学術論文

マイクロ波照射下での反応速度定数に対するエネルギー変動の影響
Effect of Energy Fluctuation on Reaction Speed Constant under Microwave Irradiation

平井隆司 [1*], 中谷 伸 [2], 佐藤元泰 [2], 永田和宏 [3]
Takashi Hirai[1*], Shin Nakatani[2], Motoyasu Sato[2], Kazuhiro Nagata[3]

1．中部大学ミュオン理工学センター　〒487-8501, 愛知県春日井市松本町 1200,
2．中部大学大学院工学研究科　〒487-8501, 愛知県春日井市松本町 1200,
3．東京工業大学名誉教授　〒224-0006, 神奈川県横浜市都筑区荏田東 3-1-13-401,

1. Center for Science and Technology, Chubu University, 1200, Matsumoto-cho, Kasugai City, Aichi, 487-8501, Japan
2. Graduate School of Engineering Studies, Chubu University, 1200, Matsumoto-cho, Kasugai City, Aichi, 487-8501, Japan
3. Prof. Emeritus, Tokyo Institute of Technology, 3-1-13-401, Eda-higashi, Tsuzuki-ku Yokohama-shi, Kanagawa, 224-0006, Japan

corresponding author*, e-mail address: heisuke2009@gmail.com
Keywords: Langevin equation, Epi-thermal distribution, Correlated noise,

Abstract

There is a research field called a fluctuating system. In systems such as Brownian motion, the particles of interest exchange kinetic energy from white noise and perform a random walk. The Langevin equation handles these events and takes up fine particle friction and microwave irradiation to confirm the operation of the system. In this paper, we incorporate microwave irradiation into the Maxwell-Boltzmann distribution and confirm that its non-thermal energy exhibits the so-called "microwave effect". As a sample case using correlated noise, two-dimensional Ising model is proposed as a specific example of Monte Carlo simulation. Results will vary depending on the strength of the noise correlation. In this way, the noise-to-noise correlation has a strong effect on physical quantities.

1. Introduction

Methodologies have been paid attention for tracking non-equilibrium thermodynamic fluctuations in the materials. Specific examples include substances such as clusters and colloids, and molecular motors.[1] It has been experimentally confirmed that fine particles such as pollen show Brownian motion, and it is theoretically known that white noise shows a random walk accompanied by the Langevin equation. The situation is further complicated by the input of energy into the system by microwaves. Friction occurs when clusters and colloids move, white noise transmission due to collisions with other particles, and microwave irradiation. They conflict with each other to determine the behavior of the system.

In this paper, we will consider how kinetic energy can be introduced into the reaction speed. We will discuss the reaction speed of the system, taking into account the three quantities of microwave, white noise, and friction.

In general, the energy loss due to friction and the white noise received from other particles compete with each other to determine the movement of the particles. For example, it is reported that the reaction time of microwaves is 4 hours and the time required for a specific reaction by heat transfer is 40 hours,[2] which is exactly the effect of microwaves. Here, noise with a time-correlation is proposed as a random number. This is used to examine the noise dependence of the reaction speed.

And then, time-correlated noise is taken as an example of statistical mechanics. It is to be important the last result of this paper.

As a system, we will consider liquid H_2O as an example of microwave active material, and the Ising model can be considered as an application using correlated noise.

2. Formulation

Since we are considering liquid H_2O as a system, it is heated by microwaves and a phase transition from liquid to gas occurs. To give a broader example, chemical reactions can be discussed in the same way. As a model, the system surrounded by a heat bath with a constant temperature and volume is treated.

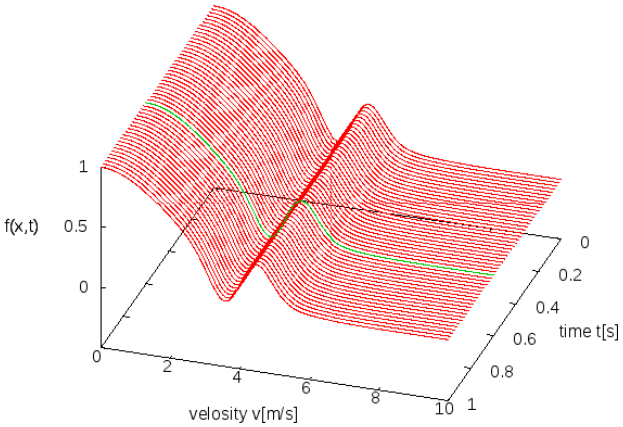

Fig. 1 Schematic diagram of the epi-thermal distribution of continuously irradiated microwave. The middle line is a cross section of the microwave at a point in time t. The distribution function does not depend on time because the system is surrounded by a heat bath.

In this system, microwave is continuously applied. At this point t, the epi-thermal distribution function is considered clipped, as shown in Fig. 1. This epi-thermal distribution function loses its peak with the passage of time due to friction between particles, and eventually becomes heated and changes to a normal distribution function. However, since the system is in contact with the heat bath, the shape of the distribution function does not change at continuous time. The time scale taken up in Fig. 1 is seconds, but the time scale until the microwave falls into heat is μs. Therefore, local temporal heating by microwaves is not observed on the scale of seconds, and it looks the same as normal heating such as electric heating.

The Langevin equation is introduced as equation of motion containing a fine particle with existing of random work. In the case of one particle surrounded by many particles, it can be written as follows.

$$m\frac{d\vec{v}}{dt} = -\gamma\vec{r} + \vec{\lambda} + \vec{P} \times \vec{E} \tag{1}$$

Here, γ is the coefficient of friction, $\vec{\lambda}$ is white noise, $\vec{P}$ is the polarization coefficient, respectively. The quantity $\vec{E}$ is electric field of single mode microwave, and the concrete formula is $\vec{E}(x,t) = \vec{E}_0 exp(ikx - i\omega t)$. The sample size (few cm^3) of this study is much smaller than $1/k$ ($k{\sim}10^{-6}$ order), so there is no need to think about spatial changes. Further mentioning the time change, since the frequency is GHz, it is an oscillation on a scale on the order of 10^{-9} [s]. The order is different by 10^3 because the time scale considered is 10^{-6} [s]. Therefore, the vibration of the electric field takes an approximation that considers only the large modulation.

If $\vec{\lambda}$ is removed from Eq. (1), it becomes the equation of motion of the polarization element in $\vec{E}$. When the average velocity is calculated from the Maxwell-Boltzmann distribution, the kinetic energy is consumed by friction, so that the average velocity does not depend on time, and there is no time evolution of the system. Since $\vec{\lambda}$ fluctuates as a function of time, Eq. (1) becomes a function of time. This is the reason why Eq. (1) includes noise and microwave.

Considering the kinetic energy, energy conservation formula is as follows,

$$W_\mu = \int_{r_i}^{r_f} dr \cdot \left(-\gamma\vec{r} + \vec{\lambda} + \vec{P} \times \vec{E}\right) \tag{2}$$

Here, r_i, r_f mean initial and final positions, respectively. White noise $\vec{\lambda}$ =$(\lambda_1, \lambda_2, \lambda_3,)$ in general,

$$\langle\lambda_i(t)\lambda_j(t')\rangle = \delta_{ij}\Delta_{t,t'} \tag{3}$$

is defined like this. The white noise defined here has a characteristic time determined by the frequency factor. That is, white noise has a value of $\Delta_{t,t'} = 1$ at $t - t' = 0.1\ [ms]$, and otherwise $\Delta_{t,t'} = 0$. On the other hand, $\delta_{ij} = 1$ for $i = j$, and $\delta_{ij} = 0$ for $i \neq$j. So, time factor $\Delta_{t,t'}$ is unusual definition of noise. But this definition is important in this study.

As the certain fine particles, molecules and polarizations generally follow the Maxwell-Boltzmann distribution function, but for the introduction of microwave monochromatic energy, one must consider that there will always be a peak in the Maxwell-Boltzmann distribution function. This is called the epi-thermal distribution.

As an example, let's define and explain a distribution function that takes two positions.

We introduce the multiplication type distribution function.[3]

$$f_M(v) = f_0(v)g_M(v) \tag{4}$$

$$f_0(v) = \sqrt{\frac{m}{2\pi k_B T}}\, exp\left(-\frac{mv^2}{2\pi k_B T}\right) \tag{5}$$

$$g_M(v) = exp\left(\delta_{v,v_\mu}\frac{W_\mu}{k_B T}\right) \tag{6}$$

$$\bar{v} = \frac{\int_0^\infty v f_M(v)dv}{\int_0^\infty f_0(v)dv} = \sqrt{\frac{2k_B T}{\pi m}}\, exp\left(\frac{W_\mu}{k_B T}\right) \tag{7}$$

Here, Eq. (4) is the epi-thermal distribution function, Eq. (5) is the usual Maxwell-Boltzmann distribution function, Eq. (6) is the epi-thermal component of distribution function, Eq. (7) is the average velocity obtained from Eqs. (4)-(6), respectively. And δ_{v,v_μ}, W_μ are Kronecker delta and kinetic energy caused by noise. It should be noted that the exp term in Eq. (7) is multiplied by the usual velocity distribution. The initial M means multiplication and indicates the monochromatic appearance of the microwave immediately after it is turned on.

Using the expression epi-thermal distribution, thermal energy and non-thermal energy are mixed on the same graph. The peak structure is non-thermal energy, and it takes μs to change to thermal energy.

We introduce an added type distribution function.[4]

$$f_A(v) = f_0(v) + f_0(v)\big(v - v_\mu\big)g_A(v) \quad (8)$$

$$g_A(v) = \sqrt{\frac{m(v-v_\mu)^2}{2\pi W_\mu}}\, exp\left(-\frac{m(v-v_\mu)^2}{2W_\mu}\right) \quad (9)$$

$$\bar{v} = \frac{\int_0^{v_c} v f_A(v)dv}{\int_0^{v_c} f_0(v)dv} \cong \sqrt{\frac{2k_BT}{\pi m}}\left[1 + W_\mu\right] \quad (10)$$

$$W_\mu = \frac{m}{2k_BT\sqrt{\pi}}\left(\frac{v_c^2}{2} + \frac{v_\mu^2}{4}\right) exp\left(\frac{2v_c}{v_\mu} - 1\right) \quad (11)$$

Here, v_μ is defined by dumping point velocity. The cutoff v_c is introduced to prevent the divergence of the integral. The initial A means to add. Eq. (8) shows the following. It means moving particles in a distribution with low kinetic energy based on the velocity of v_μ to a region with high kinetic energy by microwave energy. In order to make the cutoff easy to understand, letting, $v_c = 2v_\mu$, Eqs. (10), (11) become simple as follows.

$$\bar{v} = \sqrt{\frac{2k_BT}{\pi m}}\left(1 + \frac{\dot{W}}{k_BT}\right) \quad (12)$$

with $\dot{W} = 9me^3v_\mu^2/8\sqrt{\pi}$. It can be seen that $\dot{W}$ is introduced in the form of addition to the usual distribution function. Whether this multiplication type distribution in Eqs. (4)-(7) or addition type distribution Eqs. (8)-(12) becomes important because multiplication type shows initial state and addition type shows medium state of time scale, respectively. From multiplication to addition, the reaction speed changes shape over time.

Eqs. (4) and (8) are not normalized in the form of including microwave peaks. This is because the peak is not thermal energy. The microwave peak of the epi-thermal Maxwell-Boltzmann distribution in Eq. (4) is listed in the same figure, but is a separate physical quantity. In Eq. (8), the Maxwell-Boltzmann distribution and the microwave peak are partially mixed, and the situation is different from Eq. (8). After a few μs, the non-thermal peak turns completely thermal energy due to friction with other particles. Eq. (4) shows the state immediately after the microwave is injected, and Eq. (8) shows the state in which non-thermal energy accelerates particles slower than the peak. This means the passage of time when microwave is applied.

The reaction speeds κ_M, κ_A are obtained for the case of the definition formula Eq. (4) to be multiplied by the distribution function and the case of the definition formula Eq. (8) to be added. [4]

$$\kappa_M = \frac{q^\ddagger}{q_a q_b}\frac{k_BT}{h} exp\left(-\frac{E^* - W_\mu}{k_BT}\right) \quad (13)$$

$$\kappa_A = \frac{q^\ddagger}{q_a q_b}\frac{k_B T + \dot{W}}{h} exp\left(-\frac{E^*}{k_BT}\right) \quad (14)$$

Here, the quantities $q^\ddagger$, q_a and q_b are partition functions for phase (chemical) change, state a and state b, respectively. It is noteworthy that Eqs. (13), (14) are in perfect agreement with the results of Nagata & Kodama.[5]

The velocity v_μ and energy W_μ, $\dot{W}$ have not substantially discussed time dependence. Then, Eq. (15) is newly defined as a time-dependent kinetic energy as a value indicating the influence of these.

$$w_\mu = \sum_j P(\lambda_j) exp\left[-\frac{t - t_j}{\tau}\Theta(t_j)\right] - \sum_j \int_{r_i}^{r_f} dr_j \cdot \left(-\gamma r_j + \vec{P}_j \times \vec{E}\right) \quad (15)$$

Here, $w_\mu = W_\mu/h$ is normalized kinetic energy, $P(\vec{\lambda}_j)$ is a Gaussian distribution probability as a function of $\vec{\lambda}_j$. Also, τ is the relaxation time of the decay of kinetic energy, and $\Theta(t_j)$ is the step function. As a result, Eq. (15) defines an equation that ticks j over time at intervals of about frequency factor 10 kHz. [5] This equation takes into account friction loss, energy gain from the microwave field, and noise.

Taking the average of the random numbers of many fine particles in the first term of Eq. (15) gives the following relationship.

$$\sum_k^\infty \sum_j P\big(\lambda_{j,k}\big) exp\left[-\frac{t - t_{j,k}}{\tau}\Theta\big(t_{j,k}\big)\right] = 0 \quad (16)$$

where k is an index of fine particle number of interest. This is the numerical calculation result. The important thing is that the average of random numbers will be zero. The Eq. (16) means the kinetic energy of the system is preserved. Therefore, the problem of the many fine particles system is competition of friction and the energy given by microwave independent of one fine particle's noise.

Now let's change the topic from H_2O to magnetization. The partition function can be defined by using time-correlated noise.

$$Z = \sum_{j,k} exp\left(-\frac{W_{j,k}}{k_BT}\right) \quad (17)$$

$$W_{j,k} = W_0 P\big(\lambda_{j,k}\big) exp\left(-\frac{t - t_{j,k}}{\tau}\Theta\big(t_{j,k}\big)\right) \quad (18)$$

$$\langle X\rangle = \sum_{j,k} \frac{W_{j.k}}{Z} exp\left(-\frac{W_{j,k}}{k_BT}\right) \quad (19)$$

By using Eqs. (17)-(19) statistical mechanics quantities in time-correlated noise can be calculated. If we propose some kind of fluctuating physical quantity, a distribution function by time-correlated noise is defined and the thermodynamic quantity $\langle X\rangle$ can be calculated. Since this statistical mechanics method usually requires the accumulation of many samples, it is useful to treat the noise distribution function defined here in that the number of samples is small.

As an application example of correlated noise, the Ising model can be considered, and it is generally known that it exhibits ferromagnetism. The formulation of Ising model is,

$$H = -J\sum_{\langle i,j\rangle} S_i S_j - h\sum_i S_i \quad (20)$$

The spin of Ising model is defined by $S_i = 1/2$ for sample number $i \in [0\colon 0.5]$ and $S_i = -1/2$ for $i \in [0.5\colon 1]$ in the prepared correlation noise [0:1] defined by first term of

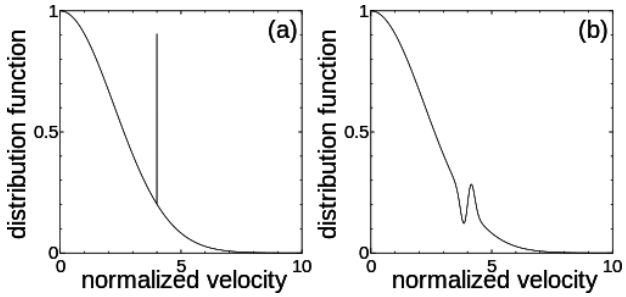

Fig.2 Extended distribution function. (a) When the distribution function is disturbed by multiplication. (b) When a disturbance is added to the distribution function by addition.

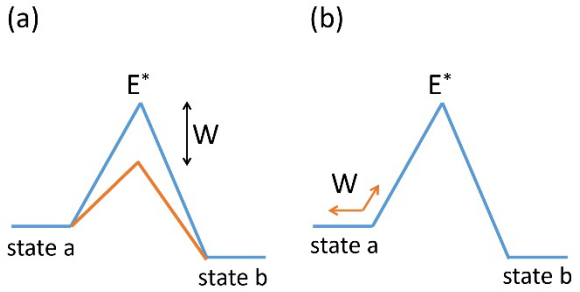

Fig.3 Schematic diagram of reaction speed by Langevin equation. (a) When the distribution function is disturbed by multiplication. (b) When a disturbance is added to the distribution function by addition. The quantities W oscillate with time.

Eq. (15). The quantities J and h is defined by interaction energy between nearest neighbor spins and exchange energy under the magnetic field, respectively.

3. Results and Discussion

The calculated results of Eqs. (4),(8) are shown in Fig. 2. In Fig. 2(a), the microwave energy has a delta functional type peak structure. On the other hand, in Fig. 2(b), the dumping structure can be seen. When a microwave is input at $t = 0$, the energy is applied to the system as a delta functional peak. Here, thermal energy (Maxwell-Boltzmann distribution) and microwave energy (peak structure) should be understood separately.

Schematic diagrams of the reaction speed are shown in Fig. 3 plotting Eqs. (13), (14). In Fig. 3(a), the energy of the activated complex E^* is reduced by the quantity W_μ. On the other hand, Fig. 3(b) shows vibration of energy $\dot{W}$ in state a. In both cases, the reaction speed is accelerated. These Figs. 2(a) and (b) correspond to Figs. 3(a) and (b), respectively. The difference in the behavior of these peaks is the passage of time. These corresponds to raising the level of basic energy, and means that phase transitions and chemical changes can occur more easily below the transition temperature.

Here, by introducing white noise with a frequency factor of 10kHz to the reaction speed again, the effect of noise can be introduced to the reaction speed. Since the

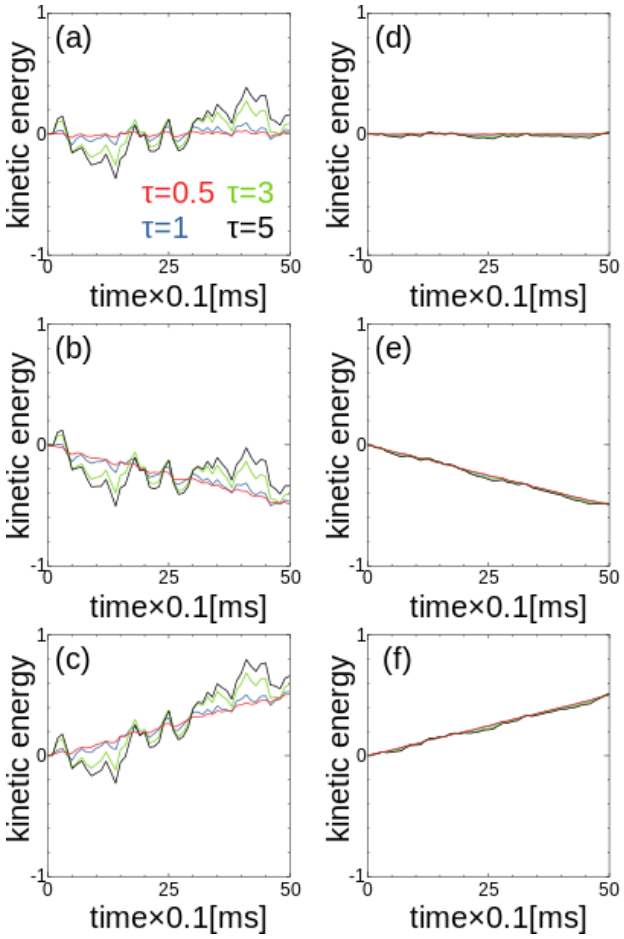

Fig.4 Time-dependent kinetic energy. (a), (d) Friction = microwave irradiation (b), (e) Friction > microwave irradiation (c), (f) Friction < microwave irradiation, respectively. And then, (a), (b), (c) for one fine particle and (d), (e), (f) for average of 100 fine particles, respectively.

relaxation time of microwaves is several μs,[3] the time resolution is much lower than the frequency factor 10kHz,[6] that is, 0.1ms. Therefore, the noise effect is updated for each frequency factor and applied to the reaction speed. Here, the Fig. 4 shows the kinetic energy defined by the Eq. (15). The noise is no longer white noise, but time-dependent correlated noise defined by the expression the first term of Eq. (15).

Fig. 4 shows three correlations of friction, microwave irradiation, and correlated noise in the Eq. (15) as a function of time. Figs. 4(a), (b) and (c) show the kinetic energy of a single fine particle, and Figs. 4(d), (e) and (f) show the average kinetic energy of 100 fine particles. This means kinetic energy is preserved at the system as in the Eq. (16). The difference in τ is the strength of the inter-noise correlation. If τ is small, the noise correlation is weak, and if τ is large, the noise correlation is strong. Since τ is the scattering memory of the fine particles, and it is generally said that the first memory is lost after three collisions, τ=3 is a reasonable number. In all discussions, when the microwave outweighs the friction, the kinetic

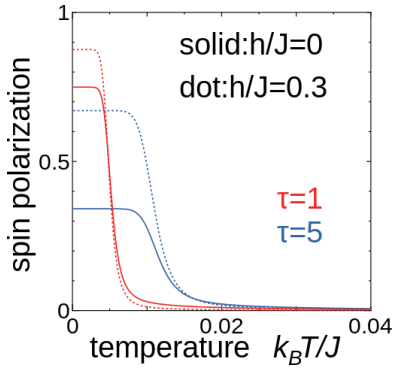

Fig.5 Spontaneous spin polarization at zero magnetic field and induced spin polarization under magnetic field in Ising model. The solid line indicates that there is no magnetic field, and the dotted line indicates that the magnetic field is applied. The noise-to-noise correlation is set to $\tau = 1, 5[ms]$.

energy rises as a function of time, and conversely, when the friction outweighs the microwave, the kinetic energy decays as a function of time.

In this calculation, the ergodic theorem that the time mean and the population mean are equal is used.

Eqs. (17)-(19) is applied to the 2D Ising model Eq. (20) with periodic boundary condition. The 100 sites of 10×10 are shown as one sheet, 50 sheets are prepared, and the Monte Carlo simulation method uses the noise represented by Eq. (15). It can be seen in Fig. 5 that the spin polarization increases and shows a constant value at low temperature region. This value rises when an external magnetic field is introduced, but it shows a constant value even at zero magnetic field. This predicts the emergence of a spontaneous magnetic field and meets the requirements of this model. The difference between $\tau = 1$ and 5 is whether the inter-noise correlation is weak or strong. The correlation of spins between cells in the Ising model is not included in the calculations by the usual Monte Carlo method. Due to the inter-noise correlation defined in this paper, the phase transition temperature at which magnetization occurs changes depending on the magnitude of τ.

4. Summary

In this paper, we have examined two ways of thinking of the Langevin equation as an epi-thermal distribution function, and have looked at the interpretation of the two reaction speeds. As a result, the reaction speed has increased in both cases. Here, we have defined the system Langevin equation as the fine particles of interest for the follow the epi-thermal Maxwell-Boltzmann distribution. Although the forms of reaction speed are different, there is no substitute for the conclusion that the reaction speed increases in both cases. The important point here is that the reaction rate is discussed below the transition temperature. Energy exceeding the transition temperature can be obtained by superimposing microwave energy on thermal energy and adding noise energy.

Furthermore, as kinetic energy, energy loss due to friction, energy acquisition by microwaves, and energy transmitted from correlated noise during particle movement have been concretely shown as a function of time. These friction and microwave energy have showed that the kinetic energy have competed as a function of time. Here, when one fine particle has moved, it has been a well-known random walk. On the other hand, when the motion of many particles has been averaged, the messiness disappears and only the friction energy loss due to noise in the entire system. Energy loss has been caused only by friction, and that to be heat by diffusion process.

The method of statistical mechanics for the 2D Ising model has been calculated as a Monte Carlo simulation. Here, time-correlation has been introduced as noise. As a result, it has become clear that the curvature of the spin component has depended on the magnitude of the correlation. In this way, when dealing with physical quantities where correlation becomes important, it has been predicted that this correlation will become important.

Thus, the effect of correlated noise determined by the frequency factor is expressed as the Brownian motion of one particle of interest. This effect defines a new correlated noise for each frequency factor with respect to reaction rate. This is different from the conventional Monte Carlo simulation.

References

1. A. W. C. Lau, D. Lacoste and K. Mallick, Phys. Rev. Lett, vol 99, (2007), pp. 158102.
2. G. Zhang and S. K. Hanson, Chem. Commun, 49, (2013), pp8371-8373.
3. T. Hirai, S. Nakatani, M. Sato and K. Nagata, JEMEA, (2022), to be published.
4. S. Takayama, M. Sato, and J. Fukushima, PSP Book, Erwann-Guenin, (2015) chapter 2.
5. K. Nagata and K. Kodama, ISIJ International, vol 62, No.8 (2022), pp. 1607-1617.
6. K. Hara, M. Hayashi, M. Sato and K. Nagata, ISIJ, vol 52, No. 12 (2012), pp. 2149-2157.

Manuscript received: Aug. 23, 2022
Revised: Nov. 15, 2022
Accepted: Nov. 18, 2022