Control of a Kinetic Monte Carlo Lattice Gas Model

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Introduction

• Macroscopic (Deterministic) Models - continuum assumption - smoothly evolving states and time - smooth derivatives

• Microscopic (Stochastic) Models - discreteness - smoothly evolving probability distribution - evolution by individual events

• When are microscopic models important?
  – Fluctuations in numbers of particles are important
  – Low order deterministic models may not exist
  – Particle location/orientation is important

• Modeling for Control Purposes
  – Model only those states (observables) necessary to accurately predict the measurements.
  – Sensitivities are necessary - How does the system respond when parameters are adjusted?

• Big Question - Are macroscopic models based on the usual closures good enough for control purposes when the process is best described by a microscopic or multi-scale model?
Literature Review

Employing Monte Carlo Models for systems level tasks is an area of active research

- Sensitivities via finite-differences and parameter estimation for KMC simulations (Raimondeau et al., 2003).

- Sensitivities of the mean via finite differences for a copper electro-deposition application (Drews et al., 2003).

- Model reduction of the chemical master equation (Gallivan and Murray, 2003), used to determine optimal open-loop temperature profiles for epitaxial thin film growth (Gallivan, 2003).

- PI control of growth rate and surface roughness in thin film growth, with a KMC model to provide interaction information (Lou and Christofides, 2003a,b)
• Coarse time stepper and direct stochastic optimization method (Hooke-Jeeves) to determine an optimal control policy for a set of reactions on a catalyst surface (Armaou and Kevrekidis, 2003).

• Coarse time stepper to identify the local linearization of the nonlinear stochastic model at a steady state of interest, standard linear quadratic control theory is then applied. (Siettos et al., 2003a).

• Previous control approach extended to spatially distributed processes Armaou et al. (2003).

• Construction of bifurcation diagrams for the mean of stochastic models (Siettos et al., 2003b).
Case Study - Surface CO Oxidation

• Overall Reaction

\[ \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 \]

• Reaction Mechanism

\[ \text{CO}(g) + *_i \xrightarrow{\alpha} \text{CO}_{*,i} \]
\[ \text{O}_2(g) + *_i + *_j \xrightarrow{\beta} \text{O}_{*,i} + \text{O}_{*,j} \]
\[ \text{CO}_{*,i} \xrightarrow{\gamma} \text{CO}(g) + *_i \]
\[ \text{CO}_{*,i} + \text{O}_{*,j} \xrightarrow{k_r} \text{CO}_2(g) + *_i + *_j \]
\[ \text{CO}_{*,i} + *_j \xrightarrow{d_1} *_i + \text{CO}_{*,j} \]
\[ \text{O}_{*,i} + *_j \xrightarrow{d_2} *_i + \text{O}_{*,j} \]

• CO Repulsive Interactions

\[ k = k_0 \exp\left(-N\epsilon/(RT)\right) \]
\[ \epsilon \text{- Interaction energy per nearest neighbor CO pair} \]

• System Parameters

\[ \alpha = 1.6 \text{ s}^{-1} \]
\[ \beta = \text{control} \]
\[ \gamma = 0.001 \text{ s}^{-1} \]
\[ k_r = 1 \text{ s}^{-1} \]
\[ d_1 = 1 \]
\[ d_2 = 1 \]
\[ \epsilon = -2 \text{ kcal} \]
\[ T = 500 \text{ K} \]
Candidate Models

• Macroscopic Models
  - Mean field model
    \[
    \frac{d\theta_{\text{CO}}}{dt} = \alpha \theta_s - \gamma \theta_{\text{CO}} \exp(-4 \theta_{\text{CO}} \epsilon/(RT)) - 4k_r \theta_{\text{CO}} \theta_O \exp(-3 \theta_{\text{CO}} \epsilon/(RT))
    \]
    \[
    \frac{d\theta_O}{dt} = 4\beta \theta_s^2 - 4k_r \theta_{\text{CO}} \theta_O \exp(-3 \theta_{\text{CO}} \epsilon/(RT))
    \]
  - Quasi-chemical model (studied, not presented here)

• Microscopic Model - Kinetic Monte Carlo
  - Initialize the lattice configuration, with specified surface coverages, and slaved higher order moments
  - Count the number of each event type on the lattice \(N_i\)
  - Step forward in time according to
    \[
    \Delta t = \frac{-\log(\xi_1)}{\sum k_i N_i}
    \]
  - Select a reaction type \(j\), where:
    \[
    \frac{k_{j-1} N_{j-1}}{\sum k_i N_i} \leq \xi_2 \leq \frac{k_j N_j}{\sum k_i N_i}
    \]
  - Chose a specific reaction from the selected reaction type
  - Update the lattice and repeat
Mean Field Model - Input Step

CO molecules - Blue, O atoms - White

\[ \Theta_{CO} \]

\[ \Theta_{O} \]

\[ \beta - \text{Input} \]

Input - PO2

Time (sec)

[Images at different time points: t=1.4 sec, t=2.3 sec, t=9.0 sec]
30x30 KMC lattice - Input Step
CO molecules - Blue, O atoms - White

Coverages

\( \Theta_{CO} \)

\( \Theta_{O} \)

\( \beta - \text{Input} \)

Input - PO₂

Time (sec)

t=1.5 sec  t=4.0 sec  t=4.2 sec  t=4.5 sec  t=5.1 sec  t=9.1 sec
Tools for Using Microscopic Models - “Steady-state” Analysis

Mean steady state, $\bar{x}_{k+1} = \bar{x}_k$  Where: $\bar{x}_k = \lim_{N \to \infty} \frac{1}{N} \sum x_k$

Methods for determining Medium-time Steady States

• Solve the Master Equation - unavailable

• Integrate KMC model for a long time - breaks down for unstable steady states

• Guess the steady state, and search for parameters $\theta$ where $\bar{x}_{k+1} = \bar{x}_k$

Search algorithm:

$$(x_{k+1} - x_k)|_{\theta_{j+1}} \approx (x_{k+1} - x_k)|_{\theta_j} + \frac{\partial}{\partial \theta_j} (x_{k+1} - x_k)|_{\theta_j} \left( \theta_{j+1} - \theta_j \right)$$

$$0 = (x_{k+1} - x_k)|_{\theta_j} + (S_{k+1} - S_k) \left( \theta_{j+1} - \theta_j \right)$$

The sensitivity or an approximate sensitivity is needed for the update
What is the sensitivity?

- The sensitivity ($S$) defines how sensitive the state ($x$) is to perturbations in parameters ($\theta$).

$$ S = \frac{\partial x}{\partial \theta^T} $$

- The state evolution equation gives rise to the sensitivity evolution equation:

$$ \frac{dx}{dt} = f(x, \theta) \quad \frac{dS}{dt} = \frac{\partial f(x, \theta)}{\partial x^T} S + \frac{\partial f(x, \theta)}{\partial \theta^T} $$

- The sensitivity evolution equation is linear with respect to $S$.

- The sensitivity depends on the state, but not vice versa.
Reconstructing the sensitivity of the mean from simulation

Method I: Finite Differences

\[ S_k = \frac{\partial \bar{x}_k(\theta)}{\partial \theta^T} \approx \frac{\bar{x}(\theta + \delta_k) - \bar{x}(\theta - \delta_k)}{2||\delta_k||} \]

Requires two mean evaluations per parameter (computationally expensive; amplifies simulation noise)

Method II: First-order approximations of the sensitivity equation

\[ S_{k+1} = S_k + \Delta t \left( \frac{\partial f(x, \theta)}{\partial x^T} \bigg|_{x_k} S_k + \frac{\partial f(x, \theta)}{\partial \theta^T} \bigg|_{x_k} \right) \]

Additional twist - use a closed-form expression (mean field model) as the functional form of the partial derivatives, but use the data \( x_k \) from the KMC simulation.
Steady State Diagrams

\( \Theta_1 \) - CO coverage

\( \beta \) - Partial Pressure O_2 (u)

Mean Field

Kinetic Monte Carlo
Model Based Controller Description

- **States** - $x_k = \begin{bmatrix} \theta_{CO} & \theta_O & d_k \end{bmatrix}^T$, **Input** - $\beta \propto P_{O_2}$, **Measurement** - $\theta_{CO}$
  Where $d_k$ is an integrated input disturbance.

- **Controller Models**
  - Mean Field model linearized about the set point
  - Nonlinear Mean Field model
  - Coarse KMC model linearized about the set point

- **Regulator** - Forecast with the model and optimize the input trajectory

- **Estimator** - $\hat{x}_k = \hat{x}_k^- + L(y_k - C\hat{x}_k^-)$
  Where $L$ is the solution to the Kalman Filter recursion of the controller model, all noise is attributed to the disturbance
Control Case 1 - Set Point Change

- Initial set point - $\theta_{CO} = 0.06$
- Final set point - $\theta_{CO} = 0.52$
- Linear models linearized about final set point
Linearized Mean Field Controller

- Makes set point change successfully
- Final response is oscillatory
- Controls well in low $\theta_{CO}$ limit, where mean field assumptions are valid
- Final response is oscillatory, where mean field assumptions are not valid
• Makes set point change successfully

• Disturbance model facilitates good initial set point tracking
Control Case 2 - Disturbance Rejection

- Set point - $\theta_{CO} = 0.52$
- Input disturbance $u_k = u_k + 1.5$
  from $t=2.5$ sec to $5.5$ sec
Linearized Mean Field Controller

- Rejects disturbance without extinguishing the plant
- Oscillatory response
Nonlinear Mean Field Controller

- Disturbance extinguishes the state
- Poor set point tracking, before and after disturbance
• Disturbance model correctly models the disturbance - and rejects the disturbance

• Measurement controlled to set point within noise level of system
Conclusions

**Big Question** - Are macroscopic models based on the usual closures good enough for control purposes when the process is best described by a microscopic or multi-scale model?

**Sometimes**

- Mean field model is accurate at low $\theta_{\text{CO}}$.
- Feedback overcomes moderate model error; forecasts needed only for short times.

**Sometimes Not**

- In general, good control requires accurate forecasting and optimization of the mean of the full microscopic model (mean field model is useless at high $\theta_{\text{CO}}$)
- In general, closed-form, low-order evolution equations for the expectation of the stochastic models do not exist.
- We are developing methods to evaluate efficiently the dynamic trajectory of the expectation of the stochastic models and the sensitivity of this expectation to parameters (control decisions).
- With further development of these tools, we can apply MPC in real time directly with the microscopic models.
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