

# KINETIC MONTE CARLO SIMULATIONS OF THE ZIFF-GULARI-BARSHAD MODEL FOR SURFACE REACTIONS

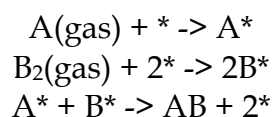
Heterogeneous catalysis and surface reactions are important for many applications, such as exhaust emission control and synthesis of chemicals, although their behavior cannot be correctly modeled using macroscopic rate laws. Python code was developed to simulate the Ziff-Gulari-Barshad model for surface reactions to help explain why carbon monoxide oxidation is rapid for some mixtures of carbon monoxide and oxygen and negligible at others. The model is extremely simple, yet complex phenomena emerges which helps explain the surface chemistry which surrounds us. Included in this work is a movie showing how too much carbon monoxide (relative to oxygen) can lead to the surface being “poisoned” by stable islands of CO which form on the surface.

## INTRODUCTION

The Ziff-Gulari-Barshad (ZGB) model has been very influential in modeling surface reactions. It deals with a generic bi-molecular, irreversible reaction, often compared to carbon monoxide oxidation. This particular reaction is a prevalent reaction in current automobiles’ catalytic converters and may be just as prevalent in the future in for fuel cell catalysis. Though it is a simple model, it shows the effects of microscopic reactions on macroscopic properties. Furthermore, it shows where macroscopic phenomenological reaction rates fail and how. Due to its simplicity, it is very applicable in interpreting a variety of surface reactions. Finally, despite its simplicity, complex phase transitions (both first- and second- order) of surface adsorbates are present and explained in the model (one of which is lacking in macroscopic models). These transitions lead to changes in reaction rate of several orders of magnitude.

## THE ZIFF-GULARI-BARSHAD MODEL

The ZGB model focuses on reactions of A and B on a surface (A could be CO and B could be O<sub>2</sub>). A adsorbs on a single surface site and gaseous B<sub>2</sub> adsorbs and instantly decomposes on two surface sites. A\* and B\* quickly react if they are nearest neighbors. We can write these reactions as follows, with freestanding asterisks indicating a surface site and X\* denoting X adsorbed on the surface:



The model treats all surface sites identically and places them uniformly on a square lattice. The gas molecules impinge the surface according to the kinetic theory of gases with a sticking probability of 1 (on empty sites, zero otherwise). The only controllable parameter is the mole fraction (in the gas phase) of A (with the balance being B<sub>2</sub>). This parameter is often times referred to as  $y$ . This model omits phenomena such as surface diffusion, desorption of A or B, lateral interactions, surface reconstruction, and other relevant processes which can add much complexity. What is captured by the model is that the surface can be fully covered with A or B (depending on  $y$ ), thus inhibiting any reaction at all (this is referred to as poisoning in the catalysis community, for obvious reasons).

## KINETIC MONTE CARLO: VARIABLE STEP SIZE METHOD

Kinetic Monte Carlo (kMC), in the most general sense, is a method of solving the Master Equation, or the equation governing the probabilities of and transition rates between different microstates (with each microstate being a different surface configuration). kMC does not compute these probabilities explicitly, but rather allows us to choose an initial configuration and (stochastically) propagate a system through time to different configurations *with the correct probabilities and rates*.

The Variable Step Size Method (VSSM, sometimes called the n-fold way) is the most popular algorithm for performing kMC; in fact, VSSM is often used interchangeably with kMC, although other algorithms exist which produce identical results with different computational properties. It works in three steps:

- 1) Initialize
  - a. Generate an initial configuration,  $a$
  - b. Set time to an initial value (usually zero)
- 2) Propagate forward in time
  - a. Increase time by the following amount:  $\ln(r)/K_a$  where  $K_a$  is the sum of all transitions out of the current microstate,  $\alpha$ , and  $r$  is uniformly distributed from 0 to 1.
- 3) Change the configuration to  $b$  with probability  $W_{ba}/K_a$

## RESULTS

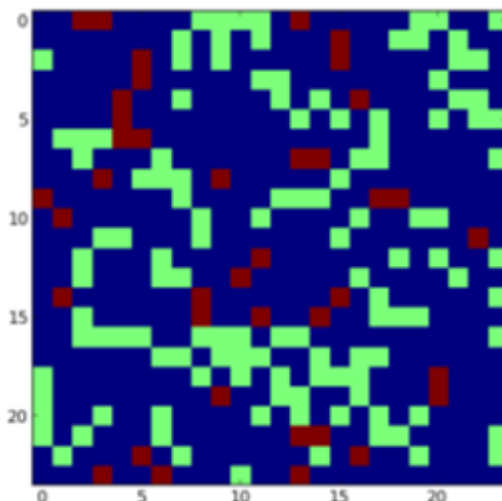


Figure 1- A picture of the surface during simulation with an initial configuration of an empty surface. Dark blue is empty sites, green is A\* and red is B\*.  $y$  is 0.85, hence A will eventually poison the surface. Notice clusters of A (and B) forming on the surface.

A graph of the simulation (shown in Figure 1) shows the system as it evolves from an empty surface to which will eventually become completely covered by A (poisoned). Of particular importance is the formation of clusters of A (and B) showing that the mean-field approximation of macroscopic rate equations does not hold true. This is due to the fact that A\* and B\* quickly react with each other, thus removing isolated species and leaving only clusters which are more stable.

There are three states for the system, depending on  $y$ , the fraction of A in the gas phase. At high  $y$  (above  $y_1$ ), the surface tends towards high A coverage. Once the surface is covered with A, there is no transition (reaction) which removes A from the surface because B cannot adsorb (the surface is poisoned with A). Conversely at low  $y$  (below  $y_1$ ), the surface tends towards being covered with B, from which it cannot recover. In the intermediate ranges of  $y$ , the system is active and produces C. Ziff et al. found these values to be  $y_1 = 0.39065 \pm 0.00010$  and  $y_2 = 0.52560 \pm 0.00001$  (1). Figure 2 shows the reaction rate (production of C) as a function of time as the system becomes more and more covered with A.

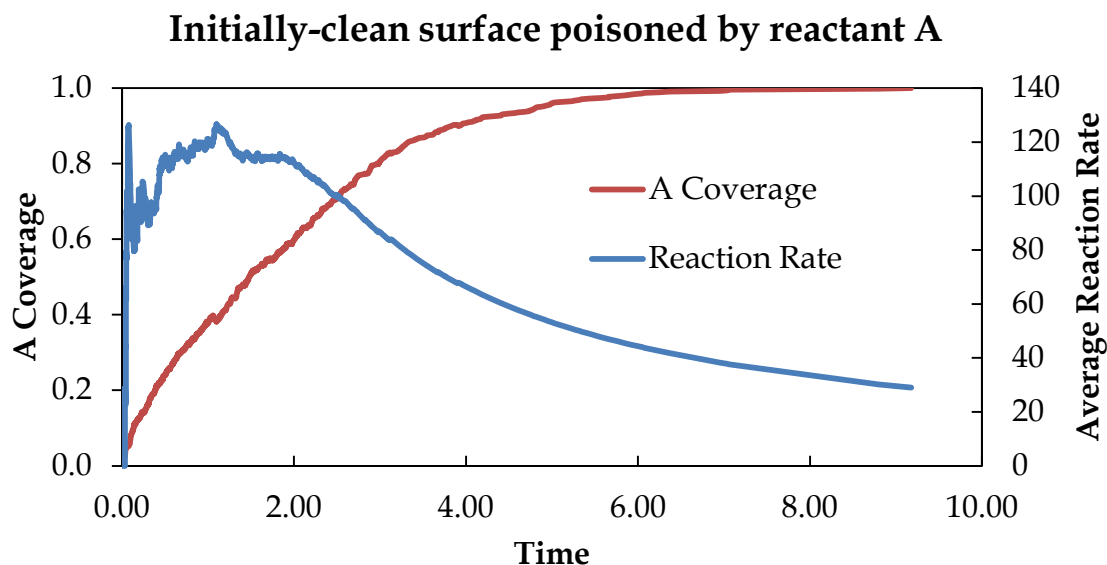


Figure 2 - A graph of the system evolving from clean to poisoned with A, due to the formation of stable islands of A

## CONCLUSIONS

In this work, code was written from scratch to simulate the ZGB model for surface reactions. The results agree with the results from literature and help explain the complex phenomena observed during heterogeneous catalysis. The model does not include many relevant features of specific reaction mechanisms, but its generic nature makes it qualitatively applicable to many reactions on surfaces.

## MOVIE CAPTION

This movie shows a kinetic Monte Carlo simulation of surface chemistry, namely the Ziff-Gulari-Barshad model for carbon monoxide oxidation (and other reactions). What you see is a colored representation of the surface during simulation with an initial configuration of an empty surface. Dark blue is empty sites, green is A\* and red is B\*. A\* and B\* quickly react to form C which promptly desorbs. The mole fraction of A in the gas phase is 0.85 in this simulation, which happens to be above a critical value of  $y_1$  - above which the surface will become completely covered with A (so-called poisoning!). Sadly, A will eventually poison the surface. Watch as stable islands of adsorbed A form which overtake the surface and end all reactivity!

## REFERENCES

- 1) R.M. Ziff, B.J. Brosilow, *Phys. Rev. A* **46**, 4630 (1992)