Opensource **M**icro**K**inetic **M**odeling Toolkit

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https://github.com/VlachosGroup/openmkm

Medasani, B. et al. *J. Chem. Inf. Model.* **2023**, *63 (11)*, 4319–4355.

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Motivation: Why use OpenMKM?

- OpenMKM is an open-source micro-kinetic modeling toolkit built in C++
- It automates the generation and simulation of the differential algebraic equations (DAE) that make up the MKM and performs sensitivity analysis (SA)
- No hand-calculations or programming is required to run OpenMKM
- Uses standardized input files (YAML) and (generates) output files (OUT, CSV) which are human-readable
- Inputs can be generated systematically using pMuTT[1] (also part of VLab)
- Uses state-of-the-art numerical libraries (Cantera[2], Sundials[3], Boost C++[4])
- Interfaces to Python (sensitivity analysis), RenView[5] for Path Visualization

[1] https://vlachosgroup.github.io/pMuTT/
[2] https://cantera.org
[3] https://computing.llnl.gov/projects/sundials
[4] https://www.boost.org/
[5] https://github.com/VlachosGroup/renview

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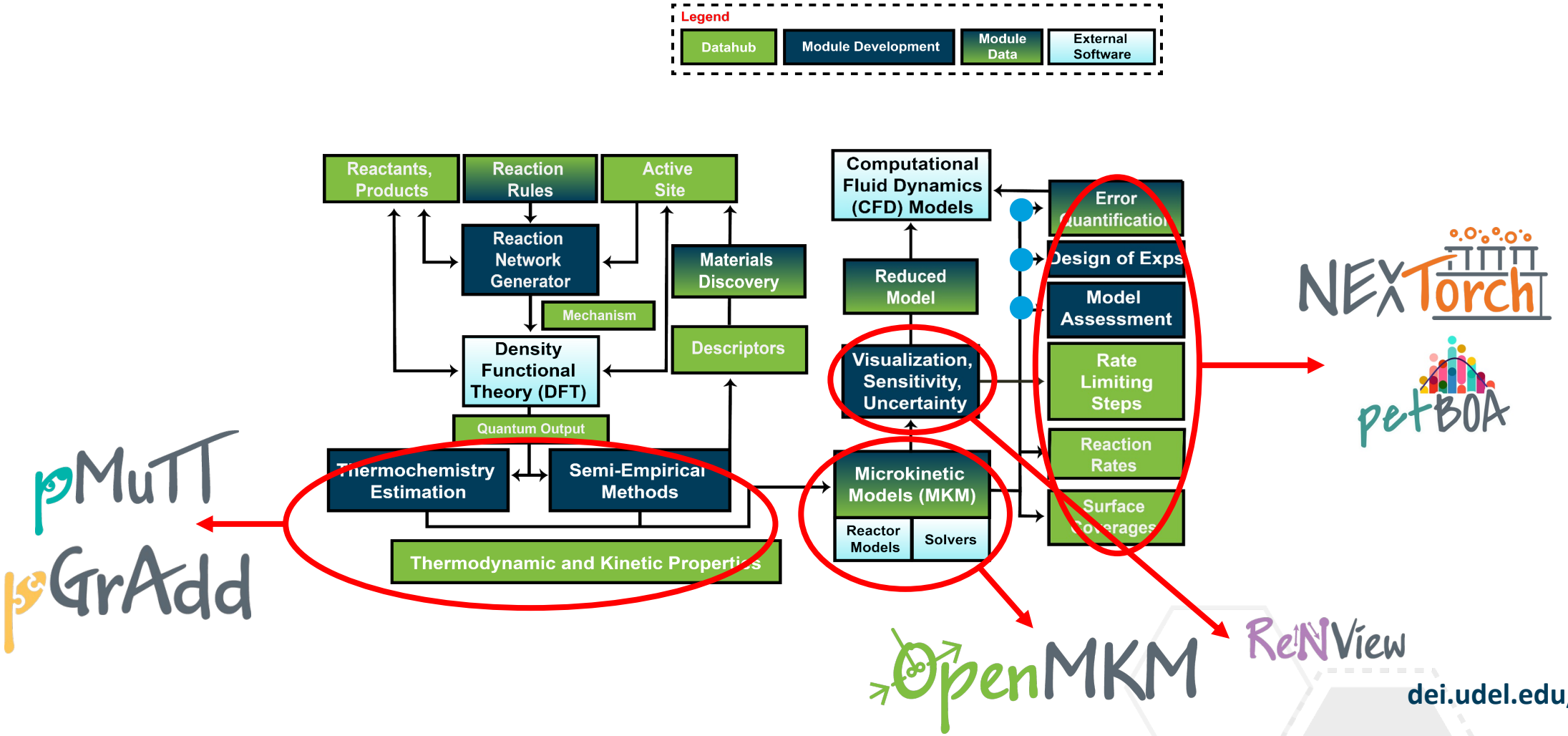
Where does OpenMKM fit in V-Lab?

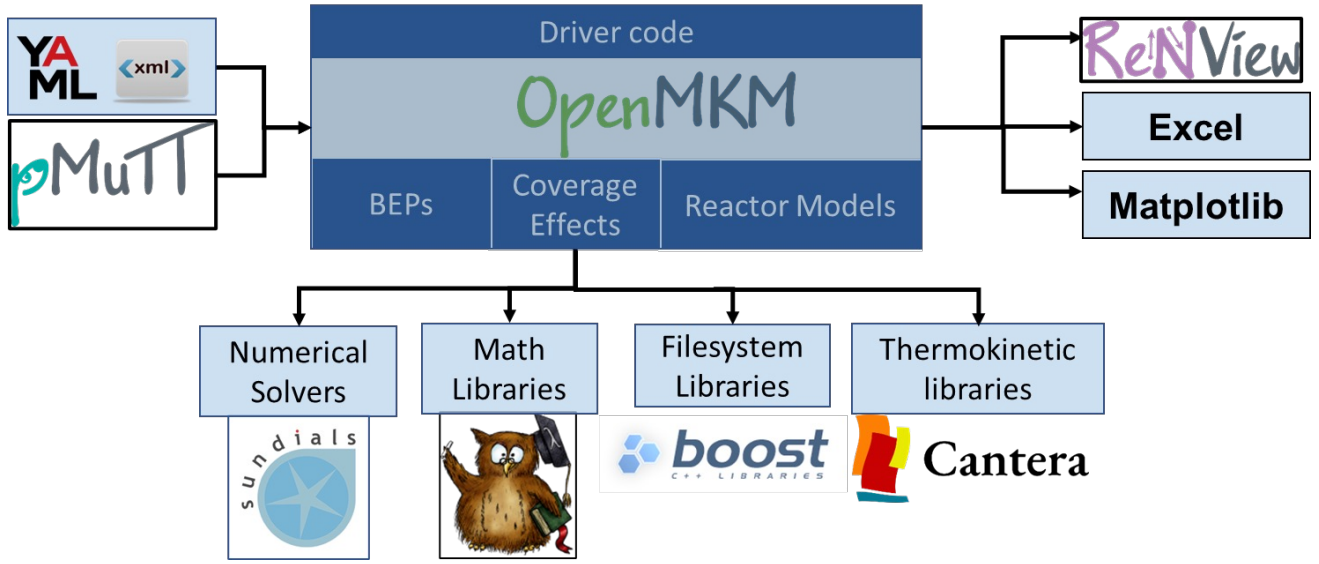
Bridge between atomic/meso scale data and macro-scale observables.



OpenMKM: Core Modules

Uses state-of-the art libraries for stability and robustness.

- OpenMKM's core modules are derived from:
  - The Cantera[1] library
  - Sundials[2] ODE/DAE solvers
  - Boost[3] C++ libraries
- YAML Input files are generated easily using
  - The pMuTT[4] library
  - Optionally also using YAML[2] API



Cantera sundials boost YAML pMuTT

[1] https://cantera.org
[2] https://computing.llnl.gov/projects/sundials
[3] https://www.boost.org/
[4] https://vlachosgroup.github.io/pMuTT/
[5] https://yaml.org/

Microkinetic Model Inputs: Reactor Conditions

Q_0 = 1 mL s^{-1}

Inlet composition, x_0:

- N_2
- H_2
- Inert

T = 673 K

P = 100 bar

V = 1 cm^3

m_{cat} = 0.1 g Ru/Al_2O_3 catalyst

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Microkinetic Model Inputs: Elementary Steps

Q_0 = 1 mL s^{-1}

Inlet composition, x_0:

- N_2
- H_2
- Inert

T = 673 K

P = 100 bar

V = 1 cm^3

m_{cat} = 0.1 g Ru/Al_2O_3 catalyst

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Elementary reversible reactions:

- Adsorption/Desorption
  1. $N_2 + * \leftrightarrow N_2*$
  2. $H_2 + * \leftrightarrow 2H*$
  3. $NH_3 + * \leftrightarrow NH_3*$
- Surface Reactions
  4. $N_2* + * \leftrightarrow 2N*$
  5. $N* + H* \leftrightarrow NH*$
  6. $NH* + H* \leftrightarrow NH_2*$
  7. $NH_2* + H* \leftrightarrow NH_3*$

Microkinetic Model Inputs: Mass Balance for N_2^*

$$\frac{d}{dt}[N_2^*] = \underbrace{k_1^{fwd} P_{N_2}[*] - k_1^{rev}[N_2^*]}_{\text{Adsorption}} - \underbrace{k_4^{fwd}[N_2^*][*] + k_4^{rev}[N^*]^2}_{\text{Surface Reactions}}$$

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Elementary reversible reactions:

- Adsorption/Desorption
  1. $N_2 + * \leftrightarrow N_2^*$
  2. $H_2 + * \leftrightarrow 2H^*$
  3. $NH_3 + * \leftrightarrow NH_3^*$
- Surface Reactions
  4. $N_2^* + * \leftrightarrow 2N^*$
  5. $N^* + H^* \leftrightarrow NH^*$
  6. $NH^* + H^* \leftrightarrow NH_2^*$
  7. $NH_2^* + H^* \leftrightarrow NH_3^*$

Microkinetic Model Inputs: Modified Arrhenius Rate Constant

$$\frac{d}{dt}[N_2^*] = k_1^{fwd} P_{N_2}[*] - k_1^{rev}[N_2^*] - k_4^{fwd}[N_2^*][*] + k_4^{rev}[N^*]^2$$

$$k_j^{fwd} = \underbrace{A_j' \left(\frac{T}{T_{ref,j}}\right)^{\beta_j}}_{A_{Arrhenius}} \exp\left(-\frac{E_{A,j}}{RT}\right)$$

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

- Arrhenius equation when $\beta_i = 1$ and $T_{ref,i} = 1\ K$

Microkinetic Model Inputs: Reverse Rate Constant

$$\frac{d}{dt}[N_2^*] = k_1^{fwd} P_{N_2}[*] - k_1^{rev}[N_2^*] - k_4^{fwd}[N_2^*][*] + k_4^{rev}[N^*]^2$$

$$k_j^{fwd} = A_j' \left(\frac{T}{T_{ref,j}}\right)^{\beta_j} \exp\left(-\frac{E_{A,j}}{RT}\right) \xrightarrow{\text{By microscopic reversibility}} k_j^{rev} = \frac{k_j^{fwd}}{K_j^{eq}}$$

$$K_j^{eq} = \exp\left(-\frac{\Delta G_j}{RT}\right)$$

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Microkinetic Model Inputs: Adsorption Preexponential

$$\frac{d}{dt}[N_2^*] = k_1^{fwd} P_{N_2}[*] - k_1^{rev}[N_2^*] - k_4^{fwd}[N_2^*][*] + k_4^{rev}[N^*]^2$$

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

By collision theory

$$A'_{ads,j} = \frac{s_j}{(\sigma)^{n_{surf}}}\sqrt{\frac{RT}{2\pi M_i}}$$

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Microkinetic Model Inputs: Surface Reaction Preexponential

$$\frac{d}{dt}[N_2^*] = k_1^{fwd} P_{N_2}[*] - k_1^{rev}[N_2^*] - k_4^{fwd}[N_2^*][*] + k_4^{rev}[N^*]^2$$

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

By transition-state theory

$$E_{A,j} = \Delta H_j^{\neq}$$

$$A'_{surf,j} = \frac{k_B}{h} \frac{1}{(\sigma)^{n_{surf}-1}} \exp\left(\frac{\Delta S_j^{\neq}}{R}\right)$$

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Microkinetic Modeling Input Summary

Set by user

- Reactor conditions
  - T, P, Q, V, x_{i0}, m_{cat}
- Elementary steps
  - Adsorption
  - Surface reactions
- Reaction parameters
  - s_j, σ, $T_{ref,j}$, β_j

Calculated by MKM

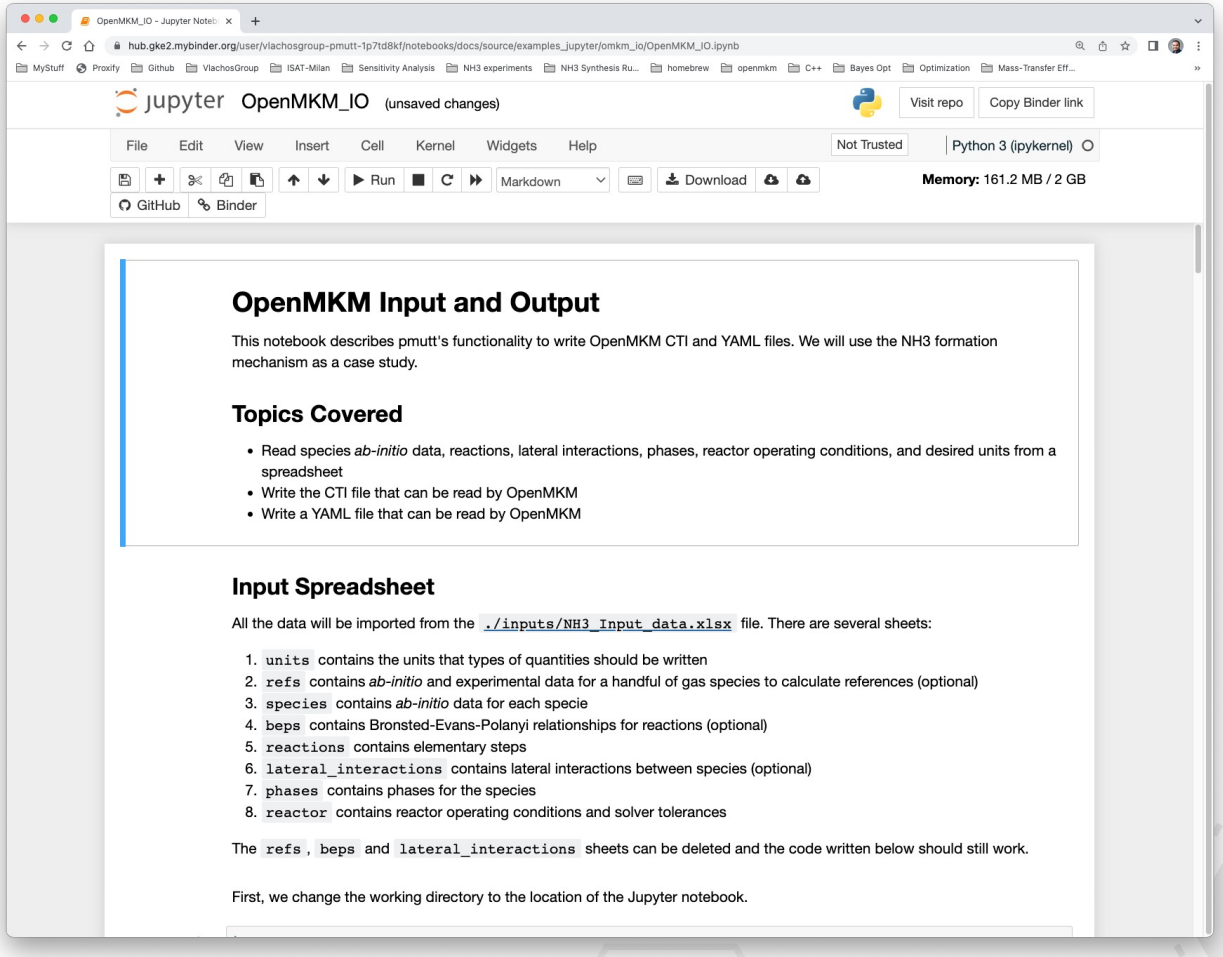
- Surface coverages
- Gas-phase compositions
- Rates

Derived from DFT/GA

- Enthalpies (H) and entropies (S) of:
  - Reactants
  - Products
  - Intermediates
  - Transition states

How to make input files for OpenMKM?

- **YAML Input files are generated easily using pMuTT**
  - Detailed pMuTT[1] documentation to generate the input files.



[1] https://vlachosgroup.github.io/pMuTT/

OpenMKM: Features Summary

Mechanisms

- Gas phase only
- Surface only
- Gas phase + multiple surfaces

Additional Features

- Support for BEP relations
- Coverage dependent enthalpies
- Parametric Studies
- Sensitivity Analysis
- Reaction Path Analysis
- Parameter Estimation

Supported Reactor Models

- Batch
- CSTR
- PFR
- PFR with T-profile

Temperature Modes

- Isothermal
- Adiabatic
- Heat transfer
- Temperature ramp (For TPD)
- Custom T-Profile (PFR 1-D only)

Demo 1: OpenMKM I/O

See Jupyter Notebook at:

ACS-Workshop-Aug-2023/omkm_demo/omkm_io

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Demo 2: PFR-1D T-Profile

Ethane dehydrogenation MKM

See Example at: ACS-Workshop-Aug-2023/omkm_demo/pfr1d_tprofile

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Demo 3: Sensitivity Analysis

Ethane dehydrogenation MKM

See Example at: ACS-Workshop-Aug-2023/omkm_demo/sa_and_rpa

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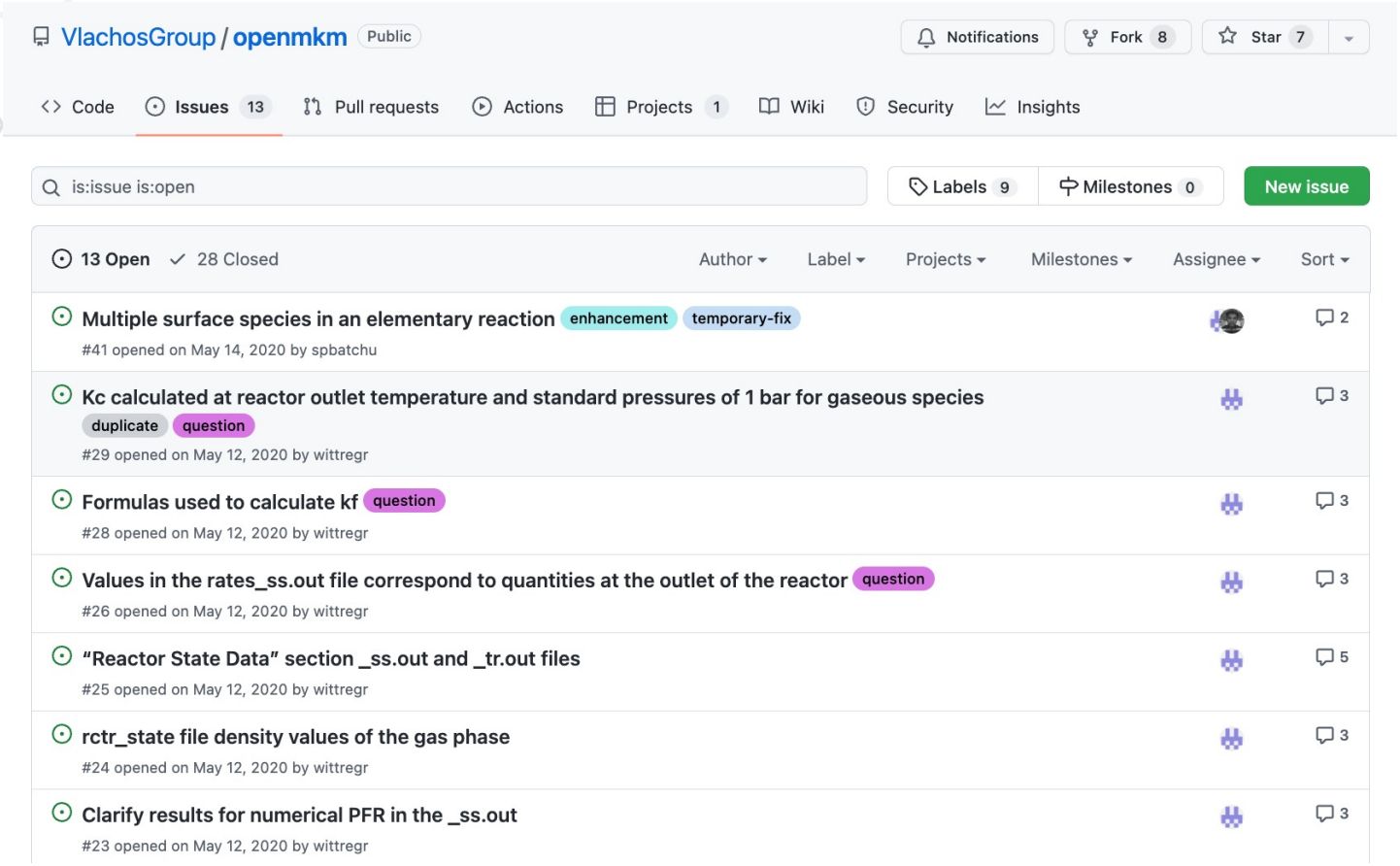
Active Open-Source Development



- Vlachos Group active on GitHub for OpenMKM software development.
- Users can report issues and provide feature requests.
- New features can be added.
- Bugs are typically fixed rapidly.

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2. RAPID (AIChE)
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