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

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CMMD Seminar, July 2009

Outline

Reaction-Diffusion Particle Models

- 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.

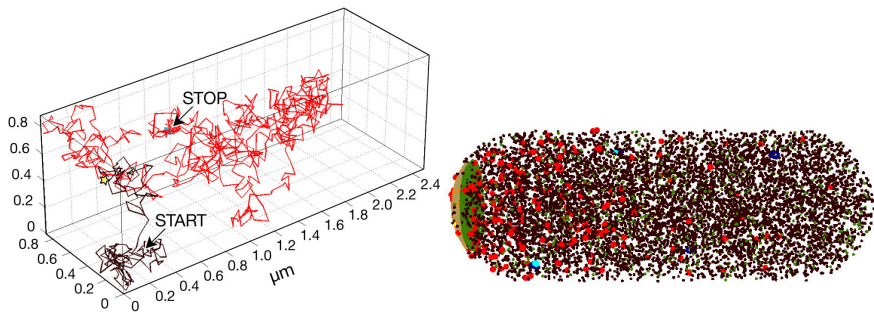# Example: Chemotaxis in *E. Coli.*

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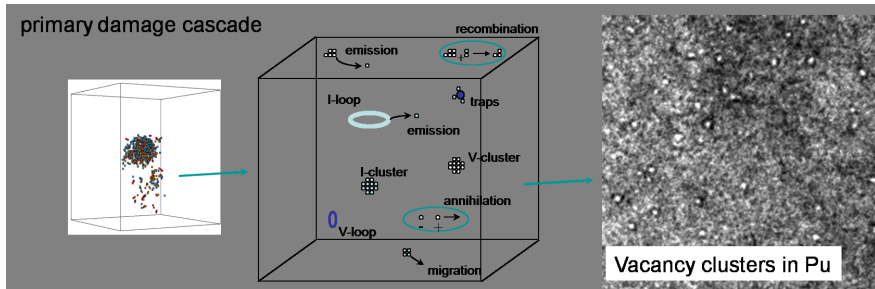
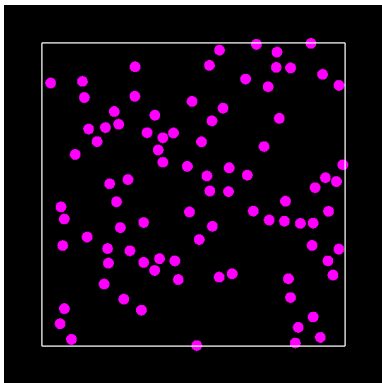# Example: Radiation Damage

Figure: Defect creation and clustering in metals during irradiation.

Diffusion Kinetic Monte Carlo

(MNG)

- 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.

Green's Function Diffusion Theory
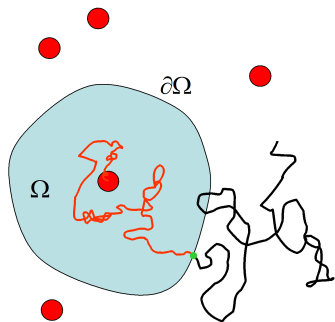
- Given a region of space Ω, one can determine the probability distributions for when and where (on $\partial\Omega$) a particle will first leave that region (*first-event prediction*).

- 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)
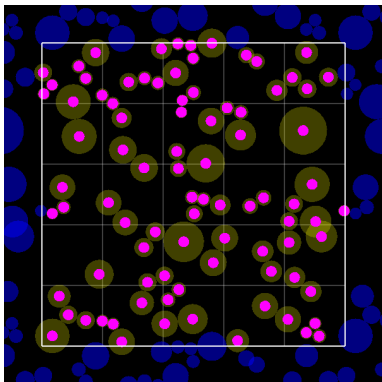
(MNG)

- 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.

FPKMC for Radiation Damage

- Diffusion-reaction model for **radiation damage in metals**: diffusing and reacting *vacancies* and *interstitials* and their clusters
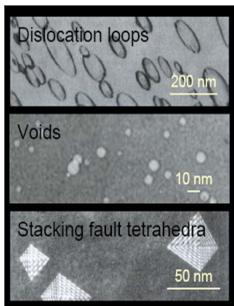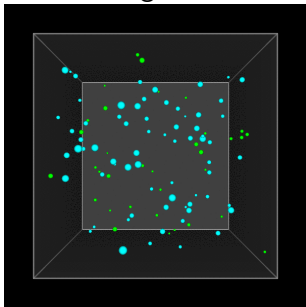
- A Kinetic Monte Carlo (KMC) simulation faithfully follows every **atomistic event**: *cascade insertion*, *diffusion hop*, *annihilation*, *recombination*, *clustering*, *dissociation*, *trapping*, *escape*, etc [4].

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

Model contd.

- **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

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

  $$E_b(c) = E_f + [E_b(2) - E_f] \frac{c^{2/3} - (c-1)^{2/3}}{2^{2/3} - 1}.$$
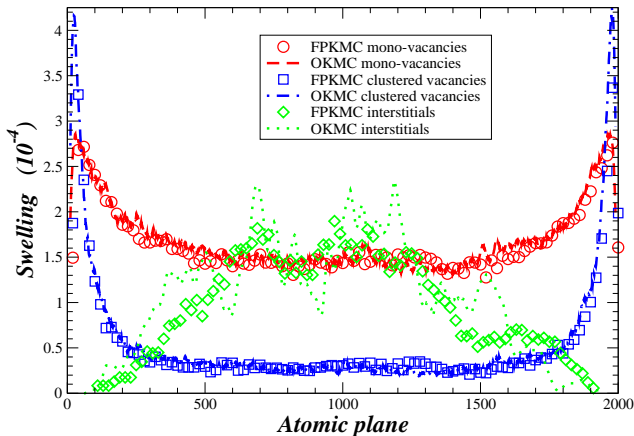
Validation

Figure: Comparison of the density profile between FPKMC (symbols) and CEA OKMC code from LAKIMOCA [5] (lines) simulations of a $0.287\mu m$-thick film of α-iron subjected to 120 seconds of electron radiation at a temperature $T = 200^o C$.

Computational Extrapolation

- We can develop FPKMC models that match *accelerator* (e.g., JANNUS) experiments (**high dose rate**) then use the same models to simulate material behavior over a *nuclear reactor* lifetime (**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 **atomistic fidelity** up to *realistic doses* (10dpa)!

- But the model is **too simple** to capture realistic physics! Work is underway at CEA to develop more detailed and accurate models.
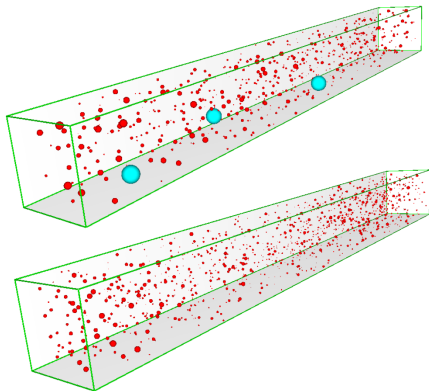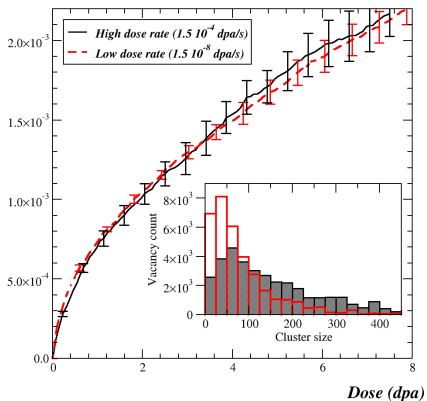
Lab vs. Reactor

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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