First-Passage Kinetic Monte Carlo Algorithm for Complex Reaction-Diffusion Systems

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Outline

1. Introduction

2. First-Passage Kinetic Monte Carlo

3. Results: Radiation Damage in Fe
Systems of diffusing particles that react with other particles upon collision are a common model in computational materials science: reaction-diffusion models.

Examples include: diffusion-limited chemical reactions, signal transduction in cells, radiation damage in metals, dopant implantation in semiconductors, epitaxial deposition and growth of thin films, population dynamics, etc.

Continuum models are often unable to correctly capture some key property, notably the strong heterogeneity in space/time (e.g., clustering), and intrinsic fluctuations (e.g., nucleation).

Continuous-Time Markov Chain models are an attractive but expensive alternative: A collection of Brownian hard spheres that diffuse through a homogeneous continuum and react upon collision with other particles or surfaces.
Example: Chemotaxis in *E. Coli.*

Figure: **Bacterial chemotaxis** as studied using *Smoldyn* by Karen Lipkow and Steven Andrews [*J. Bacteriol.* 187(1):45-53, (2005)]
Example: Radiation Damage

Figure: Defect creation and clustering in metals during irradiation.
Some or all unit events are diffusion hops: a set of $N$ hard objects walking randomly on a lattice or in continuum space.

- Upon collision particles *react* (collision events).
- Example: Diffusion-controlled annihilation $A + A \rightarrow 0$.
- Great many diffusion hops necessary to bring particles to collisions at low density.

Traditional *synchronous* $n$–fold event-driven algorithm (BKL). Other types of Poisson events (birth, decay, boundary, etc.) are easy to handle.
Given a region of space $\Omega$, one can determine the probability distributions for when and where (on $\partial \Omega$) a particle will first leave that region (first-event prediction).

Given that a particle has not yet left that region, one can determine the probability of finding the particle at some point inside the region at a given time (no-event propagation).

For pairs of particles, reduce to two independent center-of-mass and difference walkers.
First-Passage Kinetic Monte Carlo (FPKMC)

- Construct disjoint protective regions (cubes, spheres) at $t = 0$.
- Main events are (super)hops to $\partial \Omega$. For each walker (particle or pair) randomly draw first passage time from the appropriate PDF.
- Find the earliest time in the queue, propagate the particle/pair to boundary/collision, construct a new protective region, insert back into queue with a new event time, repeat [1, 2]!
Advantages of the Algorithm

- The FPKMC algorithm is exact for continuous diffusion problems because it breaks the hard $N$-body problem into tractable one- and two-body problems.
- It is the first use we know of of time-dependent Green’s functions.
- The algorithm automatically adjusts to variable timescales: multiscale.
- We have a code that implements different types of reactions (annihilation, coalescence, chemical reactions, decay/emission, hard-sphere repulsion).
Disadvantages of the Algorithm

- The method is significantly more complicated to implement than BKL KMC and it requires analytical solutions (1-body and 2-body problems).
- Multi-particle reactions cause complications or slowdown (ex., nearly triple collisions).
- One can combine the asynchronous super-hops with local synchronous small hops in a mixed time-driven/event-driven approach [3].
- FPKMC can be viewed as a general-purpose accelerator that brings particle within interaction range quickly, after which application-specific handling should take over.
Diffusion-reaction model for **radiation damage in metals**: diffusing and reacting *vacancies* and *interstitials* and their clusters.

A Kinetic Monte Carlo (KMC) simulation faithfully follows every **atomistic event**: *cascade insertion*, *diffusion hop*, *annihilation*, *recombination*, *clustering*, *dissociation*, *trapping*, *escape*, etc [4].
Radiation Damage KMC Model

- Very simple additive hard-sphere model for **testing** purposes, based on work by Barbu *et al*.

- **Species:**
  - *monomers*, including highly-mobile interstitials ($I$) and less-mobile vacancies ($V$), with diffusion coefficient
    
    $$D_1 = D_0 e^{-E_m/kT}$$
  
  - mobile *cluster species*, including dimers ($I_2$ and $V_2$) and trimers ($I_3$ and $V_3$), with radius
    
    $$R_c \sim R_0 + (R_1 - R_0)c^{1/3}$$
  
  - *immobile* species representing clusters larger than any of the mobile species ($I_c$ and $V_c$)
  
  - *Frenkel pairs* ($IV$), inserted randomly with some rate
Reactions:

- **Coalescence**: $I + I \rightarrow I_2$ or $V + V_3 \rightarrow V_{c=4}$
- **Partial annihilation**: $I_2 + V_{c=4} \rightarrow V_2$
- **Decay or emission**: $V_{c=5} \rightarrow V_{c=4} + V$, or $I_2 \rightarrow I + I$, with rate

$$\Gamma_c = \Gamma_0 D_1 a^{-2} c^{2/3} e^{-E_b(c)/kT},$$

$$E_b(c) = E_f + [E_b(2) - E_f] \frac{c^{2/3} - (c - 1)^{2/3}}{2^{2/3} - 1}.$$
Figure: Comparison of the density profile between FPKMC (symbols) and CEA OKMC code from LAKIMOCA [5] (lines) simulations of a 0.287 µm-thick film of α-iron subjected to 120 seconds of electron radiation at a temperature $T = 200^\circ C$. 
We can develop FPKMC models that match accelerator (e.g., JANNUS) experiments \textbf{(high dose rate)} then use the same models to simulate material behavior over a nuclear reactor lifetime \textbf{(low dose rate)}: computational extrapolation.

Approximate scaling of results from the accelerated testing experiments is achieved when the temperature is raised sufficiently so as to keep the ratio of vacancy diffusion coefficient to irradiation rate constant.

FPKMC allows us to quantify the mismatch with \textbf{atomistic fidelity} up to \textit{realistic doses} (10dpa)!

But the model is \textbf{too simple} to capture realistic physics! Work is underway at CEA to develop more detailed and accurate models.
Swelling ($\Delta V / V$)

*Figure:* Swelling due to 10dpa electron irradiation in a pure Fe film
Future Directions

- **Apply** FPKMC to a wider range of problems, notably, **systems biology** (compare to Smoldyn library).
- Extend first-passage to **lattice models** (discrete space), notably, defect diffusion through **dense alloys**.
- Approximately handle **continuous interaction potentials** (ala Brownian Dynamics), and most importantly, **long-ranged interactions** (e.g., electrostatic or elastic).
- When very fast species (e.g., interstitials) are present they slow down even event-driven algorithms: multiscale methods to utilize this **separation of time-scales**.
- **Parallelization** of event-driven algorithms remains an important challenge.
- The particle model can be coupled to a more efficient **continuum** model in a **hybrid method** (see next talk).
References/Questions?

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