

# Supplementary Materials for The dynamical and thermodynamical origin of dissipative chaos: Chemical Lorenz system

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## Contents

<b>1 Fokker-Planck equation</b>	<b>2</b>
<b>2 Chemical Lorenz model with chaos</b>	<b>4</b>
<b>3 On the chemical potential difference</b>	<b>5</b>
<b>4 Potential-flux landscape</b>	<b>8</b>
<b>5 Lyapunov exponent</b>	<b>10</b>
<b>6 Kolmogorov-Sinai entropy</b>	<b>11</b>
<b>7 Entropy production rate</b>	<b>12</b>

# 1 Fokker-Planck equation

In a coarse-grained description, the system state is determined by the vector of total particle numbers  $\mathbf{X} = \Omega \mathbf{x}$ , where  $\Omega$  is the volume of container and  $x_i$  stands for the particle density of  $i$ -th species. From microscopic perspective, the  $n$ -th reaction occurs with the probability  $W_n(\mathbf{X}, \mathbf{X} - \mathbf{v}_n)$  jumping from state  $\mathbf{X} - \mathbf{v}_n$  to  $\mathbf{X}$  per unit time. Here, the stoichiometric coefficients are written as the vector form  $\mathbf{v}_n$ , where the components  $v_{ni}$  is the stoichiometric coefficient of  $i^{th}$  species in  $n^{th}$  reaction. Such a stochastic system can be described by the master equation

$$\dot{P}(\mathbf{X}) = \sum_n [W_n(\mathbf{X}, \mathbf{X} - \mathbf{v}_n)P(\mathbf{X} - \mathbf{v}_n) - W_n(\mathbf{X} + \mathbf{v}_n, \mathbf{X})P(\mathbf{X})] \quad (1)$$

where  $P(\mathbf{X})$  is the probability of the system staying in the state  $\mathbf{X}$ .

The concentration  $\mathbf{x}$  is usually an invariant with respect to the volume of container  $\Omega$ . For instance, in the thermodynamic limit or macroscopic limit, the concentrations hold fixed  $\mathbf{X}/\Omega = \text{constant}$ , while  $\mathbf{X} \rightarrow \infty$  and  $\Omega \rightarrow \infty$ . So, it is easy to obtain a scaling transform for the master equation[1]

$$\dot{\rho}(\mathbf{x}) = \Omega \sum_n \left[ w_n \left( \mathbf{x}, \mathbf{x} - \frac{\mathbf{v}_n}{\Omega} \right) \rho \left( \mathbf{x} - \frac{\mathbf{v}_n}{\Omega} \right) - w_n \left( \mathbf{x} + \frac{\mathbf{v}_n}{\Omega}, \mathbf{x} \right) \rho(\mathbf{x}) \right] \quad (2)$$

with the scaling maps

$$\begin{aligned} \mathbf{X} &= \Omega \mathbf{x}, \\ P(\mathbf{X}) &= \Omega^{-1} \rho(\mathbf{x}), \\ W_n(\mathbf{X}) &= \Omega w_n(\mathbf{x}). \end{aligned} \quad (3)$$

For a system with a large volume  $\Omega \gg 1$ , we can take the Taylor expansion for the master equation with respect to  $\mathbf{v}_n/\Omega \rightarrow 0$ . Note that the stoichiometric coefficients  $\mathbf{v}_n \sim 1$ . By taking the Taylor expansion up to second order, we obtain the Fokker-Planck equation as a continuous approach for the master equation[1]

$$\dot{\rho}(\mathbf{x}) = -\nabla \cdot \mathbf{J} \quad (4)$$

with the expression for the probability flux

$$\mathbf{J} = \mathbf{F}\rho - \Omega^{-1} \nabla \cdot (\mathbf{D}\rho), \quad (5)$$

where the drift terms[1]

$$F_i(\mathbf{x}) = \sum_n v_{ni} w_n(\mathbf{x}) \quad (6)$$

and the diffusion terms[1]

$$D_{ij}(\mathbf{x}) = \frac{1}{2} \sum_n v_{ni} v_{nj} w_n(\mathbf{x}). \quad (7)$$

## 2 Chemical Lorenz model with chaos

In a specific chemical reaction model, the backward reactions can be taken as very small rates, so that the chemical dynamics is dominated by the forward reactions. In this case, the specific value of the product concentrations and the backward reaction rates do not appear in the species dynamical equations. The parameters in the chemical reaction model are taken as follows

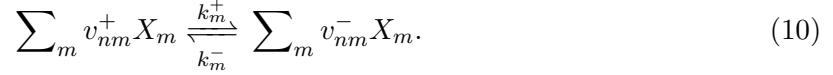
$$\begin{aligned}r_2 &= 1, \quad r_3 = 1, \\k_1 &= 0.001, \quad k_2 = 1, \quad k_3 = 10000, \quad k_4 = 0.0001, \quad k_5 = 1, \\k_6 &= 0.05, \quad k_7 = 0.005, \quad k_8 = 9900, \quad k_9 = 1, \quad k_{10} = 0.0133.\end{aligned}\tag{8}$$

We take the concentration  $r_1$  as a control parameter. The corresponding deterministic species dynamics reads from the law of mass action

$$\begin{aligned}\dot{x}_1 &= F_1 = 0.001r_1x_1x_2 - 0.1x_1^2, \\ \dot{x}_2 &= F_2 = x_1x_2 - 0.0001x_1x_2x_3 + x_2x_3 - 0.01x_2^2 - 9900x_2, \\ \dot{x}_3 &= F_3 = 10000x_3 + 0.0001x_1x_2x_3 - x_2x_3 - x_1x_3 - 0.0266x_3^2.\end{aligned}\tag{9}$$

### 3 On the chemical potential difference

Imagine that there is a chemical reaction system between some particle reservoirs. The chemical system consisted by  $M$  species and  $N$  reactions and the reaction described by the general form



In coarse-grained description, the state of system is determined by the population densities  $x_m$ . We can introduce the progress variable  $\xi_n$  for counting the reaction process for  $n^{\text{th}}$  reaction. The progress variable increases  $\xi_n \rightarrow \xi_n + 1$  with the one step  $n^{\text{th}}$  forward reaction. The disharmony among different pathways results in the accumulation in the node species with the rate

$$\dot{x}_m = \sum_m v_{nm} \dot{\xi}_n, \quad (11)$$

where

$$v_{nm} = v_{nm}^+ - v_{nm}^- \quad (12)$$

are stoichiometric coefficients.

Usually, a chemical system can be regarded as certain intermediates reacting between reactant and product reservoirs. Such an overall system can be thought of as a closed system exchanging energy but not matter with its environments. The heat flow from environment to the system reads

$$dQ = -T dS_{\text{env}} \quad (13)$$

where  $dS_{\text{env}}$  is the entropy change in the environment, and from the energy conservation

$$dQ = dU + p dV. \quad (14)$$

We introduce a thermodynamical potential  $G$  called Gibbs free energy with the form

$$G = U + pV - TS. \quad (15)$$

Then, the second law of thermodynamics described by the total entropy production can be translated to the dissipation of Gibbs free energy, i.e.,

$$dG = d(U + pV - TS) = -T(dS + dS_{\text{env}}) \leq 0. \quad (16)$$

A particle in a chemical system acquires a thermodynamical property associated with the Gibbs free energy as the form

$$\mu_m = \frac{\partial G}{\partial x_m} \quad (17)$$

called chemical potential. The chemical potential can be viewed as an effective statistical mechanical pressure on the particle creating an effective force which is called affinity defined as

$$A_n = -\frac{\partial G}{\partial \xi_n} = -\sum_m v_{nm}\mu_m, \quad (18)$$

where the progress variables  $\xi_n$  count  $n^{\text{th}}$  reaction progress and the stoichiometric coefficients

$$v_{nm} = \frac{\partial x_m}{\partial \xi_n} \quad (19)$$

reflecting the reaction structure. A spontaneous reaction occurs along positive affinities  $A_n > 0$  to reduce the Gibbs free energy.

The reactant and product reservoirs with different chemical potentials sustain the nonequilibrium in the intermediates system. The stoichiometric coefficient  $v_{nm} < 0$  for reactants and  $v_{nm} > 0$  for products. Thus, we can introduce an overall chemical potential difference between reactant and product reservoirs in the form

$$\Delta\mu = \sum_i \mu_{R_i} - \sum_j \alpha_j \mu_{P_j} \quad (20)$$

where the coefficients  $\alpha_j$  reflect the reaction structure. The chemical potential of species  $i$  can be written in the form

$$\mu_i = \mu_i^0 + RT \ln x_i \quad (21)$$

with concentration  $x_i$ , where  $\mu_i^0$  is the chemical potential of pure species  $i$ ,  $R$  is the gas constant and  $T$  is the temperature. Note that the constant  $RT$  is normalized into  $RT = 1$  in our theoretical treatment. The chemical potential difference will possess complex form due to different features of species.

For a forward dominated reaction system, we can simplify the chemical potential difference into a relatively brief structure. In such a system, the backward reactions occur with very small rates, so that the equilibrium can only be achieved with very small amount of reactants. In other words, the chemical equilibrium  $\Delta\mu \rightarrow 0$  is sustained by very small

concentration of reactants. By contrast, the finite concentrations of reactants contribute to additional chemical potential difference [between reactants and products](#)

$$\Delta\mu = \sum_i \ln r_i \tag{22}$$

where  $r_i$  is the concentration of the reactant  $R_i$ . It breaks the chemical equilibrium to create chemical reaction flows, like a higher temperature is imposed on the bottom of the atmosphere to create the buoyancy. The chemical potential difference increases with the density of reactants, while the products do not contribute to such difference. In the chemical Lorenz model, the chemical potential difference [between reactants and products](#) is given as

$$\Delta\mu = \ln r_1 \tag{23}$$

controlled by the concentration  $r_1$  of the reactant  $R_1$ .

## 4 Potential-flux landscape

The intrinsic potential and flux is obtained by solving the Hamilton-Jacobi equation [corresponding to the thermodynamical limit  \$\Omega \rightarrow \infty\$](#) . But, the Hamilton-Jacobi equation as a nonlinear partial differential equation is hard to solve. In an approximation, we replace its solution [corresponding to the thermodynamical limit  \$\Omega \rightarrow \infty\$](#)  by the numerical solution of Fokker-Planck equation [with the case of  \$\Omega \gg 1\$](#) .

One can see the general Fokker-Planck equation possesses a anisotropic inhomogeneous diffusion matrix[1]

$$D_{ij}(\mathbf{x}) = \sum_n v_{ni}v_{nj}w_n(\mathbf{x})/2. \quad (24)$$

It leads to also another difficulty in numerical treatment in practice. So, we use an isotropic homogeneous diffusion to replace the original state-dependent matrix. It is necessary to notice the isosurface of the potential in Fig.2(d)-(f) is corresponding to the solution of the Fokker-Planck equation

$$\sum_i \frac{\partial F_i \rho_{ss}}{\partial x_i} - \alpha \sum_{ij} \frac{\partial^2 \rho_{ss}}{\partial x_i \partial x_j} = 0. \quad (25)$$

In the numerical calculation, the diffusion parameter is taken as  $\alpha = 2 \times 10^7$ . In the original Fokker-Planck equation

$$\sum_i \frac{\partial F_i \rho_{ss}}{\partial x_i} - \Omega^{-1} \sum_{ij} \frac{\partial^2 D_{ij} \rho_{ss}}{\partial x_i \partial x_j} = 0, \quad (26)$$

[where](#) the diffusion matrix is approximately

$$\mathbf{D} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 16 & -8 \\ 0 & -8 & 17 \end{bmatrix} \times 10^7. \quad (27)$$

[By comparing Eqs.\(25\)-\(27\), it is easy to see that](#) the parameter  $\alpha = 2 \times 10^7$  is corresponding to an approximate volume  $\Omega \sim 10$ .

The intrinsic potential  $\phi$  contains an integral constant from the form of Hamilton-Jacobi equation, and thus the effective part is the difference

$$\phi = \phi(\mathbf{x}) - \phi_{\min}. \quad (28)$$

In addition, the intrinsic potential can be interpreted by the probability distribution  $\phi = -\alpha \ln \rho_{ss}$ . So, the integral constant is actually

$$\phi_{\min} = -\alpha \ln \rho_{ss}^{\max} \quad (29)$$



where  $\rho_{\text{ss}}^{\text{max}}$  is the maximum of the probability density in the state space. The isosurface for the effective intrinsic potential in Fig.2(d)-(f) is taken as

$$\phi_{\text{iso}} = 2\alpha. \quad (30)$$

Note that the  $\alpha$  can be thought of as a noise strength exiting the system. The system lies in the ground state  $\phi_{\text{min}} = -\alpha \ln \rho_{\text{ss}}^{\text{max}}$  without fluctuation. The isosurface  $\phi_{\text{iso}}$  outlines the states that can be exited by the noise with strength  $2\alpha$ . Obviously, the ground state  $\phi_{\text{min}}$  is surrounded by the isosurface  $\phi_{\text{iso}}$ . Furthermore, the intrinsic flux in Fig.2(g)-(i) is also approximated by the solution of the Fokker-Planck equation

$$\mathbf{V} = \mathbf{F} - \alpha \nabla \ln \rho_{\text{ss}}. \quad (31)$$

It is necessary to notice that Fig.2 is a heuristic illustration for the distribution of the potential and flux. The detailed value used in Fig.2 does not affect the further calculation of other quantities. The latter is performed by other treatment.

## 5 Lyapunov exponent

The chaos is characterized by the sensitive dependence of system behavior on initial conditions. On average, two infinitesimally closed trajectories separate exponentially fast in the form

$$|\delta\mathbf{x}(t)| \approx e^{\lambda t} |\delta\mathbf{x}(0)| \quad (32)$$

with the Lyapunov exponent  $\lambda$  providing a measure of such dynamical sensitivity.

More technically, we consider two trajectories  $\mathbf{x}(t)$  and  $\mathbf{x}'(t)$  with separation  $\mathbf{r}(t) = \mathbf{x}'(t) - \mathbf{x}(t)$ . For a general dynamics  $\dot{\mathbf{x}} = \mathbf{F}(\mathbf{x})$ , the separation rate reads

$$\dot{\mathbf{r}}(t) = \mathbf{F}(\mathbf{x}'(t)) - \mathbf{F}(\mathbf{x}(t)) \simeq \mathbf{J}(\mathbf{x})\mathbf{r} \quad (33)$$

with the Jacobian  $\mathbf{J} = \partial\mathbf{F}/\partial\mathbf{x}$ . The solution can be formally written as

$$\dot{\mathbf{r}}(t_n) = \left( \prod_i^n \exp[\tau\mathbf{J}(\mathbf{x}(t_i))] \right) \mathbf{r}(0) \quad (34)$$

where  $\tau$  is infinitesimal time increment. The global Lyapunov exponents as the chaotic measure are defined as the eigenvalues of the cumulated matrix

$$\Lambda = \lim_{n \rightarrow \infty} \frac{1}{2n\tau} \ln \left[ \left( \prod_i^n \exp[\tau\mathbf{J}(\mathbf{x}(t_i))] \right)^T \left( \prod_i^n \exp[\tau\mathbf{J}(\mathbf{x}(t_i))] \right) \right] \quad (35)$$

which describe a global property with independence of the initial condition. Usually, the largest Lyapunov exponent  $\lambda_{\max}$  is representative for measure of chaos.

## 6 Kolmogorov-Sinai entropy

We divide the  $d$ -dimensional state space into boxes with size  $\epsilon^d$ . A dynamical trajectory  $\tilde{\mathbf{x}}(t)$  can be identified by the box sequence  $i_0(0), i_1(\tau), \dots, i_n(n\tau)$  with the sampling interval  $\tau$ . Such a trajectory can be recognized with the information

$$K_n = - \sum P_{i_0 \dots i_n} \ln P_{i_0 \dots i_n}. \quad (36)$$

Accordingly, the additional information  $K_{n+1} - K_n$  is needed to predict the next boxes the trajectory passed. The Kolmogorov-Sinai entropy is defined as the average information

$$h_{\text{KS}} = \lim_{\tau \rightarrow 0} \lim_{\epsilon \rightarrow 0} \lim_{N \rightarrow \infty} \frac{1}{N\tau} \sum_{n=0}^{N-1} (K_{n+1} - K_n). \quad (37)$$

Some numerical algorithms were developed to evaluate the Kolmogorov-Sinai entropy.

## 7 Entropy production rate

The intrinsic flux gives rise to the dynamical irreversibility exhibiting the asymmetry in the probability between forward and backward trajectories. The irreversibility in the trajectory probabilities can be obtained by means of the path integral[2]. A stochastic trajectory occurs with probability

$$\mathcal{P}[\mathbf{x}(t)]\mathcal{D}\mathbf{x} = \mathcal{P}[\mathbf{x}(t)|\mathbf{x}_0]\rho_{\text{ss}}(\mathbf{x}_0)\mathcal{D}\mathbf{x} \quad (38)$$

where trajectory-dependent transition probability density  $\mathcal{P}[\mathbf{x}(t)|\mathbf{x}_0]$  can be obtained by the path integral,

$$\mathcal{P}[\mathbf{x}(t)|\mathbf{x}_0] = \prod_{t=0}^{\tau} \left[ \frac{\Omega}{4\pi|\mathbf{D}|dt} \right]^{1/2} \exp \left[ -\Omega \int_0^{\tau} \mathcal{L} dt \right]. \quad (39)$$

Each trajectory contributes a different weight by the Lagrangian

$$\mathcal{L} = \frac{1}{4} [\dot{\mathbf{x}} - \mathbf{F}(\mathbf{x})] \cdot \mathbf{D}^{-1} \cdot [\dot{\mathbf{x}} - \mathbf{F}(\mathbf{x})]. \quad (40)$$

Obviously, the Lagrangian vanishes

$$\mathcal{L}(\mathbf{x}, \dot{\mathbf{x}}) = 0 \quad (41)$$

along a deterministic trajectory  $\dot{\mathbf{x}} = \mathbf{F}(\mathbf{x})$ . For the time reversal trajectory  $\tilde{\mathbf{x}}(t) = \mathbf{x}(\tau - t)$ , we have  $\dot{\tilde{\mathbf{x}}} - \mathbf{F}(\tilde{\mathbf{x}}) = -\dot{\mathbf{x}} - \mathbf{F}(\mathbf{x}) = -2\mathbf{F}(\mathbf{x})$  and the corresponding Lagrangian

$$\mathcal{L}(\tilde{\mathbf{x}}, \dot{\tilde{\mathbf{x}}}) = \mathbf{F}(\mathbf{x}) \cdot \mathbf{D}^{-1} \cdot \mathbf{F}(\mathbf{x}). \quad (42)$$

The dynamical irreversibility is measured by

$$\begin{aligned} \frac{\mathcal{P}[\mathbf{x}(t)]}{\mathcal{P}[\tilde{\mathbf{x}}(t)]} &= \frac{\mathcal{P}[\mathbf{x}(t)|\mathbf{x}_0]\rho_{\text{ss}}(\mathbf{x}_0)}{\mathcal{P}[\tilde{\mathbf{x}}(t)|\tilde{\mathbf{x}}_0]\rho_{\text{ss}}(\tilde{\mathbf{x}}_0)} \\ &= \frac{\rho_{\text{ss}}(\mathbf{x}_0)}{\rho_{\text{ss}}(\mathbf{x}_\tau)} \exp \left[ \Omega \int_0^{\tau} [\mathcal{L}(\tilde{\mathbf{x}}, \dot{\tilde{\mathbf{x}}}) - \mathcal{L}(\mathbf{x}, \dot{\mathbf{x}})] dt \right] \\ &= \exp \left[ \Omega [\phi(\mathbf{x}_\tau) - \phi(\mathbf{x}_0)] + \Omega \int_0^{\tau} \mathcal{L}(\tilde{\mathbf{x}}, \dot{\tilde{\mathbf{x}}}) dt \right] \\ &= \exp \left[ \Omega \int_0^{\tau} \mathbf{F} \cdot \nabla \phi dt + \Omega \int_0^{\tau} \mathbf{F} \cdot \mathbf{D}^{-1} \cdot \mathbf{F} dt \right] \\ &= \exp \left[ \Omega \int_0^{\tau} [\mathbf{F} \cdot \mathbf{D}^{-1} \cdot \mathbf{F} - (\nabla \phi_0) \cdot \mathbf{D} \cdot (\nabla \phi_0)] dt \right] \\ &= \exp \left[ \Omega \int_0^{\tau} \mathbf{V} \cdot \mathbf{D}^{-1} \cdot \mathbf{V} dt \right]. \end{aligned} \quad (43)$$

On the other hand, it is particularly associated with the trajectory-dependent entropy[3]

$$\frac{\mathcal{P}[\mathbf{x}(t)]}{\mathcal{P}[\tilde{\mathbf{x}}(t)]} = \exp \left[ \int_0^\tau \dot{s}[\mathbf{x}(t)] dt \right], \quad (44)$$

where  $\dot{s}[\mathbf{x}(t)]$  is the trajectory-dependent entropy production[4] . Therefore, we obtain the density of entropy production rate

$$\begin{aligned} e_p &= \Omega^{-1} \int \dot{s}(\mathbf{x}) \rho_{ss}(\mathbf{x}) d\mathbf{x} \\ &= \int \mathbf{V} \cdot \mathbf{D}^{-1} \cdot \mathbf{V} \rho_{ss}(\mathbf{x}) d\mathbf{x} \geq 0. \end{aligned} \quad (45)$$

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