

Analysis of the Lattice Lotka-Volterra Model

Amanda Lampton*

Texas A&M University, College Station, Texas, 77843-3141

December 7, 2007

*Graduate Research Assistant, Flight Simulation Laboratory, Aerospace Engineering Department, Student Member AIAA, alampton@tamu.edu.

Contents

1	Introduction	5
2	LLV Model	6
2.1	Original LLV Model Lattice Simulations	8
2.2	Modified LLV Model Lattice Simulations	8
3	Examples	10
3.1	Case 1: Original LLV Method	10
3.2	Case 2: Radius of Reactivity = 1	12
3.3	Case 3: Radius of Reactivity = 5	14
3.4	Case 2: Radius of Reactivity = 50	14
3.5	Radii of Reactivity Summary	16
4	Conclusions	17

List of Figures

1	Phase Space	7
2	Original and Modified LLV Neighboring Sites	9
3	Concentrations of X_1 and X_2 Molecules for Original LLV Model	11
4	Global X_1 and X_2 Molecule Concentrations for Original LLV Model	12
5	Concentrations of X_1 and X_2 Molecules for a Radius of Reactivity of 1	13
6	Global X_1 and X_2 Molecule Concentrations for a Radius of Re- activity of 1	13
7	Concentrations of X_1 and X_2 Molecules for a Radius of Reactivity of 5	14
8	Global X_1 and X_2 Molecule Concentrations for a Radius of Re- activity of 5	15
9	Concentrations of X_1 and X_2 Molecules for a Radius of Reactivity of 50	15
10	Global X_1 and X_2 Molecule Concentrations for a Radius of Re- activity of 50	16
11	Global X_1 and X_2 Molecule Concentrations for a Radii of Reactivity	17

List of Tables

1	Monte Carlo Simulation Constant Parameters	11
---	--	----

1 Introduction

Restricted reactive processes are reactions that take place if the reactive species are adsorbed on the surface of a catalyst.^[1] Reactions are restricted to occurring only between neighboring molecules. As a result, basic mean-field requirements, such as homogeneity of the species and high diffusivity, no longer hold. Examples of such reactions are CO oxidation on the surface of Pt and NO reduction on the surface of Pt. Traditional mean-field approaches are not adequate in describing the dynamical behavior of these processes.

The lattice Lotka-Volterra (LLV) model was developed to model the catalytic processes of simple bimolecular reactive systems. The traditional Lotka-Volterra model was originally intended to describe the dynamics of a system of competitive biological species.^[1] This was due to its ability to describe oscillatory schemes. When applied to reactive processes, the traditional model is essentially a mean-field model containing a bimolecular autocatalytic reactive step, a creation step, and an annihilation step. When considering the phase portrait of the dynamics of such a system, there is a center that dominates the image. This center and the closed trajectories that form around it account for the oscillatory schemes. Unfortunately, the traditional model is space independent and cannot be realized on a lattice.^[1]

The LLV model is a space dependent model in which two kinds of reacting molecules and empty sites exist.^[1] There are three bimolecular reaction steps consisting of X_1 , X_2 , and S , where X_1 and X_2 are considered as on-lattice adsorbed sites and S denotes empty lattice sites.^[1]

Several different reaction applications have been analyzed. Reference 1 considers the dynamical behavior of one set of reactions using LLV and comparing local processes with the behavior predicted by mean-field analysis. Reference 2 analyzes the dynamical behavior of a similar set of reactions using LLV and also comparing to the behavior predicted by mean-field analysis. Reference 1 and 2 constrain the reactions only between neighboring molecules on the lattice. In simulation the lattice is randomly distributed with the two molecules and empty sites.^[1] As reactions occur local oscillations develop even though global oscillations are minimal, though such oscillations are predicted by the mean field analysis.^[2] Local clustering also occurs.^[1, 2] Reference 3 examines the dynamical behavior of initially inhomogeneous distributions such as stripes.

It shows how the molecules behave over time in cohesive groupings. They form several homogeneous layers and propagate through the lattice.[3]

This report examines a set of reactions using the LLV model described by the literature. The original LLV model in the form of the mean-field dynamics are analyzed and verified in Section 2. The LLV model lattice simulation is described in Section 2.1 as well the slightly modified version that is unique to this report. The original LLV model restricts reactions to those four closest neighbors on the lattice. This report proposes expanding the reactivity radius allowed in which a given site can react. This method is described in Section 2.2. The mean-field dynamics are analyzed and verified in Section 2. The mean-field dynamics are examined and compared to the dynamics of the LLV model with various radii of reactivity in Section 3.

2 LLV Model

As state previously, the LLV model considers a small system consisting of three bimolecular reactions and three species. The interactions of the three species are defined as follows



where the first step represents an autocatalytic reaction, the second the desorption of a partical, and the third the cooperative adsorption of a partical.

Let x_1 , x_2 , and s represent the total concentrations of the species X_1 , X_2 , and S , respectively. This allows for the LLV model dynamics to be represented by

$$\begin{aligned} \frac{dx_1}{dt} &= k_2x_1s - k_sx_1x_2 \\ \frac{dx_2}{dt} &= k_sx_2x_1 - k_1x_2s \\ \frac{ds}{dt} &= k_1x_2s - k_2x_1s \end{aligned} \tag{2}$$

The system of equations can be reduced by noticing that the sum of the concentrations of all three species must equal 1.

$$x_1 + x_2 + s = 1 \tag{3}$$

Using Equation 3 the system in Equation 2 can be reduced by eliminating the dynamic function $s(t)$. Thus a 2D nonlinear system is left as seen in Equation

4.

$$\begin{aligned}\frac{dx_1}{dt} &= k_2 x_1 \left(1 - x_1 - \frac{k_2 + k_s}{k_2} x_2 \right) \\ \frac{dx_2}{dt} &= -k_1 x_2 \left(1 - x_2 - \frac{k_1 + k_s}{k_1} x_1 \right)\end{aligned}\tag{4}$$

The dynamical system described by Equation 4 has four fixed points. There are three saddle points located at $(x_1^*, x_2^*) = (0, 0)$, $(0, 0)$, and $(0, 0)$. The characteristic center is located at

$$\left(\frac{k_1}{k_1 + k_2 + k_s}, \frac{k_2}{k_1 + k_2 + k_s} \right)$$

The phase portrait of the system is shown in Figure 1. The reaction constants used to generate the image are $k_1 = 0.9$, $k_2 = 0.3$, and $k_s = 0.1$.

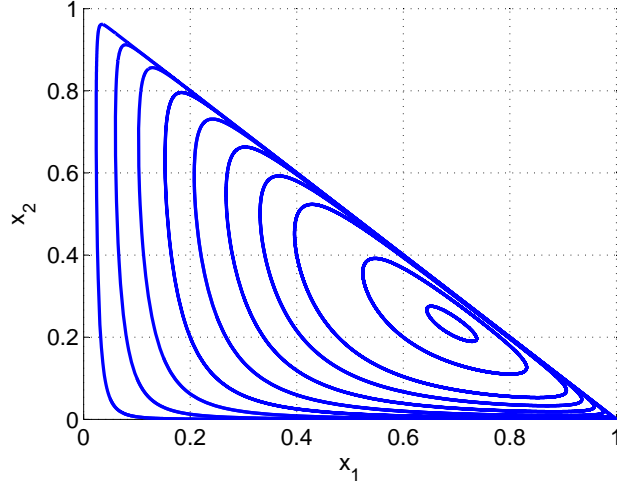


Figure 1: Phase Space

As suggested by the illustration, there are infinitely many closed trajectories around the center. These trajectories describe the oscillatory response expected from the mean-field dynamics. Additional trajectories defining the three saddle points are not important because there cannot be negative concentrations, and the sum of the concentrations cannot be greater than one. The area of interest for this case is the center.

2.1 Original LLV Model Lattice Simulations

The purpose of the lattice simulations is to allow the molecules adsorbed to lattice sites to only interact with local neighbors, meaning the four closest neighboring lattice sites. This is designed to emulate the “microscopic” picture of chemical reactions. This method effectively bars a given molecule from reacting with the mean field of all the particles. The reactions between molecules are also effectively random.

This kind of reaction is simulated using a Monte Carlo (MC) algorithm. The following summary of steps of the algorithm are for a two-dimensional square lattice and are taken almost directly from Reference 2.

1. Initially the lattice is filled at random with particles X_1 , X_2 according to a given initial condition. The lattice may also contain empty sites S .
2. At every elementary MC step, one lattice site is chosen at random.
3. If the chosen site is occupied by a particle X_1 , and a randomly chosen neighbor contains X_2 , then the molecule X_1 is replaced by a particle X_2 with reaction probability $p_s = k_s / (k_1 + k_2 + k_s)$.
4. If the chosen site is occupied by a particle X_2 , and a randomly chosen neighbor is an empty site, then the molecule X_2 desorbs and the site is vacated with probability $p_1 = k_1 / (k_1 + k_2 + k_s)$.
5. If the chosen site is empty, and a randomly chosen neighbor contains X_1 , then a second X_1 adsorbs on the S site with adsorption probability $p_2 = k_2 / (k_1 + k_2 + k_s)$.
6. In all other cases the lattice remains unchanged.
7. The algorithm returns to the second step for a new reaction event to start.

Each cycle through the MC procedure is a potential reactive event. Every MC time unit in the simulations consists of LxL attempted reactive events, where L is the linear size of the lattice.

2.2 Modified LLV Model Lattice Simulations

The modification integrated into the original LLV model involves the reaction potential of a given site. Rather than restricting reactions to only occurring

between neighboring sites, the radius of reactivity is expanded to allow molecules adsorbed to lattice sites to interact with other molecules within a certain radius of the site of interest. Figure 2 illustrates this concept.

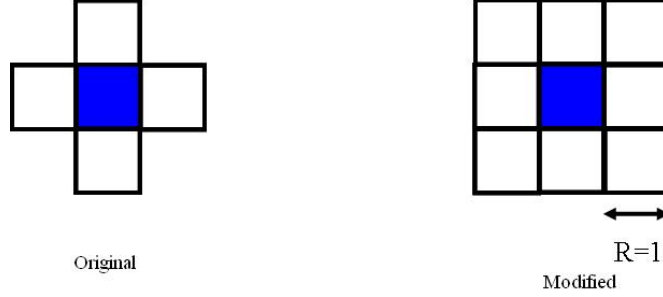


Figure 2: Original and Modified LLV Neighboring Sites

Based on the figure, the MC algorithm can be modified as follows.

1. Set the radius of reactivity, R , where R is a natural number and $1 \leq R \leq L$.
2. Initially the lattice is filled at random with particles X_1 , X_2 according to a given initial condition. The lattice may also contain empty sites S .
3. At every elementary MC step, one lattice site is chosen at random.
4. If the chosen site is occupied by a particle X_1 , and a randomly chosen neighbor no further than R lattice sites removed contains X_2 , then the molecule X_1 is replaced by a particle X_2 with reaction probability $p_s = k_s / (k_1 + k_2 + k_s)$.
5. If the chosen site is occupied by a particle X_2 , and a randomly chosen neighbor no further than R lattice sites removed is an empty site, then the molecule X_2 desorbs and the site is vacated with probability $p_1 = k_1 / (k_1 + k_2 + k_s)$.
6. If the chosen site is empty, and a randomly chosen neighbor no further than R lattice sites removed contains X_1 , then a second X_1 adsorbs on the S site with adsorption probability $p_2 = k_2 / (k_1 + k_2 + k_s)$.
7. In all other cases the lattice remains unchanged.

8. The algorithm returns to the third step for a new reaction event to start.

To further illustrate, here is a simple example. Let $R = 2$ and $L = 15$. The resulting lattice is 15×15 sites with a total of 225 sites. Let each site be uniquely defined by a set of two coordinates, so the sites range from $(1, 1)$ to $(15, 15)$. The randomly chosen lattice site is $(13, 5)$. Rather than just four neighboring sites to react with, this site now has the following sites to possibly react with:

$$\begin{aligned}
 & (11, 3), (11, 4), (11, 5), (11, 6), (11, 7) \\
 & (12, 3), (12, 4), (12, 5), (12, 6), (12, 7) \\
 & (13, 3), (13, 4) \qquad (13, 6), (13, 7) \\
 & (14, 3), (14, 4), (14, 5), (14, 6), (14, 7) \\
 & (15, 3), (15, 4), (15, 5), (15, 6), (15, 7)
 \end{aligned}
 \tag{5}$$

A site to react with is randomly chosen from the above list. Reactions occur based on the rules outlined in the fourth, fifth, and sixth lines of the modified MC algorithm. Then a new reaction event begins.

3 Examples

In order to fully explore the nuances of the previously discussed algorithms, several example cases are presented in this section. The mean-field approach, the LLV model, and the modified LLV model are compared and analysed for several radii or reactivity. All of the cases utilize the constants listed in Table 1.

Three radii of reactivity are examined. In addition to considering the evolution of the molecule concentrations on the global level, the concentrations of a series of lattice subsets are also recorded and analyzed.

3.1 Case 1: Original LLV Method

Recall that the original LLV model restricted reactions to occur only between a site and its four nearest neighbors. The MC simulation was allowed to run for a total of $L * L * MC = 27000000$ iterations. The concentrations of a series of subsets of the lattice were recorded and compared to the concentration evolution

Table 1: Monte Carlo Simulation Constant Parameters

Parameter	Value
k_1	0.9
k_2	0.3
k_s	0.1
p_1	0.692
p_2	0.231
p_s	0.078
L	300
MC	300

predicted by the mean-field system of ODEs. These concentrations are shown in Figure 3. To better compare the progression of the global concentrations of the two molecules, they are again illustrated alone in Figure 4.

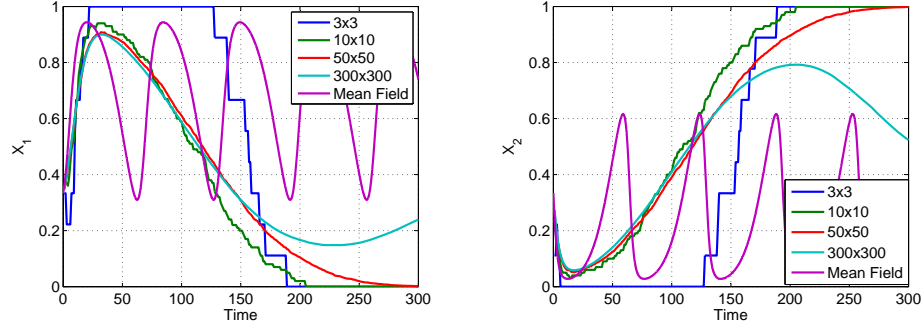


Figure 3: Concentrations of X_1 and X_2 Molecules for Original LLV Model

For both molecules at the “microscopic” level (3×3), the concentrations appear to be oscillating with no evidence of decay. To make a firm conclusion about this, however, the simulation needs to be run for many more MC time units. Unfortunately, the computational time necessary to conduct such a simulation is prohibitive. As the subset under consideration is expanded, however, there is a noticeable decay in the amplitude of the oscillations in concentration. This suggests that on the global level (300×300) the concentrations will approach some concentration and oscillate closely around it, which is not what was predicted by the mean-field simulation, shown as much shorter period, constant

amplitude oscillations. This trend holds with what was found in References 1 and 2.

3.2 Case 2: Radius of Reactivity = 1

The first radius examined is $R = 1$. This radius only adds four extra sites with which to possibly react, as seen in Figure 2. As before the concentrations of a series of subsets of the lattice were recorded and compared to the concentration evolution predicted by the mean-field system of ODEs. These concentrations are shown in Figure 5. To compare the progression of the global concentrations of the two molecules, they are again illustrated in Figure 6.

For both molecules at the “microscopic” level (3×3), the concentrations appear to be oscillating very slowly, much more slowly than the original method, with no evidence of decay. As the subset under consideration is expanded there is a noticeable decay in the amplitude of the oscillations in concentration. The decay in these figures is more evident than in the previous case, especially at the global level. This again suggests that on the global level (300×300) the concentrations will approach some concentration and oscillate closely around it, which is not what was predicted by the mean-field simulation, shown as

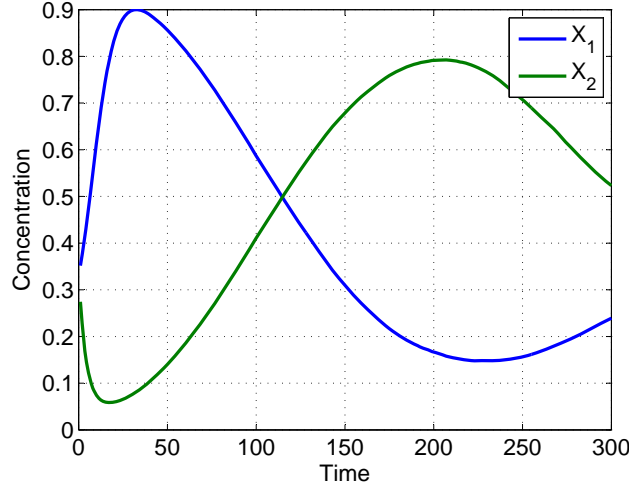


Figure 4: Global X_1 and X_2 Molecule Concentrations for Original LLV Model

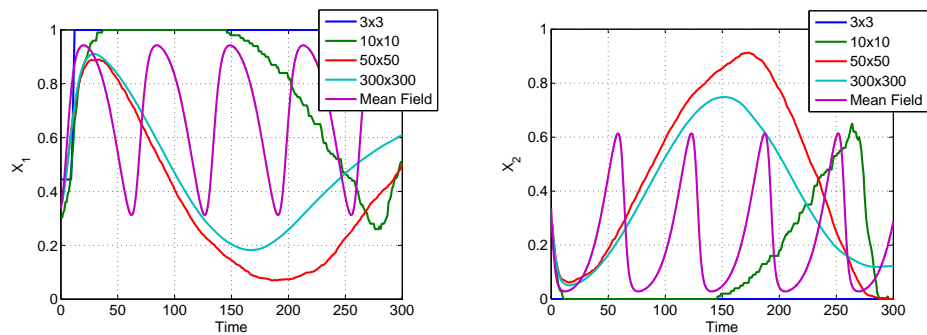


Figure 5: Concentrations of X_1 and X_2 Molecules for a Radius of Reactivity of 1

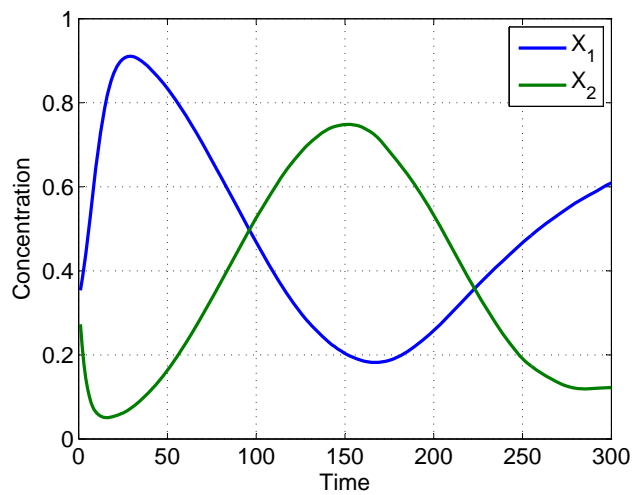


Figure 6: Global X_1 and X_2 Molecule Concentrations for a Radius of Reactivity of 1

much shorter period, constant amplitude oscillations. The period, however, is marginally closer to that of mean-field dynamics.

3.3 Case 3: Radius of Reactivity = 5

The next radius examined is $R = 5$. This radius adds 120 extra sites with which to possibly react. As before the concentrations of a series of subsets of the lattice were recorded and compared to the concentration evolution predicted by the mean-field system of ODEs. These concentrations are shown in Figure 7 and 8.

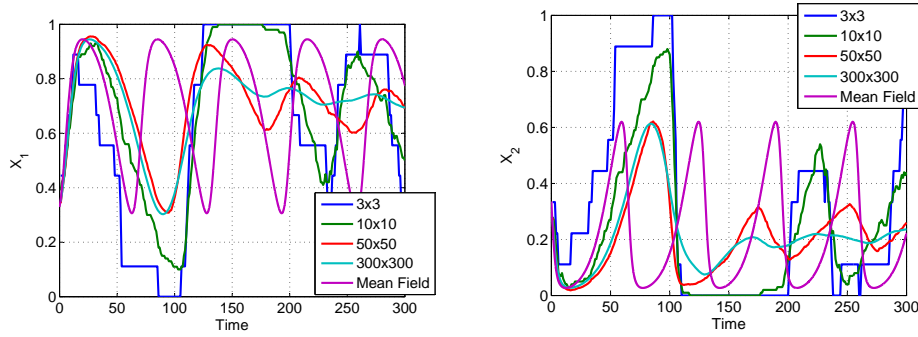


Figure 7: Concentrations of X_1 and X_2 Molecules for a Radius of Reactivity of 5

The concentration oscillations for both molecules at the “microscopic” level (3×3) in this case are much more pronounced. There is evidence of decay in this short time span. As the subset under consideration expands, the decay in the amplitude of the oscillations in concentration becomes much more noticeable. The decay in these figures is more evident than in the previous cases, even at the penultimate subset shown in Figure 7. The period of the global oscillations is only slightly larger than that of the mean-field dynamics. It appears that as the radius of reactivity increases, the global oscillations become more similar to the oscillations predicted by the mean-field dynamics.

3.4 Case 2: Radius of Reactivity = 50

The final radius examined is $R = 50$. This radius adds 2600 extra sites with which to possibly react. As before the concentrations of a series of subsets of

the lattice were recorded and compared to the concentration evolution predicted by the mean-field system of ODEs. These concentrations are shown in Figure 9 and 10.

The concentration oscillations for both molecules at the “microscopic” level (3×3) in this case behave differently than in previous cases. There are noticeable oscillations, and they follow the other concentrations closely. There is minimal

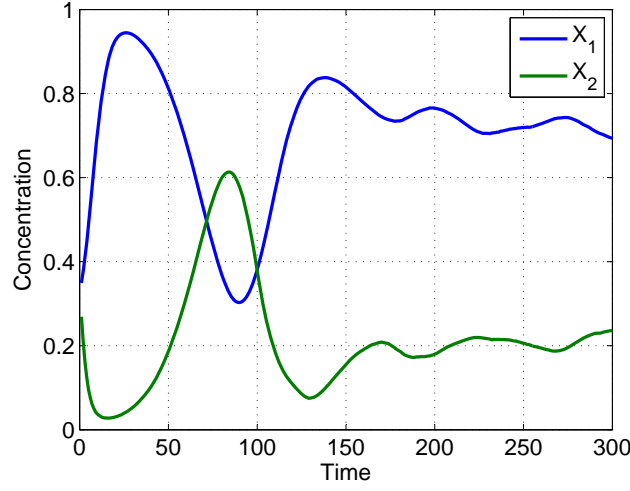


Figure 8: Global X_1 and X_2 Molecule Concentrations for a Radius of Reactivity of 5

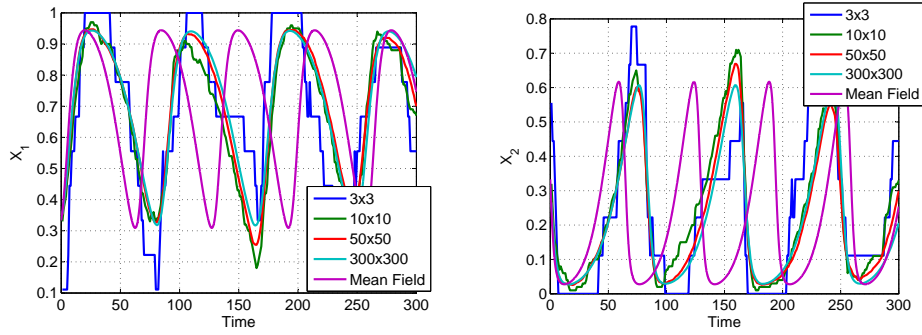


Figure 9: Concentrations of X_1 and X_2 Molecules for a Radius of Reactivity of 50

decay. As the subset under consideration expands, the oscillations in the concentrations change only slightly. The period for all subsets are very close to that of the mean-field dynamics. In addition, the amplitudes of all subsets are comparable to that predicted by the mean-field ODEs. The trend in global oscillations as the radius of reactivity increases is better illustrated in the next section.

3.5 Radii of Reactivity Summary

As shown in all the previous cases, there is a significant trend in the global oscillations of the molecule concentrations as the radius of reactivity changes. All of the global concentration dynamical responses are gathered and displayed in Figure 11.

The original LLV model has very slow, large amplitude oscillations. Based on evidence from the literature and the other times histories, it is likely that the amplitude of the oscillations will decay and hover around some final concentration. The simulation with radius of reactivity of 1 is very similar to the original method, which is to be expected given that there are only a few extra

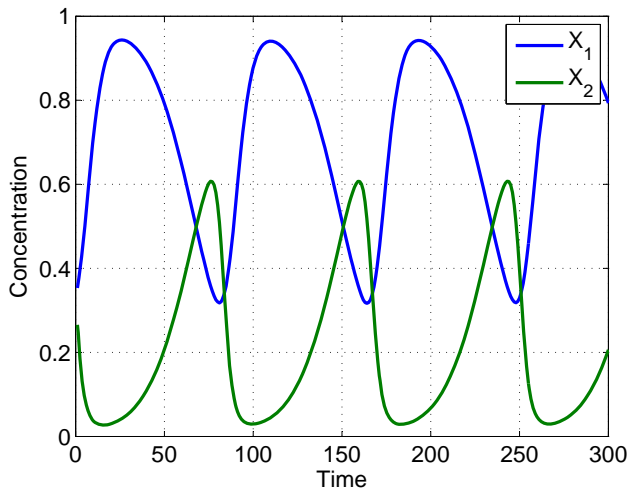


Figure 10: Global X_1 and X_2 Molecule Concentrations for a Radius of Reactivity of 50

sites with which to react. The response shows a slightly shorter period with more evidence of decay. The simulation with radius of reactivity of 5 exhibits a very fast decay. After this initial decrease in amplitude, the concentrations oscillate fairly quickly, but with small amplitude. Between a radius of 5 and a radius of 50, the dynamical response changes. The period shortens further and approaches the period of the mean-field dynamics. There is also no evidence of decay in the amplitude of the oscillations. A reasonable conclusion is that if the radius of reactivity were to increase to include the entire lattice, then the response would approach that of the mean-field dynamics.

4 Conclusions

The mean-field dynamic approximation of basic catalytic chemical reactions and the lattice Lotka-Volterra model were implemented to explore the dynamical response of the chemical reaction system given a slight modification to the model algorithm. This modification was in the form of less stringent restrictions on the reactions taking place between molecules adsorbed to lattice sites. Several examples were presented to illustrate the changes in dynamics as the restrictions were reduced in the form of increasing the number of potential molecules with which a chosen molecule may react.

All of these results suggest that on the local level, the dynamic response is different from that seen on the global level for small radii of reactivity. As the radius increases the local and global dynamical response become more similar. They also begin responding in a similar manner as the mean-field dynamics. If

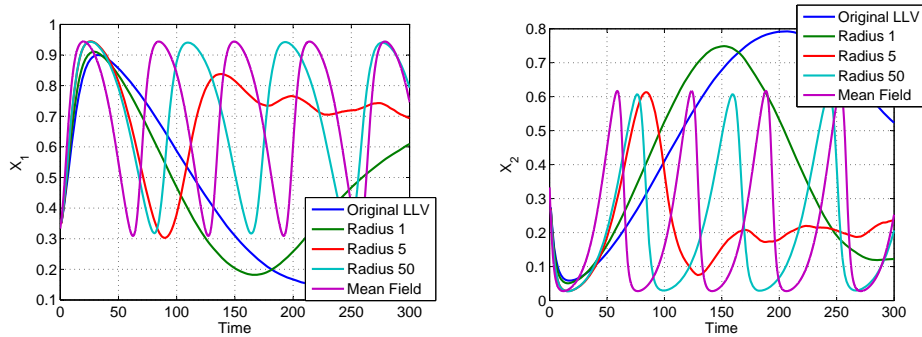


Figure 11: Global X_1 and X_2 Molecule Concentrations for a Radii of Reactivity

the radius were to include the entire lattice, it is likely that the response would closely match that of the mean-field dynamics.

References

- [1] Tsekouras, G. A., and Provata, A., “Fractal properties of the lattice Lotka-Volterra model,” *Physical Review E*, Volume 65, Number 016204, December 2001.
- [2] Shabunin, A. V., Baras, F., and Provata, A., “Oscillatory reactive dynamics on surfaces: A lattice limit cycle model,” *Physical Review E*, Volume 66, Number 036219, September 2002.
- [3] Provata, A., and Tsekouras, G. A., “Spontaneous formation of dynamical patterns with fractal fronts in the cyclic lattice Lotka-Volterra model,” *Physical Review E*, Volume 67, Number 056602, May 2003.