

Mass Action Equations for Autocatalytic Systems

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The origin of life (OoL) on earth is still in search of a satisfactory explanation. The field is dominated by many facets and partial explanations. Facets include frequency of planetary systems, climatology of early earth, chirality in naturally occurring compounds, abiotic production of molecules, etc. Partial explanations include the naturally occurring self-reproducing molecules, quasispecies and hypercycles, an RNA world, natural formation of micelles, etc. However, most of these explanations are incomplete or based on speculation.

Many other fields in the biosciences have benefited from the introduction of formal models, which forced researchers to be explicit about assumptions made, and allowed mathematical reasoning to be applied and computational experiments to be performed. Such models have been introduced in the context of the OoL, but research in them has not been very dominant so far. However, as OoL research gains pace, they will be given more attention. Examples of formal models related to OoL are Conway, von Neumann (1967), Ganti (1997), Kauffman (1986), and Steel (2000). For formal models to be useful they should capture some essence of the empirical problem and as time passes they should be forced towards increasingly realistic descriptions of the phenomena. The formalisation of catalytic reaction systems by Steel (2000), based on an initial idea by Kauffman, consists of

- a set of molecule types;
- a set of reactions where each reaction converts one set of molecules (reactants) into another set (products);
- a set of catalysations: molecules that accelerate a reaction (or set of reactions);
- a food set: a small set of molecules assumed to be freely available and constantly replenished.

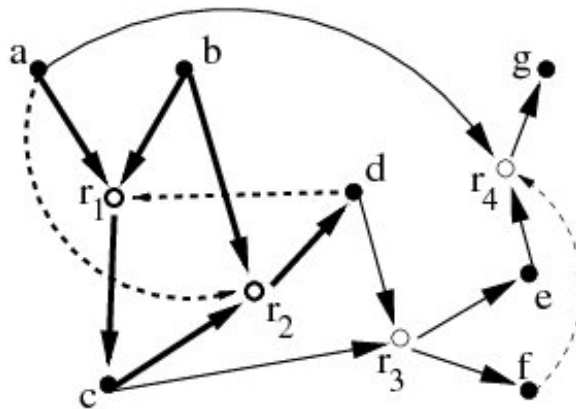


Figure 1: An example of a catalytic reaction system (CRS) from Hordijk and Steel (2004). *a, b* are here food. The subset of reactions $\{r_1, r_2\}$ (shown in bold) is an RAF set.

The questions of interest in these models are conditions for the appearance of (sub)sets of molecules/reactions that are self-sustainable: each reaction in the set is catalysed by at least one molecule from the set, and each molecule can be created, starting from the food set, by repeated reactions from the same set. This idea of *autocatalytic sets* was introduced in Kauffman (1986), and formalised as *RAF sets* and subsequently studied more extensively in Steel (2000), Hordijk and Steel (2004), and Mossel and Steel (2005). Investigations into these models represent significant progress relative to less precise models, but the Steel model needs elaboration to be more realistic in addressing the probability of spontaneous occurrences of RAF sets. A Constructively Autocatalytic Food (CAF) set is a RAF where all molecules can be constructed started by the food set.

RAF/CAF are boolean concepts and it could of interest to explore analogous models that described the concentrations of the molecules. It would be natural to assume a well-stirred medium. For the above illustration we would have the following initial conditions and mass action equations.

Initial conditions:

- $a(t)=b(t)=k$ *food molecule concentrations are constant.*
- $c(0)=d(0)=e(0)=f(0)=g(0)=0$

Mass action equations:

- $c'(t) = a(t)b(t)d(t)k_3 - c(t)b(t)a(t)k_3$
- $d'(t) = a(t)b(t)c(t)k_3$
- $e'(t) = -a(t)e(t)f(t)k_3$
- $f'(t) = 0$
- $g'(t) = a(t)e(t)f(t)k_3$

The reaction $(c,d) \rightarrow (e,f)$ does not occur in these equations as it isn't catalyzed by any molecule. k_3 is the rate of a third order reaction. The above equation system would be the analogue of CAF, while if the initial conditions were changed so all molecules had a background concentration of ϵ would correspond to the analogue of RAF. One could also consider to let the concentration of the catalyst enter as an indicator function instead of a concentration and the first equation would become $c'(t) = a(t)b(t)I_{\{d(t)>0\}}k_3 - c(t)I_{\{b(t)>0\}}a(t)k_3$.

In a general model, we will additionally assume that all reactions were 2nd or 3rd order equations as these are the predominant chemical reactions. One could also choose to have all chemicals removed by a certain rate and the systems would probably converge toward an equilibrium. General equations:

Notation:

- $x(t)$ is n -dimensional vector with the concentrations of the molecules. 0 otherwise
- T is trilinear form with $c3$ at (i,j,k) , $-c3$ at (i,k,j) and at (j,k,i) if i and j can collide and create k .
- B is bilinear form that has $c2$ at (i,j) and $-c2$ at j,i if i mutates (isomerizes) into j . B will also have similar entries for the reaction $i \rightarrow (j,k)$. 0 otherwise
- M multiplies $-c1$ on each entry of $x(t)$ corresponding to dilution or decay. 0 otherwise
- F has ϵ for each food molecule corresponding to continued replenishment and 0 otherwise.

Initialisation: $x(0)=0.0$; Dynamics: $x'(0) = T[x(t)] + B[x(t)] + M[x(t)] + F$;

What would one expect of the behaviour of such a system that is new relative to the boolean version? Simulating it for a chosen reaction system should be fairly straightforward using standard numerical techniques. One would probably expect that RAF/CAF molecules would have a concentration that stood out compared to the rest.

In the mass action RAFs one could imagine competition between different RAFs if they used the same resources. This would not occur for boolean RAFs where all that matters is the absence/presence of molecules. Clearly competition can occur in any systems, if inhibitions are allowed.

However, it would be especially interesting if this was done for graphs representing real molecules and the predictions would then also be about real molecules.

Project

- Read basic literature on RAFs and Mass Action dynamical systems
- Implement simulation tool for simulation of the above system.
- Find sets of molecules of high concentration and compare to predicted RAFs for analogous boolean system.
- Design a system that can lead to different RAFs dependent on minor perturbation in parameters.
- Design a system that builds up RAFs in stages ie when one RAF has reached a certain concentration, then this RAF can be expanded or a second RAF become possible.

References

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