学術論文

強い電磁場下での熱外放射分布によるマイクロ波効果の仮説
A Hypothesis of Microwave Effects Induced by An Epi-thermal Radiations Distributions under Intense

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Abstract

In the handling of microwave heating, it is useful to consider the same type of equations, the heat conduction equation and the diffusion equation. Due to the difference in the diffusion coefficients of each equation, there is a time delay between the energy applied by the microwave and the thermal energy. From this delay, microwave energy is stored non-thermally, which directly breaks the bonds of the crystal (it means phase transition) before it becomes thermal energy. Also, non-thermal energy is treated as acoustic phonon in the crystal. Therefore, we propose to treat phonon as an epi-thermal distribution function with an extended Bose-Einstein distribution, and in fact the application of microwaves forms a monochromatic peak in the distribution function. Its peak decays over time and becomes thermal energy. Such a process is one of the indicators of how to understand the phenomenon of microwave heating.

1. Introduction

Microwave heating is described in the form of the interaction of microwaves with charged and mass substances. The presence of a finite mass causes a phase lag in response to microwave, thus increasing the phase component. Since this is an irreversible process, microwave energy is absorbed by the system and does not return.[1][2]

Since microwaves have a monochromatic frequency, the response of microwaves is described by the Maxwell-Boltzmann distribution function when considering a multi-particle system with a finite temperature. By considering dumping here, it is known that there is a way to record a monochromatic peak due to microwave in the distribution function.[3] However, when considering solid, it is not appropriate to describe the behavior of the system with the Maxwell-Boltzmann distribution function.

In such situations, it is possible and useful to define lattice vibration (phonon).[4] If microwave is considered as photon, photon and phonon are connected by electric distortion in the single crystal that constitutes the substance, and interact to exchange energy. In this case, the Bose-Einstein distribution function can be used instead of the Maxwell-Boltzmann distribution function to describe the behavior of the system for microwave. The Bose-Einstein distribution function can directly bring in the energy of microwave and describe the response of the system without taking the procedure of converting the energy obtained by microwave into the momentum of particles with effective mass. Also, since phonon have a Bose-Einstein distribution, it is important that the same energy can be accumulated.

When a substance is irradiated with microwave, a non-thermal energy field called phonon and thermal energy can be considered. This is treated as separate equations in this paper, and it is assumed that phonon is first accumulated as a non-thermal energy field, and that

energy diffuses into thermal energy after a short but finite transition time. It is important to envision this transitive process, and such claims have not existed in previous studies.

In addition, it is experimentally reported that a physicochemical reaction that cannot be explained by ordinary thermal energy occurs in the microwave process, which is called "microwave non-thermal effect".[5]-[11]

In this paper, we treat the issue as same type two equations and assume that phonons are stored primary as a non-thermal energy field and that energy diffuses into thermal energy after a short but finite transition time. It is important to envision this transitive process, and such claims did not exist in previous studies. Section 2 shows the system and model, and Section 3 shows the derivation and solution of the theoretical formula, and the entropy generation process of the phonon field. Section 4 introduces computational examples and discusses the application of theory to latent heat processes in phase transition.

Here, methane hydrate is applied as an object of microwave heating. Methane hydrate is a microwave-sensitive substance, but the ice produced by the solid-solid-phase transition is a microwave-insensitive substance. Therefore, microwave acts only on the material before the phase transition. This allows for more general phase transitions and similar discussions during chemical changes.

2. Theoretical models and Experimental devices

As a model, we consider a closed system excluding radiation containing microwaves as energy to enter and exit. In fact, this model can be realized as an experimental system with heat insulating material and vacuum double glazing. So, it can be said that this model is a feasible model both theoretically and experimentally.

The methane hydrate produced in the laboratory is several centimeters large l, the wavelength of the microwave L is long enough ($l \ll L$), and it can be considered that there is no spatial dependence of the microwave. In addition, since microwave is directional electromagnetic wave, when a single mode is considered as a device, the direction of irradiating microwave is the x-axis, and the amplitude of the electric field is the y-axis.

In this paper, we consider the following two types of microwave irradiation; (i) pulse incident and (ii) continuous incident. We will discuss by comparing these two examples.

3. Formulation

The pulse incident of microwave needs to be an extremely short time. Theoretically, the delta function can be used, but experimentally it requires a finite time of incidence, albeit for a short time. Specifically, the vibration time of microwave is about [ns], and as will come out later, the time for mechanical vibrations of microwaves to decay in the system is several [μs]. By handling a certain amount of vibration, it can be said that microwave is sufficiently on the order of delta functions. On the other hand, when the system is continuously irradiated with microwaves, the microwaves continue to be incident from $t = 0$, so the theoretical and experimental image is straight forward to understand.

We examine the epi-thermal distribution function of the system containing microwave. For that purpose, it is important to deal with two equations, the heat conduction equation and the diffusion equation. These are similar equations, but the heat conduction equation deals with the diffusion of thermal energy in a substance, and the diffusion equation deals with the diffusion of energy space. These are independent and have different meanings. The difference between these two equations is the magnitude of the diffusion coefficients. For the diffusion coefficient D_P of the diffusion equation, the diffusion coefficient D_T of the heat conduction equation can be tentatively set as $D_T = 10D_P$. As we will see later, this assumption has been confirmed to be reasonable. These equations with different diffusion coefficient confirm the time dependence of microwaves. This assumption that the diffusion coefficients are different will be very important in future discussions. Here, in general, D_P and D_T depend on the temperature, but since the temperature change is small, both are easily set to constants.

The heat conduction equation and diffusion equation are defined below.

$$\frac{\partial T(r,t)}{\partial t} = D_T \nabla^2 T(r,t)\,, \tag{1}$$

$$\frac{\partial \phi(r,t)}{\partial t} = D_P \nabla^2 \phi(r,t)\,. \tag{2}$$

The following analytical solutions are derived for the thermal energy $Q_T(t)$ and the mechanical vibration energy $Q_P(t)$ for the microwave pulse incident.

$$Q_T(t) = CT_0[1 - exp\,(-t/\tau_T)]exp\,(ikx)\,, \tag{3}$$

$$Q_P(t) = \phi_0 exp\,(-t/\tau_P)exp(ikx)\,. \tag{4}$$

Here, the quantities are defined as $Q_T(t) = CT(t)$ and $Q_P(t) = \phi(r,t)$, where C is heat capacity. The quantity $\tau_P = 1/D_P k^2$ is calculated by the velocity of the acoustic phonon, and we can set $\tau_P = 10\tau_T$ as described above. As we will see later, microwave energy creates electric distortion in the crystal, which is stored as phonon.

Then, the thermal energy due to continuous irradiation of microwave and the energy of mechanical vibration due to continuous irradiation are calculated by the following formulas;

$$\hat{Q}_T(t) = \int_{t'=0}^{t} dt' \frac{Q_T(t')}{\tau_T}\,, \tag{5}$$

$$\hat{Q}_P(t) = \int_{t'=0}^{t} dt' \frac{Q_P(t')}{\tau_P}\,. \tag{6}$$

Here, the epi-thermal distribution function is calculated by thermal relaxation including monochromatic microwave energy. As the distribution function, the Bose-Einstein distribution function can be considered because the energy of the system is stored in phonon.

Since there is a monochromatic energy inflow in this distribution function, the distribution function has a peak at the point corresponding to the microwave. This peak is suppressed as a function of time, and the distribution

function converts the peak energy into thermal energy. The epi-thermal Bose-Einstein distribution function is defined as follows.

$$F(E,t) = f(E)g(E,t)\,, \tag{7}$$

$$f(E) = \frac{1}{exp(E/k_BT) - 1}\,, \tag{8}$$

$$g(E,t) = exp\left(\delta_{E,\varepsilon}\frac{Q_P(t)}{k_BT}\right). \tag{9}$$

Here, the quantity $\varepsilon = \hbar\omega_M$ with $\omega_M = 2.45$ [GHz] is defined.

As a specific thermodynamic quantity, entropy by phonon can be considered. This is given by the well-known harmonic oscillator entropy.

$$S(t) = Nk_BT\left[\frac{\hbar\omega}{2k_BT}coth\frac{\hbar\omega}{2k_BT} - ln\left(2sinh\frac{\hbar\omega}{2k_BT}\right)\right]. \tag{10}$$

Here, $T = T(t)$ is a function of time, and the entropy can be calculated by substituting Eq. (3) or Eq. (5) into Eq. (10).

4. Results

The energy, distribution function, and entropy are plotted for (i) pulse incident and (ii) continuous incident of microwave, respectively. Let's show each case.

4.1. Pulse incident

Fig. 1(a), in which the microwave energy and thermal energy incident on the system are plotted, is calculated by Eqs. (3) and (4). It can be seen that $Q_T(t)$ takes longer to saturate than $Q_P(t)$.

Distribution function Fig. 1(b) is calculated by Eqs. (4), (7), (8), (9). This distribution function has a peak at 2.45 [GHz] and decays over time. Looking at Fig. 1(b), the peak actually disappears at about 3 [μs]. The distribution function absorbs the peak energy and the temperature rises slightly. Specifically, in Fig. 1(b), the distribution function is drawn by defining T=1 [K] at t=0 [μs], but when t=0.05 [μs] temperature T=1.22 [K] and t= 0.3 [μs] temperature T=2.2 [K].

The phonon entropy shown in Fig. 1(c) is calculated by Eqs. (3) and (10). Entropy can be seen to converge around t=3 [μs]. A certain amount of energy is applied to the system, and it is a stable time until it is completely stored in the system as thermal energy. So, the entropy decays with respect to the time required for diffusion.

4.2. Continuous incident

Fig. 2(a), which shows the energy of the system, is calculated by the following formula by Eqs. (5) and (6). The quantity $\hat{Q}_p(t)$ starts from zero at the start of microwave incident $t = 0$ [μs] and becomes constant at about 3 [μs], but the quantity $\hat{Q}_T(t)$ rises exponentially at t =0[μs] to 3[μs], and almost linearly from t = 3[μs].

The distribution function shown in Fig. 2(b) is calculated by Eqs. (6), (7), (8), and (9). Unlike pulse incident, no peak occurs at $t = 0$. The peak once rises, falls again, and then gradually rises. The temperatures are T=1[K] at t=0[μs], T=1.48[K] at t=0.15[μs], T=2.31 [K] at t=0.25[μs], T=5.94[K] at t=0.75[μs], and T=18.66 at t=1[μs]respectively.

Entropy is calculated by equations (5) and (10). Entropy does not converge even at time t = 5 [μs].

In Fig. 3, the peak structure of Fig. 2(b) is described as a function of time. The increase or decrease of this value is essentially different from that of pulse incident.

5. Discussion

First, we consider the microwave of the pulse incident. In Fig. 1(a), microwave is first stored in the system as mechanical energy and absorbed in the system as non-thermal energy at about 0.3 [μs]. On the other hand, the thermal energy becomes stable at about 1 [μs].

In Fig. 1(b), the epi-thermal Bose-Einstein distribution function is taken up as the epi-thermal distribution function. Methane hydrate is formed as a guest molecule containing methane in the bond of H_2O molecule, but even if we try to think of H_2O itself as a distribution function, the molecule is trapped in the crystal structure, so the effective mass is considered. However, it cannot be handled by the Maxwell-Boltzmann distribution because effective mass of H_2O is not a good approximation because H_2O is fixed at the crystal and does not move

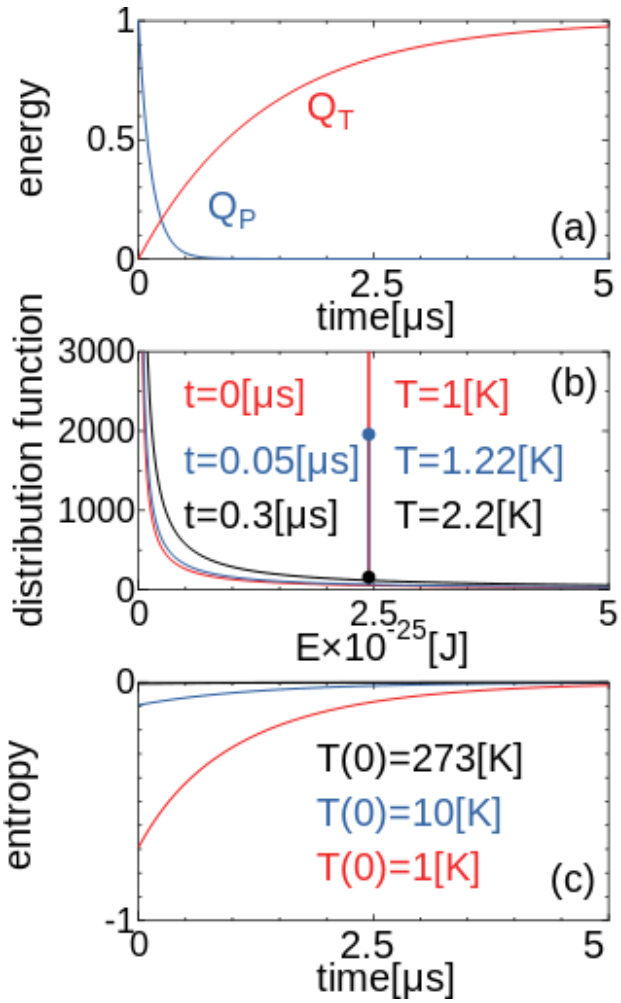

Fig.1 (a) thermal energy $Q_T(t)$ and pulse microwave energy $Q_p(t)$. (b) epi-thermal Bose-Einstein distribution function. (c) entropy plotted as a function of temperature. $T(0)$ is the temperature at t=0[μs].

freely. Thus, we focus on the phenomenon that ultrasonic wave is generated in the crystal from the electric distortion generated when microwave is applied to the crystal and accumulate as phonon, and we decided to handle the distribution function of phonon with the extended Bose-Einstein distribution.

In Fig.1(c), entropy approaches stable over time. Since the amount of energy input to the system is constant, when the energy incident by microwave is completely converted to thermal energy, it will not evolve any further. This is the reason why the entropy converges to a constant value in about several tens of [μs].

Then, we consider the microwave of the continuous incident.

In Fig. 2(a), the microwave supply and the process of conversion to heat are balanced, and the microwave energy converges to a constant value. This occurs in about 3 [μs] time scale. Thermal energy always receives energy from microwave and continues to be heated, so it rises almost linearly except for t =0[μs] to 0.3[μs].

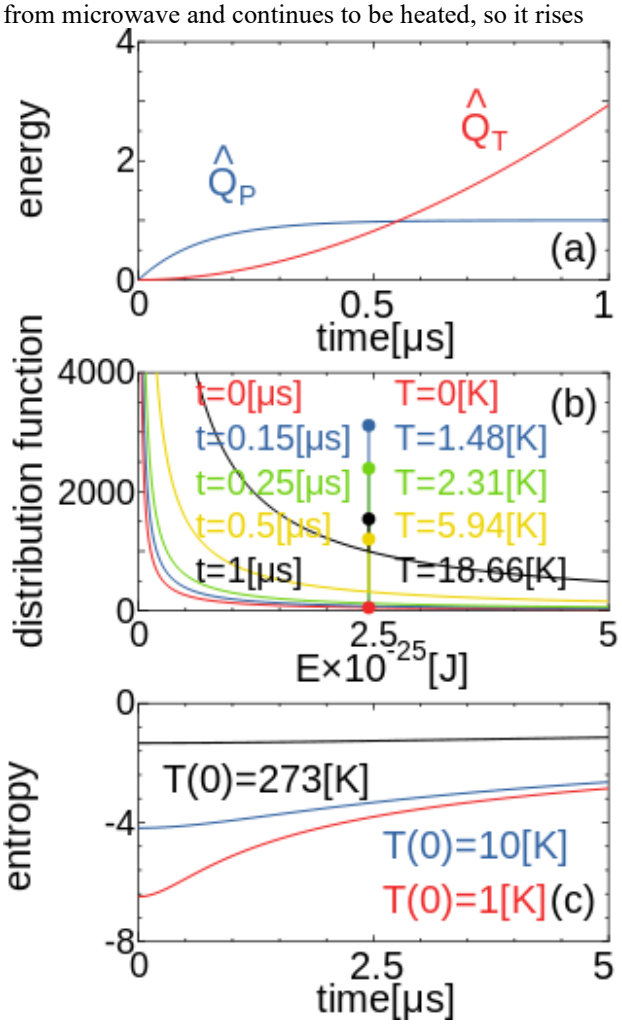

Fig.2 (a) thermal energy $\hat{Q}_T(t)$ and continuous microwave energy $\hat{Q}_p(t)$. (b) epi-thermal Bose-Einstein distribution function. (c) entropy plotted as a function of temperature. $T(0)$ is the temperature at t=0[μs].

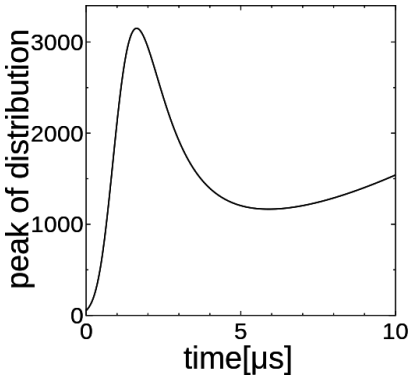

Fig.3 the peak structure as a function of time plotted at Fig. 2(b).

In Fig. 2(b), since the microwave started to enter at $t = 0$ [μs], the result that the peak in the microwave distribution function starts to rise from zero is valid. The behavior of the peak is complicated, but in the region where t is small ($0 < t < 2.5$ [μs]), the peak rises once because the mechanical energy input to the system heats up due to the difference in relaxation time between $\hat{Q}_T(t)$ and $\hat{Q}_p(t)$. This is because it is stored as non-thermal energy in the system before it changes to. So, this peak drops once at about 0.5 [μs]. After that, as a result, the peak value rises on the distribution function. Such peak behavior is shown in Fig.3 as a function of time. This is the effect of the continuous exposure of microwaves to the system, which is a major difference from pulse injection.

In Fig. 2(c), the entropy does not become stable no matter how much time passes. This is because the system is constantly being supplied with energy by microwaves. In other words, entropy generation continues at any time. While microwave energy is transformed into thermal energy and distributed, more microwave is supplied. So, the entropy does not settle to a constant value. Since the system undergoes a gradual phase transition due to microwave, phonon is no longer a good physical quantity over time. Thus, the phase transition proceeds before the entropy continues to rise to stable, the methane hydrate collapses, and the method of handling this system exceeds the range covered in this study.

When the problem of "microwave non-thermal effect" is considered, it is necessary to consider the energy path as mentioned above. (a) The system is irradiated with microwaves. (b) Microwave energy changes to electric distortion. (c) Electric distortion induces phonon in the single crystal. (d) The molecular structure of H_2O is broken by the accumulation of this phonon. If $D_T = D_P$, the path from (a) to (d) does not need to be considered. The input microwave energy is immediately relaxed and converted into heat. However, in reality, $D_T = D_P$ is not always the case, so a mechanism for storing non-thermal energy inside the crystal is indispensable. This is a positive reason why non-thermal energies such as electric distortion and phonon must be considered.

In fact, when microwave energy falls below the

hydrogen bond energy of H_2O, which is about 0.2 [eV], if microwave is considered as photon, it is necessary to store about 100,000 times photon energies. This is the reason why $D_T = 10D_P$ is defined by changing the size of D_P and D_T.

The time required for the accumulation of about 30,000 times photons is calculated to be about 2.5 [μs], which is consistent with the time scale in which the mechanical vibration energy generated by microwaves becomes thermal energy. As a result, it is shown to be on the same scale as the discussion so far, demonstrating the validity of this paper.

As an example of the discussion on chemical changes, the reaction $FeO + CO \rightarrow Fe + CO_2$ is taken as an example, which is a reduction reaction at 800 [℃], is taken as an example.[12] The binding energy is an order of magnitude different from that of hydrogen bonds, so set it to 1 [eV]. Then, using the same calculation as for methane hydrate, about 600,000 times photon accumulations are required to break the bond. According to the same calculation as before, about 25 [μs] is required for photons to accumulate. Since the frequency factor of reaction of this reaction is 7.7 [kHz] and it required for photon accumulation reciprocal is 13 [μs], it is the same order as the time.

Therefore, it can be said that this methodology is general and that the contents discussed here are also useful for other systems that react with microwave.

6. Summary

The non-thermal effect on irradiating methane hydrate with microwave has been discussed. The heat conduction equation and the diffusion equation have been taken up, and discussions have been carried out from the standpoint that their diffusion coefficients are different. Two types of microwave injection methods have been dealt with in this system. That is, (i) pulse incident and (ii) continuous incident. In (i) and (ii), the behaviors of microwave energy and thermal energy have showed completely different behaviors, respectively. The Epi-thermal distribution function is also different, and the appearance of peaks depends on the assumptions of (i) and (ii). It is important to be aware of this difference in actual experiments.

In contrast to the physical phenomenon of breaking hydrogen bonds with microwave energy, the current situation is that it is necessary to accumulate microwaves as photon about 30,000 times in terms of photon energy. On the other hand, when $D_P \neq D_T$, it is indispensable to consider a mechanism for storing non-thermal energy inside the crystal, and this is a situation where it is necessary to go through a non-thermal process called electric distortion and ultrasonic phonon.

In reality, the input microwave does not completely heat up inside the system, but it is necessary to consider the energy loss.[13] It is necessary to consider this energy when comparing it with the experiment.

In this paper, as an example, the phenomenon that occurs when methane hydrate is irradiated with microwaves is shown. This argument holds true not only for methane hydrate, but also for phase transitions and chemical changes that differ in microwaves, as in the case of the reducing action of iron.

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