Proceedings of Equadiff-11
2005, pp. 343–352
ISBN 978-80-227-2624-5

A MATHEMATICAL ASPECT FOR LIESEGANG PHENOMENA*

ISAMU OHNISHI† AND MASAYASU MIMURA‡

Key words. Liesegang band, reduced KR model, singular limit, reaction diffusion system

AMS subject classifications. 35B50, 35B10, 35B25, 45G10

1. Introduction. Liesegang phenomena are macroscopic pattern formations which appear in a gel-containing system [1]. We can observe normal striped patterns, especially in the presence of large concentration gradients in initial data. These striped patterns are called "Liesegang band", because they were discovered and studied by R.E. Liesegang in 1896 [1] for the first time. In this paper, we discuss the mechanism of this kind of very regularly striped pattern formation.

Liesegang band is obtained by the following procedure, for example. A solution of one soluble electrolyte, for instance, lead nitorate ($Pb(NO_3)_2$), at relatively low concentration is placed in a test tube to which a gel-forming material is added. After a gel is formed, another electrolyte solution, such as the potasium iodide (KI), normally at substantially higher concentration, is poured on the top of the gel containing $Pb(NO_3)_2$. The iodine-ions (I^-) diffuse into the gel and react with lead ions (Pb^{2+}) to form lead iodide (PbI_2) which is almost insoluble,

$$\mathrm{Pb}^{2+} + 2\mathrm{I}^- \longrightarrow \mathrm{PbI}_2.$$

One of interesting points of this striped pattern is that the crystals do not precipitate continuously, but it occurs discontinuously. It is also well-known that these striped patterns satisfy three geometrically beautiful laws, *spacing law*, *time law*, and *width law* in chemical experiments [2]. *Spacing law* can be described as $X_{N+1} = p_1 X_N$, where X_N is the distance of the N-th band location from an original junction and p_1 is a positive constant. *Time law* and *width law* are expressed as $\sqrt{t_N} = p_2 X_N$ and $w_N = p_3 X_N$ respectively, where t_N, w_N, p_2 and p_3 are the interval from the time when the experiment started to formation time of the N-th band, the width of the N-th band and positive constants. It is considered that these laws are due mainly to the diffusion.

We define "quasi-periodic" as the striped pattern formation which satisfies these laws to distinguish it from "periodic", which means repeating with the exactly same interval temporarily and spatially. There have been a number of models and theories of Liesegang phenomena proposed and discussed, and *time law* and *spacing law* have been already shown by a numerical simulation. But as long as we know, there is no mathematical rigorous work which reveals the mechanism and structure of Liesegang phenomena.

*This work was supported by Grant No.: 15540122 of JSPS.
†Department of Mathematical and Life Sciences, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, Hiroshima, 739-8526 Japan, (isamu_o@math.sci.hiroshima-u.ac.jp)
‡Department of Mathematics, School of Science and Technnology, Meiji University, Kawasaki, Kanagawa, 214-8571 Japan, (mimura@math.meiji.ac.jp)

2. Preliminaries. Our basic model equation is the following, which is called the reduced KR model. Here, without loss of generality, we make the diffusion constant equal to one to change the reduced KR model to the dimension less form.

$$\begin{cases} c_t = c_{xx} + b_0 S'(t)\delta\left(x - S(t)\right) - qP(c,d), & 0 < t < T,\ x \in \mathbb{R}^+, \\ d_t = qP(c,d), & 0 < t < T,\ x \in \mathbb{R}^+, \\ (B.C.)\ c_x(t,0) = 0, & 0 < t < T, \\ (B.C.)\ \lim\limits_{x\to\infty} c(t,x) = 0, & 0 < t < T, \\ (\ I.C.)\ \ c(0,x) = 0, \quad d(0,x) = 0, & x \in \mathbb{R}^+, \end{cases} \tag{2.1}$$

where δ means the Dirac δ in one-space dimension,

$$P(c,d) = \begin{cases} (c - C_a)_+, & \text{on} \quad \{x \in \mathbb{R}^+;\, c > C_s \text{ or } d > 0\}, \\ 0, & \text{otherwise}, \end{cases}$$

$$q > 0,\ b_0 > 0,\ C_s \geq C_a \geq 0 \quad : \text{given constants},$$
$$S(t) = \alpha\sqrt{t} \ \ (\alpha > 0) : \text{given function}.$$

$\mathbb{R}^+$ is defined by

$$\mathbb{R}^+ = \{x \in \mathbb{R}; x \geq 0\}.$$

(We note that $\mathbb{R}^+$ includes 0.) In this section we consider (2.1) in case of $C_a = 0$. Originally, in 1981, Keller and Rubinow derived a model system composed of four equations, which is called KR model now, see [3]. The system (2.1) is a kind of a singular limit of the KR model of the Liesegang phenomena. We refer to [4] for details about this reduction.

We first define a weak solution of (2.1). Let $c(\cdot,\cdot) \in L^1\left(0,T\,;\,W^{1,\infty}(\mathbb{R}^+)\right)$, $d(\cdot,\cdot) \in L^\infty\left((0,T)\ \times \mathbb{R}^+\right)$. If these functions satisfy

$$\begin{aligned} c(t,x) &= \int_0^t \frac{1}{(4\pi(t-s))^{\frac{1}{2}}} \left(\mathrm{e}^{-\frac{(x-S(s))^2}{4(t-s)}} + \mathrm{e}^{-\frac{(x+S(s))^2}{4(t-s)}} \right) b_0 S'(s)\ \mathrm{d}\xi\ \mathrm{d}s \\ &\quad -q \int_0^t \int_{\mathbb{R}^+} \frac{1}{(4\pi(t-s))^{\frac{1}{2}}} \left(\mathrm{e}^{-\frac{(x-\xi)^2}{4(t-s)}} + \mathrm{e}^{-\frac{(x+\xi)^2}{4(t-s)}} \right) P(c,d)\ \mathrm{d}\xi\ \mathrm{d}s, \\ d(t,x) &= q \int_0^t P(c,d)\,\mathrm{d}s, \end{aligned} \tag{2.2}$$

then we call the couple (c,d) a weak solution of (2.1).

Now we refer to the forthcoming paper [5] for the exsitence theorem of a time global solution. Moreover, in [5] we have proved that the precipitation becomes discrete spatially and temporarily. In addition to this, in [6], we report about some numerical simulations for the model system and verify the three laws by them. In this note, as we assume that the solution exists globally in time and is smooth enough away from the support point of the Dirac δ, see [5]. We concentrate on revealing the mathematical mechanism by which the quite regular patterns emerge.

3. Time law & spacing law. We first consider the problem in the original scale. The interval $\left(\underline{R_N}, \overline{R_N}\right)$ is defined as the maximal open interval where the N-th precipitation happens, and $\overline{t_N}(> 0)$ is defined as the solution of the equation: $S(\overline{t_N}) =$

$\overline{R_N}$. Especially, it is known that $\underline{R_1} = 0$. By the definition of $P(c, d)$, $\left(\underline{R_N}, \overline{R_N}\right)$ must be an open interval with finite length.

We now think about the dynamics of the system after the N-th precipitation settled down and until the $(N+1)$-st precipitation occurs. For this purpose, we separate the half line $[0, \infty)$ to $[0, \overline{R_N}]$ and $(\overline{R_N}, \infty)$. We prove that

(1) The $(N+1)$-st precipitation will never occur in $[0, \overline{R_N}]$, and
(2) The $(N+1)$-st precipitation really occurs in $(\overline{R_N}, \infty)$, which satisfies *time law* rigorously and *spacing law* approximately.

We first prove (1).

Theorem 3.1. *The $(N+1)$-st precipitation will not occur in $[0, \overline{R_N}]$.*

Proof. We define $\overline{t_N^*}$ as the time when the solution has just come down away from C_s the N-th time at all the spatial points. Even if $\overline{t_N^*} > \overline{t_N}$, it is easily seen that the next precipitation does not occur in $\left(\overline{t_N}, \overline{t_N^*}\right)$. Therefore we consider the next precipitation only in $t > \overline{t_N^*}$.

We now see

$$c(\overline{t_N^*}, x) \leq C_s, \qquad 0 \leq x \leq \overline{R_N}.$$

In what follows we prove that $c(t, x)$ goes to 0 actually for any $x \in [0, \overline{R_N}]$. For this purpose, we use the integral expression in the rescaled system. In the integral expression, let us substitute t_N^* for T_0, and we get

$$\begin{aligned} \hat{c}\,(t, y) =& \hat{c}(t_N^*, y) \\ &- \frac{q\alpha(t - t_N^*)}{(4\pi)^{\frac{1}{2}}} \int_0^1 \int_0^\infty \frac{\left(\mathrm{e}^{-\frac{\alpha^2(y-\eta)^2}{4(1-p)}} + \mathrm{e}^{-\frac{\alpha^2(y+\eta)^2}{4(1-p)}}\right) \hat{P}(\hat{c}, \hat{d})}{(1-p)^{\frac{1}{2}}} \, \mathrm{d}\eta \, \mathrm{d}p. \end{aligned} \tag{3.1}$$

By the rescaling, the precipitation interval moves to the left-hand side. Therefore, we estimate the value of $\hat{c}\left(t, \sqrt{\frac{t_N^*}{t}} y\right)$. On the moving point $\sqrt{\frac{t_N^*}{t}} y$, it is seen that

$$\begin{aligned} &\hat{c}\left(t, \sqrt{\frac{t_N^*}{t}} y\right) \leq \hat{c}\left(t_N^*, \sqrt{\frac{t_N^*}{t}} y\right) \\ &- \frac{q\alpha(t - t_N^*)}{(4\pi)^{\frac{1}{2}}} \left(\frac{t_N^*}{t}\right)^{\frac{1}{2}} \int_0^1 \int_0^\infty \frac{\left(\mathrm{e}^{-\frac{\frac{t_N^*}{t}\alpha^2(y-\zeta)^2}{4(1-p)}} + \mathrm{e}^{-\frac{\frac{t_N^*}{t}\alpha^2(y+\zeta)^2}{4(1-p)}}\right) \hat{c}(t, \sqrt{\frac{t_N^*}{t}}\zeta)}{(1-p)^{\frac{1}{2}}} \, \mathrm{d}\zeta \, \mathrm{d}p, \end{aligned} \tag{3.2}$$

where ζ is defined by

$$\eta = \sqrt{\frac{t_N^*}{t}} \zeta.$$

We take a constant $l \in (0, C_s)$ and a subinterval $[y_1', y_2'] \subset [0, \overline{R_N}]$ such that $\hat{c}\left(t, \sqrt{\frac{t_N^*}{t}} y\right) > l$ for any $y \in (y_1', y_2')$, and fix them. Therefore, there exists a constant

$B^* > 0$, which depends on y'_1, y'_2 and is independent from y, t, t^*_N, such that the second term on the right-hand side of (3.2) is smaller than

$$-\frac{q\alpha(t-t^*_\beta)}{(4\pi)^{\frac{1}{2}}}\left(\frac{t^*_\beta}{t}\right)^{\frac{1}{2}} lB^*$$

On the other hand, it is easily seen that

$$0 \le \hat{c}\left(t^*_N, \sqrt{\frac{t^*_N}{t}}y\right) \le C_s,$$

for any $t > t^*_N$. Therefore, as $t \to \infty$, we see that $\hat{c}\left(t, \sqrt{\frac{t^*_N}{t}}y\right)$ converges to 0, taking into account that $l > 0$ can be chosen arbitrarily. □

Remark 3.2. *According to the proof above, we have proved that*

$$\lim_{t\to\infty} c\,(t,x) = 0,$$

for $x \in [0, R_N]$ *uniformly.*

Next, we will prove (2). We remark that c has never reached C_s so far in $x > \overline{R_N}$, $t \le \overline{t_N}$. We define functions $\varphi_N(t)$, $\eta_N(t)$, and $\psi_N(x)$ by

$$\begin{aligned} &\varphi_N(t) = c(t, \overline{R_N}) && t > \overline{t_N}, \\ &\eta_N(t) = c_x(t, \overline{R_N}) && t > \overline{t_N}, \\ &\psi_N(x) = c(\overline{t_N}, x) && 0 < x < \infty, \end{aligned}$$

for the solution c of the original problem (2.1). By the maximality of $(\underline{R_N}, \overline{R_N})$,

$$0 \le \psi_N(x) < C_s \quad (\overline{R_N} < x < \infty), \tag{3.3}$$

and c solves the following:

$$\begin{cases} c_t = c_{xx} + b_0 S'(t)\delta(x - S(t)), & t > \overline{t_N},\ \overline{R_N} < x < \infty, \\ (B.C.)\ c(t, \overline{R_N}) = \varphi_N(t), & t > \overline{t_N}, \\ (B.C.)\ \lim\limits_{x\to\infty} c(t,x) = 0, & t > \overline{t_N}, \\ (\ I.C.)\ c(\overline{t_N}, x) = \psi_N(x), & \overline{R_N} < x < \infty. \end{cases} \tag{3.4}$$

One of our main tools is the comparison principle for parabolic equations with the homogeneous Dirichlet boundary condition at $x = 0$. Therefore, we extend (3.4) naturally into the interval $[0, \overline{R_N}]$. For this purpose, we consider the following problem:

$$\begin{cases} \tilde{c}_t = \tilde{c}_{xx}, & t > \overline{t_N},\ 0 < x < \overline{R_N}, \\ (B.C.)\ \tilde{c}(t, \overline{R_N}) = \varphi_N(t), & t > \overline{t_N}, \\ (B.C.)\ \tilde{c}_x(t, \overline{R_N}) = \eta_N(t), & t > \overline{t_N}, \\ (\ I.C.\ )\ \tilde{c}(\overline{t_N}, x) = \psi_N(x), & 0 < x < \overline{R_N}. \end{cases} \tag{3.5}$$

There is a unique solution $\tilde{c}$ of (3.5), and by use of the comparison principle (see [7]),

$$\tilde{c}(t,x) > c(t,x) \geq 0$$

is satisfied in $t > \overline{t_N}$, $0 < x < \overline{R_N}$. Finally, let us consider the following evolution problem:

$$\begin{cases} v_t = v_{xx} + b_0 S'(t)\delta(x - S(t)), & t > \overline{t_N},\ 0 < x < \infty, \\ (B.C.)\ v(t,0) = \eta_N(t), & t > \overline{t_N}, \\ (B.C.)\ \lim\limits_{x\to\infty} v(t,x) = 0, & t > \overline{t_N}, \\ (\,I.C.\,)\ v(\overline{t_N}, x) = \psi_N(x), & 0 < x < \infty, \end{cases} \tag{3.6}$$

which has a unique solution v. Moreover, v satisfies

$$v(t,x) = \tilde{c}(t,x) > c(t,x)$$

in $t > \overline{t_N}$, $0 < x < \overline{R_N}$, and also

$$v(t,x) = c(t,x)$$

in $t > \overline{t_N}$, $\overline{R_N} < x < \infty$.

Without loss of generality, we normalize $\overline{t_N} = 1$, as we fix $N \in \mathbb{N}$. In order to investigate the behavior of the solution of (3.6), we study the following homogeneous problem:

$$\begin{cases} f_t = f_{xx} + b_0 S'(t)\delta(x - S(t)), & t > 1,\ x > 0, \\ f(t,0) = 0, & t > 1, \\ \lim\limits_{x\to\infty} f(t,x) = 0, & t > 1, \\ f(1,x) = 0, & x > 0, \end{cases} \tag{3.7}$$

Furthermore, we need to consider the next problem to see properties of a solution of (3.7).

$$\begin{cases} g_t = g_{xx} + b_0 S'(t)\delta(x - S(t)), & t > 0,\ x > 0, \\ g(t,0) = 0, & t > 0, \\ \lim\limits_{x\to\infty} g(t,x) = 0, & t > 0, \\ g(0,x) = 0, & x > 0 \end{cases} \tag{3.8}$$

An important difference between (3.7) and (3.8) is the time when the initial data is given. It is 1 in (3.7), although it is 0 in (3.8).

Problem (3.8) has a unique time global solution. As $g(t,x)$ is transformed by the following change of variables:

$$\begin{cases} t' = \lambda^2 t, \\ x' = \lambda x, \end{cases} \tag{3.9}$$

$g(t',x')$ solves the same problem (3.8). Therefore, it holds that

$$g(t,x) = g(\lambda^2 t, \lambda x) \quad (\lambda > 0). \tag{3.10}$$

We let $\lambda = \frac{1}{\sqrt{t}}$, and we see

$$g(t,x) = g(1, \frac{x}{\sqrt{t}}). \tag{3.11}$$

Moreover we use the rescaling $x = S(t)y$ to get

$$g(t,x) = g(1, \alpha y). \tag{3.12}$$

We remark that the right-hand side of (3.12) does not depend on t. Let us define Ψ^D by

$$\Psi^D(y) = g(1, \alpha y),$$

and this is a stationary solution of the equation rescaled by $x = S(t)y$. Namely, Ψ^D solves

$$\begin{cases} 0 = \frac{1}{\alpha^2}\Psi_{yy} + \frac{y}{2}\Psi_y + \frac{b_0}{2}\delta(y-1), & y > 0, \\ \Psi(0) = 0, \\ \lim_{r\to\infty} \Psi(y) = 0. \end{cases} \tag{3.13}$$

This means that the solution of (3.8) has the "similar" shape to Ψ^D and its maximum point moves to the right-hand side.

On the other hand, we make the change of variables, $x = S(t)y$ and $t = e^\tau$, for the equation (3.7). If we define h by $h(\tau, y) = f(t, x)$, then the rescaled equation is

$$\begin{cases} h_\tau = \frac{1}{\alpha^2}h_{yy} + \frac{y}{2}h_y + \frac{b_0}{2}\delta(y-1), & \tau > 0,\ y > 0, \\ h(\tau, 0) = 0, \\ \lim_{y\to\infty} h(\tau, y) = 0, \\ h(0, y) = 0. \end{cases} \tag{3.14}$$

Now, let us consider the function $\Psi^D - h$, which satisfies the heat equation with the homogeneous Dirichlet boundary condition and with the initial condition Ψ^D. Therefore, $\Psi^D - h$ converges to 0 uniformly in y, which means that f is monotone increasing and

$$f(t, S(t)y) \to \Psi^D(y)(= g(1, \alpha y)), \qquad \text{uniformly in } y,$$

as $t \to \infty$ (namely $\tau \to \infty$).

We next define C^{**} by $C^{**} := \Psi^D(1) > 0$, and study the shape of $\Psi^D(y)$.

Lemma 3.3 (Estimate for $\Psi^D(y)$).

$$\begin{aligned} &\Psi^D(y) > 0, && \textit{in } (0,\infty), \\ &\Psi^D_y(y) > 0, && \textit{in } (0,1), \\ &\Psi^D_y(y) < 0, && \textit{in } (1,\infty), \end{aligned}$$

and $\Psi^D(y)$ attains its maximum C^{**} at $y = 1$.

Proof. $\Psi^D(y) > 0$ in $(0,\infty)$ is clear.

We will show that $\Psi^D_y(y) > 0$ in $(0,1)$ by contradiction. In $(0,1)$, Ψ^D solves

$$\begin{cases} 0 = \frac{1}{\alpha^2}\Psi^D_{yy} + \frac{y}{2}\Psi^D_y & \text{in } (0,1), \\ \Psi^D(0) = 0, \\ \Psi^D(1) = C^{**} > 0. \end{cases} \tag{3.15}$$

If there exists $y_0 \in (0,1)$ such that $\Psi^D_y(y_0) = 0$ then we define $G(y)$ by

$$G(y) \equiv \Psi^D(y_0),$$

and G solves

$$\begin{cases} 0 = \frac{1}{\alpha^2} G_{yy} + \frac{y}{2} G_y, \\ G_y(y_0) = 0, \\ G(y_0) = \Psi^D(y_0). \end{cases}$$

By use of the uniqueness theorem of the solution of the initial value problem for second order linear partial differential equations, this does not have any solution other than G. Therefore, the solution of (3.15) must correspond to G. Thus we see $\Psi(y) \equiv 0$ (for any $y \in (0,1)$) from $\Psi^D(0) = 0$. But this contradicts the fact that $C^{**} > 0$, so that $\Psi^D_y(y) \neq 0$ for any $y \in (0,1)$.

Taking $C^{**} > 0$ into account, we get $\Psi^D_y(y) > 0$ for any $y \in (0,1)$. We can prove that $\Psi^D_y(y) < 0$ for any $y \in (1,\infty)$ in the same manner, so we omit it. □

For the non-homogeneous problem (3.6), we make a change of variables as before and we define $w(\tau,y) = v(t,x)$ to get

$$\begin{cases} w_\tau = \frac{1}{\alpha^2} w_{yy} + \frac{y}{2} w_y + \frac{b_0}{2}\delta(y-1) & \tau > 0,\ y > 0, \\ w(\tau,0) = \eta_N(e^\tau), & \tau > 0, \\ \lim\limits_{y\to\infty} w(\tau,y) = 0, & \tau > 0, \\ w(0,y) = \psi_N(\alpha y), & y > 0. \end{cases} \tag{3.16}$$

Lemma 3.4 (Estimate for (3.16)). *If $C_s < C^{**}$, then the solution of (*3.16*) continues to attain its maximum at $y = 1$ after some finite time.*

Proof. The difference $w - h$ between solutions of (3.16) and (3.14) solves classically the following problem:

$$\begin{cases} z_\tau = \frac{1}{\alpha^2} z_{yy} + \frac{y}{2} z_y, & \tau > 0,\ y > 0, \\ z(\tau,0) = \eta_N(e^\tau) > 0, & \tau > 0, \\ \lim_{y\to\infty} z(\tau,0) = 0, & \tau > 0, \\ z(0,y) = \psi_N(\alpha y) > 0, & y > 0. \end{cases} \tag{3.17}$$

By the maximum principle, we see

$$w > h, \tag{3.18}$$

for any $\tau > 0$, $y > 0$.

We now separate the interval where $w(\cdot,\tau$ is defined to $(0,1)$ and $(1,\infty)$. In $(0,1)$, w solves

$$w_\tau = \frac{1}{\alpha^2} w_{yy} + \frac{y}{2} w_y, \quad \tau > 0,\ 0 < y < 1,$$

classically. We apply the maximum principle to see $w(\tau, y)$ attaining its maximum either at $\tau = 0$, $y = 0$ or $y = 1$. On the other hand, we have already known that the next precipitation does not occur in $[0, \overline{R_N}]$ by THEOREM 3.1. Moreover, taking (3.18), LEMMA 3.3, and the fact that $h \to \Psi^D$ as $t \to \infty$ into account, we conclude that, if $C_s < C^{**}$, then w continues to attain its maximum at $y = 1$ after some finite time.

In $(1, \infty)$, we take $R > 0$ large enough and fix it. We prove the same property in $[1, R]$. Finally we use the fact that $\lim_{y\to\infty} w(\tau, y) = 0$. We eventually see w attaining its maximum at $y = 1$ after some finite time. □

In what follows, we define τ'_{N+1} as the time when the solution w of (3.14) hits C_s the $(N+1)$-st time, and also define

$$t'_{N+1} = e^{\tau'_{N+1}}.$$

In the original temporal and spatial scale, R'_{N+1} is defined as the spatial point where the solution c hits C_s the $(N+1)$-st time.

THEOREM 3.5 (Time law). *If $C_s < C^{**}$, then $R'_{N+1} = \alpha\sqrt{t'_{N+1}}$.*

Proof. By LEMMA 3.4, $w(\tau, 1)$ continues to attain the maximum value and hits C_s in some finite time, if $C_s < C^{**}$. Therefore, in original scale, it means that

$$R'_{N+1} = \alpha\sqrt{t'_{N+1}},$$

which means *time law.* □

We define τ''_{N+1} as the time when the solution h of (3.16) hits C_s the $N+1$-st time, and also define $t''_{N+1} = e^{\tau''_{N+1}}$. Moreover, we define $R''_{N+1} = S(t''_{N+1})$ and $\overline{\tau_N} = \log \overline{t_N}$,.

THEOREM 3.6 (Spacing law). *Assume that there exists a small constant $\varepsilon_1 > 0$ such that, for any $i, j \in \mathbb{N}$,*

$$\sup_{x>0} \left|\psi_i(x + \overline{R_i}) - \psi_j(x + \overline{R_j})\right| < \varepsilon_1. \tag{3.19}$$

Then there are constants $C^* > 0$ and $\delta_0 \geq 0$ such that

$$\frac{R'_{N+1}}{\overline{R_N}} = C^* + o(\varepsilon_1^{\delta_0}),$$

if $C^{**} > C_s$ and if $|C^{**} - C_s|$ is small enough.

Proof. In the interval $[\overline{R_N}, \infty)$, we can separate the solution v of (3.6) to the following three parts:

$$v(t,x) = f(t,x) + U(t,x) + V(t,x),$$

Here $f(t,x)$ solves (3.7), $U(t,x)$ solves the following:

$$\begin{cases} U_t = U_{xx}, & t > \overline{t_N}, \quad x > \overline{R_N}, \\ U(t,0) = 0, & t > \overline{t_N}, \\ \lim_{x\to\infty} U(t,x) = 0, & t > \overline{t_N}, \\ U(\overline{t_N}, x) = \psi_N(x), & x > \overline{R_N}, \end{cases} \tag{3.20}$$

and $v(t,x)$ solves the following:

$$\begin{cases} V_t = V_{xx}, & t > \overline{t_N}, \quad x > \overline{R_N}, \\ V(t, \overline{R_N}) = \varphi_N(t), & t > \overline{t_N}, \\ \lim\limits_{x\to\infty} V(t,x) = 0, & t > \overline{t_N}, \\ V(\overline{t_N}, x) = 0, & x > \overline{R_N}. \end{cases} \tag{3.21}$$

For the solution U of (3.20), there exists a positive constant M_8 such that

$$\begin{aligned} \sup_{x\in[0,\infty)} |U(t,x)| &\le \frac{1}{(4\pi t)^{\frac{1}{2}}} \int_0^{2\pi} \int_0^{\infty} |\psi_N(x)| \,\mathrm{d}x \,\mathrm{d}\theta \\ &\le \frac{M_8}{\sqrt{t}} \to 0, \quad (t \to \infty). \end{aligned}$$

Taking the assumption (3.19) into account, there exists a positive constant M_9 such that

$$\sup_{x>0,t>0} \left| U^{(i)}(t+t_i, x+\overline{R_i}) - U^{(j)}(t+t_j, x+\overline{R_j}) \right| \le M_9 \varepsilon_1, \tag{3.22}$$

for any $i, j \in \mathbb{N}$. Here $U^{(i)}$ is the corresponding solution to (3.20) with $N = i$ for any $i \in \mathbb{N}$.

The solution of (3.21) satisfies that

$$\lim_{t\to\infty} |V(t,r)| = 0, \tag{3.23}$$

because $\lim_{t\to\infty} \varphi_N(t) = 0$ by Remark 3.2. Therefore f is only related to the $(N+1)$-st precipitation. We first consider the solution f of (3.7). We have already made a rescaling of (3.7) to get (3.14).

Let us remark that the right-hand side of (3.14) is independent from τ, and there exists a positive constant M_{10} independent of N such that, for any $N \in \mathbb{N}$, it holds that

$$\tau''_{N+1} - \overline{\tau_N} = M_{10}.$$

In the original scale of space and time it means that

$$\begin{aligned} \log t''_{N+1} - \log \overline{t_N} &= M_{10}, \\ \frac{t''_{N+1}}{\overline{t_N}} &= \mathrm{e}^{M_{10}}. \end{aligned}$$

Furthermore, because $R''_{N+1} = S(t''_{N+1})$, we get

$$\begin{aligned} \frac{R''_{N+1}}{\overline{R_N}} &= \sqrt{\frac{t''_{N+1}}{\overline{t_N}}}, \\ &= \mathrm{e}^{\frac{M_{10}}{2}}. \end{aligned}$$

We next think of the solution w of (3.16). By use of both (3.22) and (3.23), we see that the difference between the solutions of (3.14) and (3.16) is at most $O(\varepsilon_1)$ (ε_1 is small enough). Thus there exists $\delta_0 \ge 0$ such that

$$\frac{R'_{N+1}}{\overline{R_N}} = \mathrm{e}^{\frac{M_{10}}{2}} + o(\varepsilon_1^{\delta_0}),$$

because of THEOREM 3.5 □

REMARK 3.7. The assumption (3.19) means that the difference between the shape of the solution in $x > \overline{R_i}$ at the moment when $t = t_i$ and the shape of the solution in $x > \overline{R_j}$ at the moment when $t = t_j$ is small for any $i, j \in \mathbb{N}$. It apparently seems to be difficult that we prove this in mathematically rigorous manner, because of the hystericis happening. According to numerical simulations that we have already done, it seems that this is satisfied very well. We therefore think that we have made the essential mechanism by which Liesegang phenomena occurs clear.

Moreover, we can consider the interval $(\underline{R_N}, \overline{R_N})$ very small. Therefore, as $R'_N \in (\underline{R_N}, \overline{R_N})$, we can regard the difference between R'_N and $\overline{R_N}$ as much smaller than the difference between $\overline{R_N}$ and $\overline{R_{N+1}}$. Hence we can regard THEOREM 3.6 as *spacing law*. But it is difficult that we estimate how small the interval is because of the discontinuity of $P(c, d)$.

REFERENCES

[1] R. E. Liesegang, *Chemische Fernwirkung,* Photo. Archiv. **800** (1896), 305–309.
[2] S. Kai, *Macroscopic pattern formation in precipitation process (in Japanese),* Applied Physics, **54**, (1985), 19–27.
[3] J.B. Keller and S.I. Rubinow, *Recurrent precipitation and Liesegang rings,* J. Chem. Phys. **74** (1981), 5000–5007.
[4] D. Hilhorst, R. van der Hout, M. Mimura and I. Ohnishi, *Fast reaction limits and Liesegang bans*, To Appear in Proceedings of FBP (2005).
[5] D.Hilhorst, R.van der Hout, M. Mimura and I. Ohnishi, In preparation.
[6] I. Ohnishi, T. Hamamoka, and M. Mimura, *A Mathematical Aspect for Liesegang Phenomena (In JAPANESE),* SUURI KAISEKI KEN KOUKYUUROKU **1356** (2004), 1–26.
[7] M. Protter, and H. Weinberger, *"Maximum Principles in Differential Equations",* Springer-Verlag 1984.