Theory, Applications, and Tools for Multiscale Kinetic Modeling: pMuTT to OpenMKM

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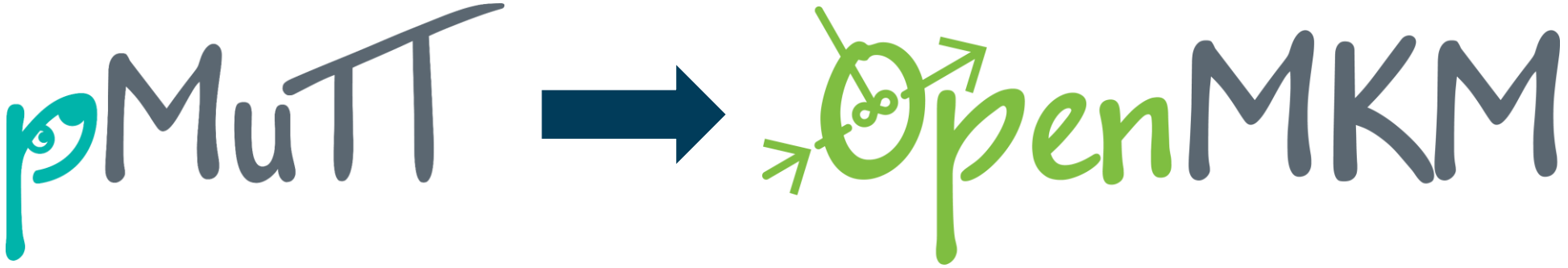


Rapid Advancement in Process Intensification Deployment

Structure of CTI Files

- File used for thermodynamics and kinetics
- Python-like structure
- File broken into blocks:
  - Units
  - Phases
  - Species
  - Lateral Interactions (optional)
  - Reaction options (optional)
  - Reactions
  - BEPs (optional)

Structure of CTI Files: Units

```
#-----------------------------------------------------------------------
# UNITS
#-----------------------------------------------------------------------
units(length="cm", time="s", quantity="mol", energy="kcal/mol",
      act_energy="kcal/mol", pressure="bar", mass="g")
```

- Specifies units throughout the CTI file

```
site_density = 1.66e-9
```

- Users can specify different units for quantities using tuples:

```
site_density = (1.0e15, "molec/cm2")
```

- OpenMKM supports any unit that Cantera supports:

https://cantera.org/tutorials/cti/cti-syntax.html#recognized-units

Structure of CTI Files: Phases

Ideal Gas

```
ideal_gas(name="gas",
          elements="H Ar N",
          species="N2 NH3 H2 Ar")
```

Stoichiometric Solid

- Usually the bulk phase of a material
- Primarily used for book-keeping

```
stoichiometric_solid(name="bulk",
                     elements="Ru",
                     species="RU(B)",
                     density=12.4,
                     note="Ru Metal")
```

Structure of CTI Files: Phases

Interacting Interface

- Specify associated species, reactions, phases, lateral interactions, BEPs.

```
interacting_interface(name="terrace",
                      elements="H N Ru",
                      species="""N2(T) N(T) H(T) NH3(T) NH2(T) NH(T)
                                 RU(T)""",
                      phases="gas bulk",
                      site_density=2.1671e-09,
                      interactions=["0000 to 0004"],
                      reactions=["0000 to 0003", "NH2-H_cle_0001",
                                 "NH-H_cle_0001", "N-H_cle_0001"],
                      beps="NH2-H NH-H N-H",
                      note="Ru(0001)")
```

Structure of CTI Files: Species

- Accepts multiple polynomials:
  - NASA
  - NASA9
  - Shomate
- All species require name and composition.
- Composition important for balancing chemical reactions.

Structure of CTI Files: Species in NASA Format

$$\frac{C_P}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

$$\frac{H}{RT} = a_1 + a_2 \frac{T}{2} + a_3 \frac{T^2}{3} + a_4 \frac{T^3}{4} + a_5 \frac{T^4}{5} + a_6 \frac{1}{T}$$

$$\frac{S}{R} = a_1 \ln T + a_2 T + a_3 \frac{T^2}{2} + a_4 \frac{T^3}{3} + a_5 \frac{T^4}{4} + a_7$$

```
species(name="NH3(T)", atoms="N:1 H:3", size=1.0,
        thermo=(NASA([298.0, 461.9183673469388],
                     [ 1.16759533E+00,  2.05732170E-02, -3.66958772E-05,
                       4.56112325E-08, -2.49628744E-11, -1.42311185E+04,
                      -4.80504278E+00]),
                NASA([461.9183673469388, 800.0],
                     [ 1.58312977E+00,  1.57753291E-02, -1.71587153E-05,
                       1.15414255E-08, -3.21958978E-12, -1.42567384E+04,
                      -6.35076167E+00])))
```

Structure of CTI Files: Species in Shomate Format

$$C_P = A + Bt + Ct^2 + Dt^3 + E\frac{1}{t^2}$$

$$H = At + B\frac{t^2}{2} + C\frac{t^3}{3} + D\frac{t^4}{4} - E\frac{1}{t} + F$$

$$S = A\ln t + Bt + C\frac{t^2}{2} + D\frac{t^3}{3} - E\frac{1}{2t^2} + G$$

```
species(name="Ar", atoms="Ar:1",
        thermo=Shomate([298.0, 6000.0],
                       [ 2.07860000E+01,  2.82591100E-07, -1.46419100E-07,
                         1.09213100E-08, -3.66137100E-08, -6.19735000E+00,
                         1.79999000E+02]))
```

Structure of CTI Files: Lateral Interactions

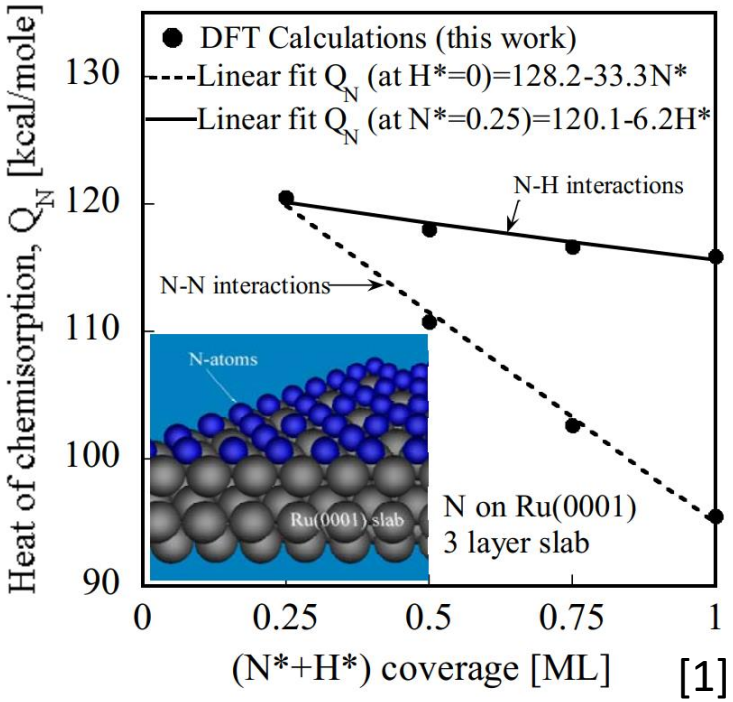
```
lateral_interaction("N(T) N(T)", [0., -33.3], [0., 0.25], id="0000")
lateral_interaction("N(T) H(T)", [-6.2],      [0.],       id="0001")
```

Species i

Species j

Slope(s) ω_{ijk}

Interval(s) in monolayer (ML)



[1]

$$H_i(T, \boldsymbol{\theta}) = H_i(T, \theta_* \rightarrow 0) + \sum_{j}^{\text{Adsorbates}} \omega_{ijk}\theta_j + b_{ijk}$$

[1] Mhadeshwar, A. B. et al. *Catal. Letters* **2004**, *96* (1–2), 13–22.

Structure of CTI Files: Adsorption Reaction

$$k_{ads,j}^{fwd} = \frac{s_j}{(\sigma)^{n_{surf}}} \sqrt{\frac{RT}{2\pi M_i}} \left(\frac{T}{T_{ref,i}}\right)^{\beta_j} \exp\left(-\frac{E_{A,j}}{RT}\right)$$

```
surface_reaction("H2 + 2 RU(T) <=> 2 H(T) + 2 RU(B)",
                 stick( 0.5,    0,       0), id="0000")
```

Stick keyword specifies adsorption

Sticking coefficient, s_j

Modified Arrhenius parameter, β_j

Activation Energy, $E_{A,j}$

Structure of CTI Files: Surface Reaction

$$k_{surf,j}^{fwd} = A'_{surf,j} \left(\frac{T}{T_{ref,j}}\right)^{\beta_j} \exp\left(-\frac{E_{A,j}}{RT}\right)$$

```
surface_reaction("NH3(S) + RU(S) <=> NH2(S) + H(S) + RU(B)",
                 [ 4.69452e+19, 1,  1.26026e+01], id="NH2-H_cle_0002")
```

Pre-exponential factor, $A'_{surf,j}$

Modified Arrhenius parameter, β_j

Activation Energy, $E_{A,j}$

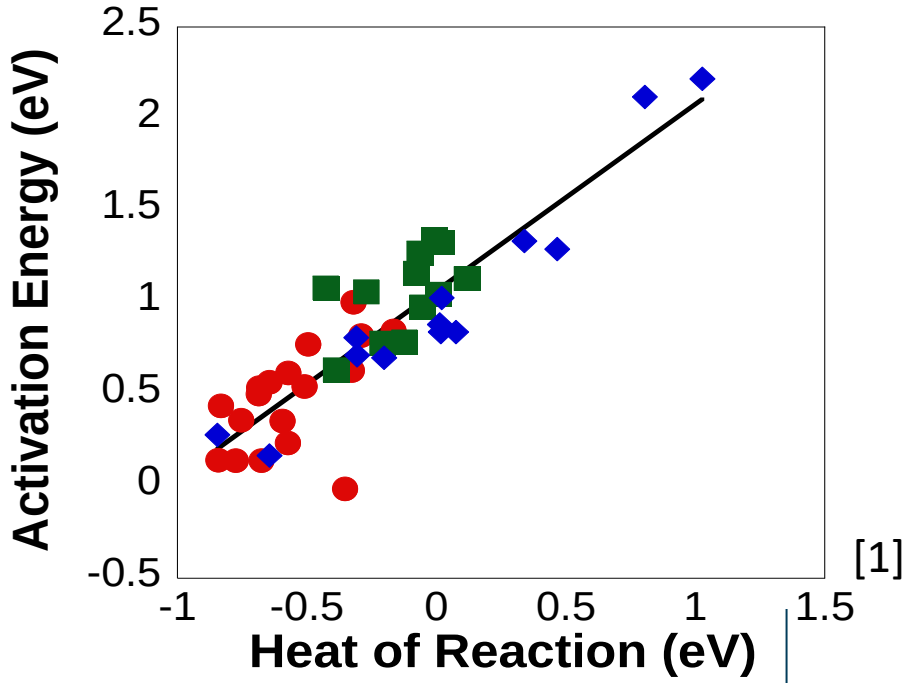
If ID is associated with BEP, then BEP will override $E_{A,j}$

Structure of CTI Files: Surface Reaction

$$E_{A,j} = \omega \Delta H_j + \Delta E_0$$

Directions supported:

- Synthesis ($NH_2^* + H^* \rightarrow NH_3^*$)
- Cleavage ($NH_3^* \rightarrow NH_2^* + H^*$)



[1]

```
bep(id="NH2-H",
    slope=0.71,
    intercept=23.69,
    direction="cleavage",
    cleavage_reactions=["NH2-H_cle_0001 to NH2-H_cle_0002"],
    synthesis_reactions=[])
```

[1] Sutton and Vlachos, *ACS Catal.*, **2**, 1624 (2012)