Kinetic Monte Carlo Approach to Cluster Growth in Magnetron Plasmas

K. Fujioka *, L. Rosenthal, S. Wolf, M. Bonitz
Institut für Theoretische Physik und Astrophysik der Christian-Albrechts-Universität Kiel, Germany

Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

TR 24 complex plasmas

Abstract

The control of nanoscale structures is of great importance to the development of technologies. Specifically, the nanoparticle may be considered as the essential building block of a variety of structures. A recent example [1] shows that gold particles can be used as seeds for the growth of nanowires with dimensions and shape controlled by the size of the seed. We present here a kinetic Monte Carlo scheme to simulate the growth [2] and size distributions of metallic clusters formed in a magnetron discharge by the agglomeration of sputtered atoms. Given a set of experimental conditions, we show that the size distribution of emitted cluster can be determined within the growth phase. The use of the "first reaction" [3] method enables us to significantly speed-up the simulation by following only representative cluster sizes within the system. We present some preliminary results and outline the general ideas to simulate a macroscopic system.

Simulation Models

Kinetic Monte Carlo

- Physical processes occur according to predetermined rates
- Models are only as accurate as the processes that are included
- Start with a simplified base list of essential processes

Primary Processes

- Metal-Gas Collisions
- Atom/Cluster Movement
- Cluster Nucleation
- Single Atom Adhesion to a Cluster

Deconstruction to Stages

1. **Thermalization:** Highly energetic sputtered atoms equilibrate with a buffer gas background
2. **Nucleation:** 3-Body Collisions (1 gas–2 metal atoms) result in bound metal dimers that serve as the nucleus for larger clusters
3. **Growth:** Single metal atoms adhere to a cluster surface

Thermalization Model

Model Details

- 1D model of discrete spatial slices
- Space filling neutral buffer gas background described by: atomic properties (r_g, m), pressure (P_g), temperature (T_g), and a constant flow velocity $(\bar{v}_g)$
- Metal atoms followed individually through the system: atomic properties (r_m, M) and intial energy (E_m)
- Collision cross section from hard sphere model: $\sigma = \pi(r_m + r_g)^2$
- Movement rate:

$$k_{move} = v_i / l$$

- Collision rate:

$$k_{col} = \nu = n_g \sigma \sqrt{(v_i - \bar{v}_g)^2 + v_{tg}^2}$$

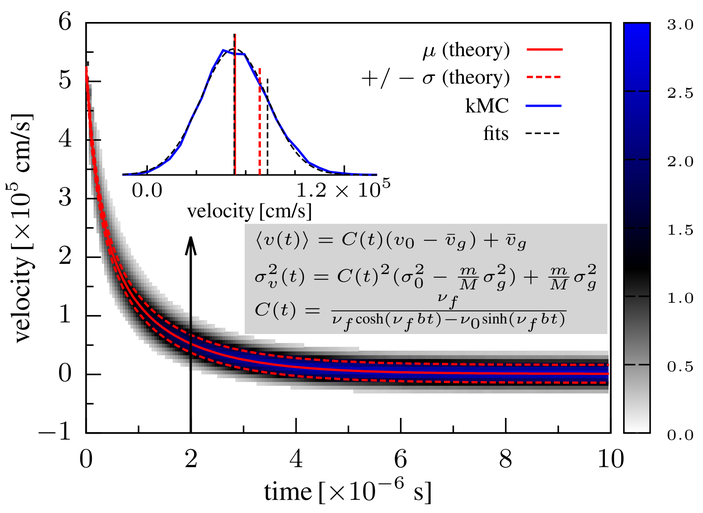


FIG. 1: Thermalization of Ag atoms in a He buffer gas Thermalization is quantified via the mean and variance of the metal atom velocity distribution. Theoretical results for the mean velocity are fully consistent with simulations, and the variance is consistent with the equilibrated state.

Example Parameters

- Spatial slices: l =0.01cm
- Sputtered Ag energy: $E_m = 15$eV corresponding to 300V magnetron discharge [4]
- He buffer temperature: $T_g = 300$K $\Rightarrow$ mean thermal veloicty $v_{tg} = \sqrt{3k_B T_g / m}$
- He buffer pressure: $P_g = 100$ Pa $\Rightarrow$ gas number density $n_g \approx 2.4 \times 10^{16}$cm^{-3}
- Constant He flow velocity: $\bar{v}_g = 2 \times 10^3$cm/s (Space average of position-dependent flow velocity: $\bar{v}_g(x) = \frac{v_e R^2}{(R + x\tan\alpha)^2}$; chamber length $x = 4$cm, nozzle radius $R = 3$mm, walls angled at $\alpha = 45°$, and exit velocity $v_e = 2.6 \times 10^4$cm/s [4])

Theoretical Approach

- Metal atom velocity after an elastic collision:

$$v_f = v_i(1 - \mu) + \mu V_g$$

where $\mu = 2m/(M + m)$, $V_g \sim \mathcal{N}[\bar{v}_g, \sigma_g^2]$

- After many collisions (N_c):

$$v(N_c) \sim \left(e^{bN_c}\mathcal{N}[\bar{v}_0 - \bar{v}_g, \sigma_0^2 - \tfrac{m}{M}\sigma_g^2] + \mathcal{N}[\bar{v}_g, \tfrac{m}{M}\sigma_g^2]\right)$$

$b = \ln(1 - \mu)$, σ_0^2 is initial variance of metal atom velocities

- Combine:
  1) mean value approximation for $v(N_c)$ to get $\nu(N_c)$
  2) the relation $N_c(t) = \int_0^t \nu(t')\mathrm{d}t'$
  $\rightarrow$ a differential equation for $\nu(t)$, the solution is used in (2) to find:

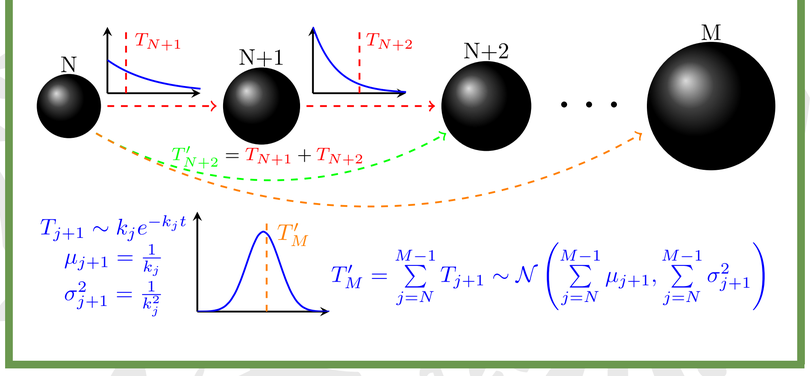
$$N_c(t) = \frac{1}{b}\left\{\ln\left[\frac{\nu_f}{\nu_f \cosh(\nu_f bt) - \nu_0 \sinh(\nu_f bt)}\right]\right\}$$

ν_f and ν_0 are the mean final and initial collision frequencies.

- $N_c(t)$ is plugged into the expression for $v(N_c)$ to give:

$$v(t) \sim \frac{\nu_f}{\nu_f \cosh(\nu_f bt) - \nu_0 \sinh(\nu_f bt)}\mathcal{N}[\bar{v}_0 - \bar{v}_g, \sigma_0^2 - \tfrac{m}{M}\sigma_g^2] + \mathcal{N}[\bar{v}_g, \tfrac{m}{M}\sigma_g^2]$$

Growth Algorithm



- Single atom growth $\rightarrow$ many MC steps: $d = 10$nm $\approx 30,000$ atoms
- "First-Reaction" kMC: events are time-ordered via rate-based exponential distributions
- Multiple growth steps contained in one MC step by summing time samples
- Central Limit Theorem for large growth events: one MC step, one time sample, many growth steps

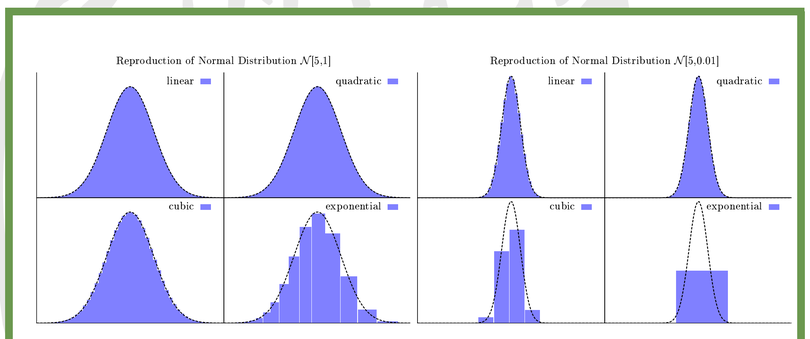


***FIG. 2: Normal Distribution Reproduction*:** Various binning schemes for representative cluster radii and their reproduction of normal distributions. While each tested scheme can reproduce a wide distribution within reason, the cubic and exponential schemes fail in representing a narrow distribution.

- Several schemes tested (Fig. 2) of representative cluster sizes (linear, quadratic, cubic, and exponential growth with an index)

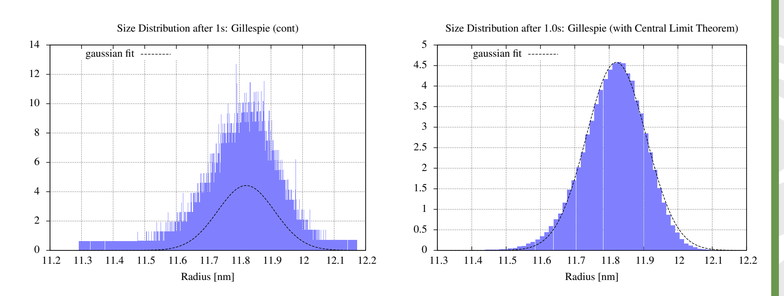


***FIG. 3: Algorithm Comparison*:** A check of the the growth algorithm comparing the quadratic scheme with the continuous growth process. Gaussian fits over the resulting distributions are nearly identical, but the simplified algorithm is computationally three orders of magnitude faster.

- Test model of cluster growth with quadratic scheme against a full calculation (Fig. 3)
- Comparing Gaussian fits: full $\rightarrow \mu = 11.8212$ and $\sigma = 0.0901856$; quadratic $\rightarrow \mu = 11.8206$ and $\sigma = 0.0871358$
- 3 orders of magnitude improvement in computation time: full $\rightarrow$ 26 hours and 5×10^{10} MC steps; quadratic $\rightarrow$ 1.5 minutes and 8×10^7 MC steps

Growth Model

- 3D treatment of clusters
- Initialize space with cluster nuclei (metal dimers)
- Constant monomer background: $n_m = 10^{13}$cm^3
- Metal assumed to be thermalized with gas background at 300 K
- Growth rate:

$$k(N_m) = k_0 N_m^{2/3} n_m$$

reduced growth constant $k_0 = \sqrt{\frac{8k_BT}{\pi M}}\pi r_m^2$, atoms in cluster N_m

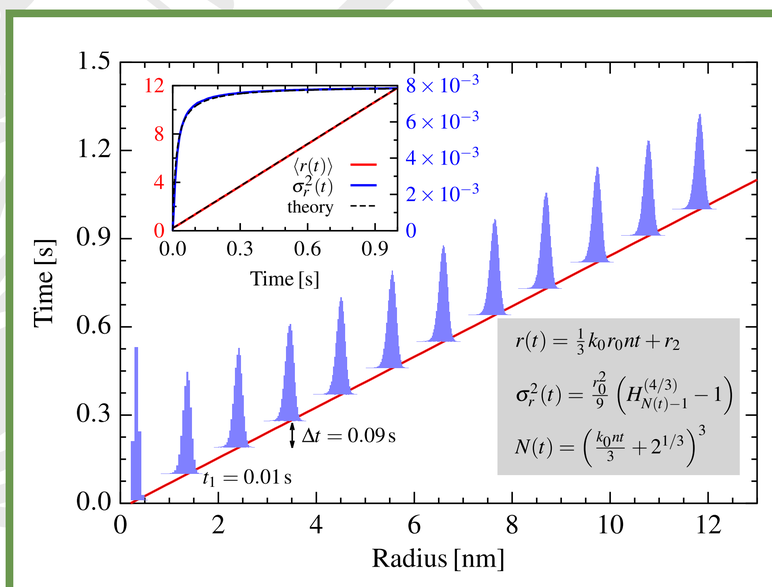


FIG. 4: *Size Distribution Evolution:* Several snapshots during the simulated growth process are shown. The mean cluster size (red lines) grows linearly in time. The inset shows the mean size and variance as functions of time along with plots of an analytical solution of the model (dashed lines) for these values.

Theoretical Approach

- $k(N_m) = \frac{dN_m}{dt}$; liquid drop model, $r = r_m N_m^{1/3}$: $\frac{dr}{dt} = \frac{1}{3}k_0 r_m n_m$
- Solution gives the mean radius:

$$\langle r(t)\rangle = \tfrac{1}{3}k_0 r_m n_m t + r_2$$

r_2 is the dimer radius ensuring cluster formation at $t = 0$.

- Taking the variance of this equation:

$$\mathrm{Var}[r(t)] = \left(\tfrac{1}{3}k_o r_m n_m\right)^2 \mathrm{Var}[t]$$

- Cumulative time variance to proceed from 2 to N_m atoms from rate-based exponential distributions:

$$\mathrm{Var}[t] = \sum_{j=2}^{N_m - 1}\frac{1}{k(j)^2} = \sum_{j=2}^{N_m-1}\frac{1}{(k_0 j^{2/3} n_m)^2}$$

$$\Rightarrow \mathrm{Var}[r(N_m)] = \frac{r_m^2}{9}\sum_{j=2}^{N_m-1}\frac{1}{j^{4/3}}$$

- Sum is a generalized harmonic number: $H_a^{(b)} = \sum_{j=1}^{a}\frac{1}{j^b}$
- Rate equation gives: $N_m(t) = \left(\frac{1}{3}k_0 n_m t + 2^{1/3}\right)^3$
- Substitute into the variance expression:

$$\mathrm{Var}[r(t)] = \frac{r_m^2}{9}\left(H^{(4/3)}_{\left(\frac{1}{3}k_0 n_m t + 2^{1/3}\right)^3 - 1} - 1\right)$$

Outlook

- Detailed comparison of models to experiments
- Treatment of nucleation stage to bridge thermalization and growth
- Combine stages into a single consistent simulation
- Expansion of interesting and relevant processes
  - Cluster-cluster collisions
  - Cluster charging
- Extension to reactive materials

Summary

- Successful implementation of kMC to model various stages of cluster growth
- Development of a fast growth algorithm to treat large cluster sizes
- Development of theoretical analysis to compliment simulation

References

[1] M. Heurlin et al, *Nature*, **492**, 90 (2012).
[2] B. Smirnov et al, *Phys. Scr.*, **73**, 288 (2006).
[3] D. Gillespie, *J. Comput. Phys.*, **22**, 403 (1976).
[4] P.V. Kashtanov, B.M. Smirnov, R. Hippler, *Phys. Usp.*, **50**, 455 (2007).

* Kenji Fujioka • Christian-Albrechts-Universität Kiel • Leibnizstr. 15, 24098 Kiel, Germany • +49(0)431-880-4732 • fujioka@theo-physik.uni-kiel.de