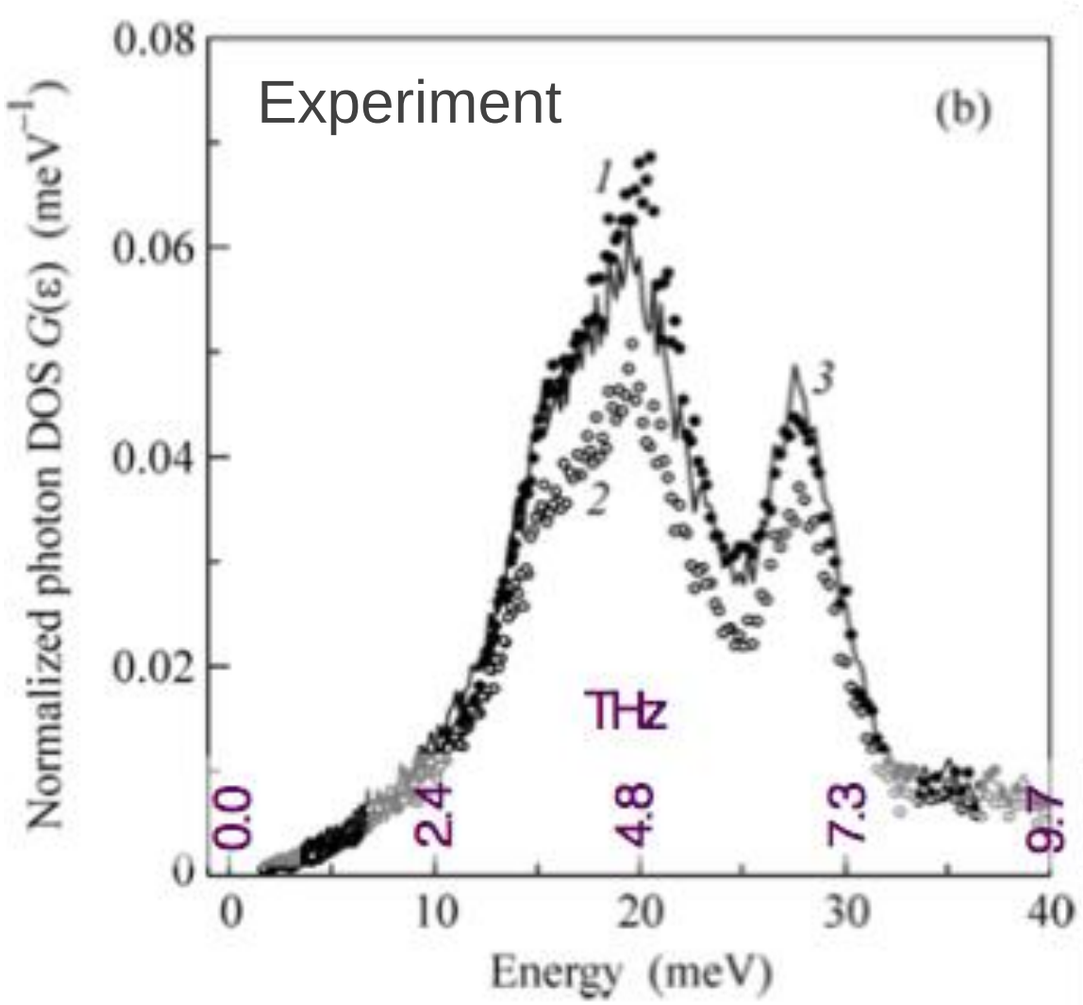


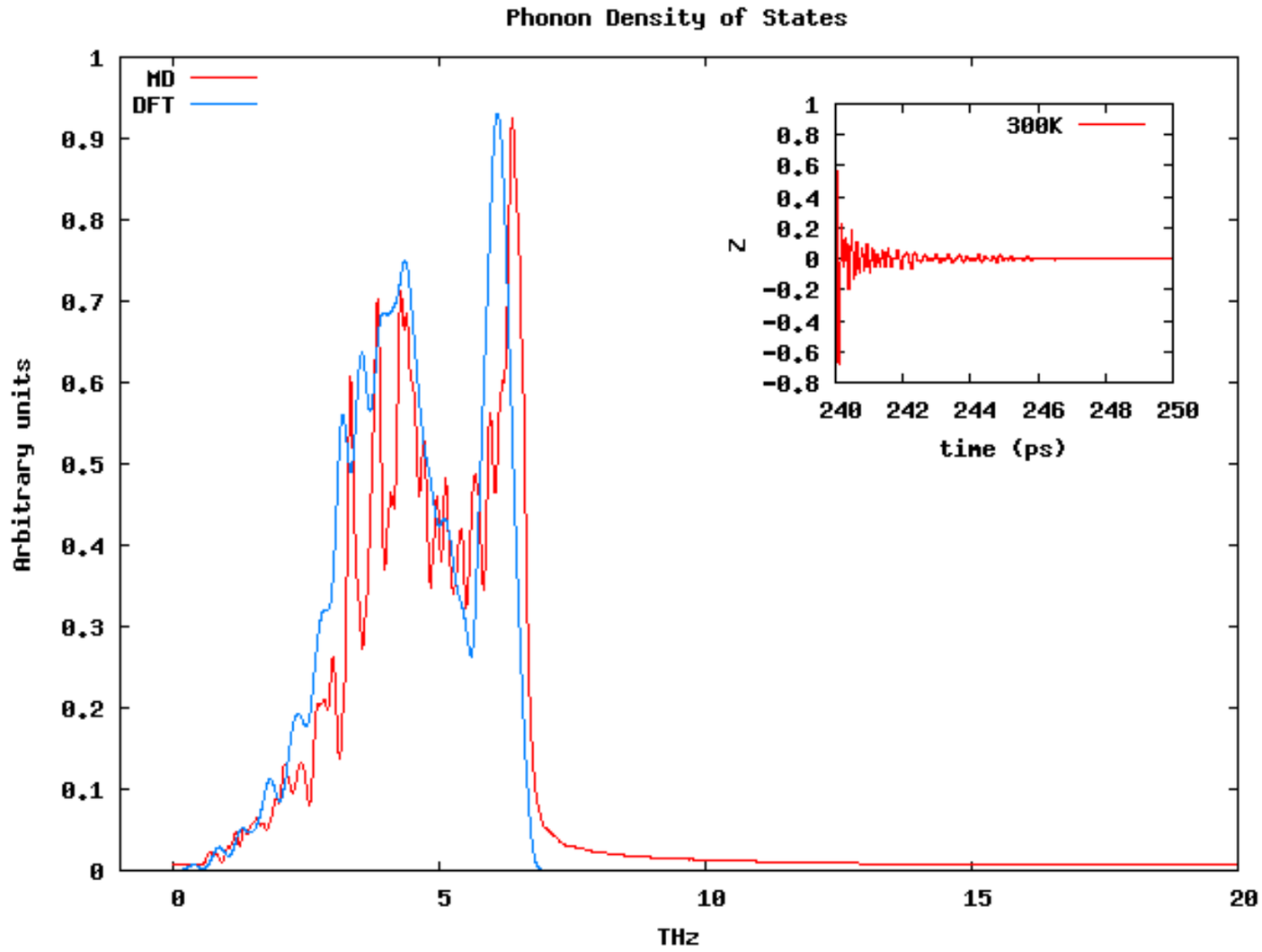
Phys. Rev. B **1994**, *50*, 2221-2226
Calphad **2007**, *31*, 95-104
Phys. Rev. B **2002**, *65*, 144306

THERMAL INTERFACE MATERIALS

Bulk Copper

Forcefield verification: Second Nearest Neighbor Modified Embedded Atom Potential (2NN-MEAM)





$$E = \sum_i \left[F_i(\overline{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} S_{ij} \phi_{ij}(R_{ij}) \right]$$

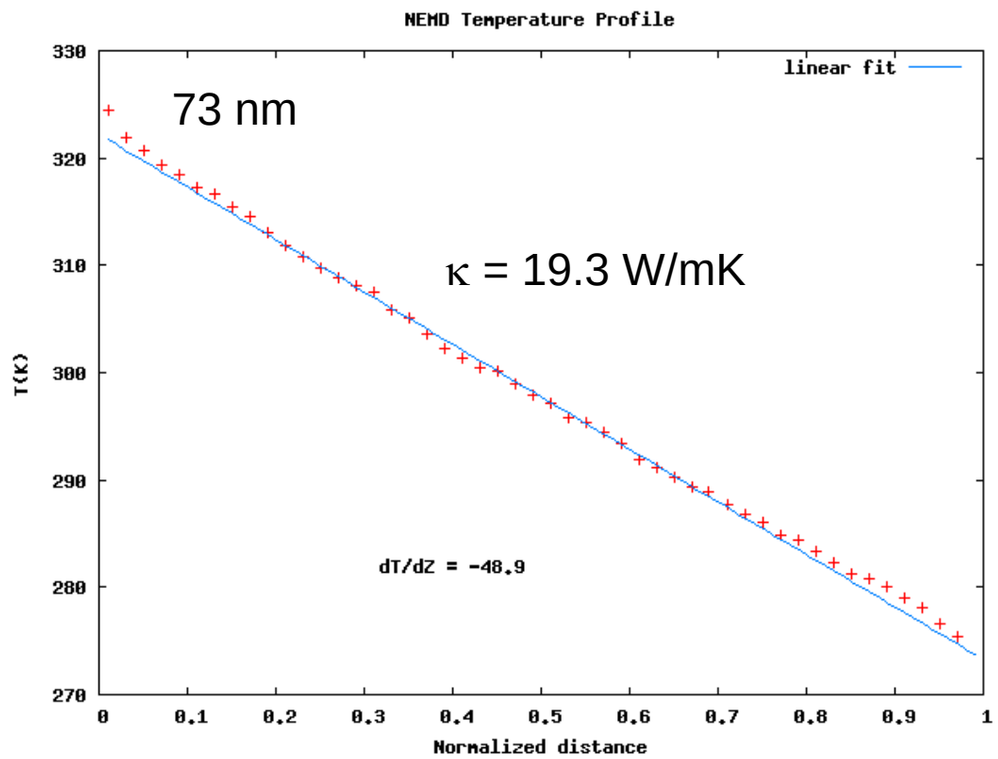
LAMMPS Younker, J. M. *in preparation*

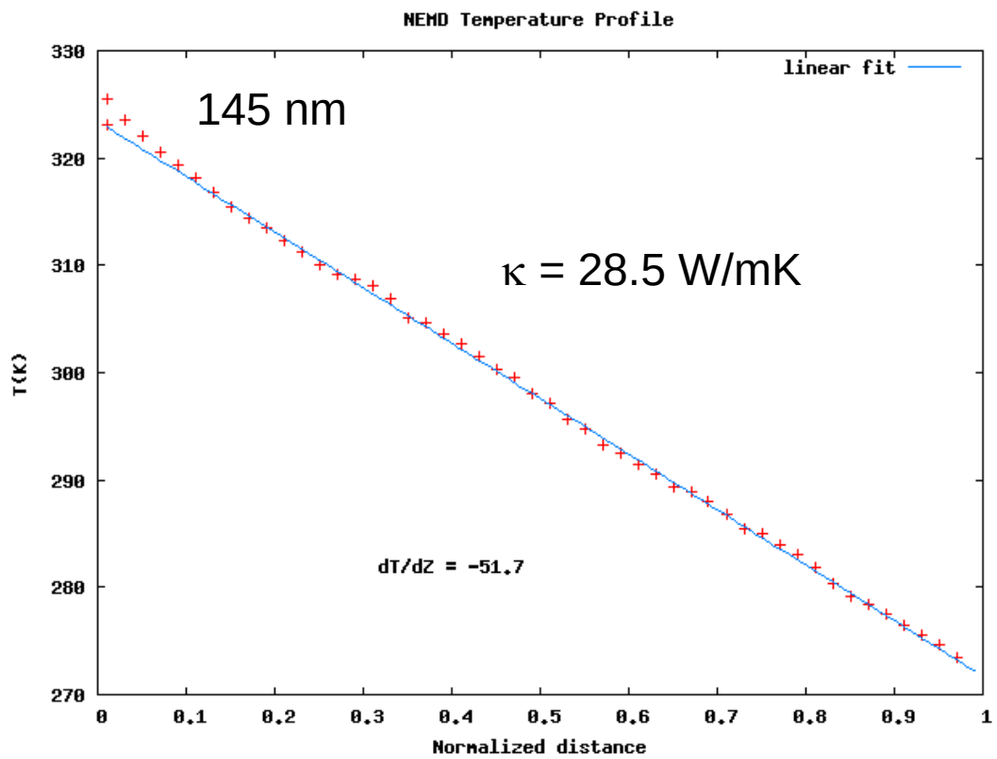
JETP Letters ***2010***, *92*, 238-243
Phys. Rev. B **2003**, *68*, 144112

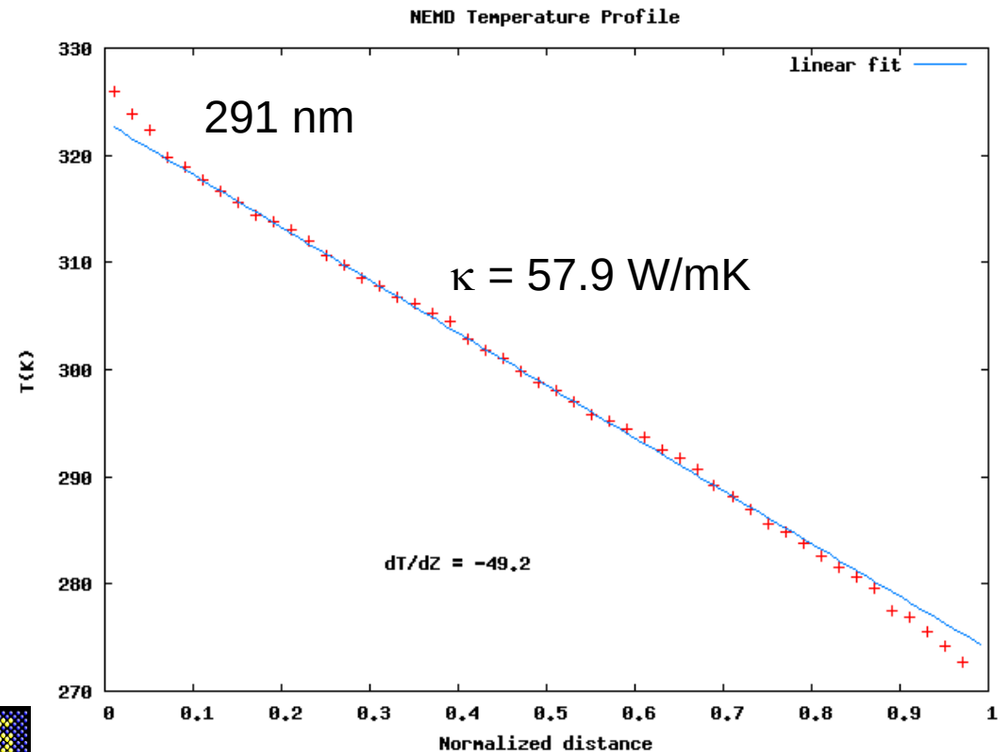
THERMAL INTERFACE MATERIALS

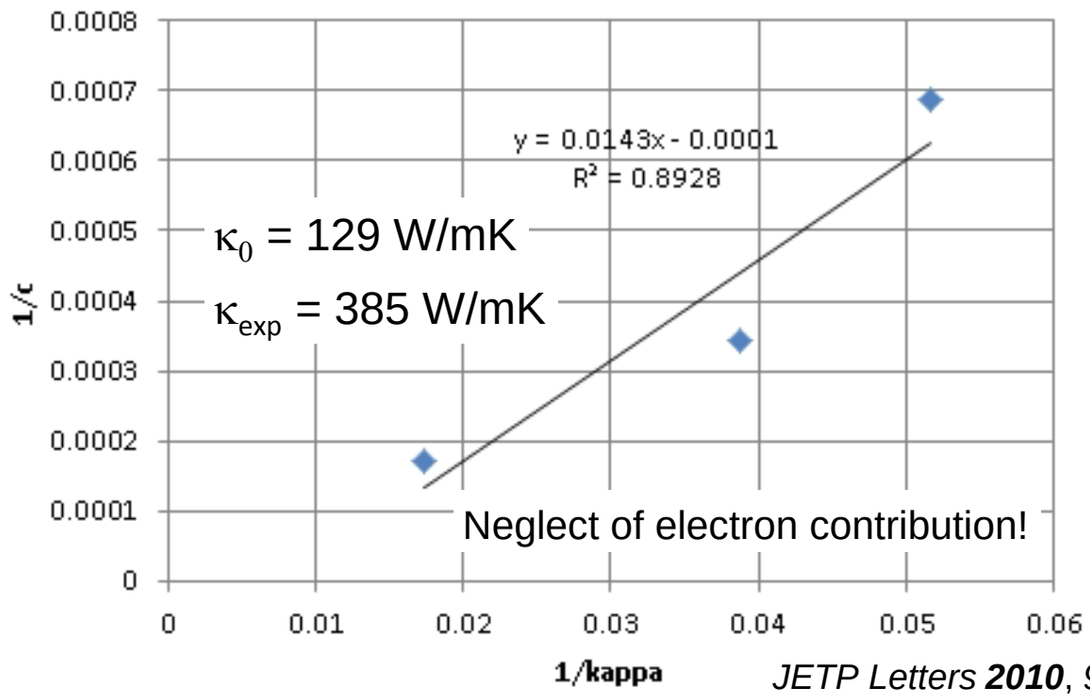
Bulk Copper

Forcefield verification: Second Nearest Neighbor Modified Embedded Atom Potential (2NN-MEAM)









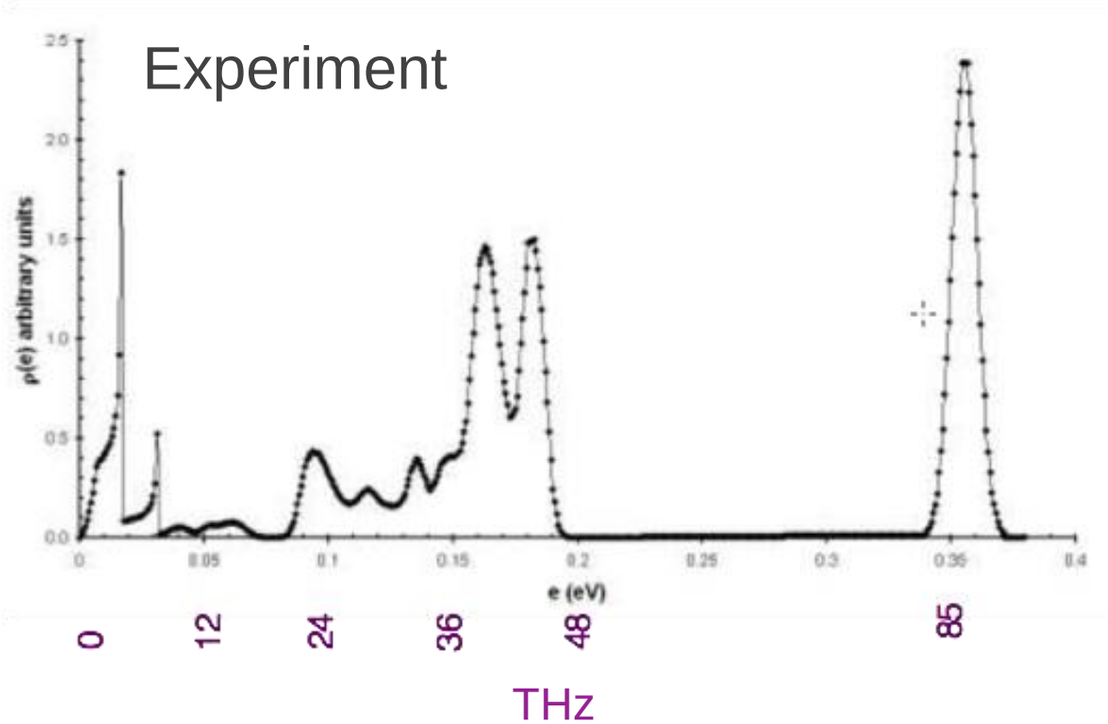
JETP Letters ***2010***, *92*, 238-243
Phys. Rev. B **2003**, *68*, 144112

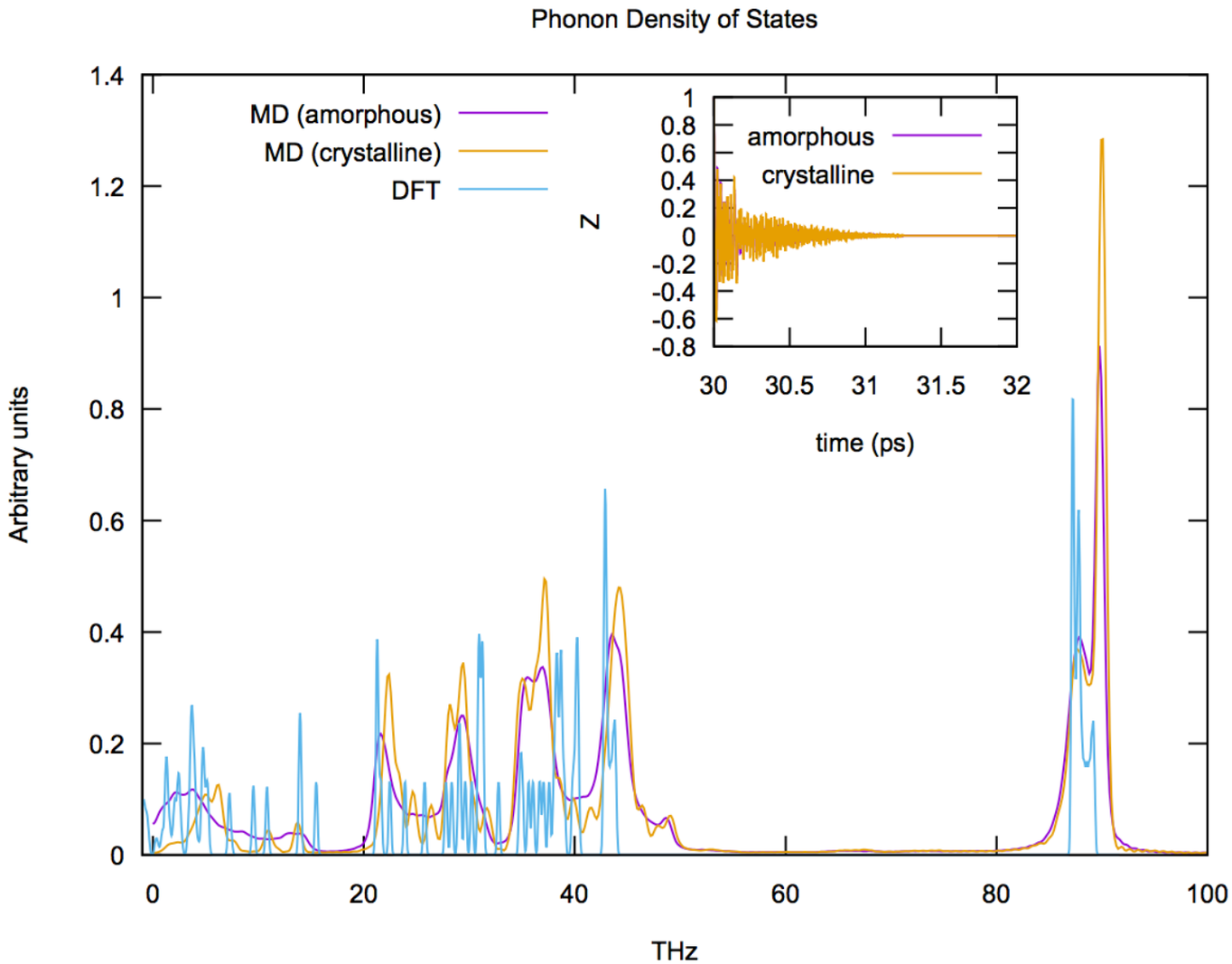
LAMMPS

THERMAL INTERFACE MATERIALS

Bulk amorphous and crystalline polyethylene

Forcefield verification: Consistent Valence Force Field (CVFF)





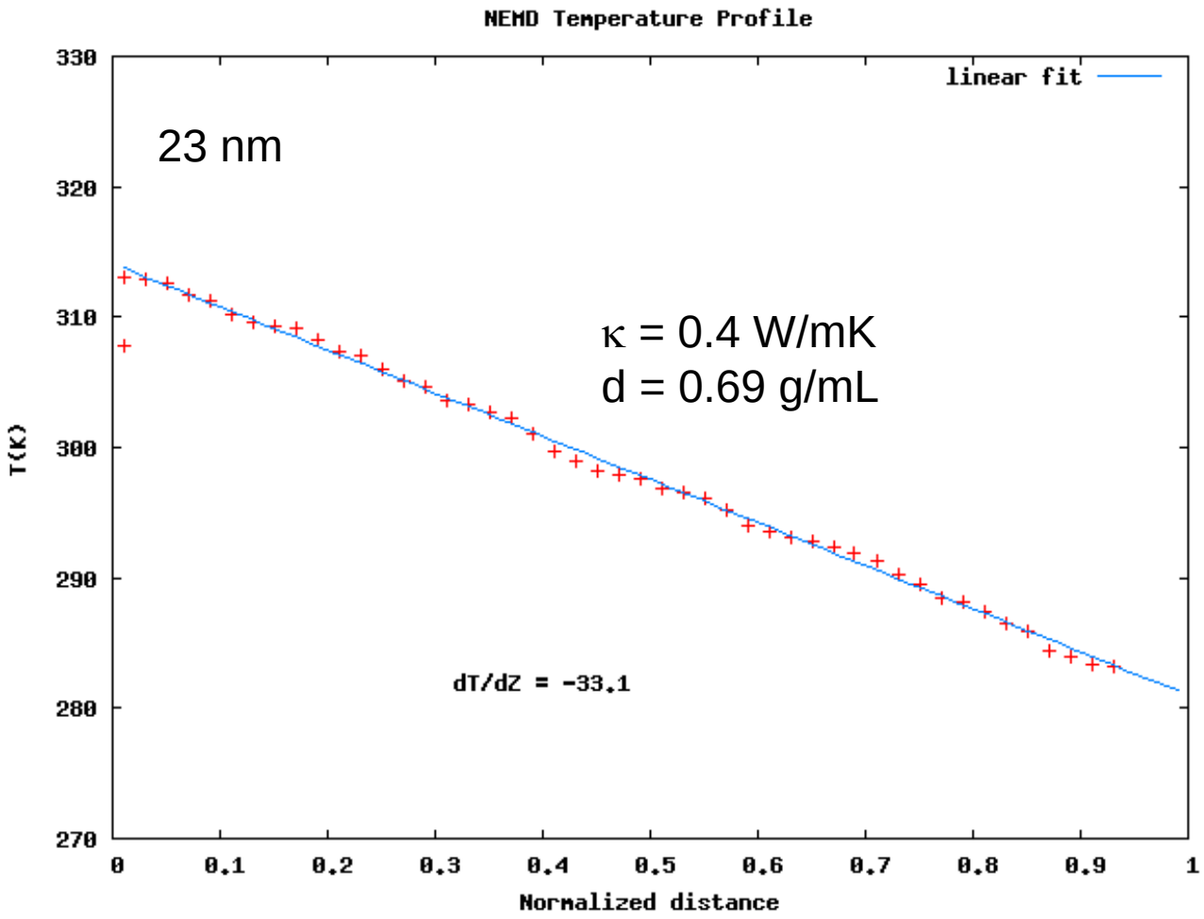
LAMMPS Younker, J. M. *in preparation*

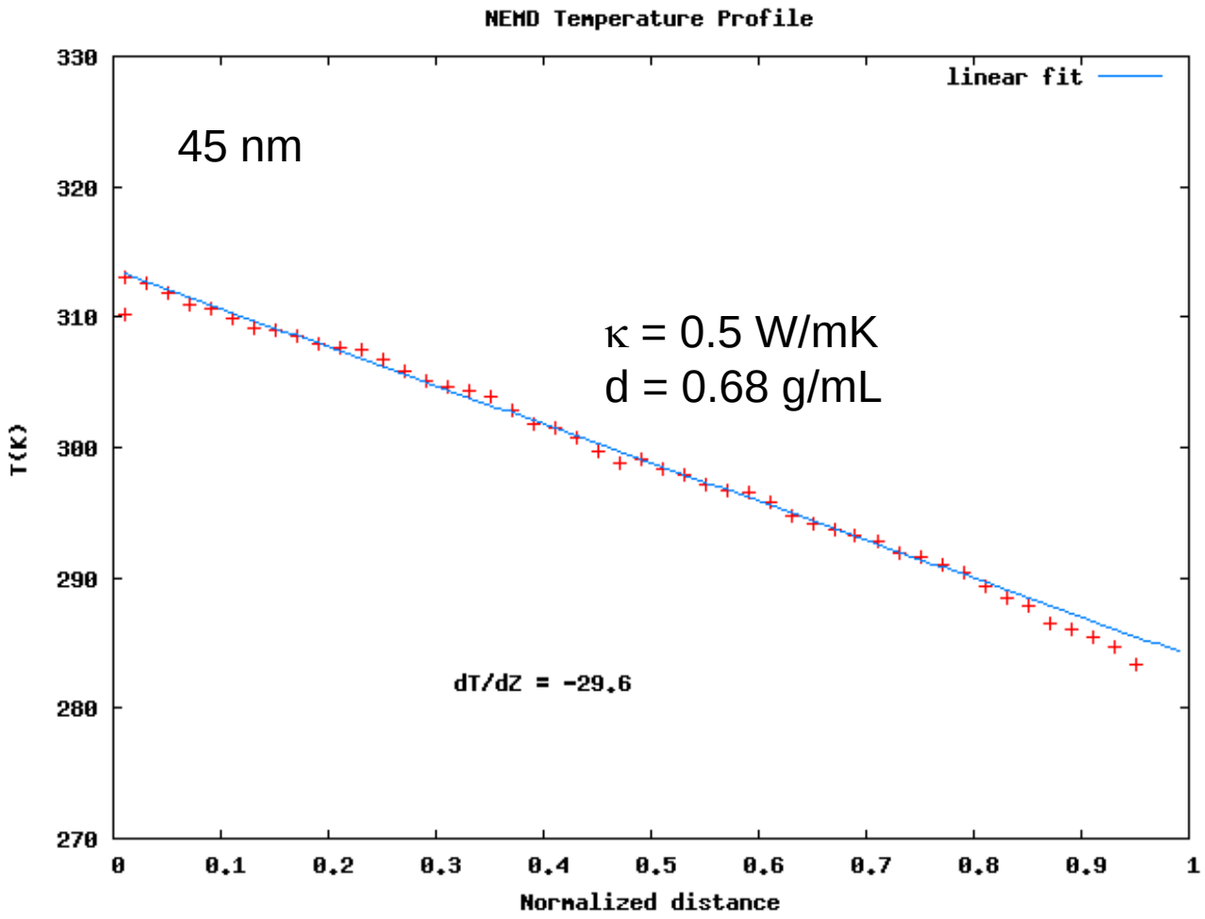
Nucl. Instrum. Meth. Phys. Res. A **2005**, *538*, 686-691
Pro. Struct. Func. Gen. **1988,** *4*, 1-47

THERMAL INTERFACE MATERIALS

Bulk amorphous polyethylene

Forcefield verification: Consistent Valence Force Field (CVFF)





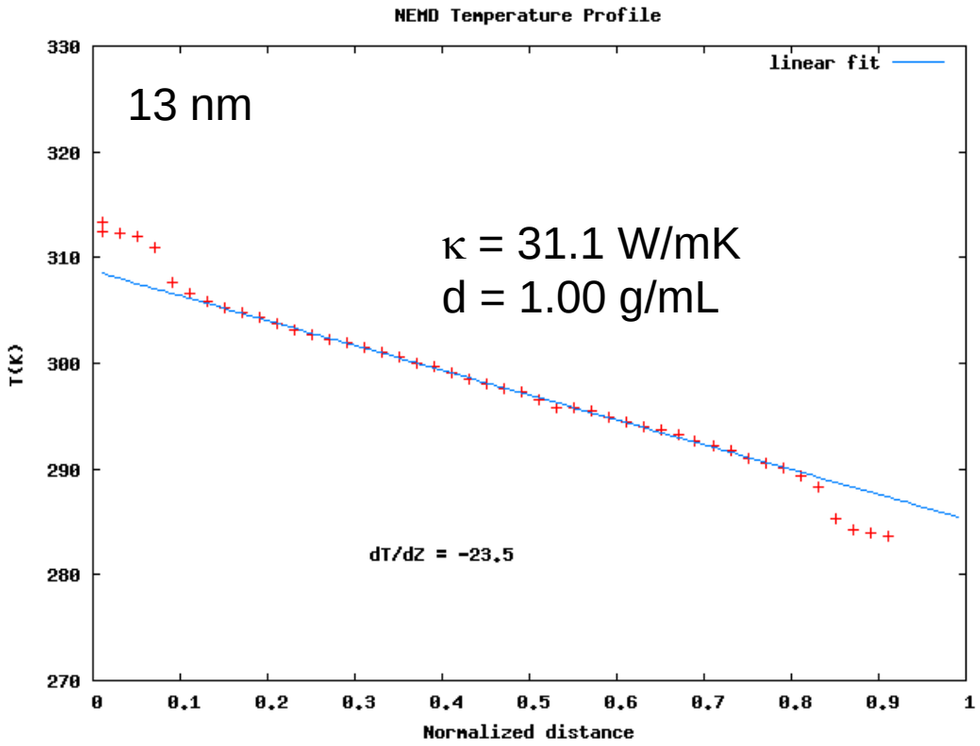
κ_{exp} = 0.5 W/mK
d_{exp} = ~0.9 g/mL

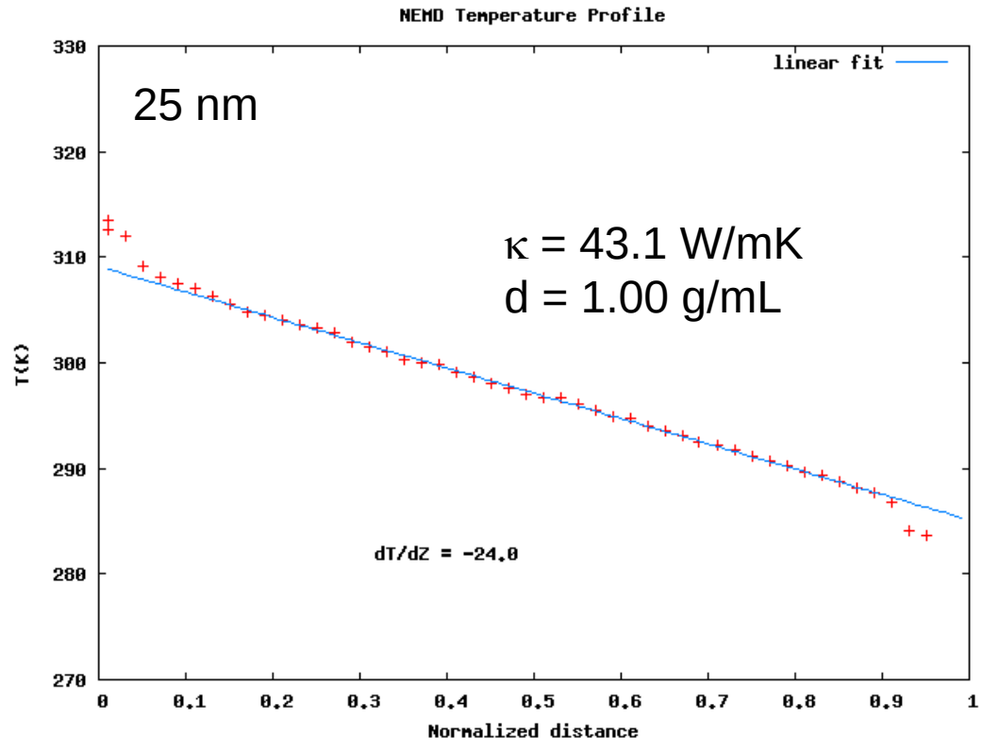
LAMMPS Younker, J. M. *in preparation*

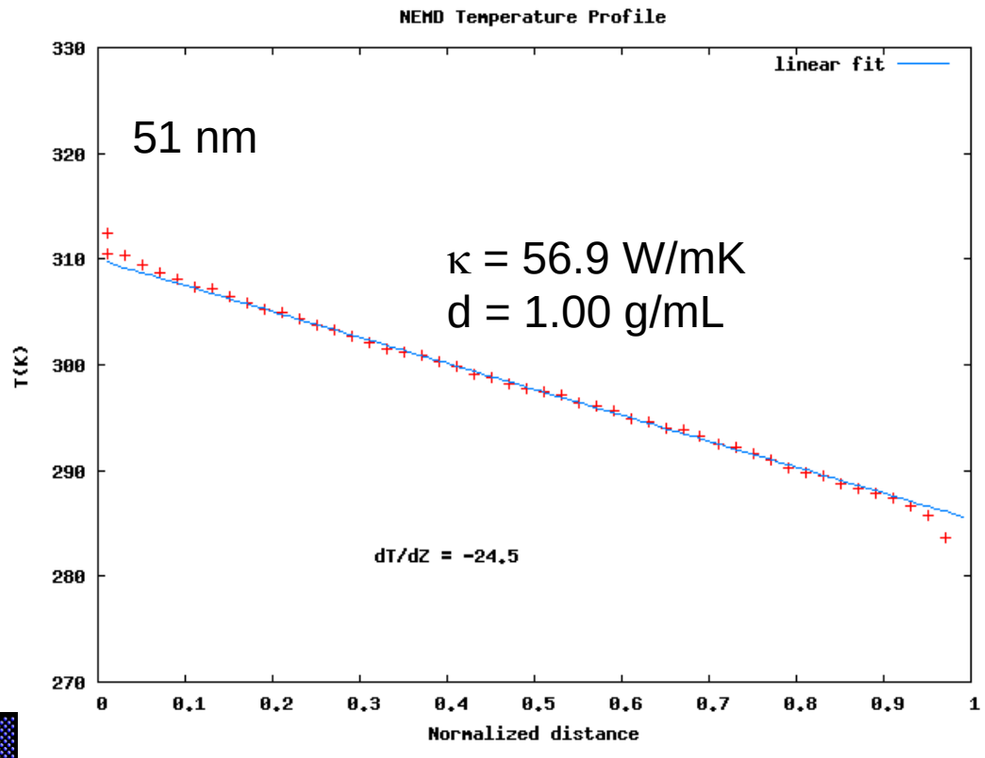
Nucl. Instrum. Meth. Phys. Res. A **2005**, *538*, 686-691
Pro. Struct. Func. Gen. **1988,** *4*, 1-47

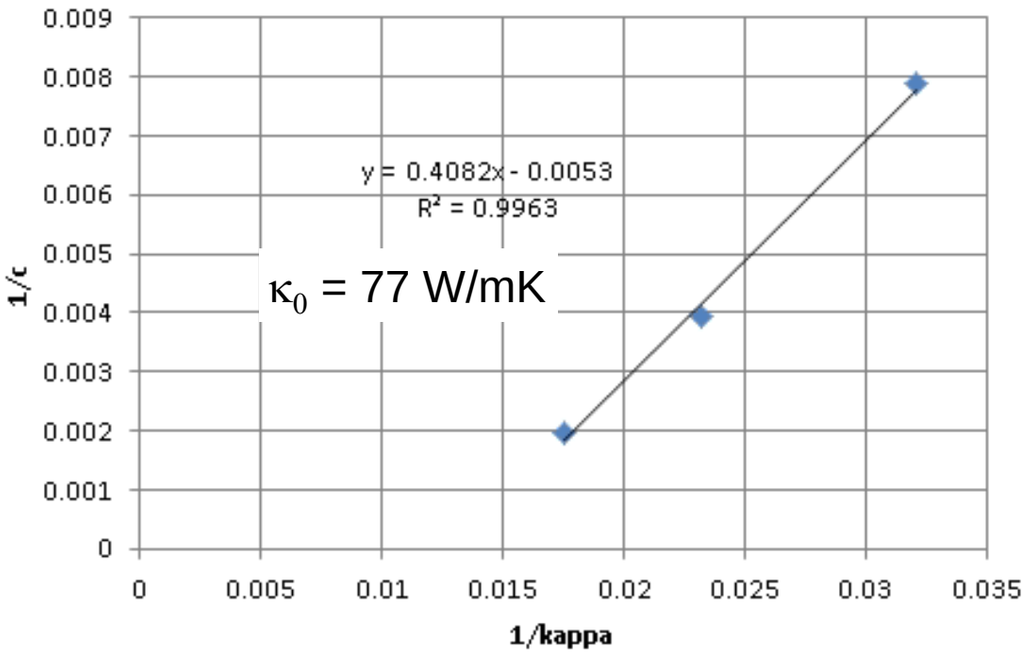
THERMAL INTERFACE MATERIALS

- Bulk crystalline polyethylene
- Forcefield verification: Consistent Valence Force Field (CVFF)









Nucl. Instrum. Meth. Phys. Res. A **2005**, *538*, 686-691
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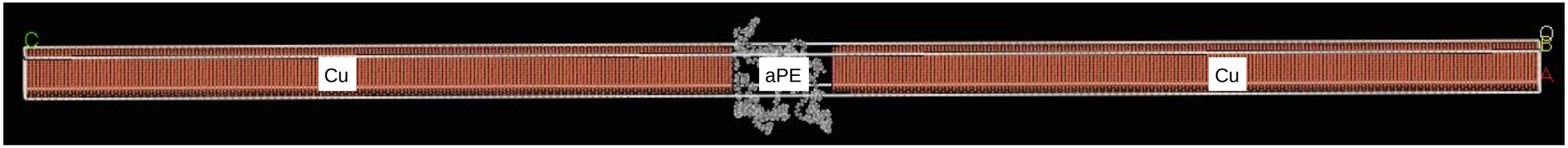
THERMAL INTERFACE MATERIALS



$$V(r) = 4\chi\varepsilon\,[(\sigma/r)^{12} - (\sigma/r)^{6}]$$

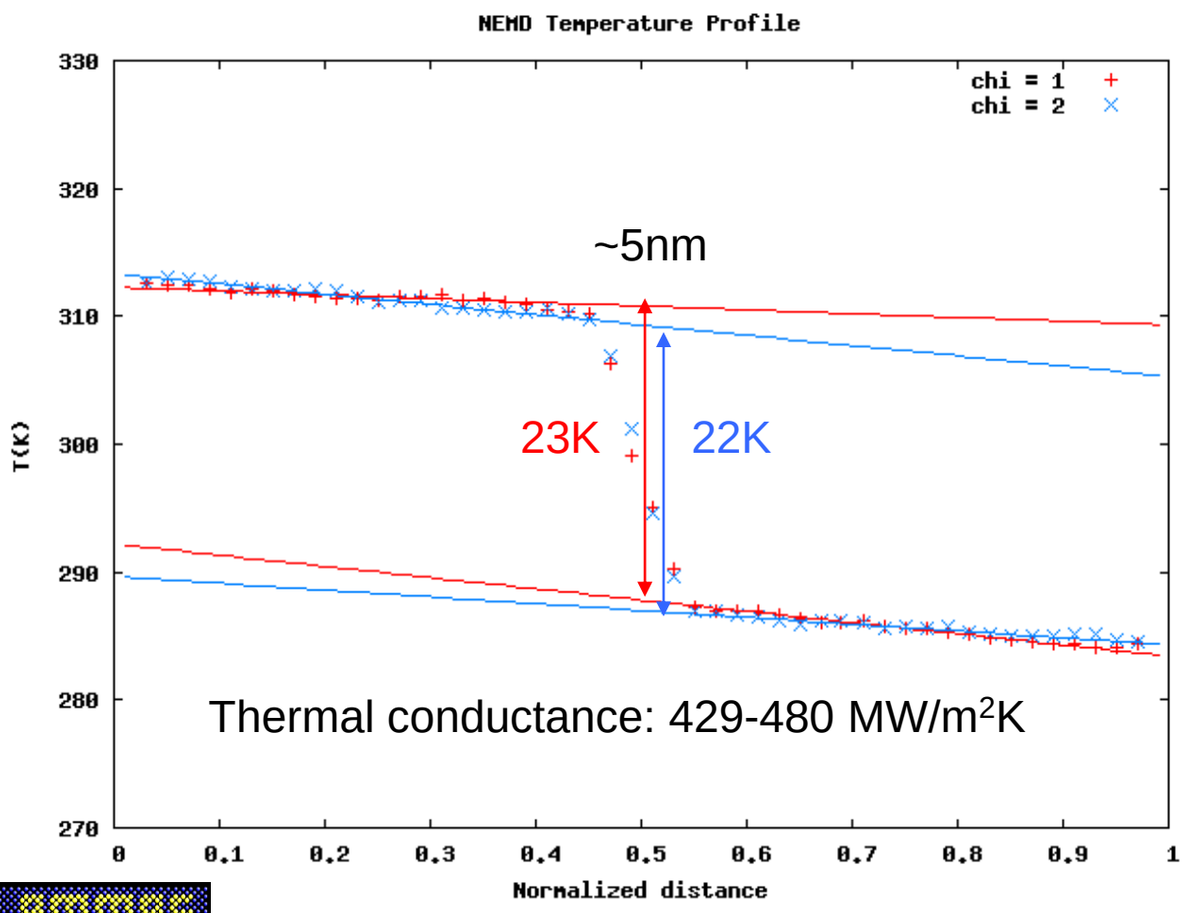
$\varepsilon_{Cu} = 409$ meV
$\sigma_{Cu} = 2.34$ Angstroms
$\varepsilon_{C} = 1.7$ meV
$\sigma_{C} = 3.88$ Angstroms
$\varepsilon_{H} = 1.6$ meV
$\sigma_{H} = 2.45$ Angstroms

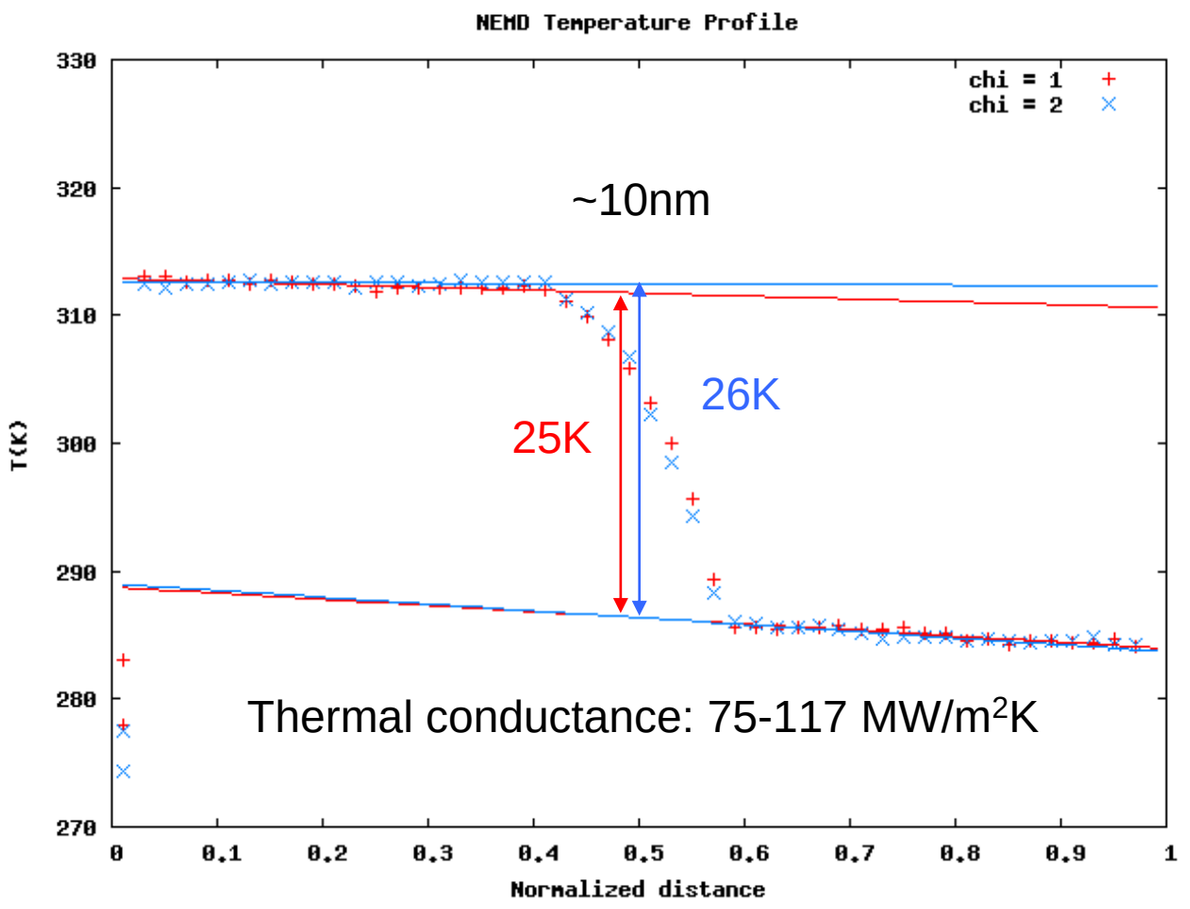
$\varepsilon_{ij} = \mathrm{sqrt}(\varepsilon_{ii}\varepsilon_{jj})$

$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$

$\varepsilon_{Cu/C} = 26.3$ meV
$\sigma_{Cu/C} = 3.11$ Angstroms
$\varepsilon_{Cu/H} = 26.0$ meV
$\sigma_{Cu/H} = 2.39$ Angstroms

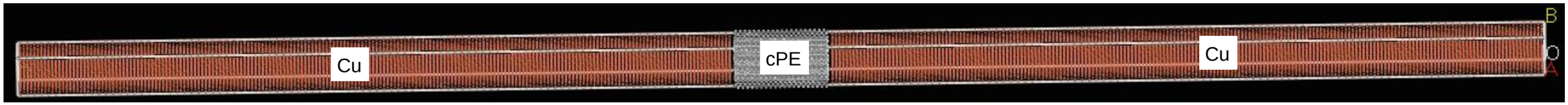
$$\Omega_K\ (\mathrm{mK/W}) = \Delta T_{interface}\,[(\kappa_{Cu}\nabla T_{Cu}^{L})^{-1} + 2(\kappa_{PE}\nabla T_{PE})^{-1} + (\kappa_{Cu}\nabla T_{Cu}^{R})^{-1}$$





LAMMPS

THERMAL INTERFACE MATERIALS



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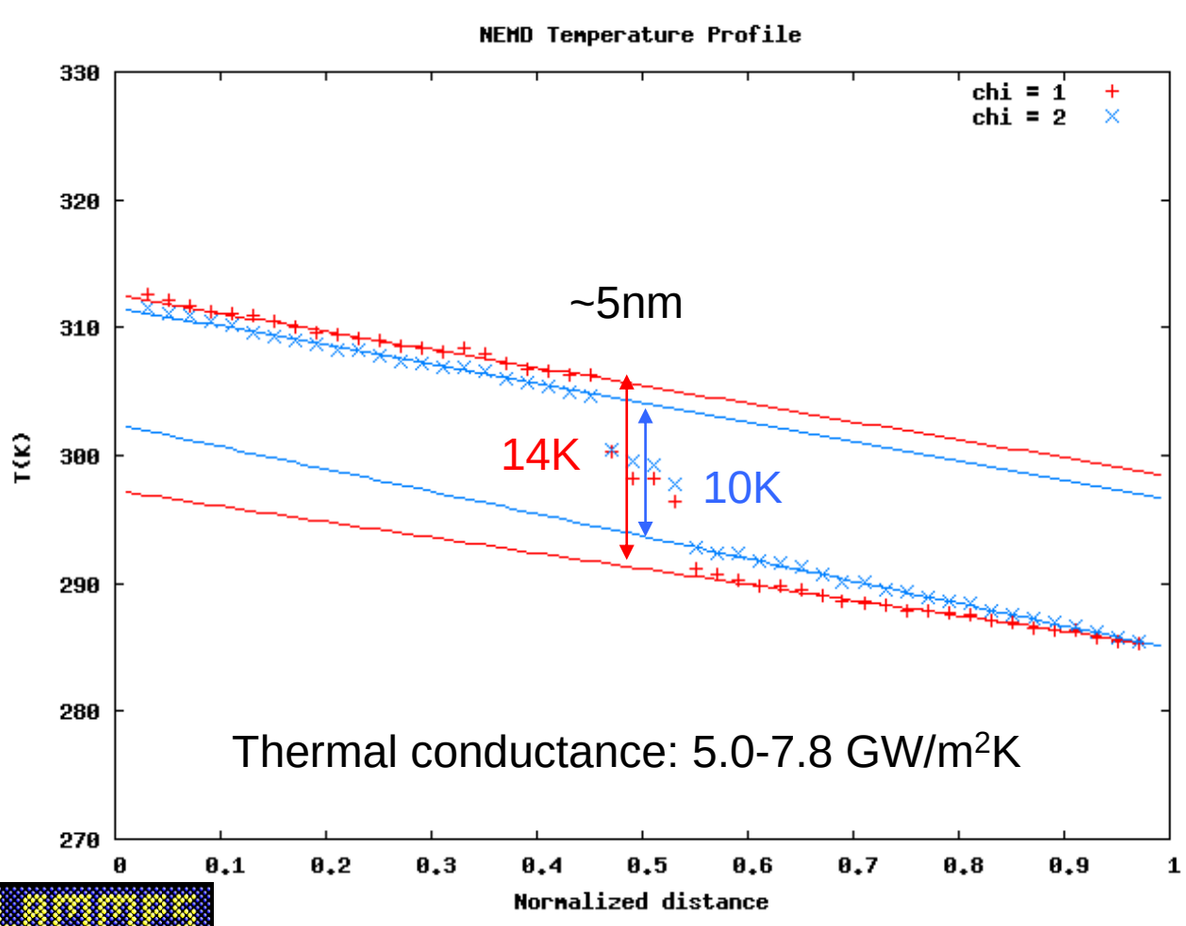
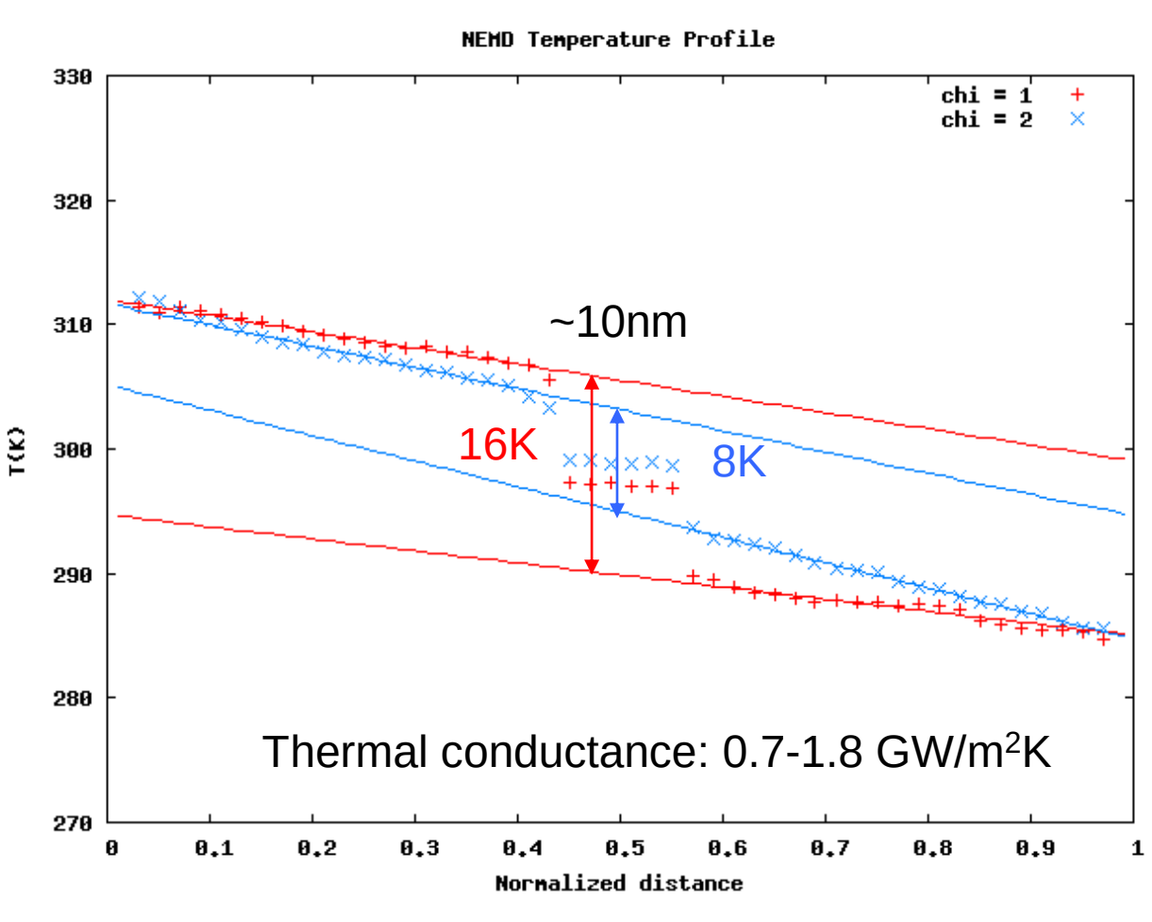
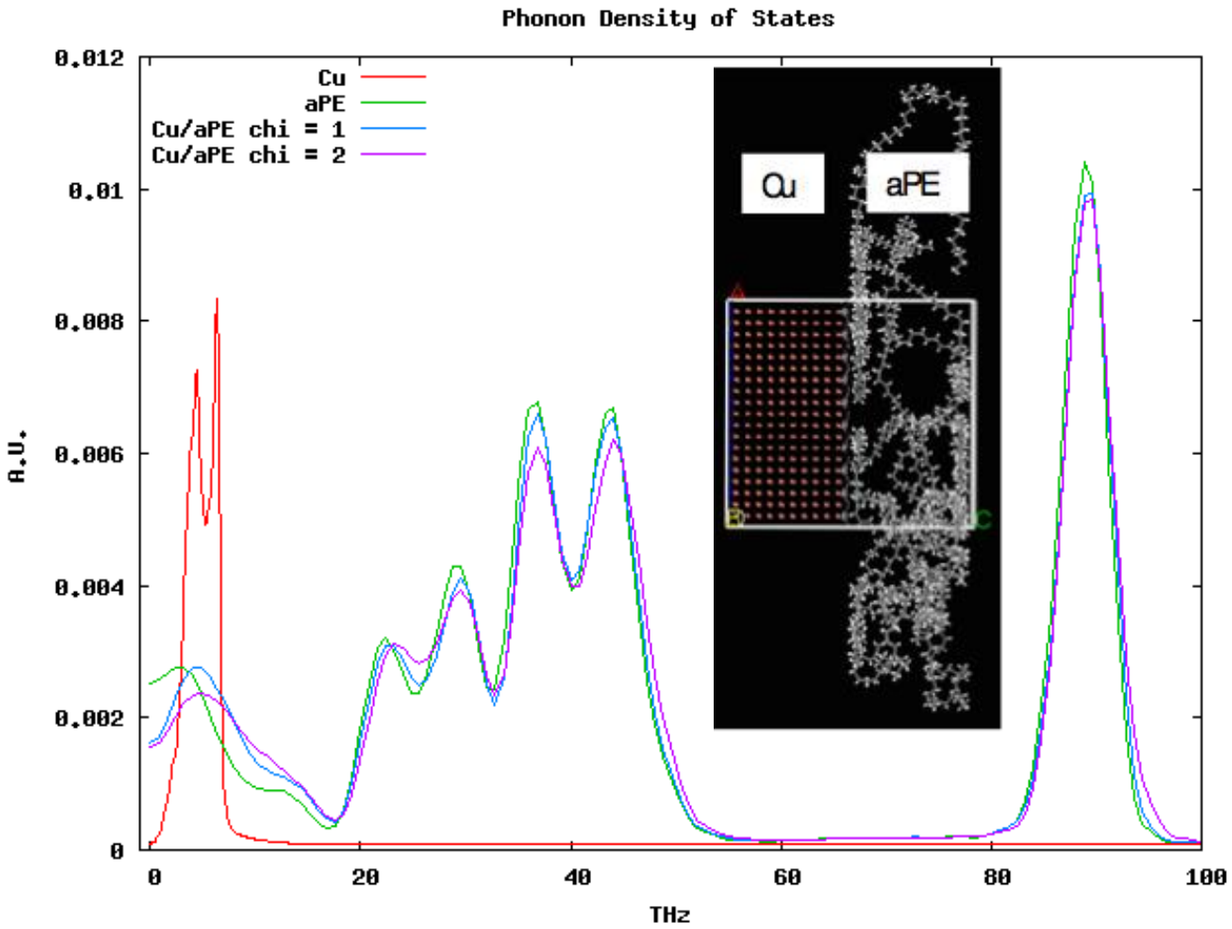


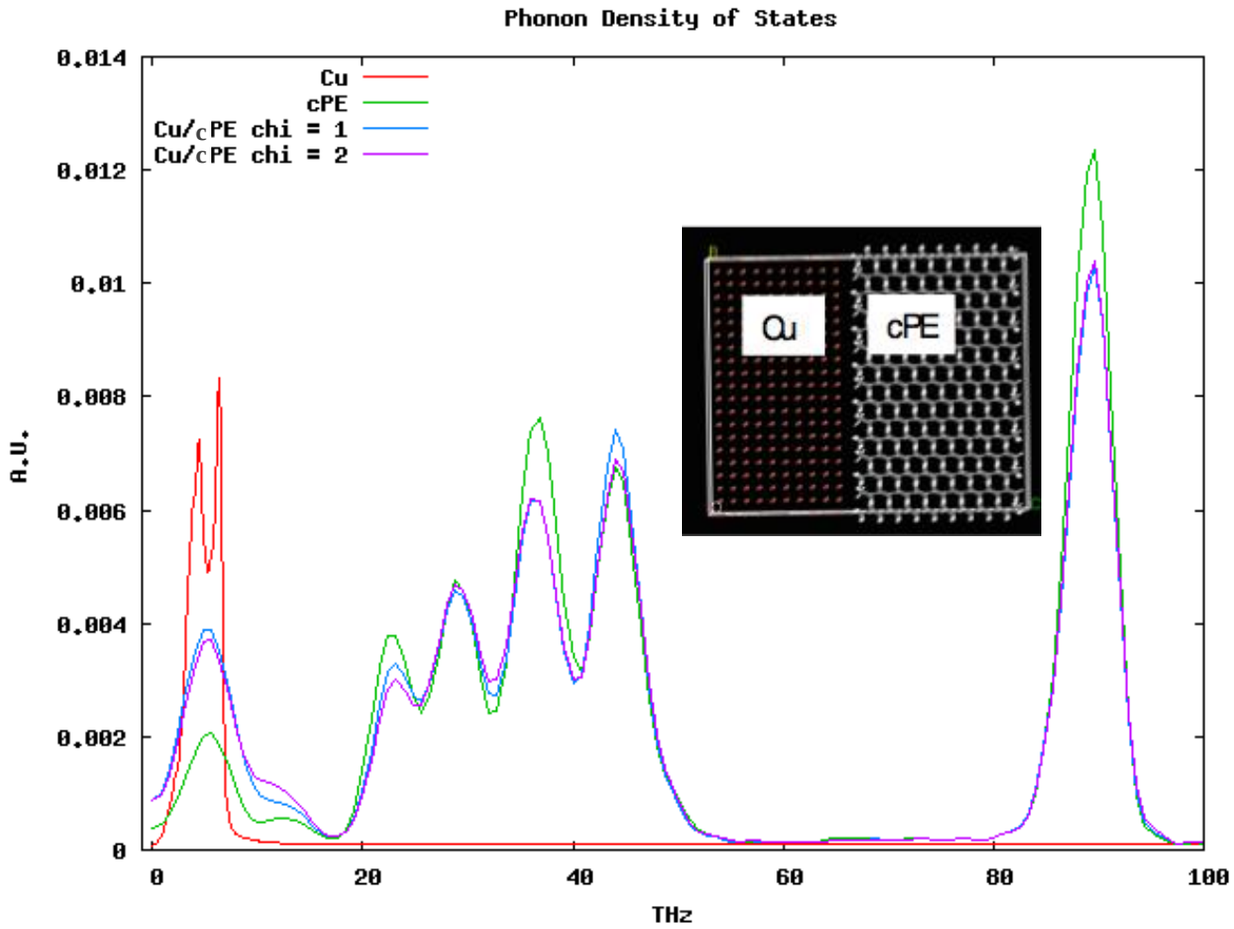


LAMMPS

THERMAL INTERFACE MATERIALS

Hypothesis: The overlap of the acoustic modes (< 20 THz) is directly correlated with thermal conductance



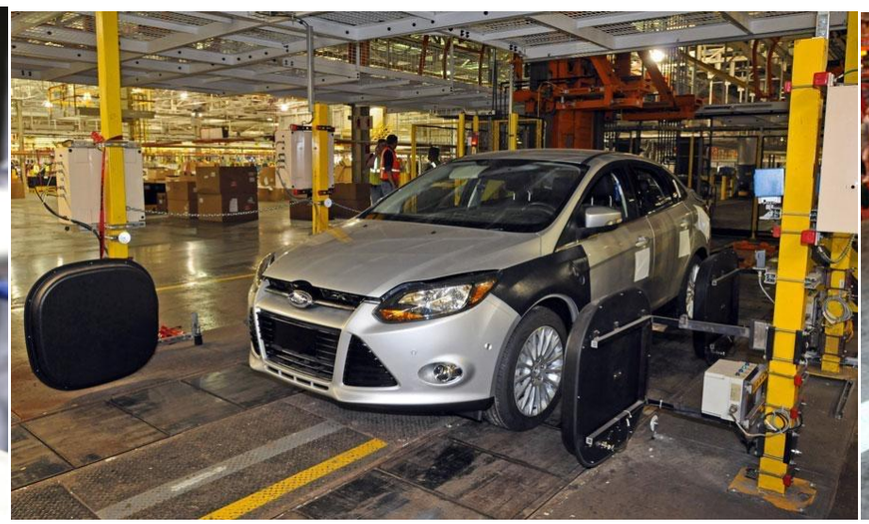


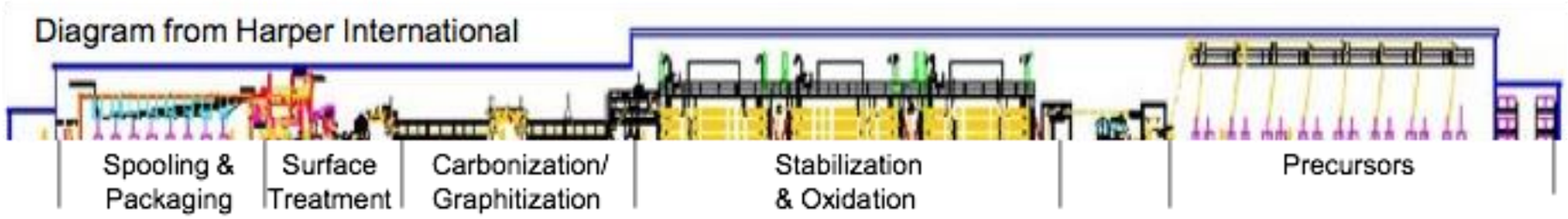
LAMMPS Younker, J. M. *in preparation*

CARBON FIBER: ALTERNATIVE PRECURSORS

Replace “most” steel components of automobiles with carbon fiber

- 10X stronger than steel with 1/4 the weight
- Reduce vehicle weight by 40% and improve fuel efficiency by 30%





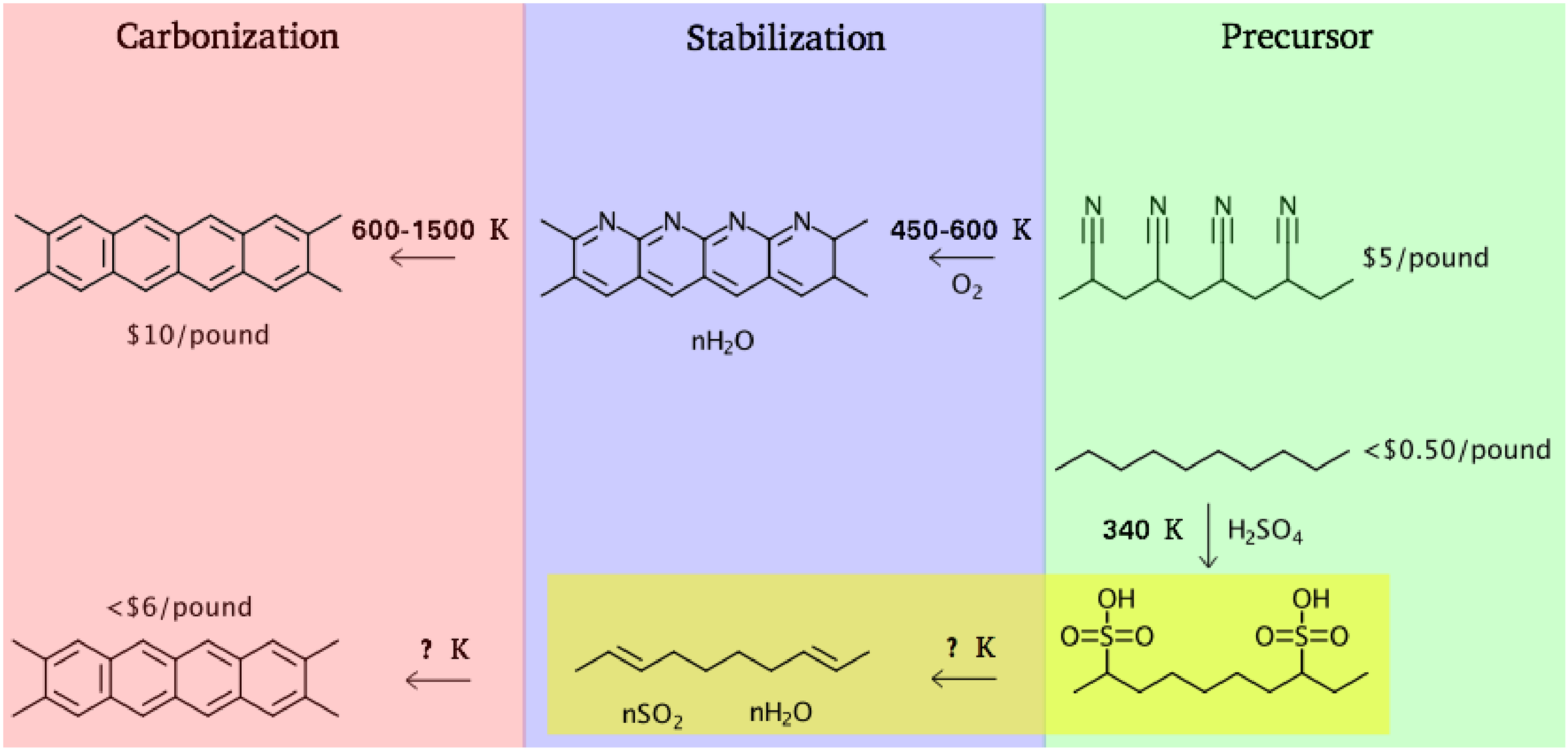
Precursor type	Yield (%)		$/lb (as-spun)	Melt-spinnable	Best achieved properties		Problem
	Theoretical	Practical			Strength (KSI)	Modulus (MSI)	
Conventional PAN	68	45-50	>4	No	500-900	30-65	High cost
Textile PAN*	~ 68	45-50	1-3	No	300-400+	30	High variation in properties
Lignin*	62-67	40-50	0.40 - 0.70	Yes	160	15	Fiber handling, low strength & slow stabilization step
Polyolefin**	86	65-80	0.35 - 0.5	Yes	380	30	Slow stabilization (sulfonation) step

“Ford--Dow Partnership Linked to Carbon Fiber Research at ORNL,” *Innovations in Manufacturing*, DOE, 2012.

“Green Car Congress," October 12, 2012.

Diagram courtesy of Harper International, Lancaster, NY. Table courtesy of Amit Naskar, ORNL.

CARBON FIBER: ALTERNATIVE PRECURSORS

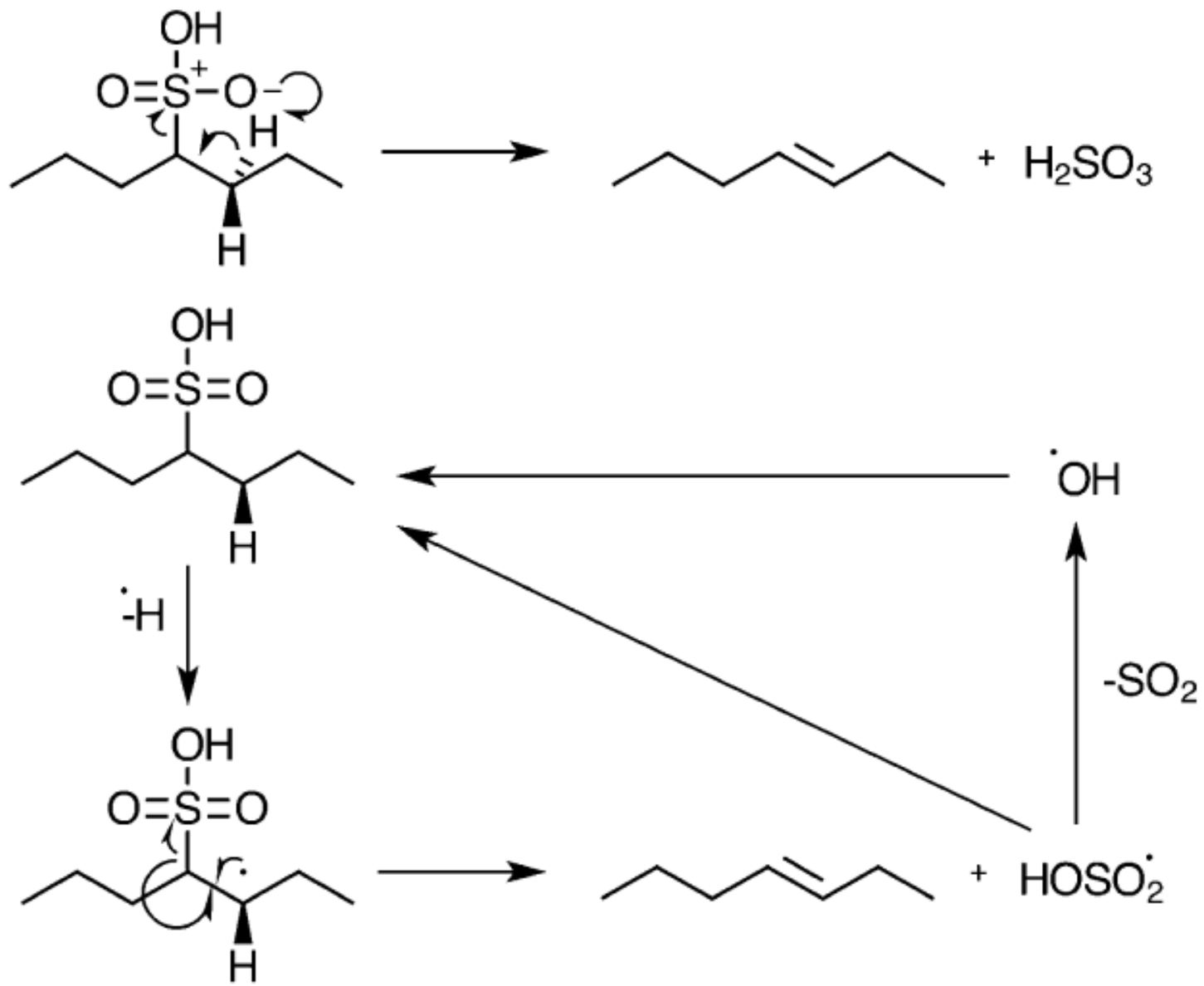


Younker *et al. J. Am. Chem. Soc.*, **2013**, *135*, 6130–6141

CARBON FIBER: ALTERNATIVE PRECURSORS

$$k(t) = \kappa(T)\frac{k_B T}{h}\frac{Q_{TS}(T)}{Q_A(T)}e^{-\Delta E/RT}$$

Radical chain reaction Internal elimination



Δ***E***: zero-point corrected activation barrier
Q: partition functions
κ: Wigner tunneling correction

Anharmonic effects incorporated for low frequency modes up to 110 cm^{-1} (Python scripted)

Second-order rate constants calculated assuming thermodynamic control: $k_i' = k_i K_{eq}$

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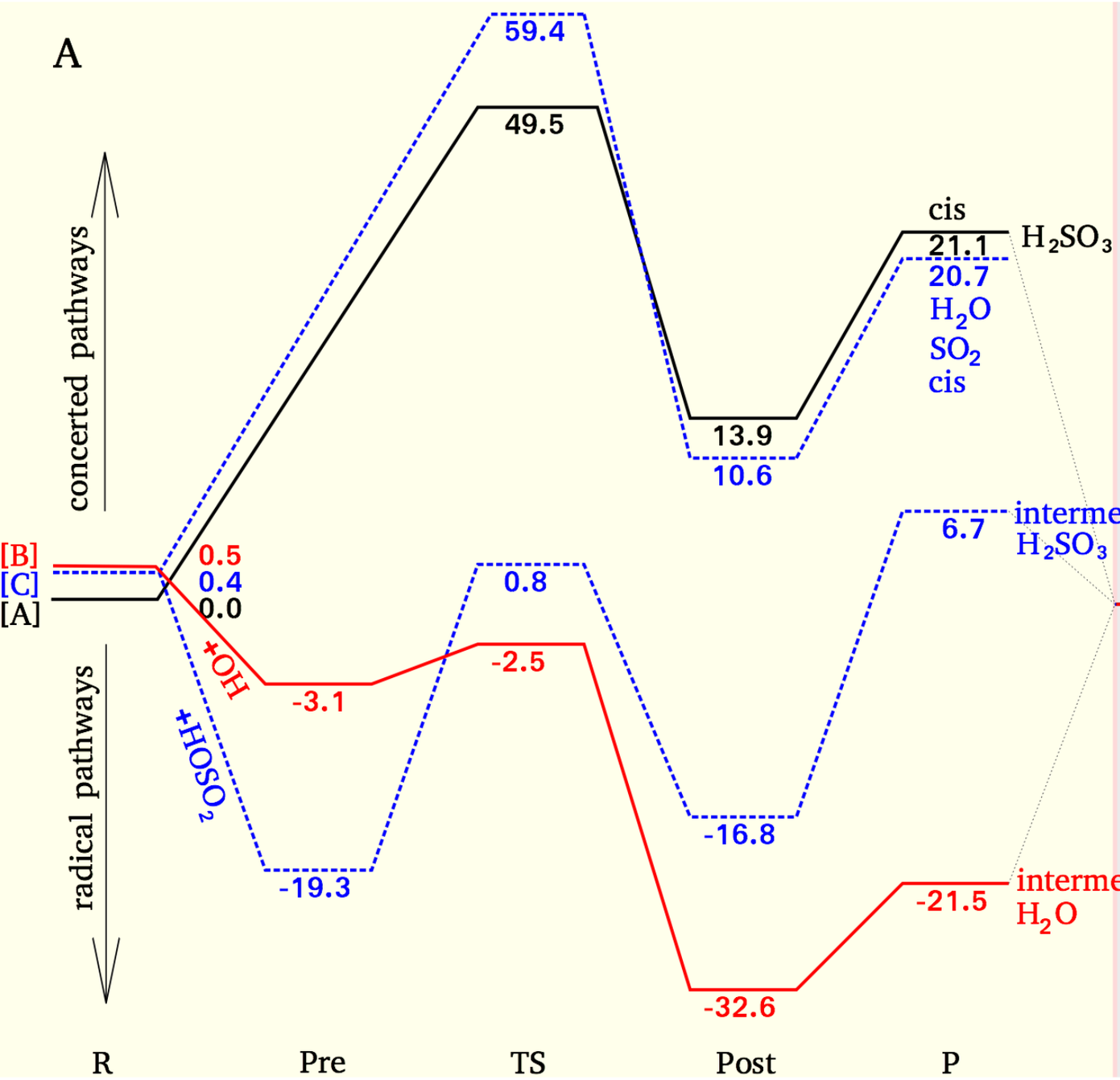
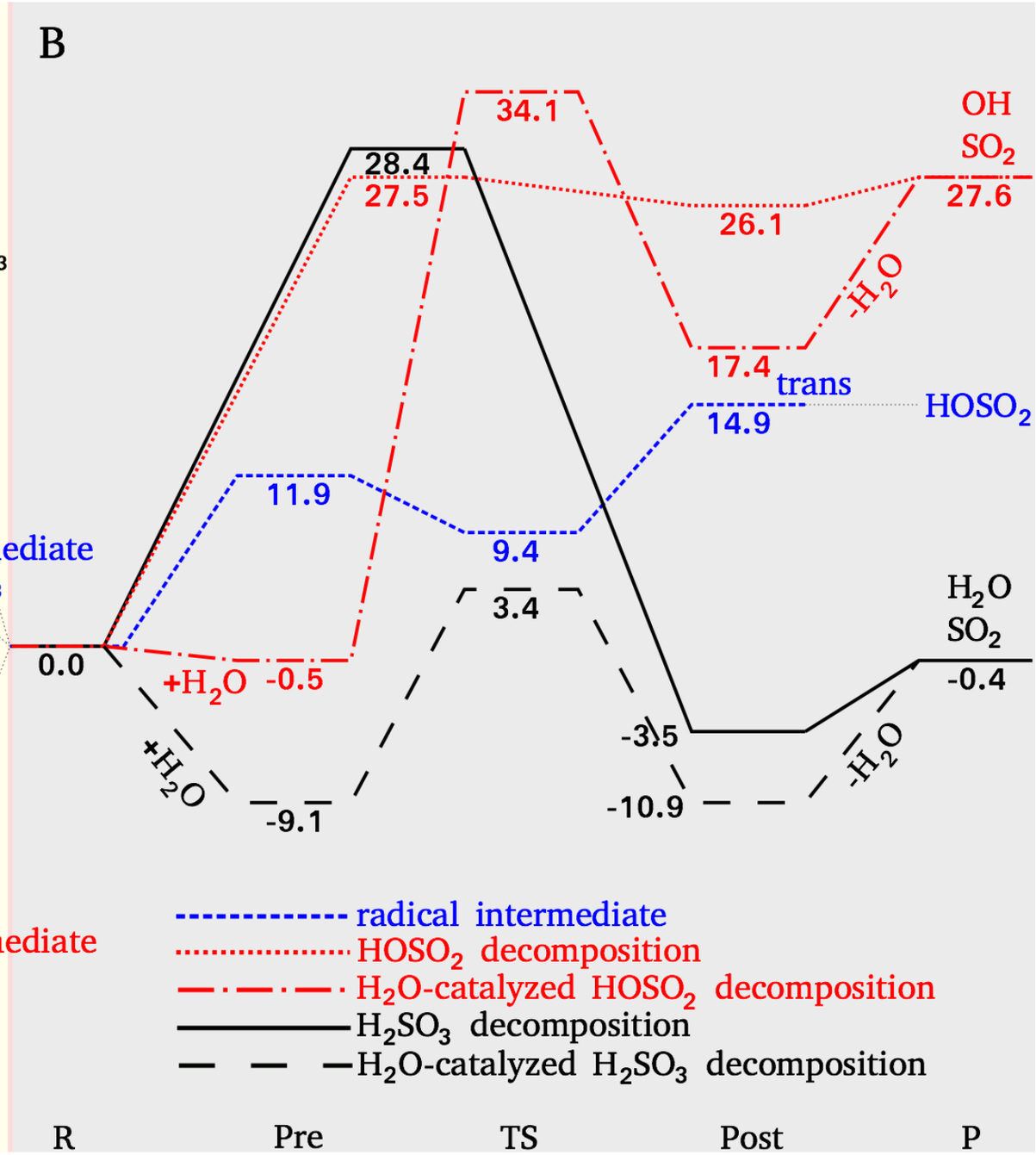
CARBON FIBER: ALTERNATIVE PRECURSORS

Calculating rate constants according to Transition State Theory





NWCHEM
HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

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CARBON FIBER: ALTERNATIVE PRECURSORS

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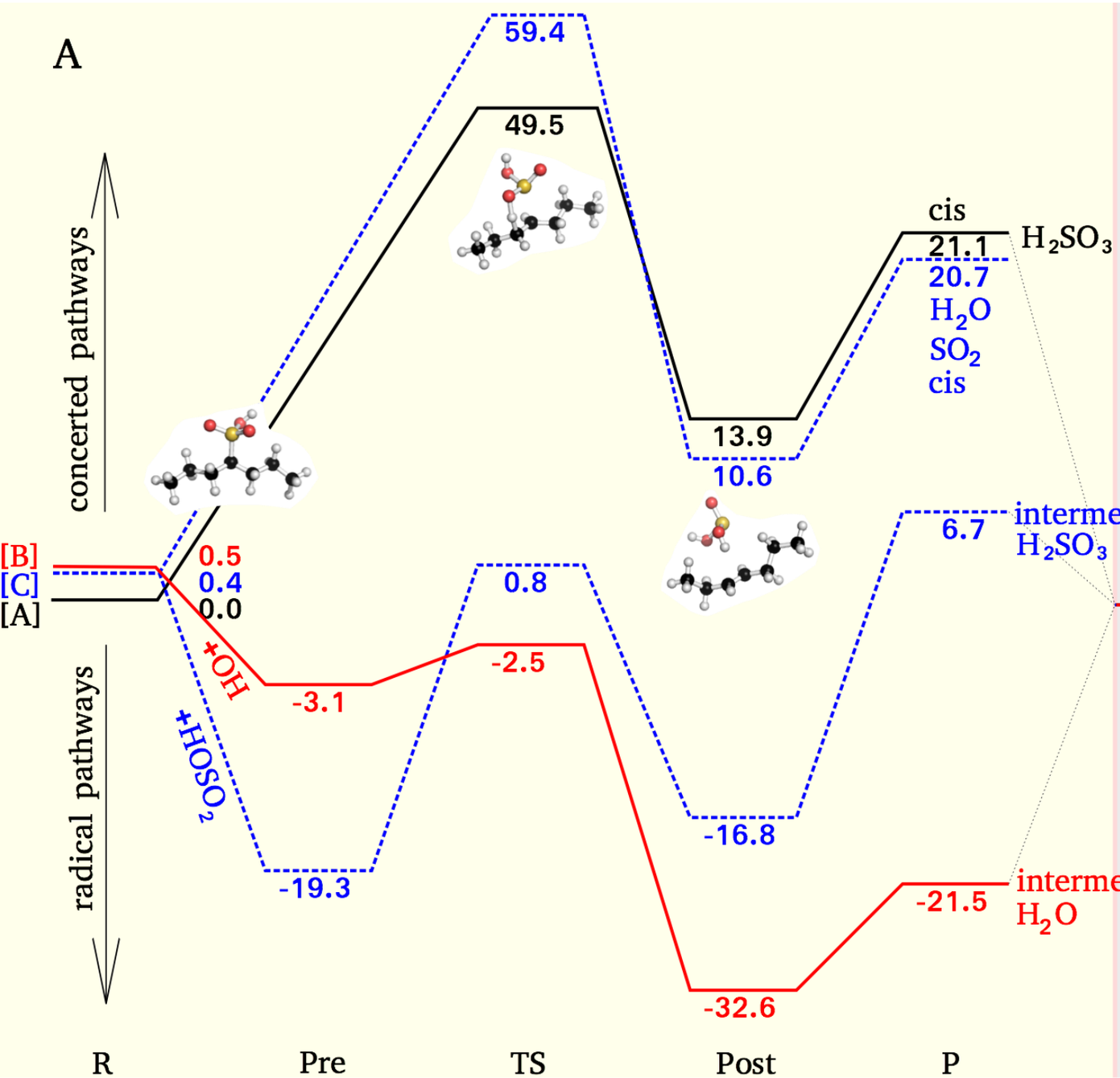

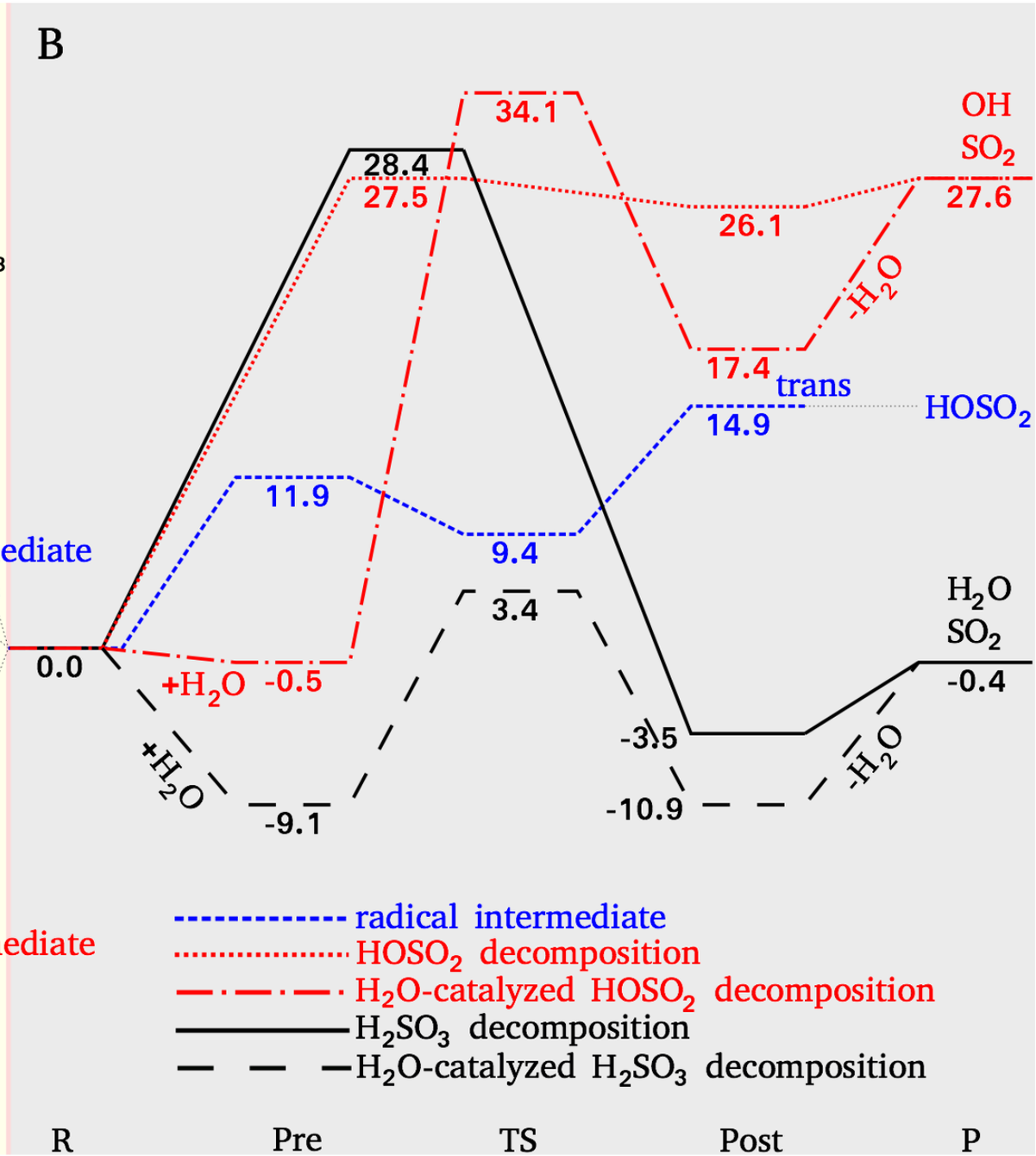

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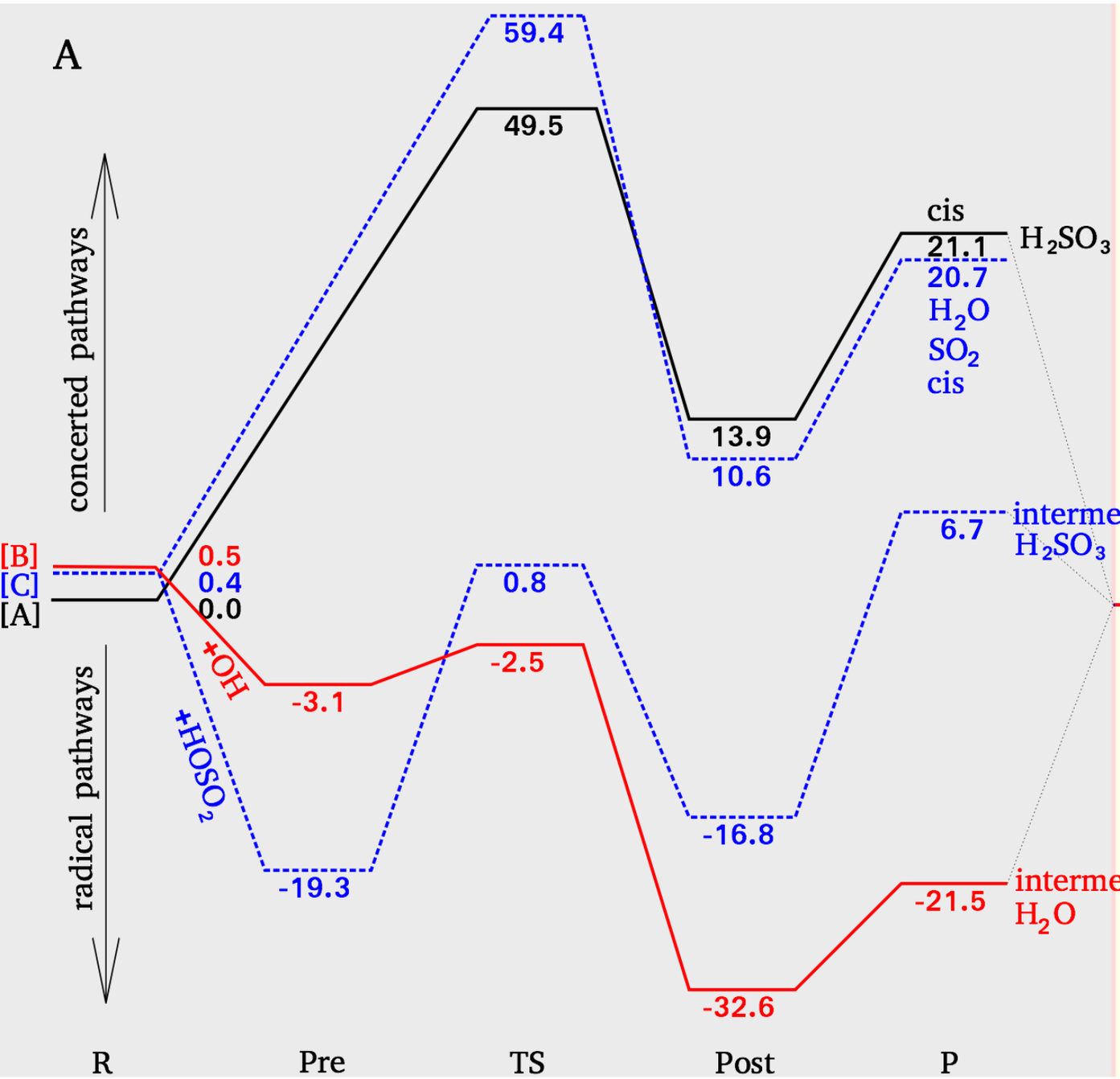

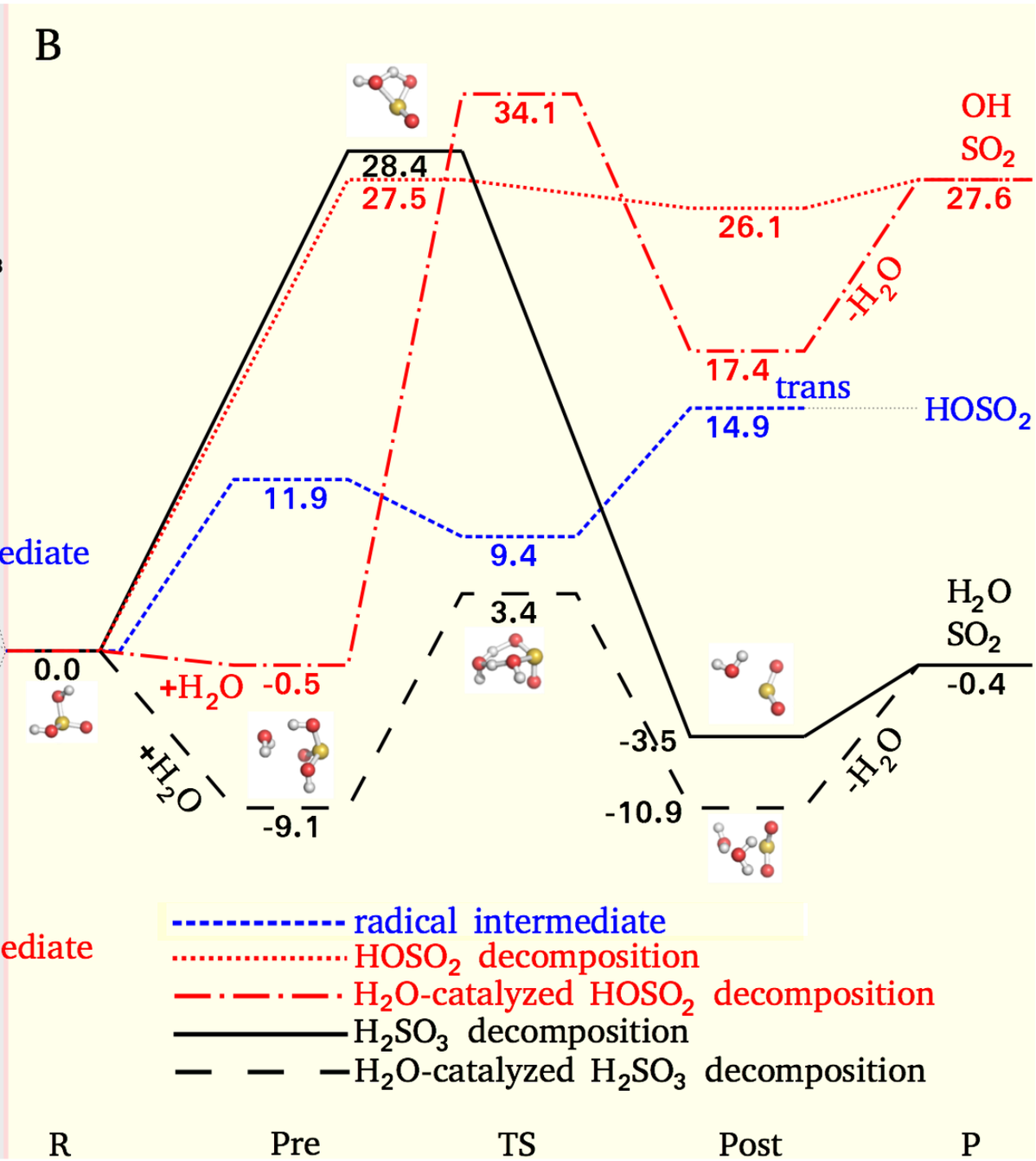

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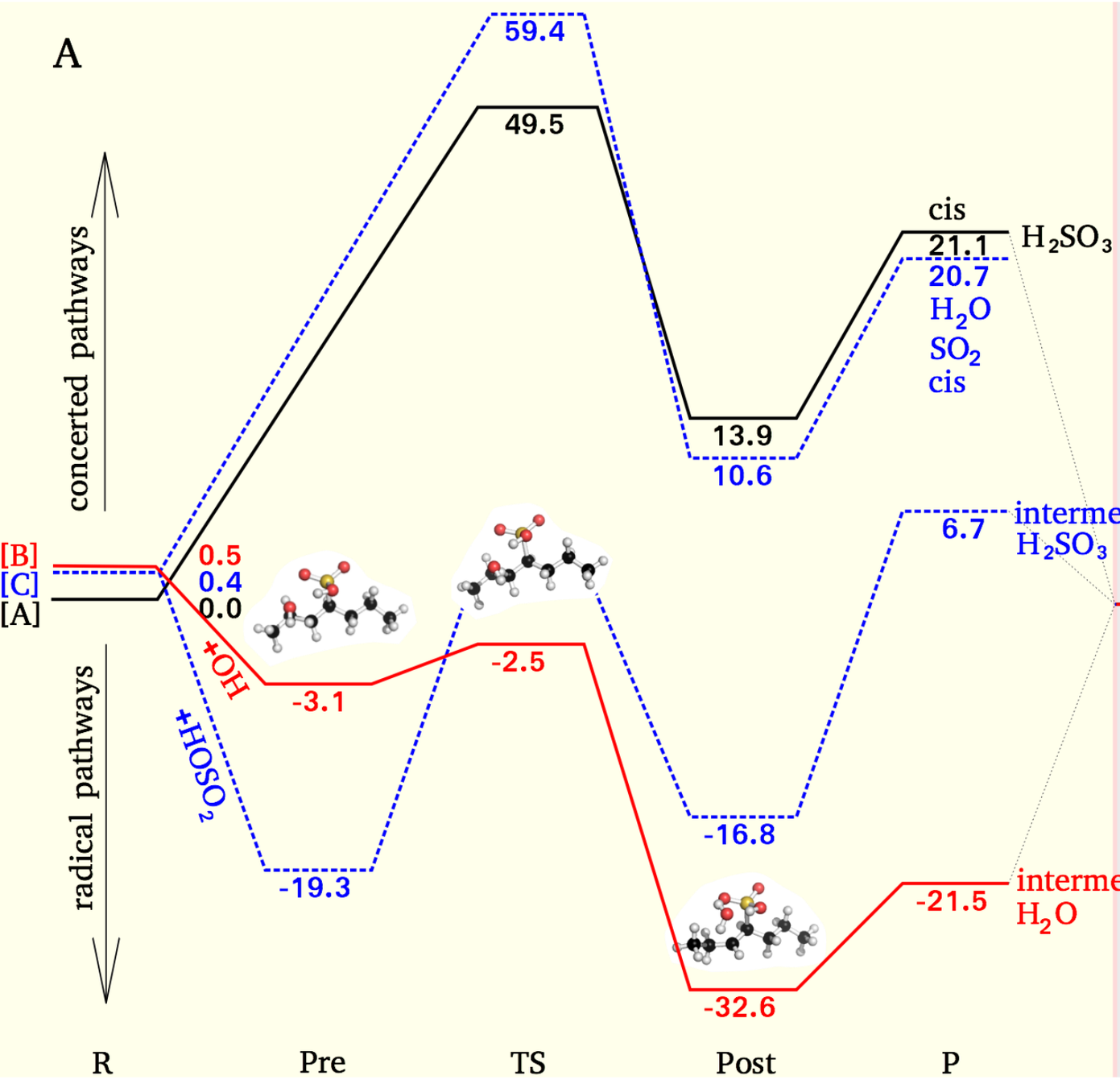

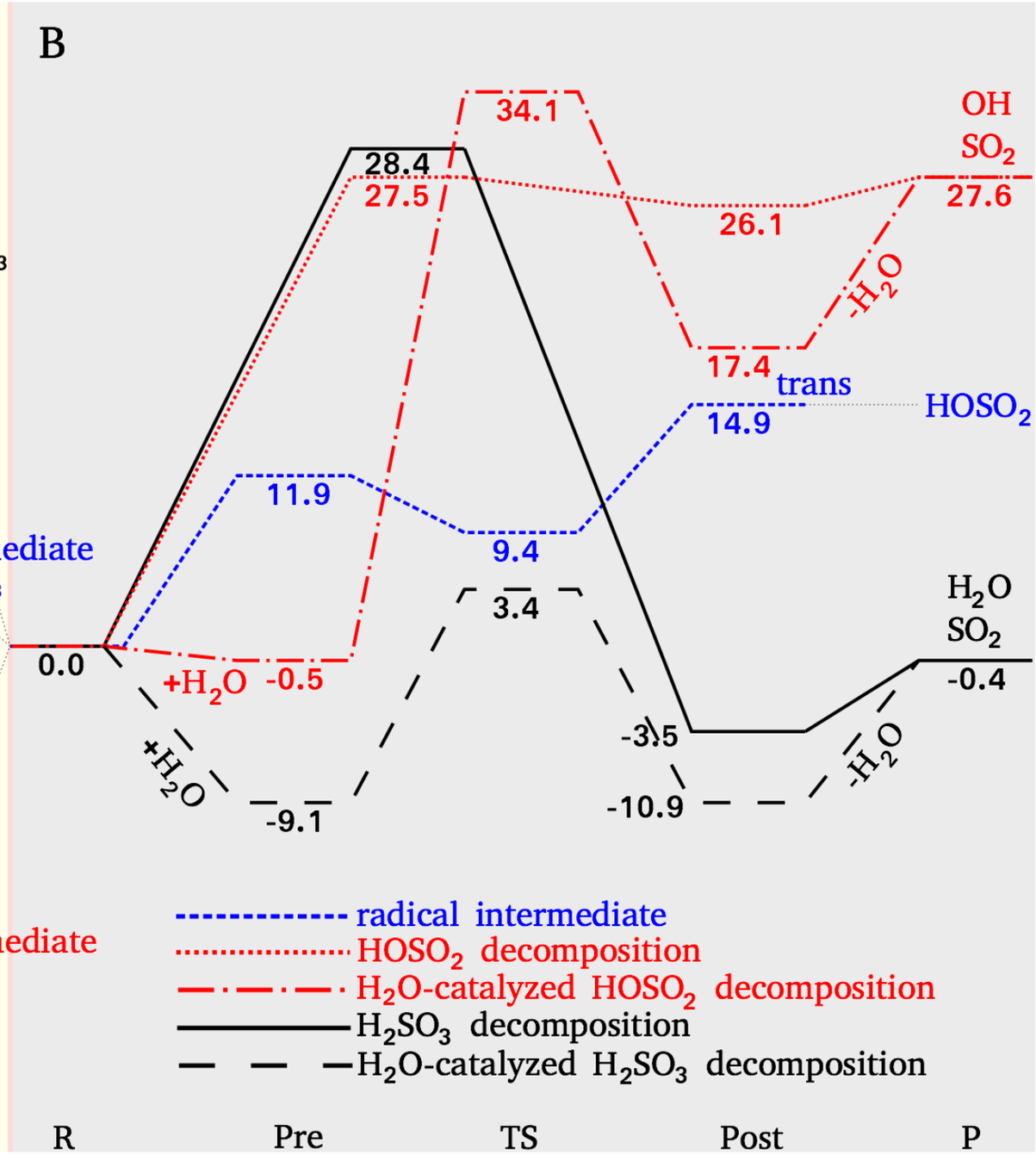

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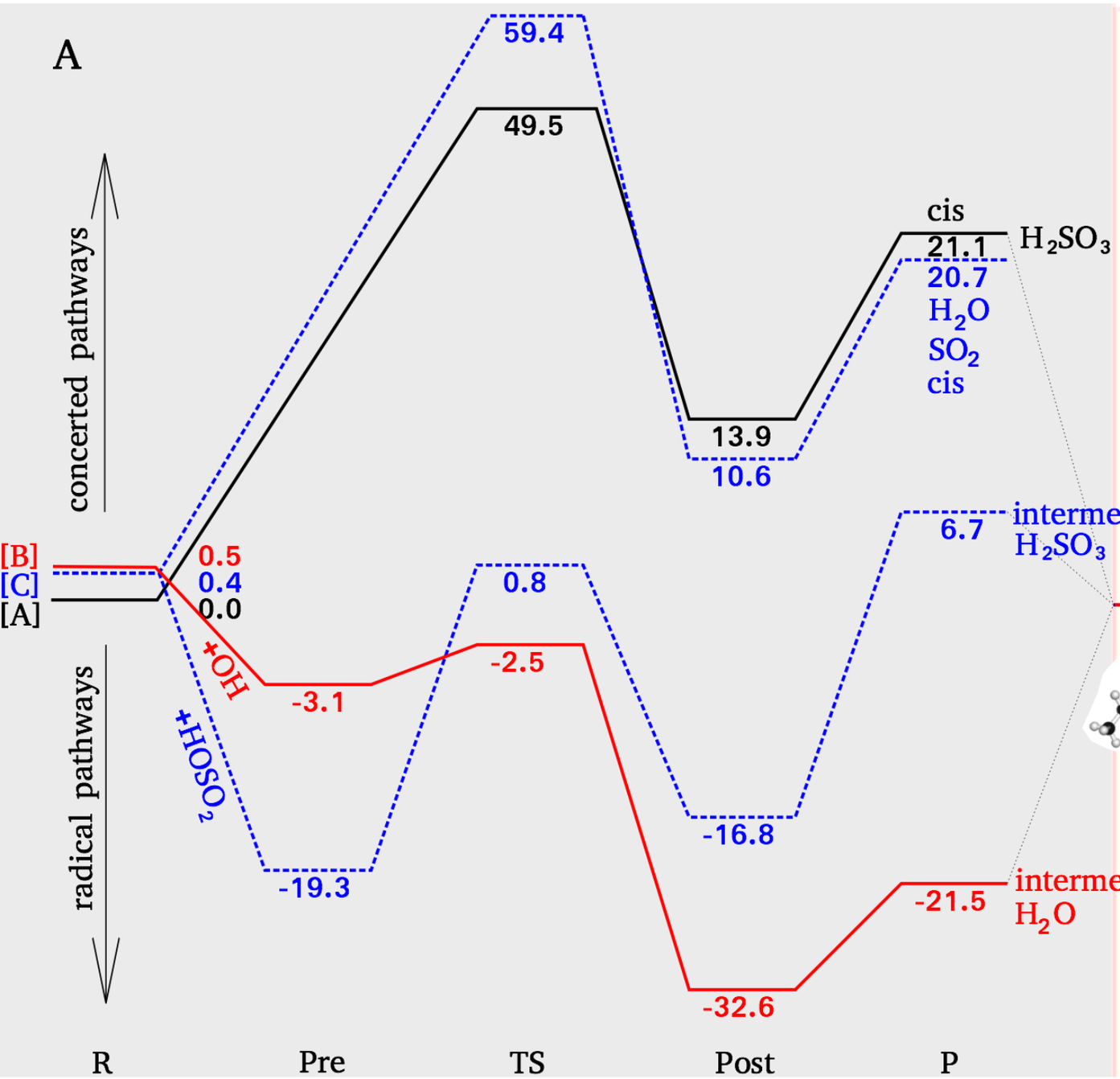

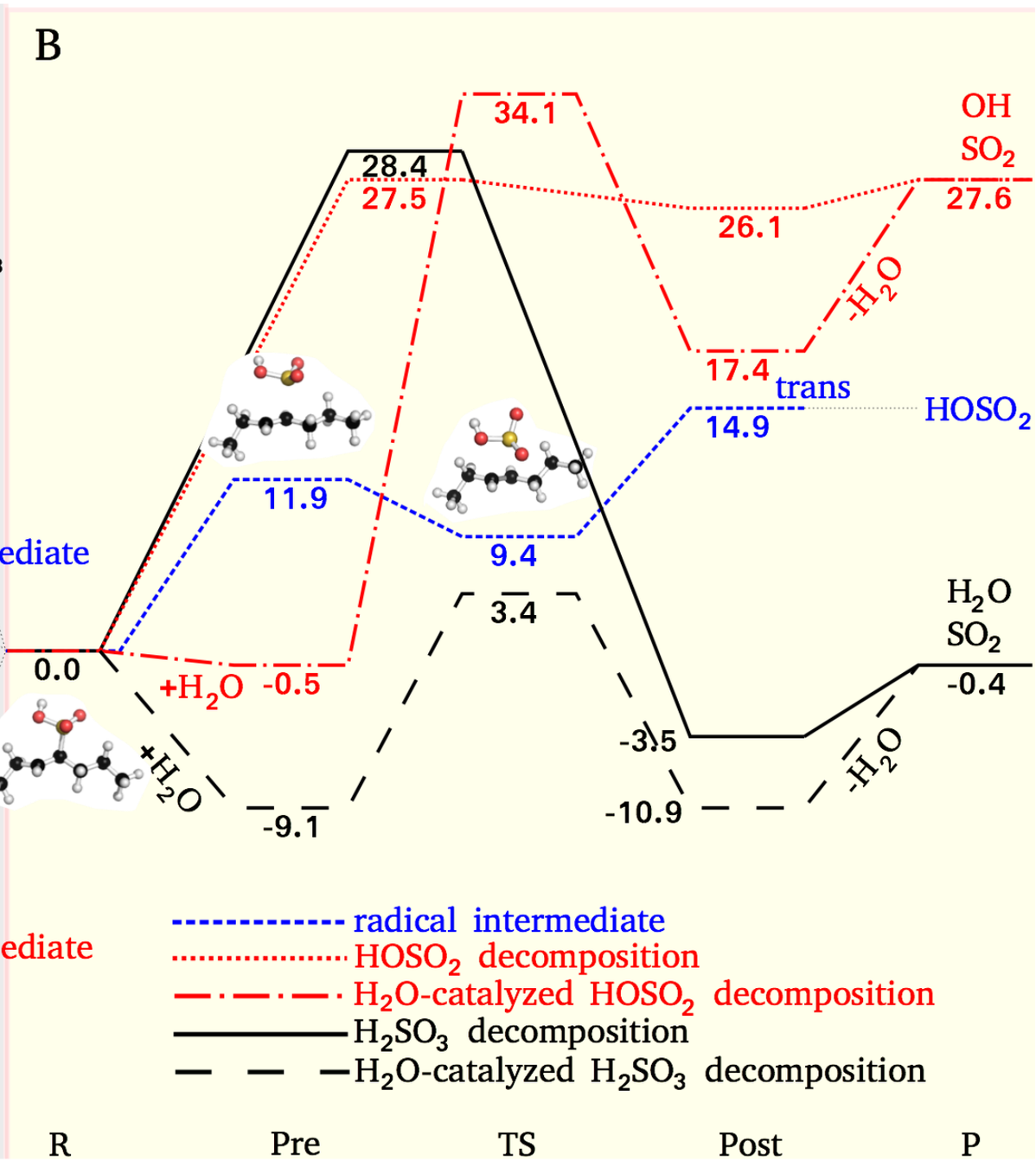

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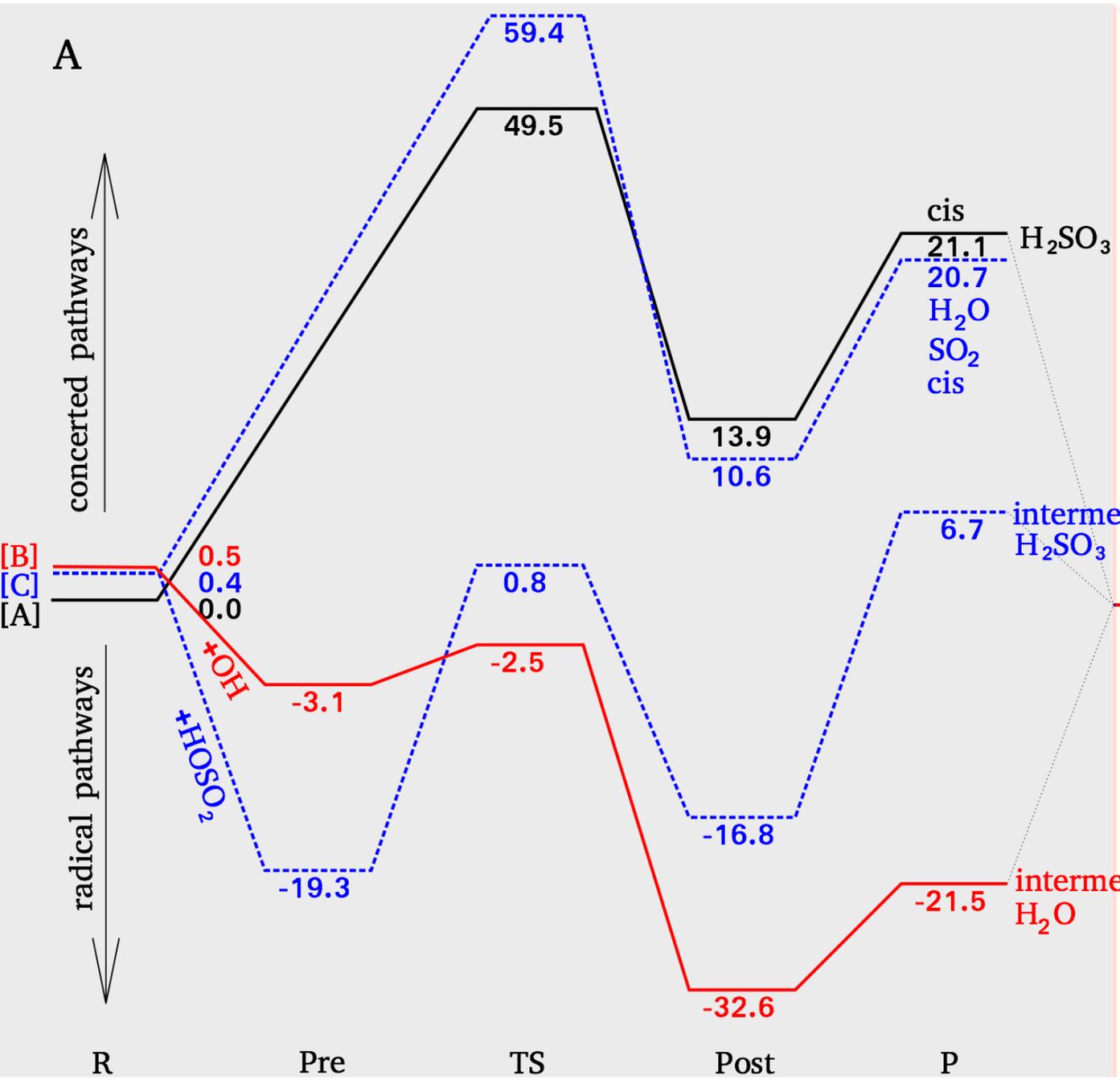

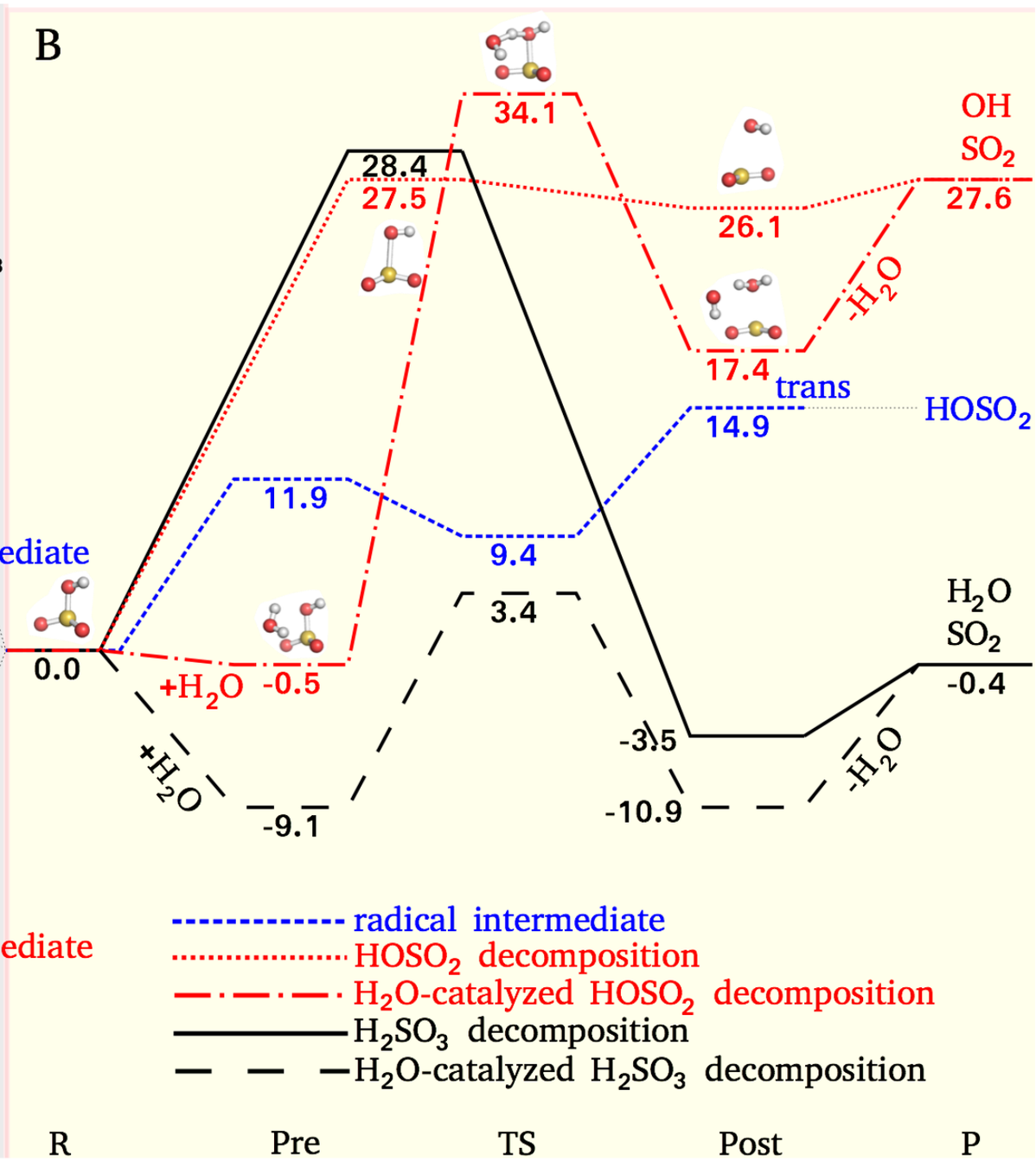

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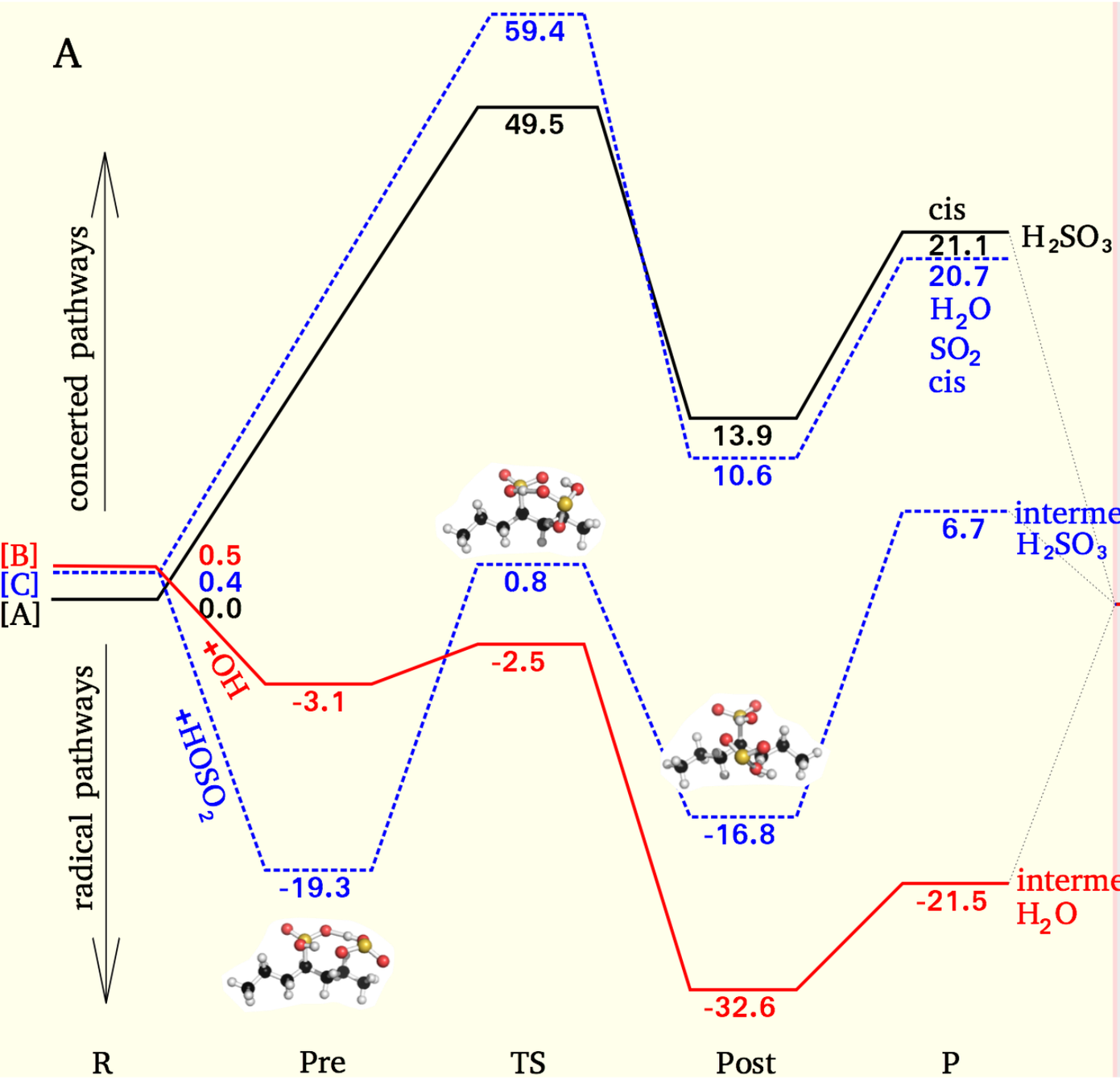

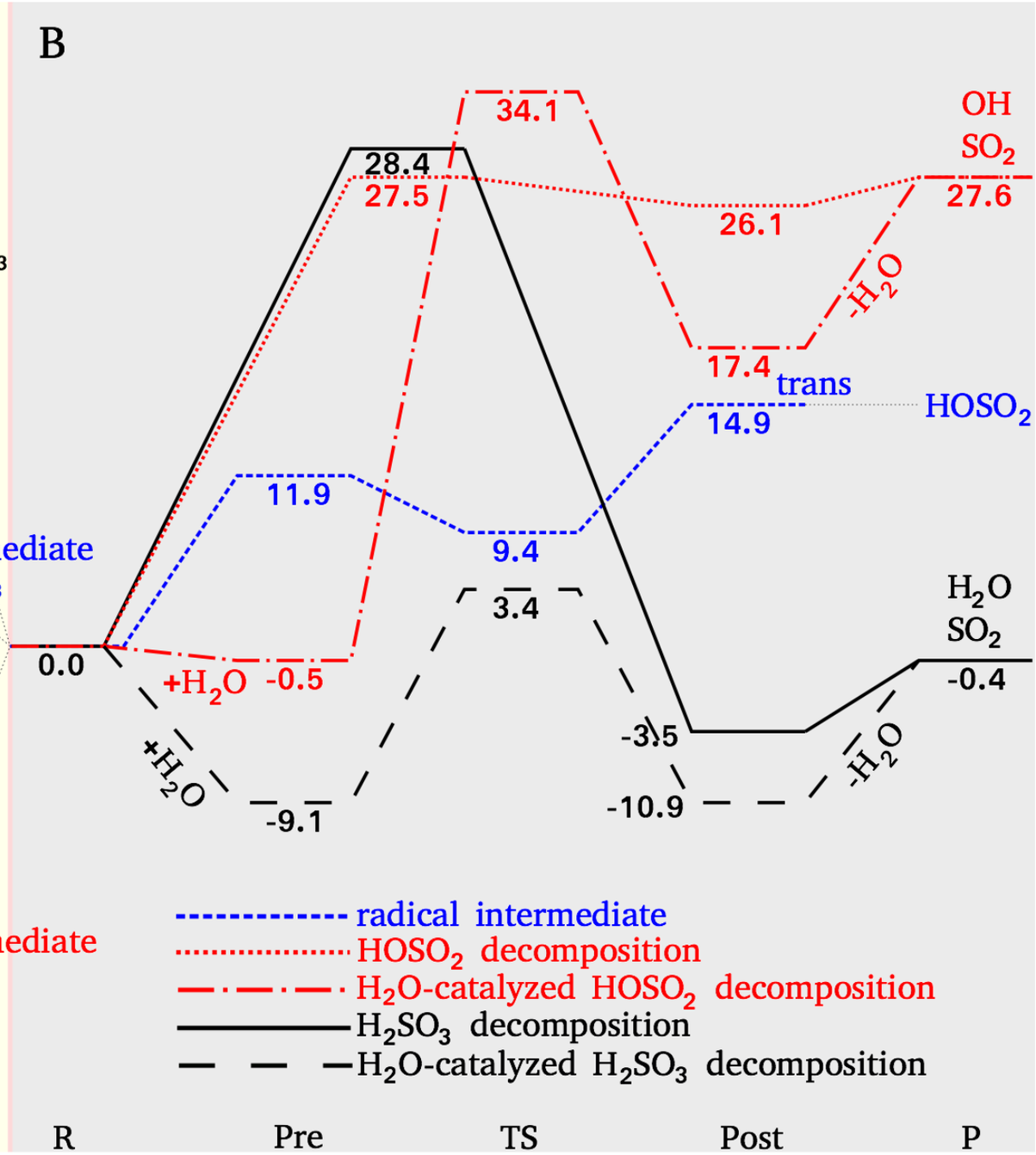

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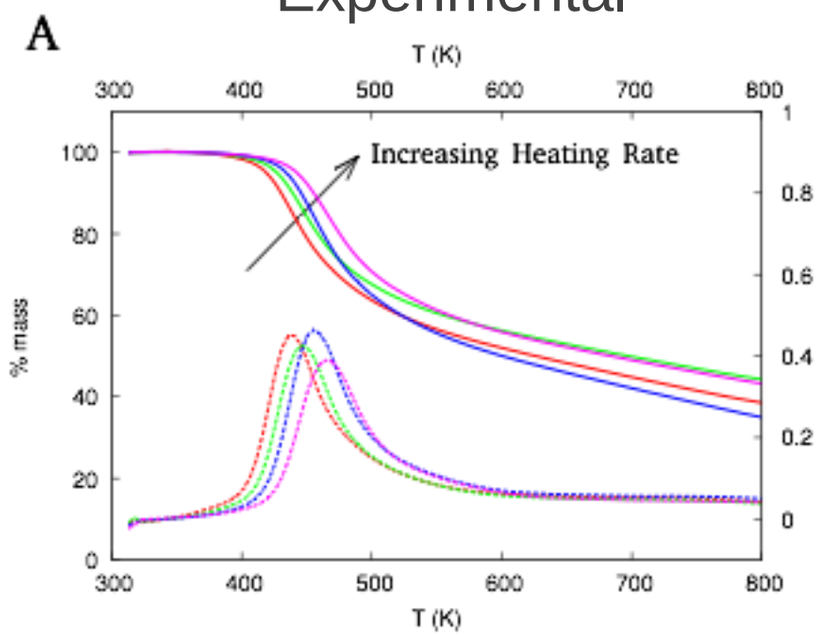
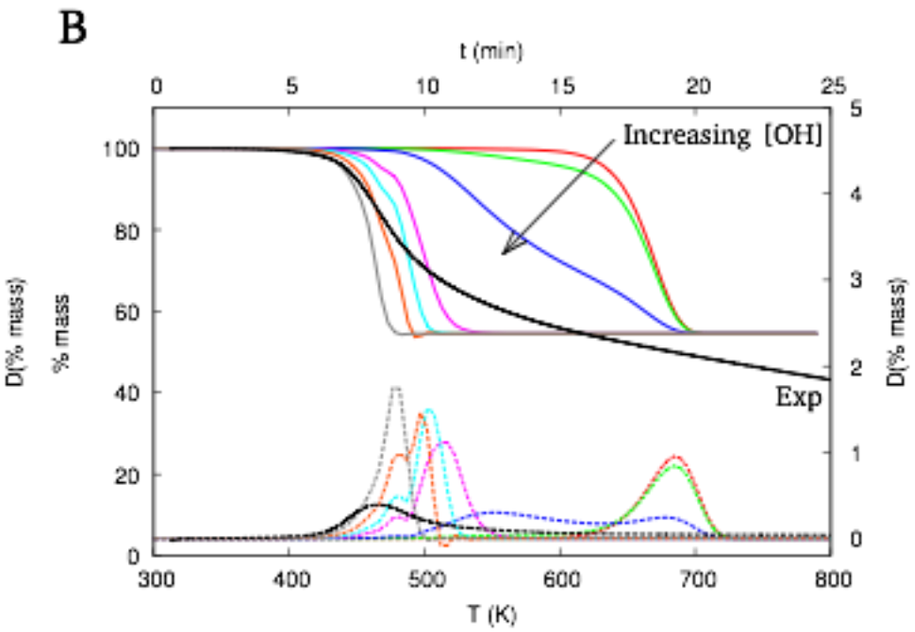
CARBON FIBER: ALTERNATIVE PRECURSORS

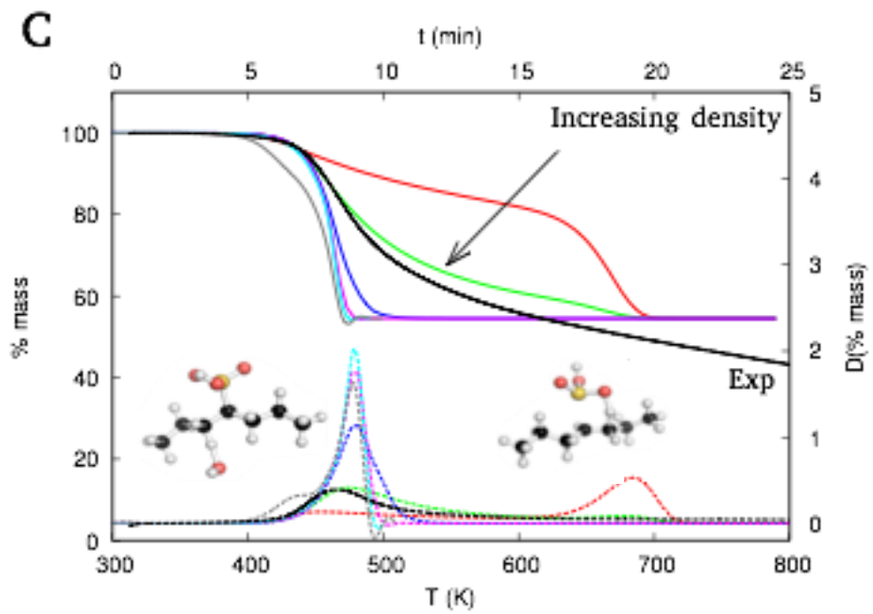
Integrate rate equations using kinetic Monte Carlo

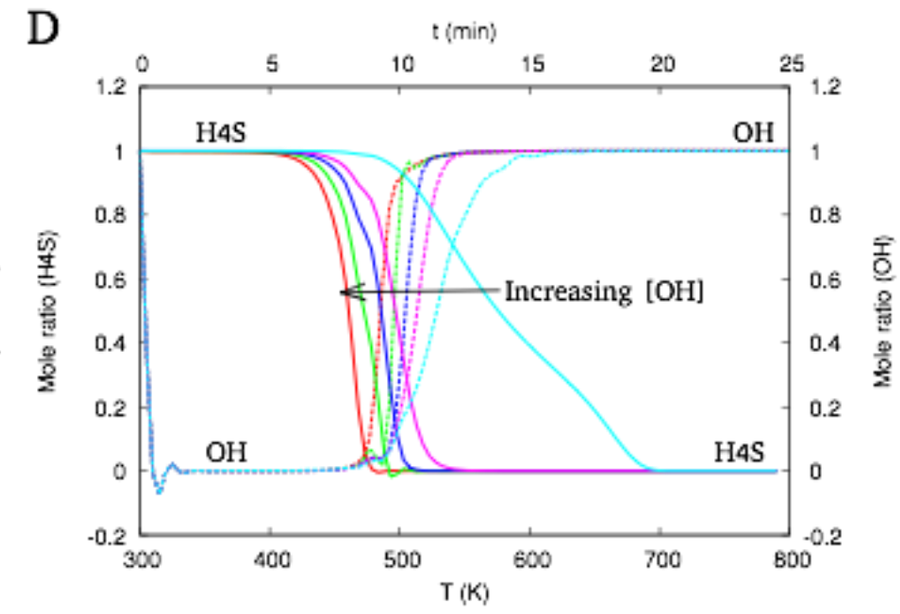
- Thermodynamically, both the elimination and radical mechanisms result in an overall similar change in energy (~27 kcal/mol).
- Kinetically, the radical mechanism is the preferred pathway at lower temperatures.
- The presence of radicals is supported by experimentally observed alkane cleavage.

Experimental









kMC simulated

SPPARKS

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ACKNOWLEDGEMENTS

DuPont

- Kerwin D. Dobbs
- Hari B. Sunkara
- Jeffrey Meth
- Keith Hutchinson
- Numerous Others

BioVia

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- Jian-Jie Liang

- Oak Ridge National Laboratory
  - Ariana Beste
  - A. C. Buchanan III
  - Amit K. Naskar
  - Tomonori Saito
  - Edoardo Apra (Pacific Northwest National Laboratory)