

Field Theory Methods in Reaction-Diffusion Systems

Gregory Szep

King's College London

April 11, 2018

1 Biochemical Processes as Dynamical Systems

In this section we will set the scene for chemical reaction systems and their methods of analysis from dynamical and topological perspectives. Dynamical methods makes use of phase space, linear stability and bifurcation analysis. Green's Functions allow for calculation of correlations and observables. Graph theory lends insight into the design principles of chemical networks. Finally a more recent approach to spatial modelling - moving local equilibria - is introduced.

1.1 Reaction Kinetics

Consider N particles of S species in a finite volume Ω . These particles can undergo R possible reactions when they meet within the volume. Suppose the timescales of equilibration with respect to volume and temperature are much faster than that of species number equilibration. This means that non-reactive collisions occur more frequently than collisions that trigger any of the R reactions.

This suggests that at any time t we may pin down the state of the system by a vector of populations $s(t) \in \mathbb{N}^S$. The reactions are characterised by a stoichiometric matrix $\mathbf{\Gamma} \in \mathbb{Z}^{S \times R}$ whose columns $\gamma \in \mathbb{Z}^S$ represent the state change vector for a reaction. Each reaction also has a propensity $\omega(s|\gamma) \in [0, \infty)$ defined through probabilities $\mathbb{P}(s, t)$ of being in state s at time t .

$$\omega(s|\gamma)dt := \mathbb{P}(s + \gamma, t + dt|s, t) \quad (1.1)$$

Suppose $\sigma(\gamma)dt$ gives the probability that the state change γ will occur within the time interval dt . The function $\sigma(\gamma)$ could be in principle calculated from the microscopic physics of the reaction. In quantum mechanics this would involve calculating the wavefunction overlap or transition rates between initial and final configurations.

This rate is proportional to the propensity, up to combinatoric multiplicity taking into account the species population s . This is the product of all component pairs $\langle s, \gamma \rangle$ of choosing $|\gamma|$ out of s particles to participate in the reaction.

$$\omega(s|\gamma) = \sigma(\gamma) \prod_{\langle s, \gamma \rangle} \binom{s}{|\gamma|} \quad (1.2)$$

1.1.1 Chemical Master Equation

By applying the laws of probability and taking the $dt \rightarrow 0$ one can derive a time-evolution equation $\mathbb{P}(s, t)$ involving the definition (1.1) which has become known as the Chemical Master Equation [1, 2].

$$\partial_t \mathbb{P}(s, t) = \sum_{\gamma \in \Gamma} \omega(s - \gamma|\gamma) \mathbb{P}(s - \gamma, t) - \omega(s|\gamma) \mathbb{P}(s, t) \quad (1.3)$$

Multiplying the Chemical Master Equation (1.3) by s and summing over all s obtains a system of differential equations for the first moment $\langle s \rangle$ in terms of vectorised propensity $\omega(s|\Gamma) \in [0, \infty)^R$ which couples to higher order moments, unfolding an infinite hierarchy.

$$\partial_t \langle s \rangle = \Gamma \langle \omega(s|\Gamma) \rangle \quad (1.4)$$

1.1.2 Reaction Equation

The mean field approximation factorises higher order moments, implying $\langle f(s) \rangle = f(\langle s \rangle)$ for any nonlinear function f . These fluctuations can be neglected in the $N, \Omega \rightarrow \infty$ thermodynamic limit [2]. This closes the infinite hierarchy (1.4) yielding a nonlinear set of coupled ordinary differential equations for a continuous vector field $\psi(t) \in [0, \infty)^S$.

$$\partial_t \psi = \Gamma \omega(\psi|\Gamma) \quad (1.5)$$

1.1.3 Lotka–Volterra Example

The Lotka–Volterra model is a canonical example of a predator-prey dynamical system. Here we may summarise the reactive behaviour between predators $A(t)$ and prey $B(t)$ in Feynman diagrams. Particles are represented by arrows \rightarrow and reactions by wavy arrows \rightsquigarrow .

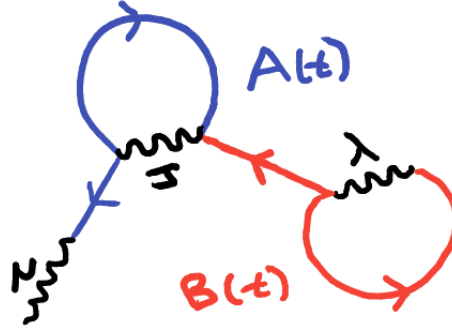


Figure 1: Feynman diagram of the Lotka–Volterra field $\begin{pmatrix} A \\ B \end{pmatrix}$ revealing autocatalytic birth rate λ for prey, constant death rate μ for predators and characteristic interaction J

Letting $s(t) = \begin{pmatrix} A \\ B \end{pmatrix}$, the stoichiometric matrix $\mathbf{\Gamma}$ and propensity $\omega(s|\mathbf{\Gamma})$ are determined from the state changes γ and the rates of each reaction.

$$\mathbf{\Gamma} = \begin{pmatrix} -1 & 0 & 1 \\ 0 & 1 & -1 \end{pmatrix} \quad \omega(s|\mathbf{\Gamma}) = \begin{pmatrix} \mu A(t) \\ \lambda B(t) \\ JA(t)B(t) \end{pmatrix} \quad (1.6)$$

1.2 Reaction Topology

1.3 Reaction-Diffusion

2 Field Theory Approach

2.1 Master Equation

2.2 Path Integrals

2.3 Green's Functions

References

- [1] D. T. Gillespie, “A rigorous derivation of the chemical master equation,” *Physica A: Statistical Mechanics and its Applications*, vol. 188, no. 1, pp. 404–425, 1992.
- [2] D. T. Gillespie, “Stochastic Simulation of Chemical Kinetics,” *Annu. Rev. Phys. Chem.*, vol. 58, pp. 35–55, 2007.