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A Mathematical Aspect for Liesegang Phenomena in two space dimensions
(空間2次元のリーゼガング現象とその数理)

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1 Introduction

図 1: Liesegang band [1]

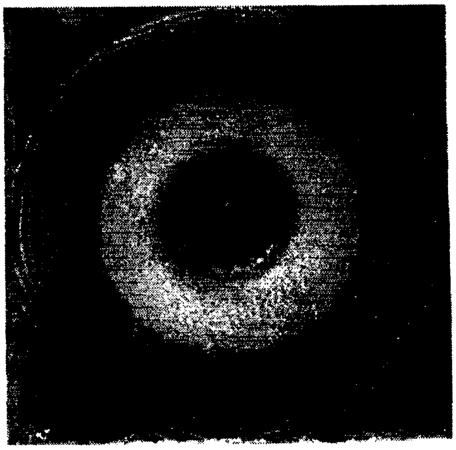


図 2: Liesegang ring [2]

We can see very beautiful pattern formation as snow in a single crystal. In case of making precipitation after crystallization, there are some cases where very strikingly regular macroscopic patterns can be seen. Especially, it is well-known that spacio-temporally periodic patterns emerge in reaction-diffusion process with precipitation in gel, if there is adequate difference of initial densities between two chemical reaction substances. In Germany, Linge first discovered this phenomena in 1855, and in 1896 Professor R.E.Liesegang studied it first as a science. In vitro, we can find band pattern and ring pattern in one space dimension and two space dimensions, respectively (Fig. 1 and Fig. 2). These are called Liesegang band and Liesegang ring, respectively, after Professor Liesegang. The interesting point is that such a spacio-temporal discontinuous pattern is formed in spite of chemical reaction occurs continuously, and this patter satisfies very strikingly regular laws (time law, spacing law, and width law).

[1]This note is based on the joint work with Professor M. Mimura in Meiji University and Dr. D. Ueyama in Hiroshima University, although, if there are mistypes or mistakes under misunderstanding, then all of them are due to the author. If you have a question, would you please mail him to the address: isamu_o@math.sci.hiroshima-u.ac.jp

In this note, we report our recent studies about such very interesting problem of Liesegang phenomena.

2 History

There have been made of tons of researches about Liesegang phenomena since the previous century. For example, there are

A)Theory of pre-nucleation:

1. super-saturation theory ([6], [7])
2. diffusion theory ([8])
3. diffusion wave theory ([9])
4. adsorption theory ([10])
5. membrane theory ([11])

B)Theory of post-nucleation:

1. theory of colloid growth and dissoluton ([3], [12])
2. theory of colloid coherence ([13]).

In the former group of theories, they consider that position of pattern is determined just when the chemical reaction occures before nucleation. This is very old way of thinking about this phenomena. On the other hand, in the latter group of theories, they consider of the position of pattern is decided after nucleation. There are some facts which cannot be explained from the former theories; for example, spiral structure or double periodic structure. Briefly speaking, we cannot understand that the following properties:

1) Colloid particles can be seen in wider area before precipitation,

2) Band or ring pattern can be formed if colloid solution with a mean radius of particles touches another with another mean radius,

3) Gavity affects the position of pattern,

4) Subring pattern can be often seen,

5) The Second structure can be made in a ring or band pattern,

6) Spacial bifurcation often occurs,

7) Spacing laws can be stochastic if the density difference is less.

Keller-Rubinow model is famous in the super-saturation theory. In the next section we briefly state some numerical simulations and insufficient points in this model.

3 Super-saturation theory

3.1 Summary

In the super-saturation theory, Keller and Rubinow assumed the following two points ([7]):

1) Precipitation occurs if the density reach the super-saturation density bigger than the saturation density,

2) Reaction speed is much faster than diffusion speed,

and tried to explain Liesegang phenomena. Especially, accourding to the model, the discontinuous presipitation emerges. In the next section, we introduce Keller-Rubinow model in detail to make numerical simulations.

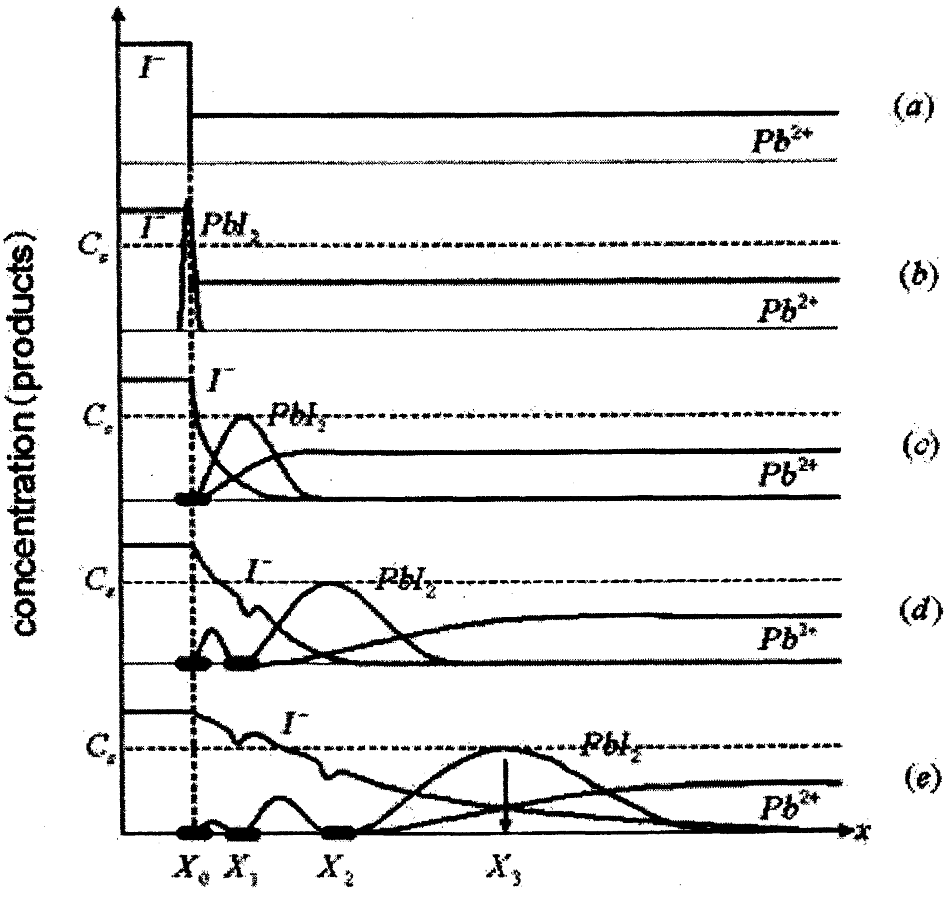


図 3: Super-saturation theory [3]

3.2 Keller-Rubinow model

In 1981, Professors J.B.Keller and S.I.Rubinow made the model called Keller-Rubinow model nowaday, with effect of adsorption of colloid combined with the super-saturation theory. This is the following:

$$v_A A^+ + v_B B^- \overset{k}{\rightleftarrows} v_C C, \tag{1}$$

$$C \overset{qP}{\rightarrow} D, \tag{2}$$

with k_+, k_- chemical reaction constants, v_A, v_B, v_B, stoichiometric coefficients, qP precipitation rate, q precipitation coefficient. Here, we make $v_A = v_B = v_C = 1$, $k_- = 0$. We can make this be the following system of partial differential equations:

$$\begin{cases} a_t = D_A \Delta a - kab, \\ b_t = D_B \Delta b - kab, \\ c_t = D_C \Delta c + kab - qP(c,d), \\ d_t = qP(c,d), \end{cases} \tag{3}$$

where, a, b, c, d are density of each ingredient, D_A, D_B, D_C are diffusion coefficients, $k = k_+$ chemical reaction constant. The diffusion of D can be negligible. $P(c,d)$ has the following form:

$$P(c,d) = \begin{cases} (c - C_a)_+, & \text{if } c > C_s \text{ or } d > 0 \\ 0, & \text{otherwise} \end{cases} \tag{4}$$

where C_a, C_s are saturation density and super-saturation density of C, respectively ($C_s > C_a > 0$). (Fig. 4)

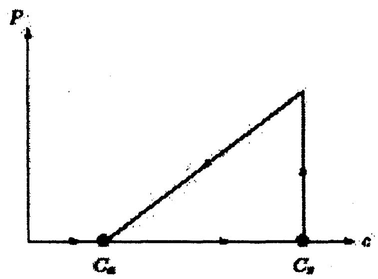


図 4: Precipitation $P(c,d)$

3.3 Numerical simulation

3.3.1 One space dimension

The initial conditon is

$$a(0,x) = c(0,x) = d(0,x) = 0,\ b(0,x) = B_0, \tag{5}$$

and the boundary condition is

$$\begin{aligned} &a(t,0) = A_0, b_x(t,0) = c_x(t,0) = 0,\ 0 < t < T \\ &a_x(t,L) = b_x(t,L) = c_x(t,L) = 0,\ 0 < t < T \end{aligned} \tag{6}$$

with $A_0 >> B_0 > 0$. (parameters are the followings: $A_0 = 10.0$, $B_0 = 1.0$, $D_A = D_B = D_C = 0.001$, $C_a = 0.2$, $C_s = 0.8$, $k = 50.0$, $q = 50.0$,$L = 1.5$)

The result is Fig. 7. Spacing law and time law are satisfied enough very well, but width law cannot be satisfied. This means that Keller-Rubinow model is good for the point that the precipitation occurs discretely, although it is not enough in point of view of width of precipitation. But Keller-Rubinow model is simple and good for understanding the mechanism by which precipitation occurs discretely and satisfies time law and spacing law. In fact, we have already given a mathematically rigorous proof which ensure Keller-Rubinow model has a mathematically rigorous solution satisfying time law and spacing law under natural assumptions. See in detail [15], [16], [17], and [18].

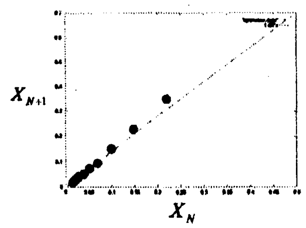


図 5: spacing law

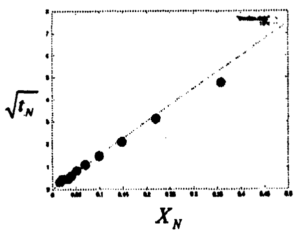


図 6: time law

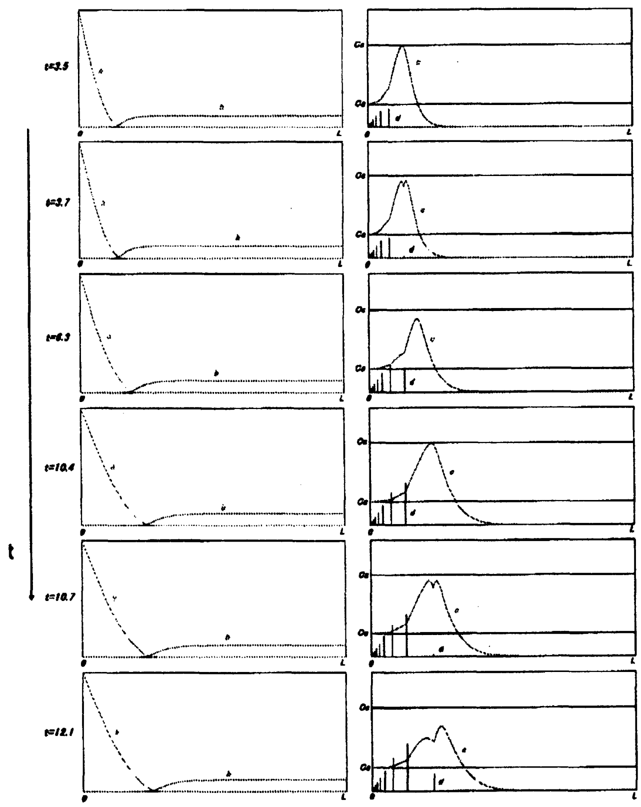


図 7: One space dimension

4 Theory of colloid growth and dissolution

4.1 Kai's theory

Professor S. Kai (Kyushu University) made a theory which explained mechanism of Liesegang phenomena in view of colloid growth and dissolution in [4]. We use it to try to make a new mathematical model of Liesegang phenomena.

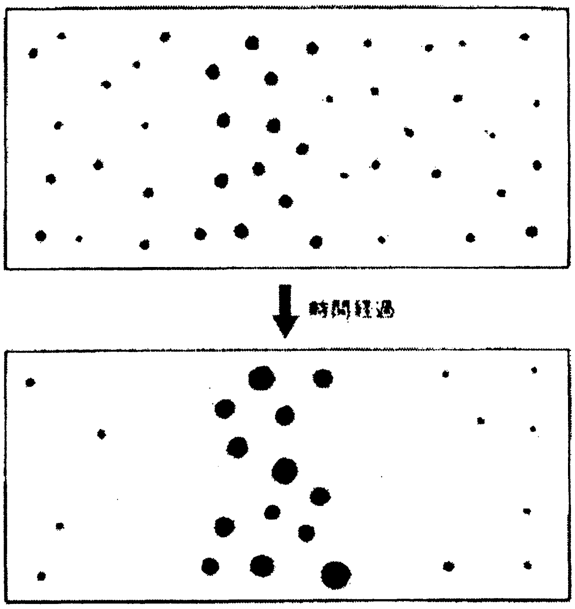


図 8: colloid growth and dissolution

4.2 Simple application of Kai's theory

We consider about the following system of equations:

$$v_A A^+ + v_B B^- \overset{k}{\rightleftarrows} v_C C \tag{7}$$

$$C \overset{P}{\rightarrow} D \tag{8}$$

$$\begin{cases} a_t = D_A \Delta a - kab, \\ b_t = D_B \Delta b - kab, \\ c_t = D_C \Delta c + kab - P, \\ d_t = P, \end{cases} \tag{9}$$

where we rewrite the term P as follows:

$$\begin{aligned} P &= q\frac{\partial}{\partial t}\left(\frac{4}{3}\pi R^3\right) \\ \frac{\partial R}{\partial t} &= \frac{M}{R}(c - C_a(R)) \end{aligned} \tag{10}$$

R : radius of colloid particle, $\quad q, M$: constants,

$C_a(R)$ is the Gibbs-Thomson formula, which is exacly the following;

$$C_a(R) = C_e(1 + \frac{\alpha}{R})$$
$$\alpha = \frac{2\sigma V}{k_B T}$$

Here

C_e : saturation density of the ideal particle with radius ∞, $\quad \sigma$: surface energy,
V : volume, k_B : Boltzmann constant, T : templature.

4.3 Numerical simulation

4.3.1 One space dimension

We make comuter simulation with parameters: $A_0 = 10.0$, $B_0 = 1.0$, $D_A = D_B = D_C = 0.001$, $k = 20$, $q = 0.5$, $M = 1.0$, $\alpha = 0.05$, $L = 10.0$.

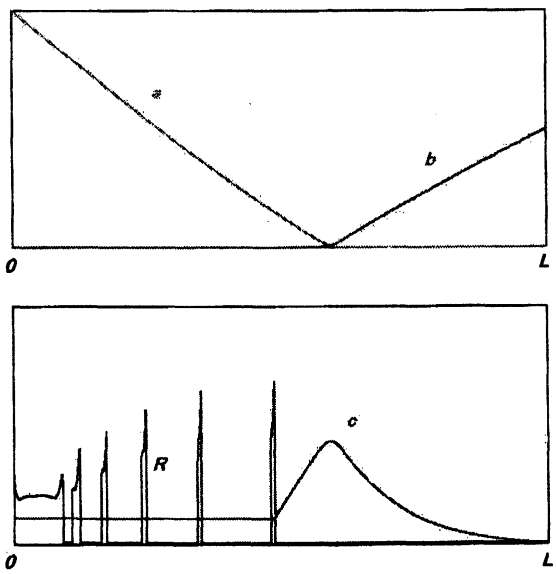


図 9: One space dimension

We try to verify the three charasteristic laws of Liesegang phenomena. Time law and spacing law are satisfied very well like the case of Keller-Rubinow model. But width law is not satisfied, although this model realizes width of the band unlike the case of Keller-Rubinow model.

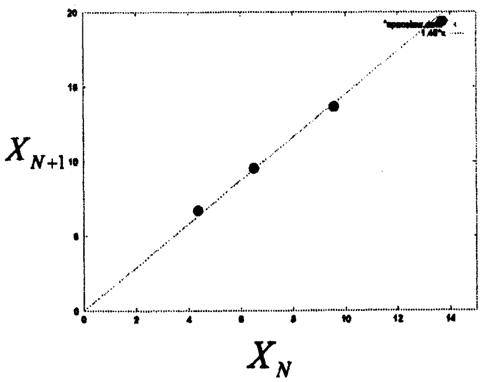


図 10: spacing law

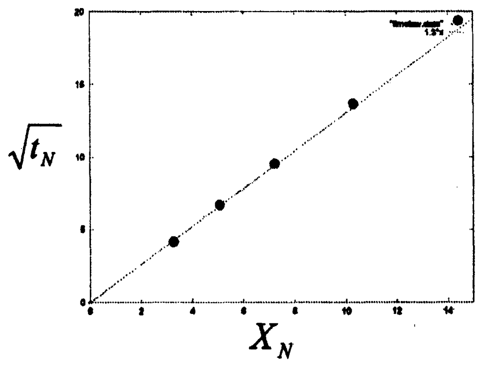
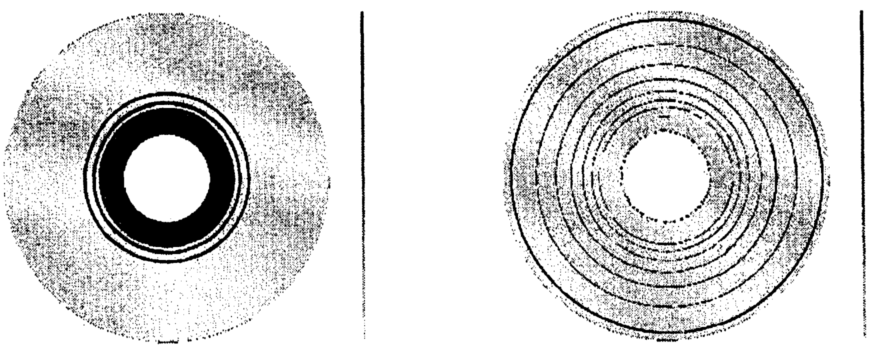


図 11: time law

4.3.2 Two space dimensions

We make two sapce dimensional simulation to get Fig. 12.



$t = 50.0$ $\qquad$ $t = 1240.0$

図 12: Two space dimensions

In this model, we can make simulations of the two dimensinal ring pattern, although the patterns dissapear after much time goes by. The result is better than in the case of Keller-Rubinow model, but we cannot be satisfied with it. In the next section we improve this model to get the result much better to discuss about the interesting view points of Liesegang phenomena.

5 Improvement of the model

We improve the model to set the ring pattern fixed adequately. Let us consider the following model:

6 Improved model

$$\begin{cases} a_t = D_A \Delta a - kab \\ b_t = D_B \Delta b - kab \\ c_t = D_C \Delta c + kab - q\dfrac{d}{dt}(\dfrac{4}{3}\pi R^3) \\ R_t = F(c, R) \end{cases} \tag{11}$$

$$F(c,R) = \begin{cases} \dfrac{M}{R}(c - \dfrac{\alpha}{R})_+ & \text{if } R_1 < R \\ \dfrac{M}{R}(c - \dfrac{\alpha}{R}) & \text{if } R_0 < R \leq R_1 \\ \dfrac{M}{R_0}(c - \dfrac{\alpha}{R_0}) & \text{if } 0 \leq R \leq R_0 \\ -hR & \text{if } R < 0 \end{cases} \tag{12}$$

Here

R_0 : minimum radius of colloid particle, R_1 : minimum radius of precipitated colloid particle
q, h : positive constants, $h \gg 1$

and $f(x)_+$ satisfies

$$f(x)_+ = \begin{cases} f(x) & \text{if } f(x) \geq 0 \\ 0 & \text{if } f(x) < 0 \end{cases}$$

7 Numerical simulation

7.1 One space dimension

Simulation result is following (Fig. 13):

(Parameters are the followings: $A_0 = 10.0, B_0 = 1.0, D_A = D_B = D_C = 0.001, k = 20.0, q = 0.05, M = 0.5, \alpha = 0.04, R_0 = 0.25, R_1 = 1.0, L = 10.0$.)

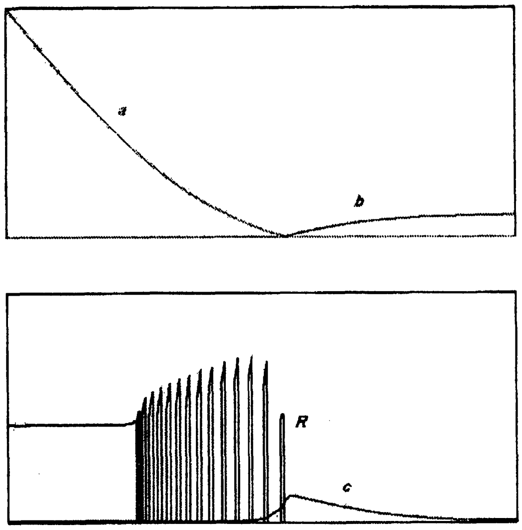


図 13: simulation of the model (11), (12)

The three laws are the followings (Fig. 14, Fig. 15, and Fig. 16):

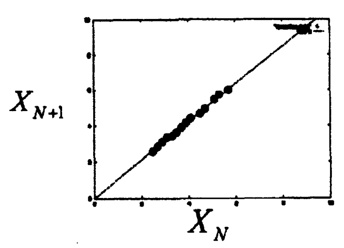


図 14: spacing law

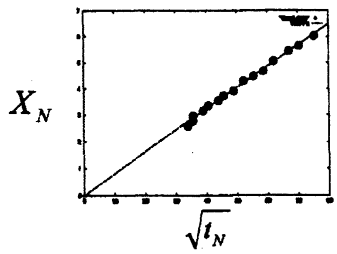


図 15: time law

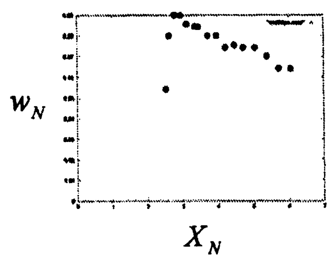
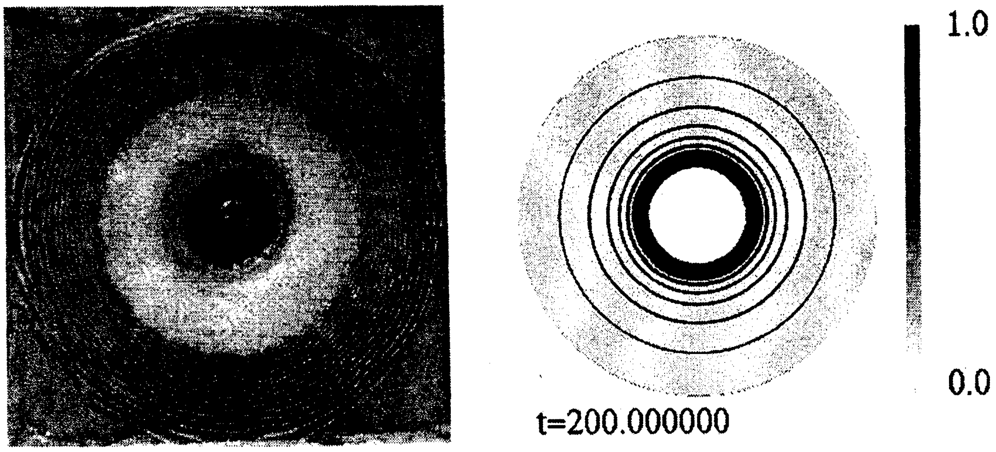


図 16: Width does not satisfiy the law.

7.2 Two space dimensions

The result is Fig. 17. ($A_0 = 10.0$, $B_0 = 1.0$, $D_A = D_B = D_C = 0.001$, $k = 20$, $q = 0.5$, $M = 1.0$, $\alpha = 0.04, R_0 = 0.1, R_1 = 1.0, R = 2.0$)



(a) (b)

図 17: (a) Chemical experiment, (b) Numerical simulation

By use of the improved model, we realize the similar pattern to the real chemical experiment unlike in the case of Keller-Rubinow model. We make an observation of the pattern in details (Fig. 18).

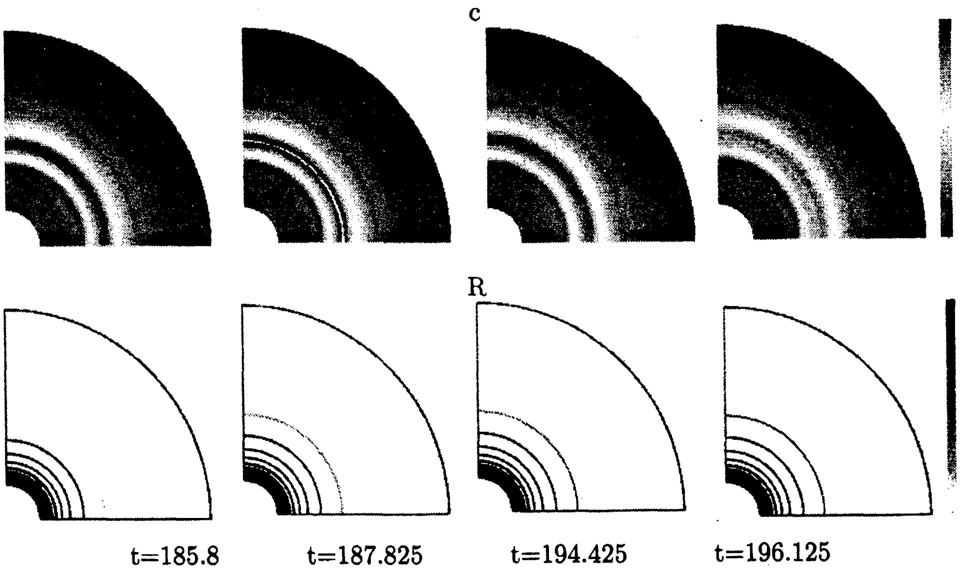
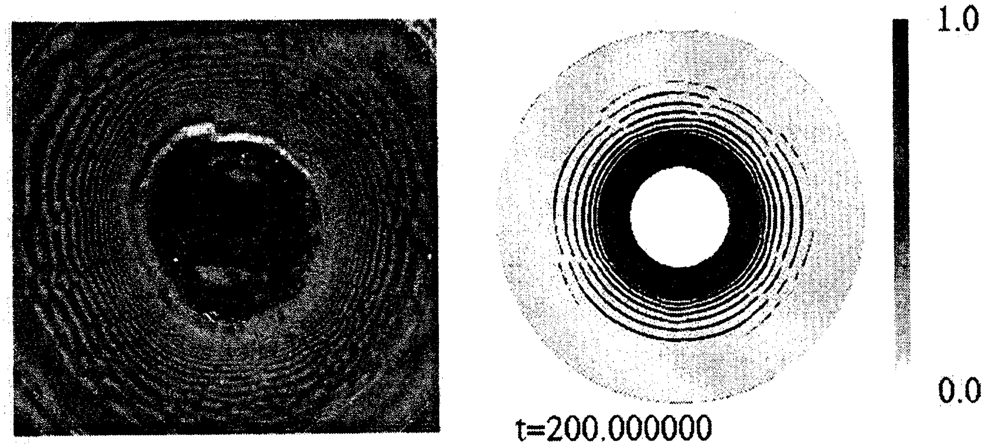


図 18: Process of making ring 17(b)

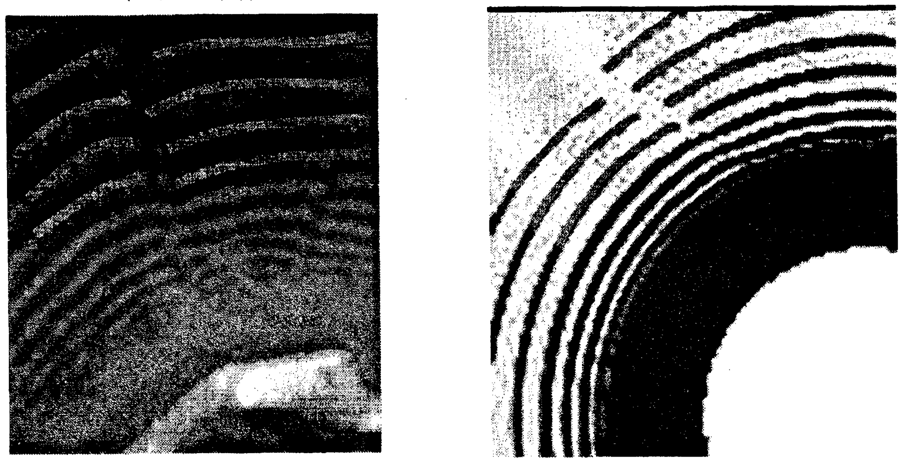
We can consider of this model as much better than the previous ones. Therefore, we try to make more simulation to realize other patterns in two space dimensions introduced in Section 2. Fig. 19(b) shows the ring pattern with intial density $B_0 = 2.0$.



(a) (b)

図 19: (a) Real experiment, (b) Numerical simulation

The ring pattern is made cut accourding to going away from the center, which is similar to the real chemical expariment. Moreover, the characteristic property of cutting ring is very similar to the real one (Fig. 20(b)).



(a) (b)

図 20: (a) Expanded figure of 19(a), (b) Expanded figure of Fig. 19(b)

Furthermore, this model realize the spiral pattern as shown in Fig. 21(b).
In real chemical experiments, ring pattern can split with initial density of B more and more. we realize this property by use of this model as following (Fig. 23):

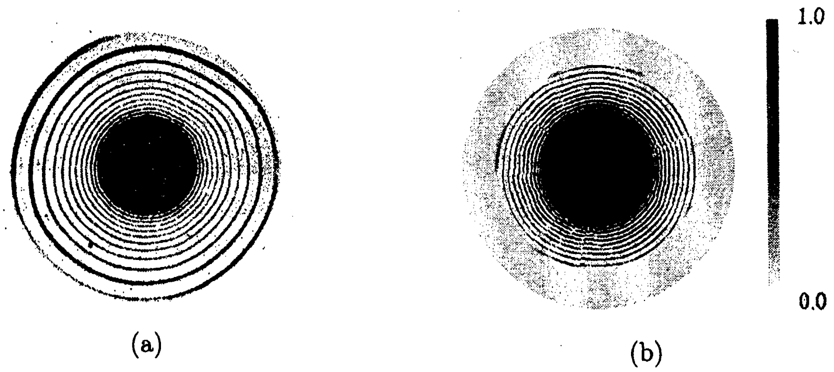


図 21: (a) Real chemical experiment, (b) Numerical spiral pattern

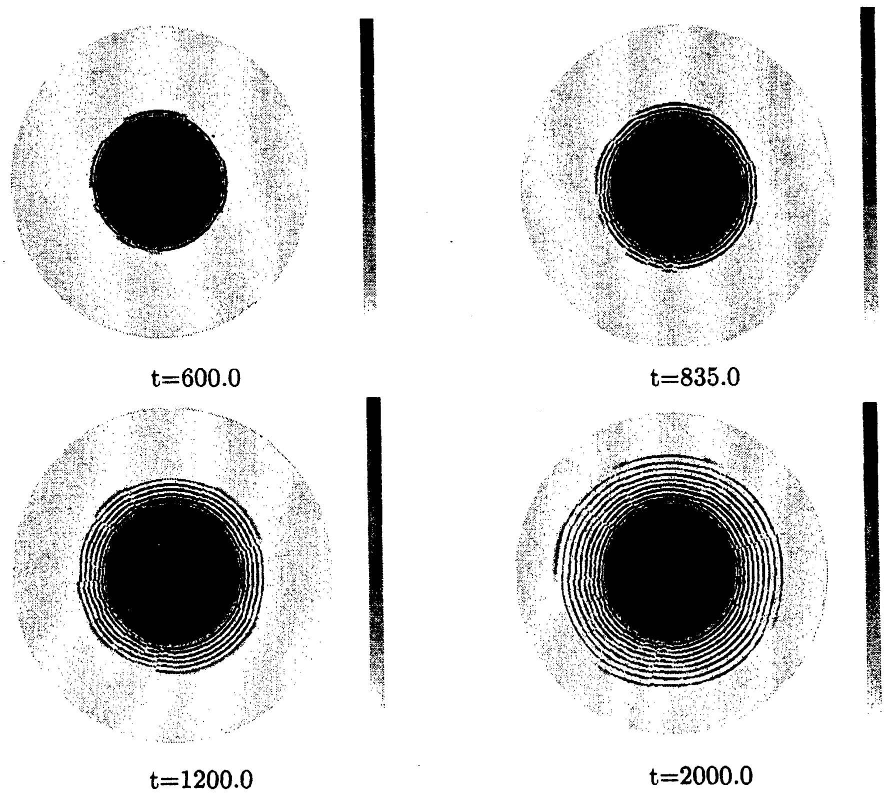
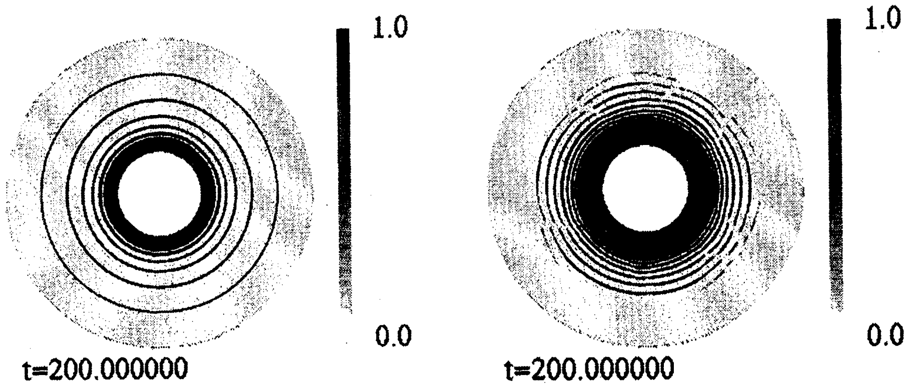


図 22: Process of makig spiral pattern



$b_0 = 1.0$ $b_0 = 2.0$

図 23: Ring splitting

Because of the above simulation results, the model 11, 12 is much better than Keller-rubinow model especially in two space dimensions. Therefore, we understand that process of colloid growth and dissolution is very important for Liesegang phenomena. But so far, it is not clear how the growth and dissolution mechanism can stop at adequate time.

8 Important suggestion

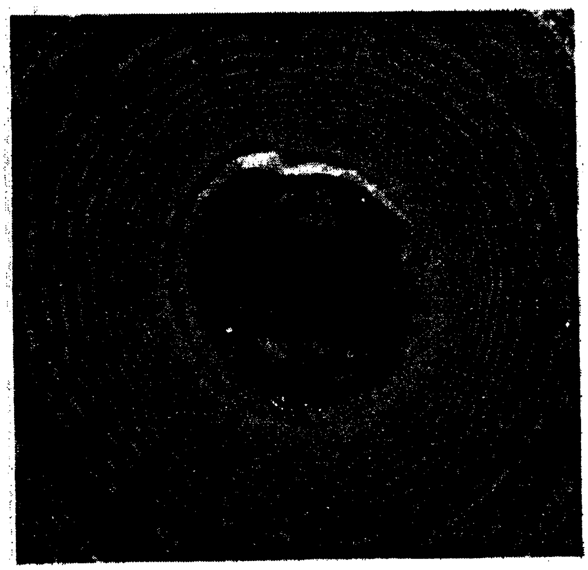
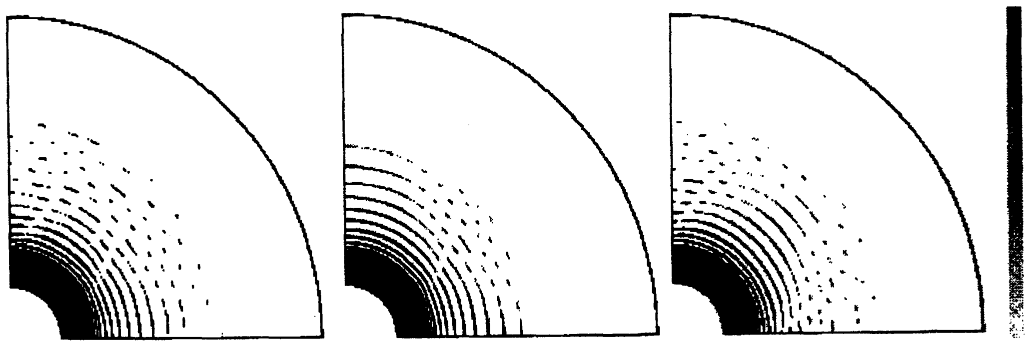


図 24: Splitting pattern

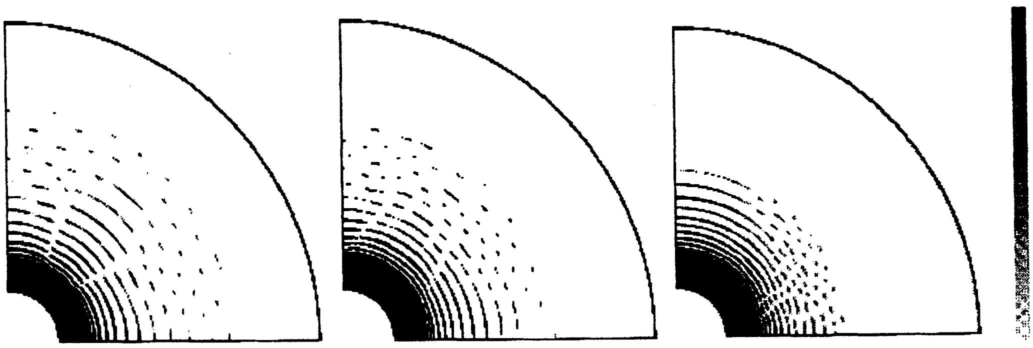
In this section we discuss about splitting phenomena of ring pattern. As long as we know, the splitting is due to the ununiformness of the real world like impurity or bruise of petri dish. But our simulation suggests that this system has an essential instablity to make the ring pattern splitting because of it. See Fig. 25.



(a) (b) (c)

図 25: (a), (b), (c) has different 5 % perturbation with different ways.(Parameters are the following: $A_0 = 10.0$, $B_0 = 2.0$, $D_A = D_B = D_C = 0.001$, $k = 20$, $q = 0.5$, $M = 1.0$, $\alpha = 0.04, R_0 = 0.1, R_1 = 1.0$)

Very tiny nonuniformness trigger it to be splitting and to be destroyed as time goes by.



(a) (b) (c)

図 26: (a)$B_0 = 1.6$, (b)$B_0 = 2.0$, (c)$B_0 = 3.0$

Fig. 26 shows that time at which the ring splits is dependent of the initial density of B. But splitting triggers destroy of the ring pattern. Because of ths fact, we consider that there is some kind of mechanism by which the ring pattern spontaneously split and is destroyed.

Furthermore, we consider about the problem of what kind of pattern is natural ? In other words, what is the final pattern if the ring pattern is unstable. See Fig. 27.

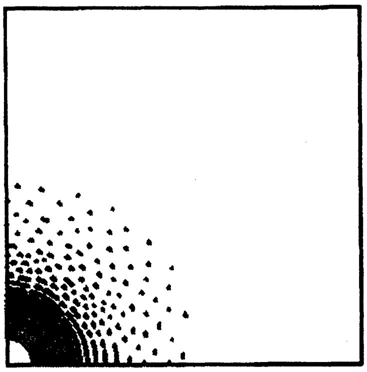
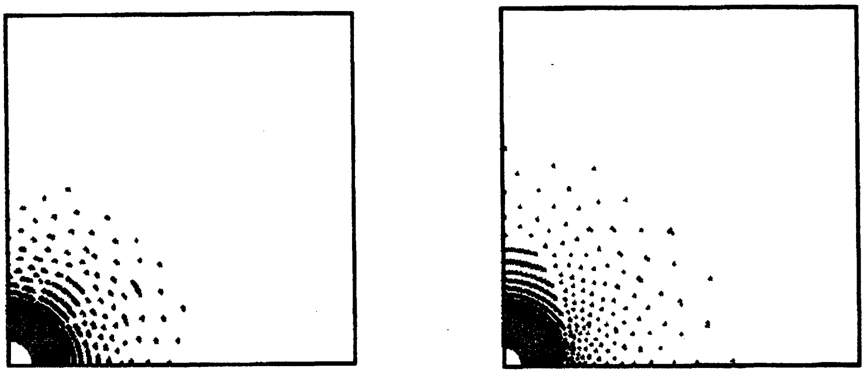


図 27: $B_0 = 2.0$

As much time goes by, the ring pattern split and is destroyed to get the final pattern with adequate size cluster. We make a conjecture that the final pattern is checker board pattern. See Fig. 28.



(a) (b)

図 28: (a)$B_0 = 1.6$, $B_0 = 3.0$

Finaly we would like to state the point of our study briefly. Accourding to our study, we can consider of this phenomena as result of contradiction and compromization between smoothing effect of diffusion and positive feedback effect of Ostwald ripning of colloid. As an important result, the final checker board pattern is regarded as very natural. This should be an important conjecture for the pattern formation in Liesegang phenomena.

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