Dynamics of chemical reacting systems in low dimensional lattices via the Equation Free Method

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Abstract. In this report we show how it is possible to reconstruct the dynamics of a chemical reacting systems on lattice via an appropriate choice of macroscopic variable set. When chemical reactions fire on a low dimensional setting the usual mean field approximation (MF) may fail to accurately describe the proper dynamics of the system. Consequently it is not possible to use the concentrations of different species as sole quantities to describe macroscopically such systems and more involved approximations are needed. Traditional approaches introduces higher order correlation functions as extra macroscopic variables, however such expansions usually require closure procedures and tend to quickly demand high number of terms even for simple systems. It is also possible to describe the system in a microscopic way via a Kinetic Monte Carlo (KMC) algorithm, but this approach requires much longer computation time. In this report we study such a problem from a different perspective using the Equation Free Method (EFM) framework; with such approach it is possible to "bridge" between the macroscopic dynamics (mean field) and the microscopic one (KMC). We analyze different techniques to move between these two descriptions of the system trying to understand what information needs to be preserved at the macroscopic level in order to recover correctly all the features of the microscopic dynamics.

1. Introduction
The dynamics of chemical reacting systems is usually described via the reaction–diffusion equation for the coverages of the different species present in the compound:

\[
\frac{\partial u_i(\vec{x},t)}{\partial t} = f_i(\bar{u}(\vec{x},t)) + D_i \nabla^2 u_i(\vec{x},t),
\]

(1)

where \(\bar{u}(\vec{x},t) = \{u_1(\vec{x},t), \ldots, u_n(\vec{x},t)\}\) is the vector of concentrations for each species \(i\) in \(\vec{x}\) at time \(t\), \(f_i\) is the mass action laws term for reactions involving species \(i\) and \(D_i\) is the matrix of diffusion coefficients.

However spatial constraints like surfaces, and low mobility of the particles may render such macroscopic description not accurate enough to capture all the microscopic fluctuations which arise at the microscopic level. In case of nonlinear reactions such fluctuations are enhanced and appear also at the macroscopic level, this renders (1) unable to describe the dynamics of \(\bar{u}\) [10, 12, 9].

For these cases it is possible to build a Monte Carlo propagator for the microscopic state; such propagator updates the system via a series of jump process according to given dynamic rules [2]. In this approach the evolution of the system is described by the chemical master equation.
\[
\frac{dP(\sigma, t)}{dt} = \sum_{\sigma'} [W(\sigma' \rightarrow \sigma)P(\sigma', t) - W(\sigma \rightarrow \sigma')P(\sigma, t)],
\]

where \(P(\sigma, t)\) is the probability of finding the system in configuration \(\sigma\) at time \(t\) and \(W(\sigma' \rightarrow \sigma)\) is the transition probability per unit time that the system switches from configuration \(\sigma'\) to configuration \(\sigma\). Due to the fact that the spatial location where the reaction fires is important for such simulation, these Monte Carlo methods are usually variants of traditional Kinetic Monte Carlo (KMC) methods like Stochastic Simulation Algorithm (SSA) [11], where also the reaction site is taken into account. Usual accelerated techniques (like \(\tau\) leaping) are not easily implemented in lattice KMC, unless other approximation (like some type of coarse graining [13]) are also taken into account. For a general review of such methods see [3].

2. Chemical reactions on low dimensional lattices

Throughout this text we will consider a particular example system in a one–dimensional lattice (such that \(\sigma\) is a vector of length \(N\) with periodic boundary condition, we also assume that all the lattice sites are occupied and that there is no diffusion. The reaction laws are:

\[\text{XAX} \leftrightarrow \text{XXX}. \quad (3)\]

This model contains the simplest mechanism to obtain macroscopic behaviour that non-trivially depends on the local configurations [9]. The reaction laws (3) are also typical part of realistic, more complex reaction schemes [1]. For the system of interest the mean field approximation reads [8]

\[
\frac{dx}{dt} = -x^3 + ax^2, \quad (4)
\]

where \(a, x\) are respectively the coverages for the species \(A, X\). The transition probabilities in (2) may be rewritten as lattice sites transitions, i.e. the probability that \(A \leftrightarrow X\) in a given lattice site \(j\)

\[
w(\sigma_j \rightarrow -\sigma_j, t) = \frac{1}{4} \left[1 - \sigma_{j-1}(t)\right] \left[1 - \sigma_{j+1}(t)\right],
\]

where we have set \(\sigma_j = +1\) if the site \(j\) is occupied by a \(X\) and \(\sigma = -1\) otherwise. Given the simplicity of such model system it is possible to develop a two step Monte Carlo propagator [8] for the microscopic state \(\sigma\), obeying (3), \(\sigma(n+1) = s(\sigma(n))\), as follow:

- pick randomly a lattice site \(J\) from a uniform integer distribution with range \([1, N]\);
- if \(\sigma_{j+1} + \sigma_{j-1} = -2\) then swap the element \(\sigma_J = -\sigma_J\).

At each step we advance the time by 1, so the total time of the simulation is counted in number of Monte Carlo steps.

It is possible to relate the macroscopic (4) dynamics and the microscopic (2) by expanding the latest in term of concentrations and higher orders particle correlations [9]. The main issue is that the equations for such correlations are not closed, and analytical closures have been developed such as the quasi–chemical approach where pair correlations are also taken into account [8]. However these closures depends strongly on the system considered, and when more than pair correlations are needed the set of equations becomes quickly intractable. Generally one would like to obtain the dynamics for some macroscopic quantities but also study the equilibrium states dependence on the reaction rates via bifurcation analysis, and these results might not be easily obtained with such approximations.
3. The Equation Free Method

A possible alternative is to use equation-free method [5] to develop a numerical closure procedure, this same method may also be used to derive bifurcation diagrams [7]. The basic idea of this approach is to assume that the system may be described by a set of macroscopic quantities, but that the equations of motion for such quantities are not available, for instance they might depend on unknown parameters or, as in this case the set might need a closure procedure. We proceed by building two maps which relate the set of macroscopic variables with the microscopic description and vice-versa (named lifting and restriction respectively). By the use of ad-hoc short microscopic simulations it is possible to obtain a numerical propagator for the macroscopic variables even if no analytic expression is available. Due to the fact that the lifting map (from the macroscopic description to microscopic one) is a one-to-many map we may use a sequence of lift-microscopic run-restrict steps to study the error made by approximating the microscopic system with the macroscopic variables. For a general review on Equation Free Methods (EFM) see[6]. EFM has already been used to get bifurcation results on chemical systems with lateral interactions [7].

A crucial issue in the equation-free approach is the selection of the appropriate macroscopic state variables, and the corresponding lifting operator. Lifting induces a numerical closure, in fact it assumes that all the information lost at the lifting stage, i.e. all those which are not explicitly included in the macroscopic variable set, are depending on it. In other related works [7] this is ensured by assuming that the fast reactions quickly equilibrate the system after any reaction fires, slaving all the spatial correlations to the species coverages. However in our system the lack of diffusion nullifies the slaving and consequently more involved liftings are needed.

We introduce two operators that make the transition between microscopic and macroscopic state variables. We define a lifting operator,

\[ \mathcal{L} : \mathbf{M} \mapsto \sigma, \]  

which maps a macroscopic state \( \mathbf{M} \) to a realization of a chain of length \( N \), and the associated restriction operator,

\[ \mathcal{R} : \sigma \mapsto \mathbf{M} \]  

which maps a microscopic realization to the corresponding macroscopic state.

In this work instead of analyzing possible options for \( \mathbf{M} \) we focus on the lifting map itself \( \mathcal{L} \) while keeping \( \mathbf{M} \) fixed, in the next section we show that for the system hereby considered it is enough to use the concentrations as macroscopic variables, so that \( \mathbf{M} = a \).

The restriction operator is readily defined using an empirical mean for the coverages:

\[ \mathcal{R}(\sigma) = \frac{1}{2} \left( N + \sum_{i=1}^{N} \sigma_i \right). \]  

In the lifting step, we need to generate a microscopic realization of the chain, consistent with the macroscopic state \( \mathbf{M}(t^*) \) obtained at time \( t^* \).

Let us now detail the complete algorithm. Given an initial condition for the macroscopic state variables \( \mathbf{M}(t^*) \) at time \( t^* \), one time step of the coarse time-stepper consists of a three-step procedure:

(i) **Lifting**, i.e. the creation of initial conditions

\[ \sigma(t^*) = \mathcal{L}(\mathbf{M}(t^*)), \]

for the microscopic model, consistently with the macroscopic state \( \mathbf{M} \) at \( t^* \).
(ii) **Simulation** the microscopic state is evolved over a one step time interval $[t^*, t^* + 1]$. Given the microscopic propagator $s$ defined in the previous section we set:

$$\sigma(t^* + 1) = s(\sigma(t^*)).$$

(iii) **Restriction**, i.e. the observation (estimation) of the macroscopic state at $t^* + 1$:

$$M(t^* + 1) = R(\sigma(t^* + 1)).$$

4. **Numerical Results**

Given (3) via numerical Monte Carlo simulations it is possible to show that for a 1-D ring starting from a uniform $X$ coverage, $\sigma = \{-1, -1, \ldots, -1\}$, the system reaches a steady state with $a_{eq} \simeq 0.28$. If instead we look at the solutions of the mean field equations (4) we have a steady state with equal concentrations and $a_{eq} \simeq x_{eq} = 0.5$. The choice of starting from a uniform $X$ coverage is by no mean restricting, in fact if there are some $A$, it is simply necessary to keep track of any cluster larger than a single $A$ as these clusters will not be affected by the dynamics. If we start from a uniform $X$ coverage then any $A$ appearing in the ring is always surrounded by two $X$, so any cluster longer than a isolated $A$ is physically impossible.

Therefore we might introduce two different liftings using only the coverage of $A$ as macroscopic quantity. The simplest lifting we develop uses only the coverage $M = a$ as macro variable and it returns a ring $\sigma$ with as many $A$ as $N \times a$; the position of these $A$ is completely random, we label this method lift$_R$. For the second lifting we consider the fact that there are no clustered $A$, so we proceed as the random lifting, but the position of the $A$ now is picked such that only physically allowed states may be created: specifically we create an initial ring of length $2N \times a$: $\{A,X,A,X\ldots,A,X\}$, we then insert randomly as many $X$ as needed,

$$r_X = N(1 - 2a).$$

We call this other lifting lift$_A$.

From the numerical results we observe that lift$_R$ has $a_{eq} = 0.5$ as steady state, on the other hand it is enough to take out the non physical impossible states as it is done with lift$_A$ to get already a perfect agreement between the microscopic and the macroscopic dynamics. We underline that there is no difference for these two liftings at the level of macroscopic variables, rather lift$_A$ preserves a specific feature of the microscopic dynamics, while lift$_R$ does not. For lift$_R$ we observe that by allowing the formation of any possible states at the lifting stage of the algorithm, we effectively shuffle the system at each step. This shuffling has the practical effect of stirring the system, so the mean field requirements (well stirred condition) are satisfies.

The reason of the results obtained by lift$_A$ may be explained by looking at the probability that a general element $\sigma_j$ may swap:

$$\mathcal{P}(A \rightarrow X), \quad \mathcal{P}(X \rightarrow A).$$

(10)

In the mean field limit any lattice site may swap, so $\mathcal{P}(A \rightarrow X) = \mathcal{P}(X \rightarrow A)$, for the micro dynamics (3) instead we have that at equilibrium $a < x$, this is due to the fact that not all the $X$ are allowed to swap to $A$ while all the $A$ are free to do so.

For instance, if we assume that on the ring all the $A$ are “isolated”, i.e. the distance between two $A$ is never smaller than two sites, we see that for any $A$ there are two neighboring $X$ which if chosen by the random pick will not react, we define such $X$ frozen. The number of frozen $X$ determines the concentrations value at equilibrium. For example if the sole frozen $X$ are those aside $A$ then we have a $1/3$ ratio between $A$ and $X$; looking at the probabilities we see that:

$$\mathcal{P}(A \rightarrow X) \propto \langle A \rangle,$$

$$\mathcal{P}(X \rightarrow A) \propto 1 - 3\langle A \rangle.$$
In the general case however, the $A$ will not be “isolated”, so situations like \{...A, X, A, X, A...\} might happen. In this case the ratio between $A$ and frozen $X$ is not 1/3 as before but depends on the length of the chain and it is the reason for having $a_{eq} = 0.28$ which is little less than 1/3.

In our numerical tests we observed that on average lift$_A$ produced a ring with less frozen $X$ than the corresponding microscopic state coming from the microscopic simulations, while lift$_R$ produced one with more. It is clear that while the errors in lift$_A$ are immediately corrected by the dynamics, those made in lift$_R$ reduce the possible reaction paths and the dynamics is drifted toward the mean field equilibrium value.

5. Conclusions
In this work we have proposed an alternative strategy to obtain a numerical closure for chemical reactions on low dimensional lattices. These systems cannot be described via the mean field approximation, and other approaches are needed using also higher order particle correlations. When no analytic form for the macroscopic variables is available, or when the number of equations become too large, it is possible to use the Equation Free method framework to obtain the numerical closure via the inclusion of higher order moments (pair and triplet correlations) in the macroscopic variables set.

Within the Equation Free framework we have shown that in some cases there is no need to introduce other variables if the lifting strategy retains some particular features of the microscopic description, in this way the approach is simpler and easier to apply. By carefully choosing the lifting we show that it is possible to get an equivalent macroscopic dynamics which resembles the data coming from the microscopic run, in this sense the lifting makes the numerical closure.

In more general cases it is possible to decrease the number of macroscopic variables needed by choosing carefully the lifting strategy. The general idea behind this approach trying to preserve the number of "elementary blocks" of the reactions, isolated $A$ and triplets of $X$ for the model
presented here. Currently we are working on a generalization of the procedure presented in this report that allows the treatment of more complex systems. We are also implementing a projective integration algorithm [6] for the coarse time stepper in order to accelerate the dynamics.

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