

# Reversible Gray-Scott model as a tool of thermodynamic investigation in Non-Equilibrium Chemical Systems

By

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## Abstract

In this report, we introduce the reversible Gray-Scott model as a tool of thermodynamic investigation in non-equilibrium reaction-diffusion system. This model is modified from the original Gray-Scott model in order to calculate the entropy production of a reaction-diffusion system. Here, we study the relations between the pattern formation and the thermodynamic quantities; the entropy production, the entropy flow and the entropy change. In summary, we comment the relation between the thermodynamic quantity and the mathematical analysis of pattern dynamics.

## § 1. Introduction

Many ordered structures exist in nature, especially biological system. For example, ordered arrays of stripes, dots or both appear in the skin patterns of fish [1]. These structures seem to contradict with the second thermodynamic law. Prigogine et al. succeeded to explain this contradiction and proposed a concept of the dissipative structures in the framework of the non-equilibrium thermodynamics [2, 3]. The dissipative structures are evoked through only dissipative processes under condition far from equilibrium. Therefore these ordered structures satisfy the second law of thermodynamics.

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After the proposal of dissipative structures concept, the number of studies in non-equilibrium and dissipative systems from the dynamical viewpoint increased. Especially pattern dynamics has been well studied mathematically and experimentally in reaction diffusion systems [4, 5, 6, 7]. However, the number of those studies from the thermodynamic viewpoint decreased. Thus there are a few studies that discuss the relation between the thermodynamic quantities and the pattern dynamics or behavior of the non-equilibrium system.

In order to discuss that relation, we introduced the reversible Gray-Scott model [8]. In this report, we present our studies with the numerical calculation of the entropy balance. The relations between the pattern dynamics and the thermodynamic quantities are discussed. In summary, we add comments about the relation between the thermodynamic quantities and the mathematical description of pattern dynamics.

## § 2. System

Generally, the chemical reactions are irreversible when these are used for simulations of non-linear pattern formation. However, it is impossible to calculate the entropy production of the irreversible reactions because the entropy production becomes infinite. (See Appendix A) In this paper, we use the reversible Gray-Scott model in order to calculate the thermodynamic quantities in a reaction diffusion system.

This model is called the reversible Gray-Scott model, which is modified from the original Gray-Scott model [4]. This original model was considered as a part of the Brullseter model. The model consists of two chemical reaction steps and three chemical species  $U$ ,  $W$  and  $P$ :



The equations that govern this reaction-diffusion system are as follows: Eq. 2.1

$$(2.3) \quad \begin{cases} \frac{\partial U}{\partial t} = -UW^2 + f(1 - U) + k_r W^3 + D_U \nabla^2 U \\ \frac{\partial W}{\partial t} = UW^2 - (f + k)W - k_r W^3 + k_r P + D_W \nabla^2 W \\ \frac{\partial P}{\partial t} = kW - k_r P - fP + D_P \nabla^2 P \end{cases}$$

where  $f$  is the flow rate constant;  $k$  and  $k_r$  are the rate constants of the forward and the backward reactions, respectively.  $D_U$ ,  $D_W$  and  $D_P$  are the diffusion coefficients of U, W and P, respectively, and are set to be:  $D_U = 2.0 \times 10^{-5}$ ,  $D_W = 1.0 \times 10^{-5}$  and  $D_P = 1.0 \times 10^{-6}$ .

### § 3. Results and discussion

The present system can show various pattern formations: self-replicating pulse, stretching line, chaotic pattern and also co-existing patterns [9, 10]. Here, thermodynamic quantities (entropy production, entropy flow and entropy change) are calculated in the two cases that a one-dimensional media shows self-replicating pulse and a propagating pulse. The relations among thermodynamic quantities are described in Appendix A. In order to calculate the entropy flow, we introduced a new chemical potential [11, 12]. The definition and calculation method of this potential is described in Appendix B.

First, we show the results in the case that the system shows self-replicating pulse (Fig.1). The one side of the system is perturbed initially and a pulse is initiated. This pulse self-replicates after a while. This pulse self-replicates three times and the system is filled with four pulses. Finally, the system becomes stable.

The entropy production increases rapidly while the pulse is self-replicating and it becomes almost stable while the pulse is not self-replicating, i.e., the system shows quasi-stable state. Finally, it becomes a constant when the system shows stable state. The entropy production is proportional to the area of black regions, and then the entropy production is an index of pattern [8, 9]. In the previous paper [8], we examined whether the entropy production could be a potential function. Unfortunately, the result shows the entropy production cannot work as a potential function and it is a counterexample of the Hanson's hypothesis that pulse replication phenomenon occurs because of the minimum entropy production principle [8].

The entropy flow shows negative values. This means that the system throws out the entropy to its environment with the flow. The absolute value of this quantity is almost the same that of the entropy production. It means that most amount of the entropy that is produced inside the system is thrown out to its environment in order to keep the system structures [11].

The absolute value of the entropy change is smaller than the other quantities. This quantity shows near zero value when the system shows quasi-stable state. On the other hands, this quantity shows a peak while the pulse is self-replicating. This quantity converges to zero, as the system becomes stable state. These behaviors of the entropy change mean that the entropy increases during the process of the pulse of self-replication and the entropy becomes stable while the system shows static stable state.

Second, thermodynamic quantities are calculated in the case the system shows a

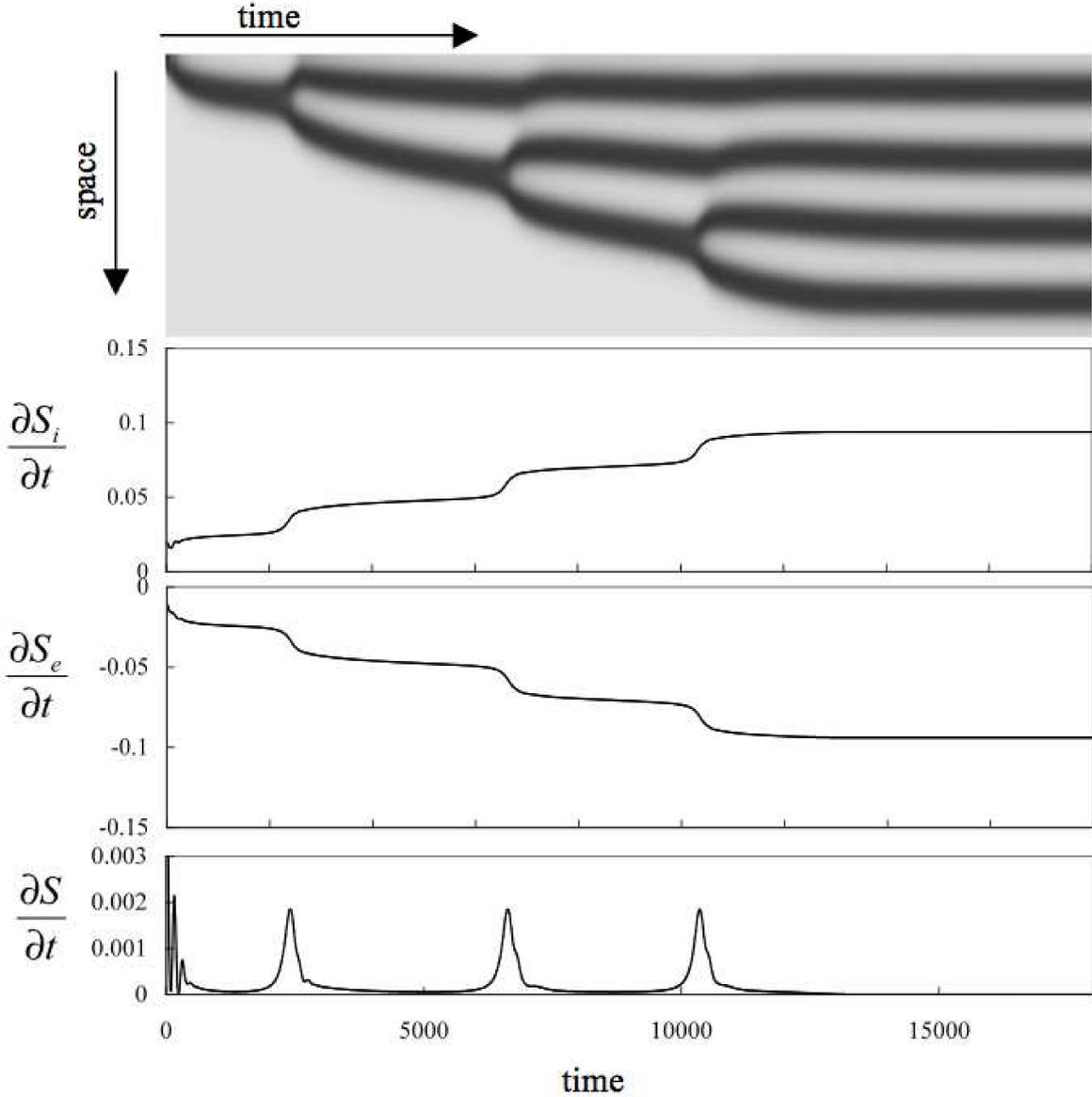


Figure 1. Time series of the one-dimensional system and thermodynamic quantities when the system shows self-replicating pulse. The system size is  $180dx$ .  $dx = 0.005$ .  $f = 0.03$ ,  $k = 0.06$ ,  $k_r = 0.001$ . The system has the Neumann boundary condition. First panel: time series of the system. The gray-scale shows the concentration of  $U$  0.0 (black) to 1.0(white). Second panel: time series of the entropy production. Third panel: time series of the entropy flow. Forth panel: time series of the entropy change.

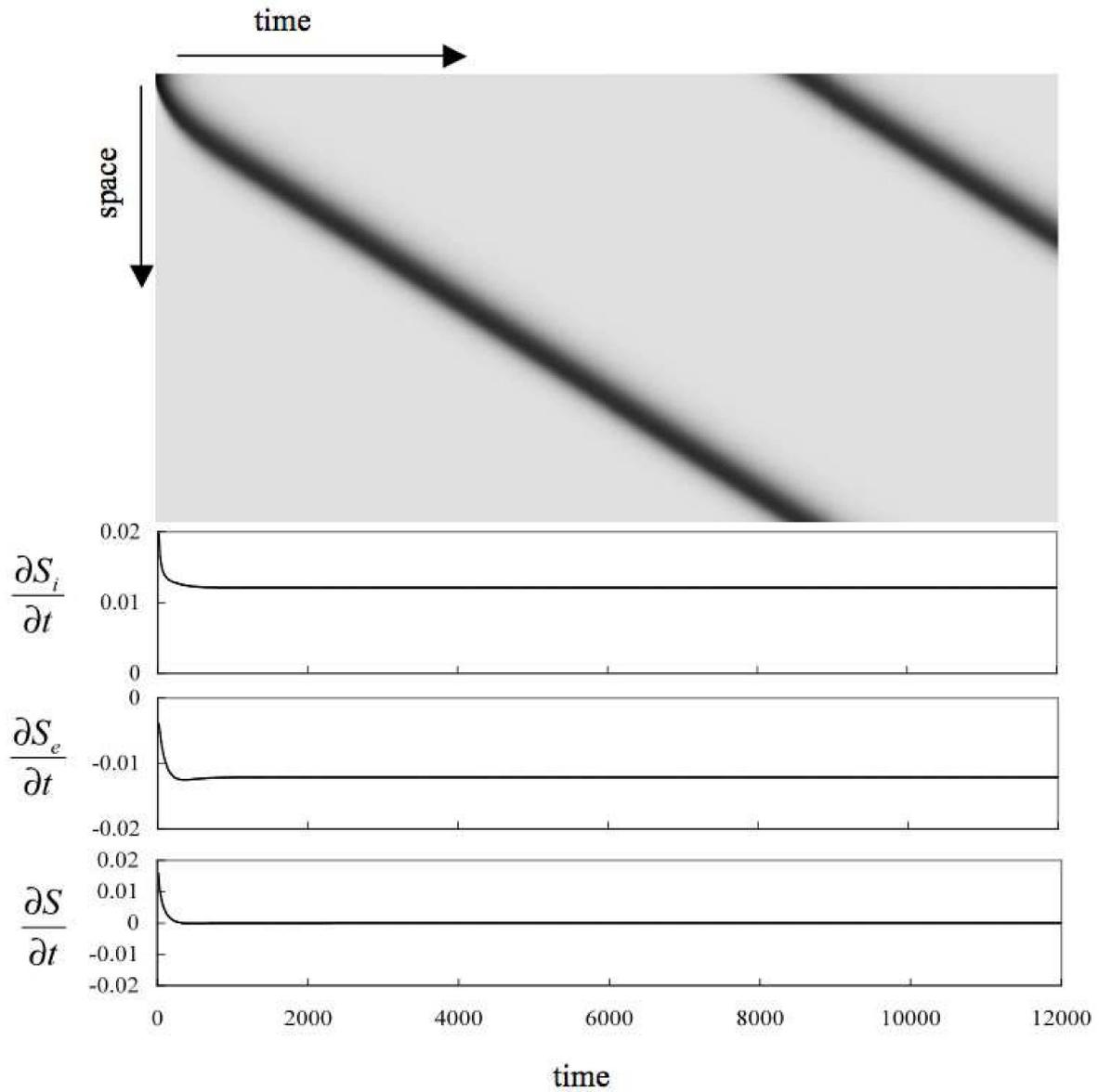


Figure 2. Time series of the one-dimensional system and thermodynamic quantities when the system shows traveling pulse. The system size is  $400dx$ .  $dx = 0.005$ .  $f = 0.01$ ,  $k = 0.047$ ,  $k_r = 0.001$ . The boundary condition is changed at  $t = 3000.0$ , from the Neumann boundary to the periodic one. First panel: The time series of the system. The gray-scale shows the concentration of  $U$  0.0 (black) to 1.0 (white). Second panel: time series of the entropy production. Third panel: time series of the entropy flow. Forth panel: time series of the entropy change.

traveling pulse (Fig.2). The system is perturbed and a pulse is initiated initially. After a while, the Neumann boundary is changed to the periodic boundary. Then the pulse is propagating with a constant velocity. All of the thermodynamic quantities become constant values after the traveling pulse is stabilized. The entropy production becomes a constant because the profile of traveling pulse is kept constantly and the entropy production is proportional to the black region [12].

The entropy flow goes to a negative constant value that is the same absolute value of the entropy production. Then the entropy change converges to zero. It means that all of the entropy that is produced inside the system is thrown out to the system and then the entropy of the system is always kept constant.

From these two cases, the thermodynamic quantities become constant. Especially when the system shows a stable solution, the entropy change becomes zero whether the system pattern is static or moves with constant velocity. The latter property coincides with the intrinsic property of the entropy, i.e., the entropy is a state function and then it shows constant value when the system is stable.

#### § 4. Summary

In this report, we calculate the entropy balance equation in a reaction-diffusion system with the reversible Gray-Scott model. In order to calculate the entropy flow and the entropy change, we introduce a new chemical potential. The property of the entropy change consists with the instinctive and intrinsic property of the entropy that the entropy is a state function of the system. Therefore, introducing the new chemical potential is useful to calculate numerically the entropy balance equation.

Here, think back on the study of Nishiura and Ueyama [6, 7]. They analyzed mathematically the mechanism of the self-replicating pulse. Their system has many stable manifolds in the norm and parameter space. These manifolds called Turing branch of  $k$  mode for stable  $k$  pulses ( $k$  is the number of the pulses)[6]. The moving point of the system travels near the saddle node bifurcation points of these branches in the case that the system shows self-replicating pulses. The moving point converges to the bifurcation point of  $k$ -mode branch when the  $k$  pulses exist in the system. After that, the moving point stays temporally near this point while the pulses are quasi-stable, in other words, while the pulses look stable. However, the moving point gets away from this point when one of the pulses begin to self-replicate. Then the moving point converges to the saddle node bifurcation of the  $k + 1$  mode branch and the system shows another quasi-stable state (looks like  $k + 1$  pulses solution). Finally, the moving point settles down on the stable manifold when the system shows a stable state. If there is no stable manifold, the system shows chaotic behaviors. From the present calculations, the entropy change converges to zero, but not zero while the pulse does

not self-replicate, i.e., the system shows a quasi-stable state. And also this quantity goes up from zero when the pulse begins to self-replicate. Therefore it looks that the entropy change shows the distance between the moving point and the stable manifold of  $k$  mode Turing branch and then there is possibility that the entropy change can be an index of that distance. Therefore, we believe that this relation is useful to reveal the detailed relation between the thermodynamic quantities and the mathematical description of the system.

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### § Appendix A. Entropy balance equation

The entropy balance equation is a basic equation for non-equilibrium thermodynamics. This equation is derived from the mass conservation law and the relation between the entropy per unit volume and mass density [2, 3]. The mass conservation law with chemical reactions is described as

$$(A.1) \quad \frac{\partial \rho_j}{\partial t} = -\text{div} \mathbf{j}_j + \sum_i v_{ji} w_i$$

where  $\rho_j$  and  $\mathbf{j}_j$  are density and flux vector of the  $j$ th chemical species, respectively.  $v_{ji}$  is stoichiometric constant of  $j$ th chemical species in  $i$ th chemical reaction.  $w_i$  is the rate of the  $i$ th chemical reaction.

The relation between the entropy per unit volume and mass density is described as

$$(A.2) \quad \frac{\partial s}{\partial t} = - \sum_j \frac{\mu_j}{T} \frac{\partial \rho_j}{\partial t}$$

where  $\mu_j$  is the chemical potential of the  $j$ th chemical species and it is described as:

$$(A.3) \quad \mu_j = \mu_j^* + k_B T \ln c_j$$

where  $\mu_j^*$  is the standard chemical potential and  $c_j$  is the concentration of the  $j$ th chemical species [2, 3]. The standard chemical potential has a constant value characteristic for each chemical species.

The entropy balance equation consists of the three thermodynamic quantities: the entropy change, the entropy production and the entropy flow. The entropy change is the time derivative of the entropy of the system,  $\partial S/\partial t$ , and the equation is described as

$$(A.4) \quad \frac{\partial S}{\partial t} = \frac{\partial S_i}{\partial t} + \frac{\partial S_e}{\partial t} = \int_V (\sigma - \operatorname{div} \mathbf{J}) dV$$

where  $\partial S_i/\partial t = \int_V \sigma dV$  is the entropy production and  $\partial S_e/\partial t = - \int_V \operatorname{div} \mathbf{J} dV$  is the entropy flow.

The entropy production represents the time derivative of the entropy that is produced inside the system. The entropy production of a reaction-diffusion system is described as:

$$(A.5) \quad \begin{aligned} \frac{\partial S_i}{\partial t} &= \int_V \sigma dV \\ &= \int_V \sum_i k_B (v_{i,+} - v_{i,-}) \ln \frac{v_{i,+}}{v_{i,-}} dV + \int_V \sum_j k_B \frac{D_j}{c_j} (\nabla c_j)^2 dV \end{aligned}$$

where  $k_B$  is the Boltzman constant;  $v_{i,+}$  and  $v_{i,-}$  are the rates of the forward and the backward reactions of the  $i$ th chemical reaction, respectively.  $D_j$  is the diffusion coefficient and the concentration of the  $j$ th chemical species.

The entropy flow represents the time derivative of the entropy that comes from or goes out to the environment across the boundary of the system. The entropy flow can be written as an integral over the system surface  $\Omega$  with the divergence theorem:

$$(A.6) \quad \begin{aligned} \frac{\partial S_e}{\partial t} &= - \int_V \operatorname{div} \mathbf{J} dV \\ &= \int_{\Omega} \sum_j \frac{\mu_j}{T} \mathbf{j}_j \cdot \mathbf{n} d\Omega \end{aligned}$$

where  $\mathbf{n}$  is the unit vector normal on the system surface.

### § Appendix B. Calculation of the entropy flow

For the calculation of the entropy flow, the flow vector  $\mathbf{j}$  and the chemical potential  $\mu$  in Eq.A.6 should be described concretely. Here, descriptions of these quantities in the present model will be given.

The flux vectors are derived from the system configurations. Here, we consider a one-dimensional reaction-diffusion system for simplicity [11]. Spatial inhomogeneity in concentrations appears along one direction  $x$  only. Then, the flow vector  $\mathbf{j}$  is described; Inward flows of chemical species are given as:

$$(B.1) \quad \mathbf{j}_U = -f\mathbf{e}_z, \mathbf{j}_W = 0, \mathbf{j}_P = 0,$$

and the outbound flows are given as:

$$(B.2) \quad \mathbf{j}_U = fU\mathbf{e}_z, \mathbf{j}_W = -fW\mathbf{e}_z, \mathbf{j}_P = fP\mathbf{e}_z,$$

where  $\mathbf{e}_z$  is the unit vector directed parallel to the surface normal vector. Here, the direction of this vector is perpendicular to the direction  $x$ . The flow terms are set to zero at the Neumann boundary conditions [11]. When the system has periodic boundary condition the system has no out or in flow term in the direction  $x$ .

The chemical potential is described with the concentrations of the chemical species and its standard chemical potential. However, we face a problem that the values of the standard chemical potentials are unknown in our model. This fact means that it is impossible to calculate the entropy flow from eqs.A.3 and A.6. To avoid this inconvenience, we introduce an alternative chemical potential,  $\mu_r$ , which is called the relative chemical potential [11].

The relative chemical potential is defined as:

$$(B.3) \quad \mu_{r,j} = \mu_j^* + k_B T \ln c_j - \mu_j^* - k_B T \ln c_{e,j} = k_B T \ln \frac{c_j}{c_{e,j}}$$

where  $c_{e,j}$  is the concentration of the  $j$ th chemical species at the equilibrium state. This equilibrium state is defined as the steady state to which the non-equilibrium system should reach if the system is suddenly isolated from its environment.

For the calculation of the relative chemical potentials in the present system, the equilibrium state  $c_{e,j}(=c_{e,j}(t))$  is calculated from the following three equations. These equations are obtained by assuming that the system is isolated, i.e.,  $f = 0.0$ .

$$(B.4) \quad \int_V (U + W + P)dV = (U_e + W_e + P_e)V,$$

$$(B.5) \quad U_e W_e^2 = k_r W_e^3,$$

$$(B.6) \quad kW_e = k_r P_e,$$

where  $V$  is the volume of the system;  $U_e$ ,  $W_e$  and  $P_e$  are the equilibrium concentrations of chemical species U, W and P, respectively. The first equation means that the total number of molecules is preserved in the reversible Gray-Scott model. The second and third equations mean that each chemical reaction step (eqs.2.1 and 2.2) should go to the equilibrium states, i.e., the principle of the detailed balance should be satisfied.